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(54) **SPANDEX FIBER WITH EXCELLENT CHLORINE RESISTANCE, AND PREPARATION METHOD THEREOF**

(57) The present invention relates to a spandex fiber containing an inorganic chlorine-resistant agent, such as a hydrotalcite compound, a mixture mineral of huntite and hydromagnesite, hydromagnesite, zinc oxide, or magnesium oxide, and a symmetrically di-hindered hydroxyphenyl-based additive, which improves the chlorine

resistance of the spandex fiber, and a production method thereof. The spandex fiber has excellent chlorine resistance, and thus can be more effectively used for sports or leisure wear such as swimwear.

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Description**Technical Field**

[0001] The present invention relates to a spandex fiber having enhanced chlorine resistance and a production method thereof, and more particularly to a spandex fiber containing a symmetrically di-hindered hydroxyphenyl-based additive and an inorganic chlorine-resistant agent, which improve the chlorine resistance of the spandex fiber while maintaining the inherent physical properties of the polyurethane polymer of the spandex fiber.

Background Art

[0002] Spandex, a typical polyurethane elastic fiber, has high rubber-like elasticity and excellent physical properties such as tensile stress and resilience, and thus is frequently used for underwear, socks, sports and leisure wear, and the like. However, the physical properties of the main component of spandex which is polyurethane show significant deterioration when it is bleached with chlorine, and the physical properties such as tenacity of swimwear made of spandex and polyamide deteriorate when they are used in swimming pools having an active chlorine content of 0.5-3.5 ppm or higher.

[0003] Efforts have been made impart spandex fibers with resistance against the deterioration caused by chlorine. Chlorine-resistant agents used in spandex include zinc oxide disclosed in US Patent No. 4,340,527, a mixture of huntite and hydromagnesite disclosed in US Patent No. 5,626,960, calcium carbonate and barium carbonate disclosed in Korean Patent Publication No. 92-03250, a MgO/ZnO solid solution disclosed in Japanese Unexamined Patent Publication No. Hei 6-81215, magnesium oxide or magnesium hydroxide or hydrotalcite disclosed in Japanese Unexamined Patent Publication No. Sho 59-133248, and a hydrotalcite treated with a higher fatty acid and a silane coupling agent, disclosed in Japanese Unexamined Patent Publication No. Hei 3-292364. In addition, phenolic compounds are also used as additives to improve the chlorine resistance of spandex fibers. For example, Japanese Unexamined Patent Publication No. Sho 50-004387 discloses a phenolic additive which is used as a stabilizer for spandex, and US Patent No. 6,846,866 discloses the technology of using a mixture of an inorganic additive and an organic additive to improve the resistance to chlorine and the resistance to discoloration caused by combustion fumes.

[0004] However, there has not yet been an additive capable of dramatically improving the chlorine resistance of spandex fibers. Thus, it is required to improve the chlorine resistance of spandex fibers.

Disclosure**Technical Problem**

[0005] Accordingly, the present invention has been made in order to satisfy the above technical requirement, and it is an object of the present invention to provide a spandex fiber which has improved chlorine resistance while maintaining the inherent physical properties of the polyurethane polymer of the spandex fiber.

[0006] Another object of the present invention is to provide a method for producing a spandex fiber, which can improve the chloride resistance of the spandex fiber while maintaining the inherent physical properties of the polyurethane polymer of the spandex fiber.

Technical Solution

[0007] One aspect of the present invention for achieving the above objects is directed to a spandex fiber having excellent chlorine resistance, which contains, based on the polyurethane solid content, 0.1-5 wt% of a symmetrically di-hindered hydroxyphenyl-based compound and 0.1-10 wt% of an inorganic chlorine-resistant agent.

[0008] Another aspect of the present invention for achieving the above objects is directed to a method for producing a spandex fiber, comprising the steps of:

reacting an organic diisocyanate with a diol to prepare a polyurethane precursor, dissolving the polyurethane precursor in an organic solvent, and then reacting the polyurethane precursor with a diamine and a monoamine, thereby preparing a polyurethane solution; and

adding, based on the polyurethane solid content, 0.1-5 wt% of a symmetrically di-hindered hydroxyphenyl-based compound and 0.1-10 wt% of an inorganic chlorine-resistant agent, to the polyurethane solution, followed by spinning.

