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(54) THERMOPLASTIC POLYURETHANE ELASTIC FIBER

(57) The present invention addresses the problem of providing a thermoplastic polyurethane elastic fiber having excellent NOx gas-induced yellowing resistance and heat resistance. The present invention relates to a thermoplastic polyurethane elastic fiber characterized by comprising 0.05 wt% to 5.00 wt% of at least one metal compound selected from the group consisting of a metal hydroxide, a metal carbonate, and a metal oxide, wherein the metal compound includes an alkali metal or an alkaline earth metal.

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Description

FIELD

[0001] The present invention relates to a thermoplastic polyurethane elastic fiber.

BACKGROUND

[0002] Polyurethane elastic fibers are commonly used in clothing and sanitary materials. The polyurethane elastic fibers used in clothing and sanitary materials must exhibit both yellowing resistance and heat resistance.

[0003] PTL 1 discloses that using a polyurethane elastic fiber obtained by adding a hindered amine-based compound and dry spinning can improve the resistance to NOx gas yellowing.

[0004] PTL 2 discloses that the NOx gas yellowing resistance of a polyurethane resin can be improved by combined use of a phenol-based antioxidant and a hindered amine-based light stabilizer, a polyester-based compound and a benzotriazole-based light stabilizer.

[0005] PTL 3 discloses that the heat resistance of a polyurethane elastic fiber can be improved by melt spinning a thermoplastic polyurethane resin obtained by reacting a double-terminated isocyanate group prepolymer obtained by reacting a polyol and a diisocyanate, with a double-terminated hydroxyl prepolymer obtained by reacting a polyol, a diisocyanate and a low-molecular-weight diol.

[0006] PTL 4 discloses that the heat resistance of a polyurethane elastic fiber can be improved by combined use of an oil agent composed of polydimethylsiloxane, with a phenol-based antioxidant.

[CITATION LIST]

[PATENT LITERATURE]

[0007]

[PTL 1] Japanese Unexamined Patent Publication No. 2006-342448
[PTL 2] Japanese Unexamined Patent Publication No. 2009-19062
[PTL 3] Japanese Unexamined Patent Publication No. 2006-307409
[PTL 4] Japanese Unexamined Patent Publication No. 2003-20521

SUMMARY

[TECHNICAL PROBLEM]

[0008] References 1 to 4 above do not, however, disclose thermoplastic polyurethane elastic fibers having both NOx gas yellowing resistance and heat resistance.

[0009] In light of the prior art described above, the problem to be solved by the invention is to provide a thermoplastic polyurethane elastic fiber having excellent NOx gas yellowing resistance and heat resistance.

[SOLUTION TO PROBLEM]

[0010] As a result of much ardent research conducted for the purpose of solving the aforementioned problem, the present inventors have completed this invention upon finding, unexpectedly, that the problem can be solved by a thermoplastic polyurethane elastic fiber characterized by comprising 0.05 wt% to 5.00 wt% of at least one metal compound selected from the group consisting of metal hydroxides, metal carbonates and metal oxides, wherein the metal compound includes an alkali metal or alkaline earth metal.

[0011] Specifically, the present invention provides the following.

[1] A thermoplastic polyurethane elastic fiber comprising 0.05 wt% to 5.00 wt% of at least one metal compound selected from the group consisting of metal hydroxides, metal carbonates and metal oxides, wherein the metal compound includes an alkali metal or alkaline earth metal.
[2] The thermoplastic polyurethane elastic fiber according to [1] above, wherein the metal compound includes an alkaline earth metal.
[3] The thermoplastic polyurethane elastic fiber according to [2] above, wherein the alkaline earth metal is magnesium.
[4] The thermoplastic polyurethane elastic fiber according to any one of [1] to [3] above, wherein the metal compound is

magnesium hydroxide.

[5] The thermoplastic polyurethane elastic fiber according to any one of [1] to [4] above, wherein the polyurethane composing the thermoplastic polyurethane elastic fiber is polyurethane polymerized from a polymer polyol, a diisocyanate and a chain extender comprising an active hydrogen compound.

[6] The thermoplastic polyurethane elastic fiber according to [5] above, wherein the chain extender is a diol having a molecular weight of 60 to 120.

[7] The thermoplastic polyurethane elastic fiber according to [5] or [6] above, wherein the diisocyanate is 4,4'-diphenylmethane diisocyanate (MDI).

[8] The thermoplastic polyurethane elastic fiber according to any one of [5] to [7] above, wherein the percentage of hard segments composed of the chain extender and the diisocyanate (the Mh ratio) is 20% to 40%.

[9] The thermoplastic polyurethane elastic fiber according to any one of [5] to [8] above, wherein the total number of moles of the chain extender and the polymer polyol is 1.001-fold to 1.100-fold with respect to the number of moles of the diisocyanate.

[10] The thermoplastic polyurethane elastic fiber according to any one of [1] to [9] above, wherein the total fineness is 160 dtex to 2000 dtex.

[11] The thermoplastic polyurethane elastic fiber according to any one of [1] to [10] above, which is a multifilament.

[12] The thermoplastic polyurethane elastic fiber according to any one of [1] to [11] above, wherein the coefficient of variation of the size unevenness in the yarn length direction is 3.0% to 10.0%.

[13] The thermoplastic polyurethane elastic fiber according to any one of [1] to [12] above, wherein the difference between the maximum size and minimum size in the yarn length direction is 10 dtex to 150 dtex.

[14] The thermoplastic polyurethane elastic fiber according to any one of [1] to [13] above, wherein the outflow start temperature of the thermoplastic polyurethane elastic fiber as determined with a flow tester is 150°C to 220°C.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0012] The thermoplastic polyurethane elastic fiber as one aspect of the invention is a thermoplastic polyurethane elastic fiber having excellent NOx gas yellowing resistance and heat resistance.

DESCRIPTION OF EMBODIMENTS

[0013] An embodiment for carrying out the invention (hereunder referred to as "the embodiment") will now be described in detail. The invention is not limited to the embodiment described below, however, and it may be modified within the scope of the gist thereof.

