**(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)**

**(19) World Intellectual Property Organization**
International Bureau

**(43) International Publication Date**
**30 May 2024 (30.05.2024)**

**(10) International Publication Number**
**WO 2024/110903 A1**

**(51) International Patent Classification:**
*C08G 18/48* (2006.01) *C08G 18/75* (2006.01)
*C08G 18/08* (2006.01) *C08G 18/76* (2006.01)
*C08G 18/32* (2006.01) *C08L 65/00* (2006.01)
*C08G 18/66* (2006.01) *D01F 6/70* (2006.01)

**(21) International Application Number:** PCT/IB2023/061811

**(22) International Filing Date:** 22 November 2023 (22.11.2023)

**(25) Filing Language:** English

**(26) Publication Language:** English

**(30) Priority Data:**
2022-188027 25 November 2022 (25.11.2022) JP

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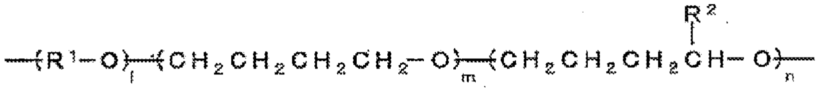
**(81) Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

**(84) Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Published:**
— *with international search report (Art. 21(3))*

**(54) Title:** POLYURETHANE ELASTIC FIBER



$$-\left(R^1-O\right)_l-\left(CH_2CH_2CH_2CH_2-O\right)_m-\left(CH_2CH_2CH_2\overset{\overset{R^2}{|}}{C}H-O\right)_n-$$

(1)

**(57) Abstract:** To provide a highly durable polyurethane elastic fiber having high stress during shrinkage, that is, recovery stress, as well as excellent antioxidative properties. A polyurethane elastic fiber comprising a polyurethane having a polyether structure in its backbone and a nitrogen-containing aromatic compound, wherein the polyether structure is represented by the following general formula (1), and the polyurethane elastic fiber contains no less than 0.05% by mass to no more than 2.0% by mass of the nitrogen-containing aromatic compound Formula (I) ($R^1$ is an alkylene group having 2 to 6 carbon atoms, $R^2$ is an alkyl group having 1 to 2 carbon atoms, and l, m, and n satisfy $4 \leq n/(l+m+n) \times 100 \leq 50$)

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# SPECIFICATION

[Title of Invention] POLYURETHANE ELASTIC FIBER

[Technical Field]

The present invention relates to a polyurethane resin composition and a polyurethane elastic fiber and particularly relates to a polyurethane elastic fiber having high stress during shrinkage, that is, high recovery stress, as well as excellent antioxidative properties and high durability.

[Background Art]

Polyurethane resins have excellent stretchability and thus are widely deployed in paint, coating agents, sealing materials, glues, adhesives, fiber processing agents, artificial leathers and synthetic leathers, raw materials for elastomers such as rollers, fiber products, and the like. In each application, in order to prevent deterioration due to thermal history when producing or processing a final product using polyurethane resin as a raw material and to improve the durability of the final product, improvements in heat resistance while maintaining stretchability (high elastic recovery and a high degree of elongation) of polyurethane resin are required.

Polyurethane elastic fibers are widely used in stretchable clothing applications such as legwear, innerwear, and sportswear and in industrial materials due to their excellent stretchability.

Similarly, polyurethane elastic fibers are required to have high elastic recovery, high strength and degree of elongation, high heat resistance, and thermosetting properties. In particular, the improvement of recovery stress has consistently been sought after in regard to elastic recovery performance.

Furthermore, in regard to heat resistance, while heat embrittlement resistance improves when the melting point is increased, because the required thermosetting properties decrease particularly when making fibers, compositions with high oxidizing properties have been required for fibers having large surface areas.

It is known that a polyurethane structure composed of a diisocyanate and a copolyether diol of tetrahydrofuran and 3-alkyl tetrahydrofuran may be a soft segment having higher stress during shrinkage, that is, higher recovery stress, than the former (patent documents 1 and 2).

Furthermore, in terms of heat resistance and thermal aging resistance, examples in which an antioxidant effect is specifically exhibited when an appropriate amount of a nitrogen-containing aromatic compound is contained in a polyurethane elastic fiber have been disclosed (patent documents 3 and 4).