Advantageous Effects

[0009] The spandex fiber according to the present invention has excellent discoloration resistance and chlorine resistance while maintaining the inherent physical properties of polyurethane, such as whiteness, holding power, tearing strength, bursting strength and elasticity. Thus, it can be effectively used in underwear such as shapewear, socks, and sportswear such as swimwear and gymnastic wear.

Mode for Invention

[0010] Hereinafter, the present invention will be described in detail.

[0011] A spandex fiber according to one embodiment of the present invention contains, based on the polyurethane solid content, 0.1-5 wt% of a symmetrically di-hindered hydroxyphenyl-based compound and 0.1-10 wt% of an inorganic chlorine-resistant agent. This spandex fiber has improved discoloration resistance and chlorine resistance while maintaining the inherent physical properties of the polyurethane polymer, and thus can be applied to various wear, such as underwear, sportswear, and casual wear.

[0012] The spandex fiber of the present invention is a fiber produced from a fiber-forming substance which is a long chain synthetic polymer comprised of at least 85% of segmented polyurethane. In other words, a polymer which is spun into the spandex fiber is a copolymer comprising a urethane bond. The polyurethane polymer which is used for the production of the spandex fiber is prepared by reacting an organic diisocyanate with a polymeric diol to prepare a polyurethane precursor, dissolving the polyurethane precursor in an organic solvent, and then reacting the polyurethane precursor with a diamine and a monoamine.

[0013] Examples of the organic diisocyanate include diphenylmethane-4,4'-diisocyanate, hexamethylene diisocyanate, toluene diisocyanate, butylene diisocyanate, hydrogenated diphenylmethane-4,4'-diisocyanate, methylene-bis(4-phenylisocyanate), 2,4-tolylene diisocyanate, methylene-bis(4-cyclohexylisocyanate), isophorone diisocyanate, tetramethylene-p-xylylene diisocyanate, and mixtures thereof.

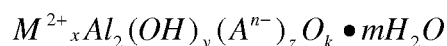
[0014] In addition, examples of the polymeric diol that is used in the present invention include polytetramethylene ether glycol, polypropylene glycol, polycarbonate diol, and the like. The diamine is used as a chain extender, and examples thereof include ethylenediamine, propylenediamine, hydrazine, 1,4-cyclohexanediamine, hydrogenated m-phenylenediamine (HPMD), 2-methylpentamethylenediamine (MPMD), and the like. More preferably, the chain extender is one or more of ethylenediamine, 1,3-propylenediamine, and 1,4-cyclohexanediamine, optionally mixed with HPMD, MPMD and/or 1,2-propylenediamine. Meanwhile, the monoamine is used as a chain terminator, and examples thereof include diethylamine, monoethanolamine, dimethylamine, and the like.

[0015] The symmetrically di-hindered hydroxyphenyl-based compound that is used in the present invention may be one or more selected from the group consisting of tetrakis [methylene-2-(3,5-di-tertiary-butyl-4-hydroxyphenyl) propionate]methane, tris(3,5-di-tertiary-butyl-4-hydroxy-5-methylphenyl) propionate, 3,3',3'',5,5',5''-hexa-tetra-butyl-a,a',a''-(mesitylene-2,4,6-trile)tri-p-cresol, hexamethylenbis[3-(3,5-di-tertiary-butyl-4-hydroxyphenyl) propionate], 1,2-bis(3,5-di-tertiary-butyl-4-hydroxyhydroxyamyl)hydrazine, N,N'-hexamethylenbis(3,5-di-tertiary-butyl-4-hydroxy-hydrocinamide), and 2,4-di-tertiary-butylphenyl-4'-hydroxy-3',5'-di-tertiary-butyl benzoate.

[0016] In the present invention, the symmetrically di-hindered hydroxyphenyl-based compound is preferably added in an amount of 0.1-5 wt% based on the polyurethane solid content. If the amount of the symmetrically di-hindered hydroxyphenyl-based compound that is added is less than 0.1 wt%, it will not significantly contribute to improving the chlorine resistance of the spandex fiber, and once more than 5 wt% is added, any further increase will not lead to an improvement in the effect thereof.