[Metal compound]

[0014] It is a feature of the thermoplastic polyurethane elastic fiber of the embodiment that it comprises at least one metal compound selected from the group consisting of metal hydroxides, metal carbonates and metal oxides, at 0.05 wt% to 5.00 wt%, preferably 0.10 wt% to 1.00 wt% and more preferably 0.30 wt% to 0.50 wt%. As a result of comprising 0.05 wt% to 5.00 wt% of at least one metal compound selected from the group consisting of metal hydroxides, metal carbonates and metal oxides, excellent NOx gas yellowing resistance and heat resistance are exhibited. The reason why the NOx gas yellowing resistance and heat resistance are improved by comprising 0.05 wt% to 5.00 wt% of at least one metal compound selected from the group consisting of metal hydroxides, metal carbonates and metal oxides is not fully understood, but is conjectured by the present inventors to be as follows. Adding at least one metal compound selected from the group consisting of metal hydroxides, metal carbonates and metal oxides at 0.05 wt% or greater results in effective NOx gas yellowing resistance, while adding it at 5.00 wt% or lower can maintain heat resistance without excessively lowering the polymer ratio in the polyurethane elastic fiber.

[0015] The metal element in the metal compound preferably includes an alkali metal or alkaline earth metal. An alkaline earth metal is more preferably included. The alkaline earth metal is preferably calcium or magnesium, with magnesium being more preferred. If the metal element is an alkali metal or alkaline earth metal then the effect of improving the NOx gas yellowing resistance will be even greater. The reason that NOx gas yellowing resistance can be improved if the metal element of the metal compound is an alkaline earth metal is not fully understood, but is conjectured by the present inventors to be as follows. Because an alkaline earth metal has high electrical charge it readily adsorbs NOx gas, thus reducing attack of NOx gas on the thermoplastic polyurethane elastic fiber, and presumably thereby improves the NOx gas yellowing resistance of the thermoplastic polyurethane elastic fiber.

[0016] The metal compound is especially preferred to be magnesium hydroxide because the effect of improving the NOx gas yellowing resistance will be even greater. The reason that NOx gas yellowing resistance can be improved if the metal compound is magnesium hydroxide is not fully understood, but is conjectured by the present inventors to be as follows.

Presumably the NOx gas yellowing resistance is improved because magnesium hydroxide is a solid base with high base strength, readily reacting with acidic NOx gas.

[Thermoplastic polyurethane]

[0017] For this embodiment, the thermoplastic polyurethane composing the thermoplastic polyurethane elastic fiber is not particularly restricted so long as it has a structure polymerized from a diisocyanate, a polymer polyol, a diol or a diamine, for example, and is thermoplastic. The polymerization method is also not particularly restricted. Examples of thermoplastic polyurethanes include polyurethanes polymerized from a diisocyanate, a polymer polyol, and a low-molecular-weight diamine as a chain extender comprising an active hydrogen compound (also referred to as "polyurethane"), or polyurethanes polymerized from a diisocyanate, a polymer polyol, and a low-molecular-weight diol as a chain extender comprising an active hydrogen compound (also referred to as "polyurethane-urethane"). A trifunctional or greater glycol or isocyanate may also be used in an amount that does not interfere with the effect of the invention. The term "thermoplastic" as used herein means that the compound has a reversible property whereby it can be melted by heating at below its decomposition temperature, exhibiting plastic flow while in the molten state, and then solidified by cooling. A polyurethane resin generally begins to decompose at 230°C or higher.

[Polymer polyol]

[0018] Polymer polyols include, but are not limited to, polymer diols such as polyether-based diols, polyester-based diols and polycarbonate-based diols. From the viewpoint of hydrolysis resistance, the polymer polyol is preferably a polyether-based polyol.

[0019] Examples of polyether-based polyols include polyethylene oxide, polyethylene glycol, polypropylene glycol, polytetramethylene ether glycol, copolymer diols as copolymers of tetrahydrofuran (THF) and neopentyl glycol, and copolymer diols as copolymers of THF and 3-methyltetrahydrofuran. Any of these polyether-based polyols may be used alone, or two or more may be used in combination. From the viewpoint of easily obtaining elastic fiber with excellent elongation, stretch recoverability and heat resistance, the number-average molecular weight of the polymer diol is preferably 1000 to 8000. Preferred polyether-based polyols from the viewpoint of photoembrittlement are polytetramethylene ether glycol, copolymer diols as copolymers of THF and neopentyl glycol, and blends of these polyols.

[Diisocyanate]

[0020] Diisocyanates include aromatic diisocyanates, alicyclic diisocyanates and aliphatic diisocyanates. Examples of aromatic diisocyanates include, but are not limited to, diphenylmethane diisocyanate (also referred to as "MDI") tolylene diisocyanate, 1,4-diisocyanatebenzene, xylylene diisocyanate and 2,6-naphthalene diisocyanate. Examples of alicyclic diisocyanates and aliphatic diisocyanates include methylenebis(cyclohexylisocyanate) (also referred to as "H12MDI"), isophorone diisocyanate, methylcyclohexane 2,4-diisocyanate, methylcyclohexane 2,6-diisocyanate, cyclohexane 1,4-diisocyanate, hexahydroxylylene diisocyanate, hexahydrotolylene diisocyanate and octahydro1,5-naphthalene diisocyanate. These diisocyanates can be used alone, or two or more may be used in combination. From the viewpoint of the stretch recoverability of elastic fiber, in particular, the diisocyanate is preferably an aromatic diisocyanate, and more preferably MDI. Using MDI increases the rigidity and improves the heat resistance, as a cyclic structure is introduced into the polymer skeleton.

[Chain extender]

[0021] The chain extender comprising an active hydrogen compound is preferably one or more selected from the group consisting of low-molecular-weight diamines and low-molecular-weight diols. A chain extender may also be one having both a hydroxyl group and an amino group in the molecule, such as ethanolamine. From the viewpoint of obtaining a thermoplastic polyurethane suitable for melt spinning, the active hydrogen compound is preferably a low-molecular-weight diol.

[0022] Examples of low-molecular-weight diamines as the chain extender comprising an active hydrogen compound include hydrazine, ethylenediamine, 1,2-propanediamine, 1,3-propanediamine, 2-methyl-1,5-pentanediamine, 1,2-diaminobutane, 1,3-diaminobutane, 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, 2,2-dimethyl-1,3-diaminopropane, 1,3-diamino-2,2-dimethylbutane, 2,4-diamino-1-methylcyclohexane, 1,3-pentanediamine, 1,3-cyclohexanediamine, bis(4-aminophenyl)phosphine oxide, hexamethylenediamine, 1,3-cyclohexyldiamine, hexahydrometaphenylenediamine, 2-methylpentamethylenediamine and bis(4-aminophenyl)phosphine oxide.