Moreover, in recent years, with growing interest in various environmental issues, there has been a demand for initiatives oriented toward a transition to a sustainable society for all organic materials, and polyurethane elastic fibers, which are contained at a relatively low content in expandable members, are no exception. Since the content in stretchable clothing and industrial materials is relatively low, it is difficult to separate and remove such, making it difficult to recycle resources, and thermal recycling may be preferable. Therefore, the use of components derived from carbon-neutral biomass resources as raw materials has been proposed (patent documents 5 and 6).

[Prior Art Documents]

[Patent Documents]

[Patent Document 1] JP H2-19511 A

[Patent Document 2] JP H9-136937 A

[Patent Document 3] JP 2008-69506 A

[Patent Document 4] WO 2009/011189

[Patent Document 5] JP 2014-522446 A (Translation of PCT Application)

[Patent Document 6] JP 2021-152139 A

[Summary of Invention]

[Problem to Be Solved by Invention]

However, recovery stress or antioxidative properties are insufficient with these conventional techniques. Thus, there is demand for a polyurethane resin composition and a polyurethane elastic fiber having high recovery stress and excellent antioxidative properties.

A problem of the present invention is to provide a high durability polyurethane resin composition and a polyurethane elastic fiber having high stress during shrinkage, that is, high recovery stress, as well as excellent antioxidative properties.

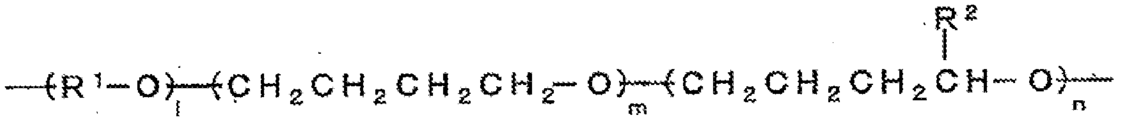
[Means for Solving Problem]

In order to solve said problem, the present inventors examined cases wherein an alkyl group is present on a carbon atom adjacent to an ether group in a tetramethylene ether. That is, this is a polyurethane structure composed of a diisocyanate and a copolyether diol of tetrahydrofuran and 2-alkyl tetrahydrofuran. As a result, it was found that a 2-alkyl group had higher recovery stress than a 3-alkyl group in the polyurethane resin composition and in the polyurethane elastic fiber. Furthermore, the present inventors found that, compared to a 3-alkyl group, a completely different heat resistant behavior is exhibited when using a 2-alkyl group. In other words, it was found that in the case of a 2-alkyl group, a nitrogen-containing aromatic compound maximizes heat resistance at a specific added amount. These phenomena are thought to be due to the fact that when an alkyl group is present on a carbon atom adjacent to an ether group in a tetramethylene ether, the steric hindrance of the alkyl group is more dominant in the 2-alkyl group than in the 3-alkyl group, and from the perspective of antioxidation, when an alkyl group is present on a carbon atom adjacent to an ether group, cleavage of the ether oxygen and the adjacent carbon can be suppressed. Thus, it was found that a polyurethane resin composition and a high durability polyurethane elastic fiber having high recovery stress and excellent antioxidative properties may be obtained. As a result, since both high heat resistance and high durability are provided even when the melting point is low and heat setting is high, low-temperature processing is possible, and energy conservation is possible with respect to environmental problems. Moreover, conventionally, the use of components derived from carbon-neutral biomass resources suitable for thermal recycling as raw materials has been proposed (patent documents 5 and 6). However, it is unreasonable to use a raw material having a new or a special chemical structure that has not been widely used thus far, and it is important to use a non-petrochemical having a known chemical structure that is a biomass raw material, that is, a biomass monomer.

In short, the present invention has a configuration such as that below.

(1) A polyurethane elastic fiber provided with a polyurethane having a polyether structure in its backbone and a nitrogen-containing aromatic compound, wherein
the polyether structure satisfies the following general formula (1),
and the polyurethane elastic fiber contains no less than 0.05% by mass to no more than 2.0% by mass of the nitrogen-containing aromatic compound.