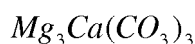
[0017] The inorganic chlorine-resistant agent that is used in the present invention may be a hydrotalcite represented by the following formula 1, a huntite represented by the following formula 2, a hydromagnesite represented by the following formula 3, zinc oxide, magnesium oxide, or the like. Inorganic chlorine-resistant agents, such as hydrotalcite, a physical mixture of huntite and hydromagnesite, basic magnesium carbonate, zinc oxide, and magnesium oxide, have the property of capturing halogen atoms, and thus are very effective at neutralizing chlorine.

[Formula 1]

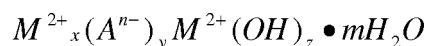


wherein M^{2+} is Mg^{2+} , Ca^{2+} or Zn^{2+} , A^{n-} is an anion having a valence of n , x and y are positive numbers of 2 or greater, Z is a positive number of 3 or smaller, k is 0 or a positive number of 3 or smaller, m is 0 or a positive number, and A^{n-} is OH^- , F^- , Cl^- , Br^- , NO_3^- , SO_4^{2-} , CH_3COO^- , CO_3^{2-} , HPO_4^{2-} , an oxalate ion, a salicylate ion, or a silicate ion.

[Formula 2]



[Formula 3]



wherein M^{2+} is Mg^{2+} or Ca^{2+} , A^{n-} is CO_3^{2-} , x is from 1 to 5, z is from 0 to 2, and m is from 0 to 5.

[0018] Huntite and hydromagnesite are minerals which are present in the form of mixtures and are difficult to separate into pure huntite or hydromagnesite.

[0019] Non-limiting examples of the hydrotalcite compound represented by formula 1 include $Mg_{4.5}Al_2(OH)_{13}CO_3 \cdot 3.5H_2O$, $Mg_6Al_2(OH)_{16}CO_3 \cdot 5H_2O$, $Mg_8Al_2(OH)_{20}CO_3 \cdot 6H_2O$, $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$, $Mg_{4.5}Al_2(OH)_{13}CO_3$, $Mg_6Al_2(OH)_{16}CO_3$, $Mg_8Al_2(OH)_{20}CO_3$, $Mg_4Al_2(OH)_{20}CO_3$, $Mg_{4.5}Al_2(OH)_{13}(CO_3)_{0.6}O_{0.4}$, $Mg_6Al_2(OH)_{16}(CO_3)_{0.7}O_{0.3}$, $Mg_{4.5}Al_2(OH)_{12.2}(CO_3)_{0.8}O_{0.6}$, $Mg_4Al_2(OH)_{12}(CO_3)_{0.6}O_{0.4}$, and any mixtures thereof.

[0020] Hydrotalcite has the property of absorbing water, and thus when it is added to a polyurethane polymer in an uncoated state, it will cause gelation and coagulation, thereby causing yarn breakage and the like in a spinning process. In order to prevent an increase in discharge pressure and yarn breakage during a spinning process by preventing water absorption into hydrotalcite and improving the dispersibility of hydrotalcite, hydrotalcite may be used after it has been coated. Even when uncoated hydrotalcite is used, sand grinding or milling of the uncoated hydrotalcite can provide the same spinning properties as those obtained when coated hydrotalcite is used.

[0021] Examples of the coating agent which may be used in the present invention include, but are not limited to, aliphatic alcohols, fatty acids, fatty acid salts, fatty acid esters, phosphoric acid esters, styrene/maleic acid anhydride copolymers and derivatives thereof, silane coupling agents, titanate coupling agents, polyorganosiloxanes, polyorgano-hydrogensiloxanes and melamine-based compounds. Among these, fatty acids, fatty acid salts and/or melamine-based compounds are preferred. Fatty acids and fatty acid salts exhibit excellent coating effects compared to other coating agents.

[0022] The coating process for hydrotalcite may be carried out by adding a coating agent to a solvent such as water, alcohol, ether or dioxane in an amount of 0.1 to 10 wt% based on the weight of hydrotalcite, adding uncoated hydrotalcite thereto and stirring the resulting solution at an elevated temperature of 60 to 180 °C (if necessary, using a high-pressure reactor) for about 20 minutes to 2 hours, followed by filtering and drying. Alternatively, the coating process may be performed by heat-melting a coating agent without using a solvent and mixing the melted coating agent with hydrotalcite at high speed.