[0023] Examples of low-molecular-weight diols as the chain extender comprising an active hydrogen compound include ethylene glycol, 1,3-propanediol, 1,4-butanediol, bishydroxyethoxybenzene, bishydroxyethylene terephthalate, 1-

methyl-1,2-ethanediol, 1,6-hexanediol and 1,8-octanediol. These low-molecular-weight diols may be used alone, or two or more may be used in combination.

[0024] The chain extender is preferably a diol with a molecular weight of 60 to 120 from the viewpoint of stretch recoverability of the elastic fiber, and from the viewpoint of improving the heat resistance and NOx gas yellowing resistance. An active hydrogen compound as a diol with a molecular weight of 60 to 120 is preferably ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol or 1,8-octanediol, more preferably 1,3-propanediol, 1,4-butanediol or 1,6-hexanediol, and most preferably 1,4-butanediol.

[Synthesis method for thermoplastic polyurethane]

[0025] The thermoplastic polyurethane may be produced by a process such as a one-shot process or prepolymer process, which may employ a publicly known technique for polyurethane reaction. For a prepolymer process, the polymer polyol and diisocyanate in a molar ratio of preferably 1.0:1.8 to 3.0 and more preferably 1.0:2.0 to 2.5 are added to a reaction tank equipped with a warm water jacket and stirrer under nitrogen purging, and reaction is carried out to obtain a prepolymer with isocyanate groups at both ends. A chain extender is then added to the prepolymer with isocyanate groups at both ends, and chain extension reaction is carried out. Solid-phase polymerization may then be carried out to obtain a polyurethane with a predetermined molecular weight. After uniform mixing of the prepolymer and the chain extender, a cylindrical pipe or a twin-screw extruder may be used for production of a polymer in a continuous or semi-continuous manner, followed by solid-phase polymerization.

[0026] The total number of moles of the chain extender and polymer polyol is preferably 1.001-fold to 1. 100-fold with respect to the number of moles of the diisocyanate in order to allow both heat resistance and NOx gas yellowing resistance to obtained. It is not fully understood why the NOx gas yellowing resistance and heat resistance are improved if the total number of moles of the chain extender and polymer polyol is 1.001-fold to 1. 100-fold with respect to the number of moles of the diisocyanate, but the present inventors conjecture as follows. If the total number of moles of the chain extender and polymer polyol is at least 1.001 times the number of moles of the diisocyanate, then it will be possible to reduce the amount of the intramolecular diisocyanate-derived structure that readily adsorbs NOx gas, thus improving the NOx gas yellowing resistance. If the total number of moles of the chain extender and polymer polyol is 1.100 times or less with respect to the number of moles of the diisocyanate, ligand exchange between the metal salt and the hydroxyl groups of the thermoplastic polyurethane will be less likely to occur, helping to exhibit the resistance of the metal salt against NOx gas yellowing, and consequently improving the NOx gas yellowing resistance. If the total number of moles of the chain extender and polymer polyol is at least 1.001 times the number of moles of the diisocyanate, then the heat resistance will also be improved since the molecular weight of the thermoplastic polyurethane will more easily increase.

[Method for producing thermoplastic polyurethane elastic fiber]

[0027] The spinning method is not particularly restricted so long as the desired properties can be obtained, and examples include a method of loading thermoplastic polyurethane chips into an extruder where they are heated, and melt spinning them, as well as a method of melting chips and then mixing them with a polyisocyanate compound and spinning, or a method of adding a reaction mixture of a prepolymer with isocyanate groups at both ends and an active hydrogen compound to a prepolymer with isocyanate groups at both ends, and continuously spinning without forming chips.

[0028] The polyurethane loaded into the extruder is metered with a metering pump and directed into the spinning head. If necessary, it may be filtered through a wire mesh or glass beads in a spinning head to remove contaminants, and then discharged from a nozzle and air-cooled with a cold air chamber, coated with a treatment agent, and wound up via a Godet roll.

[0029] In the spinning step, the die temperature, cold air speed, cold air temperature, location of convergence and spinning speed are adjusted, and the temperature profile and yarn tension of the filament are strictly controlled. The die temperature is preferably 180°C to 220°C and more preferably 200°C to 210°C. The cold air is provided by a common method of cooling for melt spinning, by contacting air perpendicular to the traveling direction of the yarn from directly below the spinneret, with a cold air speed of preferably 0.2 m/s to 2.0 m/s and more preferably 0.5 m/s to 1.2 m/s, and a cold air temperature of preferably 5°C to 20°C and more preferably 7°C to 15°C. The method of converging multifilaments may be setting a false twisting machine between godet rolls after the nozzle, and propagating twists from below by the strength of twisting, causing the filaments to converge together while controlling the heights of the convergence points. A common false twisting method may be selected, such as air false twisting with an air nozzle, or using a ring false twisting machine for contact with a rotating ring.

[0030] The method for adding at least one metal compound from among metal hydroxides, metal carbonates and metal oxides at 0.05 wt% to 5.00 wt% in the thermoplastic polyurethane elastic fiber of the embodiment is not particularly restricted, and may be, for example, a method of addition while the raw material is charged in, prior to reaction of the prepolymer with the polymer polyol and diisocyanate, a method of addition during the step of chain extension reaction

between the prepolymer and active hydrogen compound, or a method of addition of a master batch comprising the metal compound during spinning.

[0031] The thermoplastic polyurethane elastic fiber of the embodiment may also comprise a polymer other than a polyurethane, or an additive such as an antioxidant, light fastness agent, ultraviolet absorber, gas discoloration inhibitor, dye, activator, delustering agent, pigment or lubricant, so long as the desired effect of the invention is not lost.

[0032] From the viewpoint of reelability and processability for the thermoplastic polyurethane elastic fiber of the embodiment, it may also comprise a treatment agent such as an oil agent. Examples of treatment agents include, but are not limited to, silicone oils such as dimethylsilicone, mineral oils, and combinations of the same. The method of applying the treatment agent is not particularly restricted and may be a method of coating with an oiling roller, for example.