[Formula 1]



$$-(R^1-O)_l-(CH_2CH_2CH_2CH_2-O)_m-(CH_2CH_2CH_2\overset{\overset{R^2}{|}}{C}H-O)_n- \qquad (1)$$

($R^1$is an alkylene group having 2 to 6 carbon atoms, $R^2$is an alkyl group having 1 to 2 carbon atoms, and l, m, and n satisfy $4 \leq n/(l+m+n) \times 100 \leq 50$)

(2) The polyurethane elastic fiber of (1), wherein l, m, and n in the foregoing general formula (1) satisfy $6 \leq n/(l + m + n) \times 100 \leq 16$.

(3) The polyurethane elastic fiber of (1) or (2), wherein the polyurethane elastic fiber contains no less than 0.2% by mass to no more than 0.8% by mass of the nitrogen-containing aromatic compound.

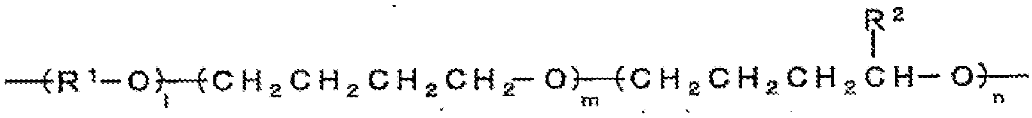
(4) The polyurethane elastic fiber of any of (1) to (3), wherein, when n' is defined as the number of $-(CH_2CH_2CH_2CHR^2\text{-}O)n-$ in the foregoing general formula (1) at terminals, $5 \leq n'/(l+m+n) \times 100 \leq 30$ is satisfied.

(5) The polyurethane elastic fiber of any of (1) to (4), wherein the number average molecular weight of the moiety of the foregoing general formula (1) is no less than 3,000 to no more than 30,000.

(6) The polyurethane elastic fiber of any of (1) to (5), wherein the bio-conversion rate by carbon isotope ratio measurement established in ISO 16620-2 is 3% or more in a carbon mass ratio.

(7) An article comprising a polyurethane elastic fiber having a polyether structure in its backbone

and a nitrogen-containing aromatic compound, wherein
the polyether structure is represented by the following general formula (1),
and the polyurethane elastic fiber contains no less than 0.05% by mass to no more than 2.0% by mass of the nitrogen-containing aromatic compound
[Formula 1]



$$-\left(R^1-O\right)_l-\left(CH_2CH_2CH_2CH_2-O\right)_m-\left(CH_2CH_2CH_2\overset{\overset{R^2}{|}}{C}H-O\right)_n- \qquad (1)$$

($R^1$ is an alkylene group having 2 to 6 carbon atoms, $R^2$ is an alkyl group having 1 to 2 carbon atoms,
and l, m, and n satisfy $4 \leq n/(l+m+n) \times 100 \leq 50$ ).

(8) The article of claim 7, wherein the article is selected from the group consisting of a fiber, a fabric, a film, and combinations thereof.
(9) The article of claim 8, wherein the fabric is selected from a knit, a woven, and a nonwoven.
[Effect of Invention]

According to the present invention, it is possible to provide a high durability polyurethane elastic fiber having high stress during shrinkage, that is, high recovery stress, as well as excellent antioxidative properties.

[Description of Embodiments]

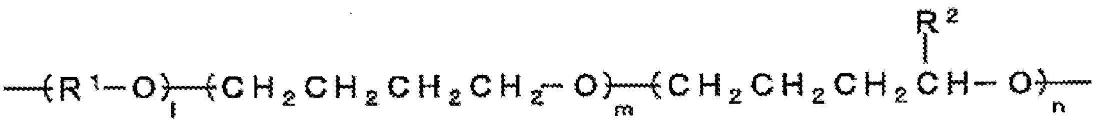
The present invention will be described in detail below along with embodiments.

First, the polyurethane used in the polyurethane resin composition and the polyurethane elastic fiber of the present invention will be described. The polyurethane described herein is preferably used as a main component, and the term main component as described herein is a component contained in the polyurethane resin composition the polyurethane elastic fiber in an amount exceeding 50% by mass.