[0023] When hydrotalcite is coated with the melamine-based compound, the coating process should be performed in water at a temperature of 160 °C or higher under pressure, because the melamine-based compound has a high melting point.

[0024] The fatty acid which may be used as the coating agent for hydrotalcite in the present invention is preferably one or more selected from mono- or poly-hydroxy fatty acids having a linear or branched hydrocarbon chain containing 3 to 40 carbon atoms. Specific examples of the fatty acid include lauric acid, caproic acid, palmitic acid and stearic acid.

[0025] The fatty acid salt which may be used in the present invention contains either a metal selected from metals of Groups I to III of the Periodic Table or zinc. The fatty acid of the fatty acid salt may be saturated or unsaturated, may contain 6 to 30 carbon atoms and may be monofunctional or bifunctional. Examples of the fatty acid salt include lithium, magnesium, calcium, aluminum or zinc salts of oleic acid, palmitic acid or stearic acid, preferably magnesium stearate, calcium stearate and aluminum stearate, more preferably magnesium stearate.

[0026] The melamine-based compound which may be used as a coating agent in the present invention may be one or a mixture of two or more selected from melamine compounds, phosphor-containing melamine compounds and melamine cyanurate compounds, which may be substituted with an organic compound having a carboxyl group.

[0027] Specifically, the melamine compound may be selected from methylene dimelamine, ethylene dimelamine, trimethylene dimelamine, tetramethylene dimelamine, hexamethylene dimelamine, decamethylene dimelamine, dodecamethylene dimelamine, 1,3-cyclohexylene dimelamine, *p*-phenylene dimelamine, *p*-xylene dimelamine, diethylene trimelamine, triethylene tetramelamine, tetraethylene pentamelamine, hexaethylene heptamelamine, melamine formaldehyde and the like.

[0028] The phosphor-containing melamine compounds comprise a phosphoric acid or phosphate coupled to the above-described melamine compounds, and specific examples thereof include dimelamine pyrophosphate, melamine primary phosphate, melamine secondary phosphate, melamine polyphosphate, and a melamine salt of bis-(pentaerythritol phos-

phate) phosphoric acid, etc.

[0029] The melamine cyanurate compounds are melamine cyanurates substituted with at least one substituent of selected from methyl, phenyl, carboxymethyl, 2-carboxyethyl, cyanomethyl, 2-cyanoethyl and the like.

[0030] The above melamine-based compounds preferably contain an organic compound having a carboxyl group. Examples of the organic compound having a carboxyl group include aliphatic monocarboxylic acids, aliphatic dicarboxylic acids, aromatic monocarboxylic acids, aromatic dicarboxylic acids, aromatic tetracarboxylic acids, cycloaliphatic monocarboxylic acids, and cycloaliphatic dicarboxylic acids. For example, the aliphatic monocarboxylic acids include caprylic acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, stearic acid, nonadecanoic acid, eicosanoic acid and behenic acid; the aliphatic dicarboxylic acids include malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, 1,9-nonanedicarboxylic acid, 1,10-decanedicarboxylic acid, 1,11-undecanedicarboxylic acid, 1,12-dodecanedicarboxylic acid, 1,13-tridecanedicarboxylic acid and 1,14-tetradecanedicarboxylic acid; the aromatic monocarboxylic acids include benzoic acid, phenylacetic acid, α -naphthoic acid, β -naphthoic acid, cinnamic acid, *p*-amino hippuric acid and 4-(2-thiazoylsulfamyl)-phthalaninoic acid; the aromatic dicarboxylic acids include terephthalic acid, isophthalic acid and phthalic acid; the aromatic tricarboxylic acids include trimellitic acid, 1,3,5-benzenetricarboxylic acid and tris(2-carboxyethyl) isocyanurate; the aromatic tetracarboxylic acids include pyromellitic acid and biphenyltetracarboxylic acid; the cycloaliphatic monocarboxylic acids include cyclohexane carboxylic acid; and the cycloaliphatic dicarboxylic acids include 1,2-cyclohexane dicarboxylic acid.