[0033] The proportion of hard segments composed of the chain extender and diisocyanate in the thermoplastic polyurethane elastic fiber of the embodiment (hereunder referred to as "Mh ratio") is preferably 20% to 40%, more preferably 20% to 35% and even more preferably 22% to 30%. An Mh ratio of 20% to 40% can improve both the heat resistance and the NOx gas yellowing resistance. While it is not fully understood why the NOx gas yellowing resistance and heat resistance can be improved if the Mh ratio is 20% to 40%, the present inventors conjecture as follows. With an Mh ratio of 20% or greater, hydrogen bonding between the urethane bonds increases and heat resistance is improved, while the abundance ratio of metal salt near the hard segments also increases, thereby improving the NOx gas yellowing resistance. If the Mh ratio is 40% or lower, then if the diisocyanate includes an aromatic ring this will reduce the amount of aromatic rings that undergo yellowing by adsorption of NOx gas, and will thereby improve the NOx gas yellowing resistance. The calculation method for the Mh ratio will be described in detail below.

[0034] The total fineness of the polyurethane elastic fiber of the embodiment is preferably 160 dtex to 2000 dtex, more preferably 300 dtex to 1500 dtex and even more preferably 600 dtex to 1000 dtex.

[0035] The polyurethane elastic fiber of the embodiment may be either a monofilament or a multifilament, although a multifilament is preferred. When the polyurethane elastic fiber is a multifilament, the number of filaments is preferably 14 to 140.

[0036] The coefficient of variation in the size unevenness in the yarn length direction of the thermoplastic polyurethane elastic fiber of the embodiment is preferably 3.0% to 10.0%, more preferably 3.0% to 9.5% and even more preferably 3.5% to 9.0%. If the coefficient of variation in the size unevenness is 3% to 10% it will be possible to improve both the NOx gas yellowing resistance and the heat resistance. While it is not fully understood why the NOx gas yellowing resistance and heat resistance are improved when the coefficient of variation in the size unevenness is 3.0% to 10.0%, the present inventors conjecture as follows. A coefficient of variation in the size unevenness of 3.0% or greater tends to cause light to undergo diffuse reflection on the fiber surfaces, resulting in non-transparent fibers and low visibility of yellowing inside the fibers, thus resulting in lighter yellowing. If the coefficient of variation in the size unevenness is 10.0% or lower, yarn breakage caused by heating at the finer parts of the fibers is reduced, thus improving the heat resistance. The method for controlling the coefficient of variation in the size unevenness is not particularly restricted so long as the desired properties can be obtained, and for example, it may be a method of widening the aperture of the spinneret used for melt spinning and generating draw resonance, a method of increasing the discharge throughput to generate sharkskin or melt fractures, or a method of changing the degree of cooling during the spinning step to cause swaying of the thread.

[0037] The difference between the maximum size and the minimum size of the thermoplastic polyurethane elastic fiber of the embodiment in the yarn length direction is preferably 10 dtex to 150 dtex, more preferably 15 dtex to 100 dtex and even more preferably 20 dtex to 80 dtex. If the difference between the maximum size and minimum size is 10 dtex to 150 dtex it will be possible to improve both the NOx gas yellowing resistance and the heat resistance. While it is not fully understood why the NOx gas yellowing resistance and heat resistance are improved when the difference between the maximum size and minimum size is 10 dtex to 150 dtex, the present inventors conjecture as follows. A difference between the maximum size and minimum size of 10 dtex or greater tends to cause light to undergo diffuse reflection on the fiber surfaces, resulting in non-transparent fibers and low visibility of yellowing inside the fibers, thus resulting in lighter yellowing. If the difference between the maximum size and minimum size is 150 dtex or lower, yarn breakage caused by heating at the finer parts of the fibers is reduced, thus improving the heat resistance. The method for controlling the size difference is not particularly restricted so long as the desired properties can be obtained, and for example, it may be a method of widening the aperture of the spinneret used for melt spinning and generating draw resonance, a method of increasing the discharge throughput to generate sharkskin or melt fractures, or a method of changing the degree of cooling during the spinning step to cause swaying of the thread.

[0038] The outflow start temperature of the thermoplastic polyurethane elastic fiber of the embodiment, as measured with a flow tester, is preferably 150°C to 220°C and more preferably 150°C to 200°C from the viewpoint of improving the heat resistance and NOx gas yellowing resistance. While it is not fully understood why the heat resistance and NOx gas yellowing resistance can be improved if the outflow start temperature is 150°C to 220°C, the present inventors conjecture as follows. An outflow start temperature of 150°C or higher reduces structural change in the thermoplastic polyurethane by heating, thus improving the heat resistance, while an outflow start temperature of 220°C or lower lowers the viscosity during melting, improving the wettability and resulting in uniform dispersion of the metal salt, thereby improving the NOx

gas yellowing resistance.

EXAMPLES

[0039] The present invention will now be explained in more specific detail through the following Examples and Comparative Examples, with the understanding that the scope of the invention is not limited by the Examples.

[0040] The methods for evaluating the physical properties used in the Examples and Comparative Examples will be explained first.

<Quantitation of constituent components of thermoplastic polyurethane>

[0041] The structure of the chain extender comprising an active hydrogen compound and the diisocyanate forming the thermoplastic polyurethane in the thermoplastic polyurethane elastic fiber was ascertained by NMR. Specifically, NMR was conducted under the following conditions, to determine the structure of the diisocyanate and chain extender. The structure of the diisocyanate and chain extender can be judged from the positions of the peaks in NMR measurement.

Apparatus: Bruker Biospin Avance600
Measurement nucleus: ^{1}H
Resonance frequency: 600 MHz
Number of scans: 256
Measuring temperature: room temperature
Solvent: Deuterated dimethylformamide
Measuring concentration: 1.5 wt%
Chemical shift reference: dimethylformamide (8.0233 ppm)

<Calculation method for ratio of total number of moles of chain extender and polymer polyol with respect to number of moles of diisocyanate (OH/NCO)>

[0042] The OH/NCO ratio of the thermoplastic polyurethane elastic fiber was calculated by the following formula:

$$OH/NCO = \{(Hh + Hs)/4\}/(Hi/x) : \text{Formula (1)}$$

using the integral value of the peak in NMR measurement.

[0043] The symbols in the formula are as follows:

Hh: integral value from methylene groups of active hydrogen compounds adjacent to urethane bonds
Hs: integral value from methylene groups of polymer polyols adjacent to urethane bonds
Hi: integral value from hydrogen compounds in diisocyanate
x: total number of hydrogens of diisocyanate.