The polyurethane used in the present invention has a polyether structure in its backbone. The polyurethane having a polyether structure in its backbone has a structure in which a polymer diol having a polyether structure and a diisocyanate serve as the starting material. Here, the phrase "having a structure in which...serve as starting material" refers to the structure of the relevant portion of the starting material in order to describe its backbone structure of the polymer, and the starting material and synthesis method thereof are not particularly limited. That is, the starting material may be, for example, a polyurethane urea composed of a polymer diol, a diisocyanate, and a low molecular weight diamine as a chain extender, or may be a polyurethane urethane composed of a polymer diol, a diisocyanate, and a low molecular weight diol as a chain extender. Furthermore, polyurethane urea, which uses a compound having a hydroxyl group and an amino group in the molecule, may be used as a chain extender. It is also preferable that trifunctional or higher polyfunctional glycols, isocyanates, and the like be used to the extent that they do not impede the effects of the present invention. Furthermore, the processing method is not particularly limited either. That is, the polyurethane may be recycled through remolding and re-spinning.

In the present invention, the polyether structure of a polymer diol having a polyether structure satisfies the following general formula (1).

[Formula 2]



$$-\!\!(R^1-O)_l\!\!-\!\!(CH_2CH_2CH_2CH_2-O)_m\!\!-\!\!(CH_2CH_2CH_2\overset{R^2}{\overset{|}{C}}H-O)_n\!\!- \quad (1)$$

($R^1$is an alkylene group having 2 to 6 carbon atoms, $R^2$is an alkyl group having 1 to 2 carbon atoms, and l, m, and n satisfy $4 \leq n/(l+m+n) \times 100 \leq 50$)

Furthermore, when l, m, and n in the foregoing general formula (1) satisfy $6 \leq n/(l+m+n) \times 100 \leq 16$, it is preferable because the balance between stress during extension and stress during extension recovery is favorable, and the same characteristics are obtained in a smaller amount of modified tetramethylene ether units as compared to conventional techniques equivalent to modified tetramethylene ether units ($CH_2CH_2CH_2CHR^2$-O), for example, ($CH_2CH_2CHRCH_2$-O). In general formula (1), l, m and n represent only the ratio. That is, respective units are not limited to only block bodies having l, m, and n as repeating units, but respective units may be random bodies connected at random.

In a case wherein $5 \leq n'/(l+m+n) x 100 \leq 30$ is satisfied when n' is defined as the number of -($CH_2CH_2CH_2CHR^2$-O)n- in the foregoing general formula (1) at terminals of the foregoing general formula (1), it is preferable because the balance between stress during extension and stress during extension recovery is more favorable, and durability, that is, resistance to thermal oxidation degradation, resistance to ultraviolet degradation, resistance to chlorine degradation, and a combined resistance to these is improved due to a synergistic action with the nitrogen-containing aromatic compound.

It is also preferable that $R^1$ take carbon atoms in a number other than 4, such as 2, 3, 5, or 6. In the case of 2, water vapor permeability increases, and moisture absorption and water absorption functions are imparted, while in the case of 6, hydrophobicity is imparted. In the case of odd carbon numbers of 3 and 5, crystals during elongation (strain-induced crystals) in the soft segment may be suppressed, thereby contributing to elongation recovery.

Furthermore, it is preferable that THF and 2-MeTHF, which are the raw materials for structural units of $(CH_2CH_2CH_2CH_2\text{-}O)$ and $(CH_2CH_2CH_2CHR^2\text{-}O)$, be used as the raw materials for components derived from carbon-neutral biomass resources suitable for thermal recycling. In such a case, the degree to which components derived from biomass resources are used as raw materials is expressed as the bio-conversion rate. The bio-conversion rate can be obtained using ISO 16620-2, which is a radiocarbon (carbon-14) concentration measurement identification method. In the present invention, the radioactive carbon (carbon-14) concentration measurement identification method of ISO 16620-2 described above may be simply referred to as carbon isotope ratio measurement. It is preferable that the polyurethane resin composition and polyurethane elastic fiber of the present invention have a bio-conversion rate of 3% or more in carbon mass ratio as determined by carbon isotope ratio measurement.