[0031] The hydromagnesite of formula 3 may be obtained from minerals or by synthesis. Examples of a coating agent which may be used for coating of hydromagnesite in the present invention include, but are not limited to, aliphatic alcohols, fatty acids, fatty acid salts, fatty acid esters, phosphoric acid esters, styrene/maleic acid anhydride copolymers and derivatives thereof, silane coupling agents, titanate coupling agents, polyorganosiloxanes, polyorganohydrogensiloxanes and melamine-based compounds. Among these, fatty acids, fatty acid salts and/or melamine-based compounds are preferred. Fatty acids and fatty acid salts exhibit excellent coating effects compared to other coating agents. The coating process for hydromagnesite may be carried out by adding a coating agent to a solvent such as water, alcohol, ether or dioxane in an amount of 0.1 to 10 wt% based on the weight of hydrotalcite, adding an uncoated hydromagnesite thereto and stirring the resulting solution at an elevated temperature of 50 to 170 °C (if necessary, using a high-pressure reactor) for about 20 minutes to 2 hours, followed by filtering and drying. Alternatively, the coating process may be performed by heat-melting a coating agent without using a solvent and mixing the melted coating agent with hydromagnesite at high speed.

[0032] When hydromagnesite is coated with the melamine-based compound, the coating process should be performed in water at a temperature of 160 °C or higher under pressure, because the melamine-based compound has a high melting point.

[0033] The fatty acid which may be used as a coating agent for hydromagnesite in the present invention is preferably one or more selected from mono- or poly-hydroxy fatty acids having a linear or branched hydrocarbon chain containing 3 to 40 carbon atoms. Specific examples of the fatty acid include lauric acid, caproic acid, palmitic acid and stearic acid.

[0034] The fatty acid salt which may be used in the present invention contains either a metal selected from metals of Groups I to III of the Periodic Table or zinc. The fatty acid of the fatty acid salt may be saturated or unsaturated, may contain 6 to 30 carbon atoms and may be monofunctional or bifunctional. Examples of the fatty acid salt include lithium, magnesium, calcium, aluminum or zinc salts of oleic acid, palmitic acid or stearic acid, preferably magnesium stearate, calcium stearate and aluminum stearate, more preferably magnesium stearate.

[0035] The chlorine-resistant agent which is used in the present invention is preferably added in an amount of 0.1-10 wt% based on the polyurethane solid content. If the amount added of the chlorine-resistant agent is less than 0.1 wt%, the chloride resistance of the spandex fiber will be insufficient, and if the amount is more than 10 wt%, the strength, elongation and modulus of the spandex fiber will deteriorate due to the excessive content of inorganic compounds.

[0036] A stabilizer may be added to the polyurethane polymer in order to prevent the discoloration and deterioration in physical properties of the spandex which result from either heat treatment during spandex processing or UV light, smog and the like. Specific examples of the stabilizer include hindered phenolic compounds, benzofuranone-based compounds, semi-carbazide-based compounds, benzotriazol-based compounds, hindered amine-based compounds, polymeric tertiary amine stabilizers (e.g., a tertiary nitrogen atom-containing polyurethane, polydialkyl aminoalkyl methacrylate, etc.), and the like.

[0037] The spandex fiber of the present invention may further include, in addition to the above-described compounds, inorganic additives such as titanium dioxide, magnesium stearate, etc. The titanium dioxide may be used in an amount of 0.1-5 wt% based on the weight of the spandex fiber, depending on the whiteness of the spandex fiber. The magnesium stearate is used to enhance the unwinding property of the spandex fiber and is added in an amount of 0.1 to 2 wt% based on the weight of the spandex fiber.

[0038] The polyurethane spinning solution may contain other various additives for specific purposes, unless these additives interfere with the effects of the present invention. These additives include stabilizers, UV light absorbers, light

resistant agents, antioxidants, anti-tack agents, lubricants such as mineral oil and silicone oils, antistatic agents, and the like. Examples of the additives include hindered phenolic stabilizers such as 2,6-di-*t*-butyl-4-methyl-phenol as a light stabilizer, antioxidants, phosphorus-containing chemicals, nitrogen oxide traps, light stabilizers, hindered amine stabilizers, metal salts such as magnesium stearate and barium sulfate, bactericides containing silver, zinc, or compounds thereof, deodorants, anti-static agents, and the like.