<Quantitation method for hard segment ratio (Mh ratio)>

[0044] The Mh ratio for the thermoplastic polyurethane elastic fiber is calculated by solving the following simultaneous equations (2) to (5):

$$Ms = \{Mdo + Mdi(N1 - N0)\}/(N1 - N0 - 1) - 2\,Mdi \quad \text{formula (2)}$$

$$Mh = \{Mda(N1 - 1) + Mdi \times N0\}/(N1 - N0 - 1) + 2\,Mdi \quad \text{formula (3)}$$

$$N0 = 0.03806\,N1^{4} - 0.3997\,N1^{3} + 1.617\,N1^{2} - 2.144\,N1^{1} + 0.8795 \quad \text{formula (4)}$$

$$Mh\ ratio\ (\%) = \{Mh/(Ms + Mh)\} \times 100 \quad \text{formula (5).}$$

[0045] The symbols in the formulas are as follows:

Ms: number-average molecular weight of soft segment portions
Mdo: number-average molecular weight of polymer polyol
Mdi: molecular weight of isocyanate
N1: molar ratio of isocyanate with respect to polymer polyol
N0: molar ratio of unreacted isocyanate with respect to polymer polyol
Mh: number-average molecular weight of hard segment portions
Mda: molecular weight of chain extender (or number-average molecular weight if two or more are used in combination),
Mdi: molecular weight of isocyanate.

<Identification and quantitation of metal compounds>

[0046] The thermoplastic polyurethane elastic fiber may be wrapped around a glass plate and analyzed by XRD (Ultima-IV by Rigaku Corp.), and the chemical composition of the metal compound may be identified by comparing the analyzed spectrum with data from a database. After the metal compound has been identified by XRD, a sample may be prepared by wrapping the thermoplastic polyurethane elastic fiber around a PP film with a hole opened at the center, without any gap, and may be analyzed by XRF (ZSX-100e by Rigaku Corp.), to allow quantitation of the metal compound content from the detected intensity of elements composing the metal compound. If necessary, a calibration curve prepared using the same metal compound may also be used during the quantitation.

<Measurement of thermoplastic polyurethane elastic fiber outflow start temperature>

[0047] The outflow start temperature of the thermoplastic polyurethane elastic fiber is measured using a Model CFT-500D flow tester (product of Shimadzu Corp.). The outflow start temperature of the thermoplastic polyurethane elastic fiber is measured without prior treatment for removal of treatment agents such as oil agents, sampling 1.5 g for each measurement. The die (nozzle) used is one with a diameter of 0.5 mm and a thickness of 1.0 mm, and a 49 N extrusion load is applied with a preheating time of 240 seconds at an initial preset temperature of 120°C, after which the temperature is increased to 250°C at a constant rate of 3°C/min and the stroke length (mm) and temperature curve during that time are determined. As the temperature increases, the polymer in the toner is heated and the polymer begins to flow out from the die. The temperature at that time is recorded as the outflow start temperature.

<Method of measuring coefficient of variation in the size unevenness>

[0048] Measurement of the coefficient of variation in the size unevenness is carried out by adjusting the rotational speeds of two godet rolls so that the thermoplastic polyurethane elastic fiber is stretched two-fold, and setting the apparatus described below between the godet rolls. The outer diameter of the elastic fiber was measured in two mutually vertical directions using a laser, and the ratio between the average deviation and average value for the diagonal length calculated by the Pythagorean theorem was recorded as the coefficient of variation in the size unevenness. The measurement data used were the average values for 50,000 data points, measured at 160 points/sec.

Apparatus: LS9006D (Keyence Corp.)
Measurement: Outer diameter
Minimum display unit: 0.0001 mm
Measuring points: 50,000
Accumulation cycle: × 100

<Size measuring method>

[0049] The size was measured by cutting the thermoplastic polyurethane elastic fiber perpendicularly and observing the thread cross-section with the following apparatus and conditions, calculating the total cross-sectional area of the thread by automatic area measurement and calculating the size per unit length using the following formula (6):

$$d = D \times 1.1\ (g/cm^3) \times 10^6 \qquad \text{formula (6)}$$

{where d is size (dtex) and D is the total cross-sectional area of the thread (cm^2)}.

Apparatus: VHX-7000 (Keyence Corp.)

Lens: VH-Z100R
Magnification: 500x
Method: automatic area measurement
Extraction mode: brightness

<Method of measuring difference between maximum size and minimum size of polyurethane elastic fiber>

[0050] Measurement of the difference between the maximum size and minimum size was conducted by cutting the thermoplastic polyurethane elastic fiber perpendicularly, observing the thread cross-section with the following apparatus and conditions, calculating the total cross-sectional area of the thread by automatic area measurement, and calculating the size per unit length from the difference between the maximum size and minimum size calculated at 10 points according to formula (6) at 5 mm spacings in the yarn length direction.

Apparatus: VHX-7000 (Keyence Corp.)
Lens: VH-Z100R
Magnification: 500x
Method: automatic area measurement
Extraction mode: brightness

<Evaluation of heat resistance>

[0051] The thermoplastic polyurethane elastic fiber was held in a 2-fold stretched state, and the time until yarn breakage while pressed against a heat source at 110°C (seconds to thermal cutting) was evaluated as an index of the heat resistance.

<Evaluation of NOx gas yellowing resistance>

1. ΔYI value

[0052] The thermoplastic polyurethane elastic fiber was used for evaluation of yellowing according to JIS-L-0855: Test method for color fastness against nitrogen oxide gas, and a weak test method. The assessment was made by comparing the yellowness index YI value, measured using a Macbeth colorimeter (Macbeth Co.), with an untreated sample YI0, determining the value of ΔYI according to the following formula (7):

$$\Delta YI = YI - YI0 \qquad \text{formula (7).}$$

[0053] A smaller ΔYI value indicates resistance to yellowing while a larger value indicates greater tendency toward yellowing.

2. Yellowing visibility

[0054] The thermoplastic polyurethane elastic fiber yellowed by the method of 1. above was compared with a color code, and assigned an evaluation score on the following 10-level scale. Specifically, ten 20-year-olds, and two 30-, 40-, 50- and 60-year-olds each (total: 18 individuals) were asked to select a color code most closely matching the color of the yellowed thermoplastic polyurethane elastic fiber, and the average score was recorded as the evaluation score for yellowing visibility. The color code and evaluation scale used were as follows, with a larger evaluation score indicating greater yellowing resistance.