It is also preferable that the other polymer diol contains a polyether-based, polyester-based diol, polycarbonate diol, or the like. Furthermore, a polyether-based diol is particularly preferably used from the perspective of imparting flexibility and elongation to a molded body obtained from the polyurethane resin composition of the present invention and to a polyurethane elastic fiber obtained from the polyurethane resin composition of the present invention. Furthermore, two or more types of these polymer diols may be used in combination.

In terms of the molecular weight of the polymer diol, the number average molecular weight is preferably 1,000 or more and more preferably 3,000 or more from the perspective of obtaining elongation, strength, heat resistance, and the like when made into an elastic fiber. By using a polyol having a molecular weight in this range, an elastic fiber having excellent elongation, strength, and heat resistance can be obtained. Furthermore, a polyol having a number average molecular weight of 30,000 or less is preferable, and 6,000 or less is more preferable. By using a polyol having a molecular weight in this range, an elastic fiber having excellent elongation, elastic recovery capabilities, heat resistance, and durability due to synergistic effects with a nitrogen-containing aromatic compound can be obtained.

Next, as the diisocyanate, aromatic diisocyanates such as diphenylmethane diisocyanate (hereinafter also abbreviated as MDI), tolylene diisocyanate, benzene 1,4-diisocyanate, xylylene diisocyanate, 2,6-naphthalene diisocyanate, and the like are suitable for synthesizing polyurethane having particularly high heat resistance and strength. Furthermore, as the alicyclic diisocyanate, for example, methylenebis(cyclohexyl isocyanate), isophorone diisocyanate, methylcyclohexane 2,4-diisocyanate, methylcyclohexane 2,6-diisocyanate, cyclohexane 1,4-diisocyanate, hexahydroxylylene diisocyanate, hexahydrotolylene diisocyanate, octahydro 1,5-naphthalene diisocyanate, and the like are preferable. Alicyclic diisocyanates may be particularly effectively used to suppress yellowing of molded articles obtained from the polyurethane resin composition of the present invention and polyurethane elastic fibers obtained from the polyurethane resin composition of the present invention. Furthermore, these diisocyanates may be used alone, or two or more types may be combined. Hereinafter, a molded article obtained from the polyurethane resin composition may be referred to as a polyurethane resin molded article.

Next, it is preferable that at least one type of low molecular weight diamine or low molecular weight diol be used as the chain extender used in synthesizing the polyurethane. Note that a type having both a hydroxyl group and an amino group in one molecule, such as ethanolamine, may also be used.

Examples of preferable low molecular weight diamines include ethylenediamine, 1,2-propanediamine, 1,3-propanediamine, hexamethylenediamine, p-phenylenediamine, p-xylylenediamine, m-xylylenediamine, p,p'-methylenedianiline, 1,3-cyclohexyldiamine, hexahydrometaphenylenediamine, 2-methylpentamethylenediamine, bis(4-aminophenyl)phosphine oxide, and the like. It is preferable to use one or two or more of these. Ethylenediamine is particularly preferable. By using ethylenediamine, an elastic fiber having excellent elongation, elastic recovery, and heat resistance can be easily obtained. A triamine compound capable of forming a cross-linked structure in these chain extenders; for example, diethylenetriamine and the like may be added to such an extent that the effect is not lost.

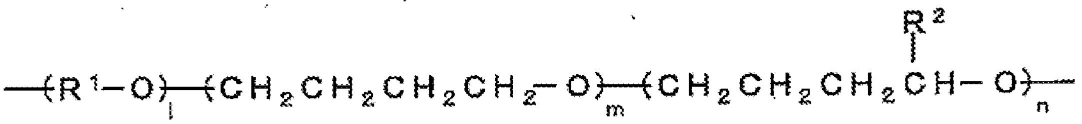
Furthermore, typical examples of low molecular weight diols include ethylene glycol, 1,3-propanediol, 1,4-butanediol, bishydroxyethoxy benzene, bishydroxyethylene terephthalate, and 1-methyl-1,2-ethanediol. It is preferable to use one or two or more of these. Particularly preferably, ethylene glycol, 1,3-propanediol, and 1,4-butanediol are used. When these are used, heat resistance increases as a polyurethane having diol elongation, and a polyurethane resin molded article and an elastic fiber having higher strength can be obtained.