[0039] Another aspect of the present invention is directed to a method for producing a spandex fiber having excellent chlorine resistance. In the inventive method for producing the spandex fiber, an organic diisocyanate is reacted with a diol to prepare a polyurethane precursor, after which the polyurethane precursor is dissolved in an organic solvent and then reacted with a diamine and a monoamine, thereby preparing a polyurethane solution. Then, based on the polyurethane solid content, 0.1-5 wt% of a symmetrically di-hindered hydroxyphenyl-based compound and 0.1-10 wt% of an inorganic chlorine-resistant agent are added to the polyurethane solution, and the resulting mixture is spun to form a spandex yarn which is then wound. The polyurethane solution may be melt-spun, dry-spun or wet-spun into spandex fibers.

[0040] In the production of the spandex fiber according to the present invention, the symmetrically di-hindered hydroxyphenyl-based compound and the inorganic chlorine-resistant agent may be added to the polyurethane polymer at any convenient point of time. For example, the inorganic chlorine-resistant agent may be added to the polyurethane solution together with other additives and be mixed with the polyurethane polymer during a sand-grinding or milling process. Alternatively, the inorganic chlorine-resistant agent may also be mixed with the polyurethane polymer in a solvent during the sand-grinding or milling process in the absence of other additives. In addition, the symmetrically di-hindered hydroxyphenyl-based compound may be added during the sand-grinding or milling process after it has been separately dissolved in a solvent. In order to improve the dispersibility of the inorganic chlorine-resistant agent, a coated inorganic chlorine-resistant agent may also be added.

[0041] The process of sand-grinding or milling the inorganic chlorine-resistant agent can be performed by milling either a mixture of the inorganic chlorine-resistant agent, a solvent and a small amount of the polyurethane polymer or a slurry mixture of the inorganic chlorine-resistant agent, a solvent, a small amount of the polyurethane polymer, and other additives, using a conventional bead mill. Herein, the small amount of the polyurethane polymer serves to increase the dispersibility of the inorganic chlorine-resistant agent. The solvent used may be one or more selected from among dimethylacetamide, dimethylformamide and dimethylsulfoxide.

Examples

[0042] Hereinafter, the present invention will be described in further detail with reference to examples. These examples are provided for illustrative purposes only and are not intended to limit the scope of the present invention. All parts, percentages, etc., are by weight unless otherwise specified.

Example 1

[0043] 518 g of diphenylmethane-4,4'-diisocyanate and 2,328 g of polytetramethylene ether glycol (molecular weight: 1,800) were reacted with stirring at 90 °C under a nitrogen atmosphere for 95 minutes to prepare a polyurethane prepolymer having isocyanate groups at both ends. After cooling the prepolymer to room temperature, 4,269 g of dimethylacetamide was added thereto to obtain a polyurethane prepolymer solution.

[0044] Subsequently, 43 g of ethylenediamine and 9.1 g of diethylamine were dissolved in 1,889 g of dimethylacetamide. The resultant solution was added to the prepolymer solution at 9 °C or below to obtain a polyurethane solution. The polyurethane solution was mixed with, based on the solid content of the polyurethane solution, 1 wt% of poly(N,N-diethyl-2-aminoethyl methacrylate) as an acid dye enhancer, 0.1 wt% of titanium oxide as a light resistant agent, 0.26 wt% of magnesium stearate as an unwinding property enhancer, and 4 wt% of the chlorine-resistant agent hydrotalcite ($\text{Mg}_3\text{Al}_2(\text{OH})_4(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$) coated with, based on the weight of the hydrotalcite, 2 wt% of stearic acid and 1 wt% of melamine phosphate. In addition, 1.5 wt% of tetrakis[methylene-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] methane as a symmetrically di-hindered hydroxyphenyl-based compound was added to and mixed with the resulting slurry, thereby obtaining a spinning solution.