#FFD500: 1 point
#FFD91A: 2 points
#FFDD33: 3 points
#FFE14D: 4 points
#FFE666: 5 points
#FFEA80: 6 points
#FFEE99: 7 points
#FFF2B3: 8 points
#FFF7CC: 9 points

#FFFBE6: 10 points

[0055] The ΔYI value and yellowing visibility evaluations are both evaluations of NOx gas yellowing resistance. Since the yellowing visibility is influenced by visibility to humans while the ΔYI value is not, it is possible to evaluate NOx gas yellowing resistance based on visibility to humans by comparing the yellowing visibility of samples with the same ΔYI value.

[Example 1]

<Synthesis of thermoplastic polyurethane resin>

[0056] A 2400 g portion of polytetramethylene ether diol with a number-average molecular weight of 1800, and 750.78 g of 4,4'-diphenylmethane diisocyanate, were reacted for 3 hours at 60°C while stirring under a dry nitrogen atmosphere, to obtain a polyurethane prepolymer capped at both ends with isocyanate groups. After adding 151.20 g of 1,4-butanediol to the polyurethane prepolymer, the mixture was stirred for 15 minutes to obtain a polyurethane with a viscosity of 2000 poise (30°C).

[0057] It was then poured out onto a TEFLON^{R} tray and annealed for 16 hours in a hot air oven at 110°C with the polyurethane in the tray, to obtain a thermoplastic polyurethane resin.

<Preparation of master batch>

[0058] The obtained thermoplastic polyurethane resin was crushed into powder with a size of about 3 mm using a Model UG-280 crusher by Horai Co. The crushed chips were dried to a moisture content of 100 ppm using a dehumidifying dryer with temperature conditions of 110°C, after which polyurethane resin powder and magnesium hydroxide were loaded into a hopper in a predetermined ratio and melted in an extruder to produce a strand, cooling the strand through a water bath at 20°C, and pelletizing it with an SCF-100 Plastic Processor by Isuzu Chemical Machinery Co., Ltd. to obtain a magnesium hydroxide master batch with 10 wt% of the active ingredient.

<Fabrication of thermoplastic polyurethane elastic fiber>

[0059] The thermoplastic polyurethane resin powder and the magnesium hydroxide master batch were mixed in a weight ratio of 95:5 to obtain magnesium hydroxide-containing polyurethane resin powder, which was measured using a gear pump mounted on the head, pressurized and filtered with a filter, and then discharged at a die temperature of 210°C from a 60-hole nozzle with a diameter of 0.23 mm, with a discharge throughput for 620 dtex. Cold air was then blown from a cold air chamber at a cold air temperature of 15 to 17°C with the cold air speed adjusted to 0.8 to 1.0 m/s, striking the fiber in a perpendicular manner for melt spinning. A ring-shaped false twisting machine was used for propagation of twisting in the multifilament, which was subsequently wound up on a paper pirn while applying a treatment agent composed mainly of polydimethylsiloxane and a mineral oil, to obtain a wound body of a 620 dtex/60 filament thermoplastic polyurethane elastic fiber. The magnesium hydroxide content of the thermoplastic polyurethane elastic fiber was 0.50 wt%, the Mh ratio was 24%, the coefficient of variation in the size unevenness was 4.0%, the OH/NCO ratio was 1.010, the seconds to thermal cutting was ≥600 seconds, the ΔYI value of the thermoplastic polyurethane elastic fiber was 8, the difference between the maximum size and minimum size was 30 dtex, the outflow start temperature was 160°C and the yellowing visibility evaluation was 10 points. The results are shown in Table 1 below.

[Examples 2 to 6]

[0060] Thermoplastic polyurethane elastic fibers were obtained by the same method as Example 1, except that the ratio of the polyurethane resin and the master batch was adjusted to increase the amount of magnesium hydroxide in each polyurethane elastic fiber. The results are shown in Table 1 below.

[Examples 7 to 12]

[0061] Thermoplastic polyurethane elastic fibers were obtained by the same method as Example 1, except that the metal compound was changed to magnesium carbonate (Example 7), magnesium oxide (Example 8), calcium hydroxide (Example 9), calcium carbonate (Example 10), sodium carbonate (Example 11) or potassium carbonate (Example 12). The results are shown in Table 1 below.

[Examples 13 to 17]

[0062] Thermoplastic polyurethane elastic fibers were obtained by the same method as Example 1, except that the chain extender comprising an active hydrogen compound was changed to ethylene glycol (Example 13), 1,3-propanediol (Example 14), 1,6-hexanediol (Example 15), 1,8-octanediol (Example 16) or 1,10-decanediol (Example 17). The results are shown in Table 1 below.

[Examples 18 and 19]

[0063] Thermoplastic polyurethane elastic fibers were obtained by the same method as Example 1, except for using methylenebis(cyclohexylisocyanate) (H12 MDI) (Example 18) and 1,6-hexamethylene diisocyanate (HDI) (Example 19). The results are shown in Table 1 below.

[Examples 20 to 26]

[0064] Thermoplastic polyurethane elastic fibers were obtained by the same method as Example 1, except that the molar ratio of the polymer polyol and diisocyanate was adjusted to increase **or decrease** the Mh ratio of each thermoplastic polyurethane elastic fiber. The results are shown in Table 1 below.

Table 1]

	Metal compound		Chain extender		Diisocyanate	Mh ratio	OH/NCO	Coefficient of variation in size unevenness	Size difference	Total fineness	Outflow start temp.	Seconds to thermal cutting	ΔYI value	Yellowing visibility
	Type	Addition (wt%)	Type	Mol. wt.	Type	(%)		(%)	(dtex)	(dtex)	(°C)	(see)		
Example 1	Magnesium hydroxide	0.50	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 see	8	10
Example 2	Magnesium hydroxide	0.05	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 see	31	5.4
Example 3	Magnesium hydroxide	0.10	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 see	12	9.2
Example 4	Magnesium hydroxide	0.30	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 see	9	10
Example 5	Magnesium hydroxide	1.00	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	553	8	10
Example 6	Magnesium hydroxide	5.00	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	144	8	10
Example 7	Magnesium carbonate	0.50	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 see	12	9.2
Example 8	Magnesium oxide	0.50	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 sec	10	9.1
Example 9	Calcium hydroxide	0.50	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 see	41	3.9
Example 10	Calcium carbonate	0.50	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 see	36	4.4
Example 11	Sodium carbonate	0.50	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 see	45	2.7
Example 12	Potassium carbonate	0.50	1,4-Butane-diol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 see	45	2.8
Example 13	Magnesium hydroxide	0.50	Ethylene glycol	62.07	MDI	24	1.010	4.0	30	620	160	245	9	10

(continued)

	Metal compound		Chain extender		Diisocyanate	Mh ratio	OH/ NCO	Coefficient of variation in size unevenness	Size difference	Total fineness	Outflow start temp.	Seconds to thermal cutting	ΔYI value	Yellowing visibility
	Type	Addition (wt%)	Type	Mol. wt.	Type	(%)		(%)	(dtex)	(dtex)	(°C)	(see)		
Example 14	Magnesium hydroxide	0.50	1,3-Propanediol	76.09	MDI	24	1.010	4.0	30	620	160	478	9	10
Example 15	Magnesium hydroxide	0.50	1,6-Hexanediol	118.17	MDI	24	1.010	4.0	30	620	160	462	9	10
Example 16	Magnesium hydroxide	0.50	1,8-Octanediol	146.23	MDI	24	1.010	4.0	30	620	160	273	9	10
Example 17	Magnesium hydroxide	0.50	1,10-Decanediol	174.28	MDI	24	1.010	4.0	30	620	160	89	9	10
Example 18	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	H12 MDI	24	1.010	4.0	30	620	160	176	9	10
Example 19	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	HDI	24	1.010	4.0	30	620	160	162	9	10
Example 20	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	18	1.010	4.0	30	620	150	213	16	8.8
Example 21	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	20	1.010	4.0	30	620	160	576	9	10
Example 22	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	22	1.010	4.0	30	620	160	≥600 see	9	10
Example 23	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	30	1.010	4.0	30	620	160	≥600 see	9	10
Example 24	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	35	1.010	4.0	30	620	160	≥600 see	14	9.2
Example 25	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	40	1.010	4.0	30	620	160	≥600 see	19	8.4
Example 26	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	45	1.010	4.0	30	620	160	≥600 see	29	6.2

[Examples 27 to 33]

[0065] Thermoplastic polyurethane elastic fibers were obtained by the same method as Example 1, except that the molar ratio of the polymer polyol, diisocyanate and diol was adjusted to change the OH/NCO ratio of each thermoplastic polyurethane elastic fiber. The results are shown in Table 2 below.

[Examples 34 to 41]

[0066] Thermoplastic polyurethane elastic fibers were obtained by the same method as Example 1, except that the spinning temperature, spinneret diameter, discharge throughput, cooling conditions and winding conditions during spinning were adjusted to change the coefficient of variation in the size unevenness of each thermoplastic polyurethane elastic fiber. The results are shown in Table 2 below.

[Examples 42 to 49]

[0067] Thermoplastic polyurethane elastic fibers were obtained by the same method as Example 1, except that the spinning temperature, spinneret diameter, discharge throughput, cooling conditions and winding conditions during spinning were adjusted to change the size difference (maximum size - minimum size) of each thermoplastic polyurethane elastic fiber. The results are shown in Table 2 below.

Table 2]

	Metal compound		Chain extender		Diisocyanate	Mh ratio	OH/NCO	Coefficient of variation in size unevenness	Size difference	Total fineness	Outflow start temp.	Seconds to thermal cutting	ΔYI value	Yellowing visibility
	Type	Addition (wt%)	Type	Mol. wt.	Type	(%)		(%)	(dtex)	(dtex)	(°C)	(see)		
Example 27	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.000	4.0	30	620	160	≥600 see	15	8.8
Example 28	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.001	4.0	30	620	160	≥600 see	13	9.4
Example 29	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.005	4.0	30	620	160	≥600 see	9	10
Example 30	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.030	4.0	30	620	160	≥600 see	9	10
Example 31	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.050	4.0	30	620	160	588	9	10
Example 32	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.100	4.0	30	620	160	571	13	9.1
Example 33	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.500	4.0	30	620	160	469	19	8.1
Example 34	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	1.0	10	620	160	≥600 see	23	4.3
Example 35	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	3.0	20	620	160	≥600 see	12	8
Example 36	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	3.5	24	620	160	≥600 see	9	10
Example 37	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	5.0	35	620	160	≥600 see	9	10
Example 38	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	9.0	60	620	160	≥600 see	9	10
Example 39	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	9.5	64	620	160	563	9	10

(continued)

	Metal compound		Chain extender		Diisocyanate	Mh ratio	OH/NCO	Coefficient of variation in size unevenness	Size difference	Total fineness	Outflow start temp.	Seconds to thermal cutting	ΔYI value	Yellowing visibility
	Type	Addition (wt%)	Type	Mol. wt.	Type	(%)		(%)	(dtex)	(dtex)	(°C)	(see)		
Example 40	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	10.0	66	620	160	477	8	10
Example 41	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	150	98	620	160	391	8	10
Example 42	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	3.5	5	620	160	≥600 see	8	4.9
Example 43	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	3.5	10	620	160	≥600 see	8	8.2
Example 44	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.0	20	620	160	≥600 see	8	10
Example 45	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.5	30	620	160	≥600 see	8	10
Example 46	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	5.0	80	620	160	≥600 see	8	10
Example 47	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	7.0	100	620	160	≥600 see	8	10
Example 48	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	8.0	148	620	160	560	8	10
Example 49	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	9.0	199	620	160	478	8	10

[Examples 50 to 54]

[0068] Thermoplastic polyurethane elastic fibers were obtained by the same method as Example 1, except that the molecular weight of the thermoplastic polyurethane was changed by adjusting the molecular weight of the polymer polyol, to change the outflow start temperature of each thermoplastic polyurethane elastic fiber. The results are shown in Table 3 below.

[Comparative Example 1]

[0069] A thermoplastic polyurethane elastic fiber was obtained by the same method as Example 1, except that no metal compound was added. The results are shown in Table 3 below.

[Comparative Example 2]

[0070] A thermoplastic polyurethane elastic fiber was obtained by the same method as Example 1, except that the amount of master batch added was adjusted to change the amount of magnesium hydroxide in the polyurethane elastic fiber to 10.0 wt%. The results are shown in Table 3 below.

[Comparative Examples 3 to 6]

[0071] Thermoplastic polyurethane elastic fibers were obtained by the same method as Example 1, except that the metal compound was changed to magnesium stearate (Comparative Example 3), calcium stearate (Comparative Example 4), zinc oxide (Comparative Example 5) or aluminum hydroxide (Comparative Example 6). The results are shown in Table 3 below.