[0045] The spinning solution was defoamed, after it was dry-spun at a spinning temperature of 260 °C and wound at a speed of 900 m/min, thereby producing a 4-filament 40-denier spandex yarn.

[0046] The chlorine resistance of the spandex yarn was evaluated, and the results of the evaluation are shown in Table 1 below. In order to evaluate the chlorine resistance of the obtained spandex yarn, the strength retention rate in chlorinated water was evaluated in the following manner. The spandex yarn was stretched at a stretching ratio of 50%, treated with water (pH 4.5; 99 to 100 °C) for 2 hours, and dried and cooled at room temperature. Then, the spandex yarn was dipped in 45 ℓ of chlorinated water (pH 7.0-7.5) containing 3.5 ppm of active chlorine at room temperature for 120 hours, and the strength retention rate thereof was calculated using the following equation. The strength of the

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spandex yarn was measured using MEI by applying 32 kgf cell to a 20 cm-long sample at a cross head speed of 1000 mm/min.

$$\text{Strength retention rate (\%)} = S/S_0 \times 100$$

wherein S_0 is strength before treatment, and S is strength after treatment.

Example 2

[0047] A spandex yarn was produced in the same manner, except that 3,3',3'',5,5',5''-hexa-tetra-butyl-a,a',a''-(mesitylene-2,4,6-trile)tri-p-cresol was used as the symmetrically di-hindered hydroxyphenyl-based compound. The chlorine resistance of the produced spandex yarn was evaluated, and the results of the evaluation are shown in Table 1 below.

Example 3

[0048] A spandex yarn was produced in the same manner, except that tetrakis[methylene-2-(3,5-di-tertiary-butyl-4-hydroxyphenyl)propionate]methane was used as the symmetrically di-hindered hydroxyphenyl-based compound and that 4 wt% of an uncoated hydrotalcite ($\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$) was added as the chlorine-resistant agent. The chlorine resistance of the produced spandex yarn was evaluated, and the results of the evaluation are shown in Table 1 below.

Example 4

[0049] A spandex yarn was produced in the same manner, except that a mixture of huntite and hydromagnesite was used as the inorganic chlorine-resistant agent. The chlorine resistance of the produced spandex yarn was evaluated, and the results of the evaluation are shown in Table 1 below.

Example 5

[0050] A spandex yarn was produced in the same manner, except that hydromagnesite was used as the inorganic chlorine-resistant agent. The chlorine resistance of the produced spandex yarn was evaluated, and the results of the evaluation are shown in Table 1 below.

Example 6

[0051] A spandex yarn was produced in the same manner, except that 2,4-di-tertiary-butylphenyl-4'-hydroxy-3',5'-di-tertiarybutyl benzoate was used as the inorganic chlorine-resistant agent. The chlorine resistance of the produced spandex yarn was evaluated, and the results of the evaluation are shown in Table 1 below.

Comparative Example 1

[0052] A spandex yarn was produced in the same manner, except that an unsymmetrically di-hindered hydroxyphenyl-based compound was used instead of the symmetrically di-hindered hydroxyphenyl-based compound. The chlorine resistance of the produced spandex yarn was evaluated, and the results of the evaluation are shown in Table 1 below.

Comparative Example 2

[0053] A spandex yarn was produced in the same manner, except that the inorganic chlorine-resistant agent was used alone without using the symmetrically di-hindered hydroxyphenyl-based compound. The chlorine resistance of the produced spandex yarn was evaluated, and the results of the evaluation are shown in Table 1 below.

[Table]

	Examples						Comparative Examples	
	1	2	3	4	5	6	1	2
Strength retention rate (%)	91.1	90.3	89.8	87.4	90.7	80.61	59.7	63.8

[0054] As can be seen from the results in Table 1 above, the inventive spandex fibers comprising both the symmetrically di-hindered hydroxyphenyl-based compound and the inorganic chlorine-resistant agent showed significantly high strength retention rates in chlorinated water compared to the conventional spandex fiber comprising either the symmetrically di-hindered hydroxyphenyl-based compound alone or the inorganic chlorine-resistant agent alone.