Table 3]

	Metal compound		Chain extender		Diisocyanate	Mh ratio	OH/NCO	Coefficient of variation in size unevenness	Size difference	Total fineness	Outflow start temp.	Seconds to thermal cutting	ΔYI value	Yellowing visibility
	Type	Addition (wt%)	Type	Mol. wt.	Type	(%)		(%)	(dtex)	(dtex)	(°C)	(see)		
Example 50	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	140	512	9	10
Example 51	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	150	≥600 see	9	10
Example 52	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	200	≥600 see	9	10
Example 53	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	220	≥600 see	12	9.4
Example 54	Magnesium hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	225	570	13	9.1
Comp. Example 1	None	0	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 sec	55	1.4
Comp. Example 2	Magnesium hydroxide	10.00	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	160	Immediate yarn breakage	9	10
Comp. Example 3	Magnesium stearate	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 sec	54	1.3
Comp. Example 4	Calcium stearate	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 sec	55	1.4
Comp. Example 5	Zinc oxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 sec	56	1.2

(continued)

	Metal compound		Chain extender		Diisocyanate	Mh ratio	OH/NCO	Coefficient of variation in size unevenness	Size difference	Total fineness	Outflow start temp.	Seconds to thermal cutting		ΔYI value	Yellowing visibility
	Type	Addition (wt%)	Type	Mol. wt.	Type	(%)		(%)	(dtex)	(dtex)	(°C)	(see)			
Comp. Example 6	Aluminum hydroxide	0.50	1,4-Butanediol	90.12	MDI	24	1.010	4.0	30	620	160	≥600 sec		54	1.3

INDUSTRIAL APPLICABILITY

[0072] The thermoplastic polyurethane elastic fiber of the invention can be suitably used in clothing such as inner wear, stockings or compression wear, or as a gather member or in sanitary materials such as diapers.

Claims

1. A thermoplastic polyurethane elastic fiber comprising 0.05 wt% to 5.00 wt% of at least one metal compound selected from the group consisting of metal hydroxides, metal carbonates and metal oxides, wherein the metal compound includes an alkali metal or alkaline earth metal.

2. The thermoplastic polyurethane elastic fiber according to claim 1, wherein the metal compound includes an alkaline earth metal.

3. The thermoplastic polyurethane elastic fiber according to claim 2, wherein the alkaline earth metal is magnesium.

4. The thermoplastic polyurethane elastic fiber according to any one of claims 1 to 3, wherein the metal compound is magnesium hydroxide.

5. The thermoplastic polyurethane elastic fiber according to any one of claims 1 to 3, wherein the polyurethane composing the thermoplastic polyurethane elastic fiber is polyurethane polymerized from a polymer polyol, a diisocyanate and a chain extender comprising an active hydrogen compound.

6. The thermoplastic polyurethane elastic fiber according to claim 5, wherein the chain extender is a diol having a molecular weight of 60 to 120.

7. The thermoplastic polyurethane elastic fiber according to claim 5, wherein the diisocyanate is 4,4'-diphenylmethane diisocyanate (MDI).

8. The thermoplastic polyurethane elastic fiber according to claim 5, wherein the percentage of hard segments composed of the chain extender and the diisocyanate (the Mh ratio) is 20% to 40%.

9. The thermoplastic polyurethane elastic fiber according to claim 5, wherein the total number of moles of the chain extender and the polymer polyol is 1.001-fold to 1. 100-fold with respect to the number of moles of the diisocyanate.

10. The thermoplastic polyurethane elastic fiber according to any one of claims 1 to 3, wherein the total fineness of the thermoplastic polyurethane elastic fiber is 160 dtex to 2000 dtex.

11. The thermoplastic polyurethane elastic fiber according to any one of claims 1 to 3, which is a multifilament.

12. The thermoplastic polyurethane elastic fiber according to any one of claims 1 to 3, wherein the coefficient of variation in the size unevenness in the yarn length direction is 3.0% to 10.0%.

13. The thermoplastic polyurethane elastic fiber according to any one of claims 1 to 3 above, wherein the difference between the maximum size and minimum size in the yarn length direction is 10 dtex to 150 dtex.

14. The thermoplastic polyurethane elastic fiber according to any one of claims 1 to 3, wherein the outflow start temperature of the thermoplastic polyurethane elastic fiber as determined with a flow tester is 150°C to 220°C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/015215

A. CLASSIFICATION OF SUBJECT MATTER

D01F 6/94(2006.01)i; ***D01F 6/70***(2006.01)i
FI: D01F6/94 A; D01F6/70 B

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)

D01F6/94; D01F6/70; C08K3/00-13/08; C08L1/00-101/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2012-132130 A (TORAY OPELONTEX CO LTD) 12 July 2012 (2012-07-12) claim 1, paragraphs [0031], [0040], [0059]	1-14
Y	JP 2014-95162 A (ASAHI KASEI FIBERS CORP) 22 May 2014 (2014-05-22) claims 1, 2, paragraphs [0033], [0044]	1-14
Y	JP 2022-514184 A (THE LYCRA COMPANY UK LTD) 10 February 2022 (2022-02-10) claims 1, 2, 8, 9, paragraph [0027]	1-14
Y	JP 2003-268629 A (NISSHINBO IND INC) 25 September 2003 (2003-09-25) claims	1-14
Y	JP 2005-48316 A (NISSHINBO IND INC) 24 February 2005 (2005-02-24) claims, paragraph [0046], example 1	1-14
Y	JP 2006-28453 A (NISSHINBO IND INC) 02 February 2006 (2006-02-02) claims, paragraphs [0061], [0065], examples 7, 8	1-14
A	JP 2003-113303 A (TOYO BOSEKI) 18 April 2003 (2003-04-18) claims, paragraph [0001]	1-14

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

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Date of the actual completion of the international search	Date of mailing of the international search report
12 June 2023	**20 June 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/015215

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2019/103013 A1 (ASAHI KASEI KABUSHIKI KAISHA) 31 May 2019 (2019-05-31) claims	1-14

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/015215

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2012-132130 A	12 July 2012	(Family: none)	
JP 2014-95162 A	22 May 2014	(Family: none)	
JP 2022-514184 A	10 February 2022	WO 2020/102044 A1 claims 1, 2, 8, 9, paragraph [0027] US 2021/0395921 A1 EP 3880874 A1 CN 112996955 A KR 10-2021-0088703 A TW 202031947 A BR 112021009097 A	
JP 2003-268629 A	25 September 2003	(Family: none)	
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