[0055] Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

Claims

1. A spandex fiber having excellent chlorine resistance, which contains, based on the polyurethane solid content, 0.1-5 wt% of a symmetrically di-hindered hydroxyphenyl-based compound and 0.1-10 wt% of an inorganic chlorine-resistant agent.
2. The spandex fiber of claim 1, wherein the symmetrically di-hindered hydroxyphenyl-based compound is one or more selected from the group consisting of tetrakis [methylene-2-(3,5-di-tertiary-butyl-4-hydroxyphenyl) propionate]methane, tris(3,5-di-tertiary-butyl-4-hydroxy-5-methylphenyl) propionate, 3,3',3'',5,5',5''-hexa-tetra-butyl-a,a',a''-(mesitylene-2,4,6-trile)tri-p-cresol, hexamethylenbis[3-(3,5-di-tertiary-butyl-4-hydroxyphenyl) propionate], 1,2-bis(3,5-di-tertiary-butyl-4-hydroxyhydroxyamyl)hydrazine, N,N'-hexamethylenbis(3,5-di-tertiary-butyl-4-hydroxy-hydrocinnamides), and 2,4-di-tertiary-butylphenyl-4'-hydroxy-3',5'-di-tertiary-butyl benzoate.
3. The spandex fiber of claim 1, wherein the inorganic chlorine-resistant agent is one or more selected from the group consisting of a hydrotalcite compound, a mixture of huntite and hydromagnesite, hydromagnesite, zinc oxide, and magnesium oxide.
4. The spandex fiber of claim 3, wherein the hydrotalcite compound is one or more selected from the group consisting of $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{CO}_3 \cdot 3.5\text{H}_2\text{O}$, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 5\text{H}_2\text{O}$, $\text{Mg}_8\text{Al}_2(\text{OH})_{20}\text{CO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Mg}_4\text{Al}_2(\text{OH})_{12}\text{CO}_3 \cdot 3\text{H}_2\text{O}$, $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}\text{CO}_3$, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$, $\text{Mg}_8\text{Al}_2(\text{OH})_{20}\text{CO}_3$, $\text{Mg}_4\text{Al}_2(\text{OH})_{20}\text{CO}_3$, $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{13}(\text{CO}_3)_{0.6}\text{O}_{0.4}$, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3)_{0.7}\text{O}_{0.3}$, $\text{Mg}_{4.5}\text{Al}_2(\text{OH})_{12.2}(\text{CO}_3)_{0.8}\text{O}_{0.6}$, and $\text{Mg}_4\text{Al}_2(\text{OH})_{12}(\text{CO}_3)_{0.6}\text{O}_{0.4}$.
5. The spandex fiber of claim 3, wherein the hydromagnesite is one or more selected from the group consisting of $\text{Mg}_4(\text{CO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mg}_3(\text{CO}_3)_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, $\text{Mg}_4(\text{CO}_3)_4 \cdot \text{Mg}(\text{OH})_2$, $\text{Mg}_3(\text{CO}_3)_3 \cdot \text{Mg}(\text{OH})_2$, and MgCO_3 .
6. The spandex fiber of claim 1, wherein the inorganic chlorine-resistant agent is coated with at least one coating agent selected from the group consisting of aliphatic alcohols, fatty acids, fatty acid salts, fatty acid esters, phosphoric acid esters, styrene/maleic acid anhydride copolymers and derivatives thereof, silane coupling agents, titanate coupling agents, polyorganosiloxanes, polyorganohydrogensiloxanes and melamine-based compounds.
7. A method for producing a spandex fiber, comprising the steps of:
 - reacting an organic diisocyanate with a diol to prepare a polyurethane precursor, dissolving the polyurethane precursor in an organic solvent, and then reacting the polyurethane precursor with a diamine and a monoamine, thereby preparing a polyurethane solution; and
 - adding, based on the polyurethane solid content, 0.1-5 wt% of a symmetrically di-hindered hydroxyphenyl-based compound and 0.1-10 wt% of an inorganic chlorine-resistant agent, to the polyurethane solution, followed by spinning.
8. The method of claim 1, wherein the inorganic chlorine-resistant agent is one or more selected from the group consisting of a hydrotalcite compound, a mixture of huntite and hydromagnesite, hydromagnesite, zinc oxide, and magnesium oxide.

REFERENCES CITED IN THE DESCRIPTION

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