Furthermore, the molecular weight of the polyurethane in the present invention is preferably within a range of no less than 30,000 to no more than 150,000 in terms of the number average molecular weight from the perspective of obtaining a polyurethane resin molded article and polyurethane elastic fiber having high durability and strength. Note that the molecular weight is measured by GPC and converted using polystyrene.

It is also preferable that one type or two or more types of terminal blocking agents in combination be used in the polyurethane. Preferable examples of terminal blocking agents include: monoamines such as dimethylamine, diisopropylamine, ethylmethylamine, diethylamine, methylpropylamine, isopropylmethylamine, diisopropylamine, butylmethylamine, isobutylmethylamine, isopentylmethylamine, dibutylamine, and diamylamine; monools such as ethanol, propanol, butanol, isopropanol, allyl alcohol, and cyclopentanol, and monoisocyanates such as phenyl isocyanate.

The polyurethane resin composition and polyurethane elastic fiber of the present invention contain no less than 0.05% by mass to no more than 2.0% by mass of a nitrogen-containing aromatic compound. This synergistically exhibits high durability with polyurethane having the polyether structure of the foregoing general formula (1) in its backbone, in particular, high durability with excellent antioxidative properties.

[Formula 3]



$$-\left(R^1-O\right)_l\left(CH_2CH_2CH_2CH_2-O\right)_m\left(CH_2CH_2CH_2\overset{\overset{\displaystyle R^2}{|}}{C}H-O\right)_n- \qquad (1)$$

($R^1$is an alkylene group having 2 to 6 carbon atoms, $R^2$is an alkyl group having 1 to 2 carbon atoms, and l, m, and n satisfy $4 \leq n/(l+m+n) \times 100 \leq 50$)

When the content of the nitrogen-containing aromatic compound is less than 0.05% by mass, there is a risk that durability of the polyurethane resin molded article and the polyurethane elastic fiber will be insufficient, and when the content exceeds 2.0% by mass, a reduction in heat resistance of the polyurethane resin molded article and the polyurethane elastic fiber will be pronounced, and there is a risk that yellowing resistance will be reduced.

A value of no less than 0.05% by weight to no more than 2.0% by weight of the content of the nitrogen-containing aromatic compound generally corresponds to the nitrogen-containing aromatic compound being present in a range of 0.25 to 13.3 milliequivalents (meq/kg) per 1 kg of elastic fiber. In contrast, because an aromatic ring containing a nitrogen atom easily undergoes thermal decomposition, when the content of the nitrogen-containing aromatic compound is too high (that is, when the aromatic ring nitrogen atom exceeds 13.3 milliequivalents), radical generation due to thermal decomposition will be more dominant than the synergistic effect of polyurethane having the polyether structure of general formula (1) in its backbone, heat resistance will be reduced, and a quinone structure will be formed, causing thermal discoloration. As a result, functions such as high heat resistance and the like will not be obtained. Furthermore, while there are cases in which a large amount of the nitrogen-containing aromatic compound is contained as a light resistant agent, effects such as high heat resistance and the like, which are objects of the present invention, cannot be obtained when the content thereof is so great as to exceed 2.0% by mass. Based on these points, it is preferable that the content of the nitrogen-containing aromatic compound be an appropriate amount that is not too great, and the preferable range is no less than 0.1% by mass to no more than 1.0% by mass, and more preferably no less than 0.2% by mass to no more than 0.8% by mass.

Furthermore, it is preferable that when n' is defined as the number of -($CH_2CH_2CH_2CHR^2$-O)n- in the polyurethane having the polyether structure of the foregoing general formula (1) in its backbone at terminals, $5 \leq n'/(l+m+n) \times 100 \leq 30$ be satisfied. In such a case, the effect of antioxidative properties with the nitrogen-containing aromatic compound may be synergistically exhibited. Furthermore, $10 \leq n'/(l+m+n) \times 100 \leq 15$ is more preferable, and the nitrogen-containing aromatic compound is more effective at a smaller amount. In these cases, the content of the nitrogen-containing aromatic compound is preferably no less than 0.1% by mass to no more than 0.6% by mass.

More specifically, the contained nitrogen-containing aromatic compound is a compound having a nitrogen-containing aromatic heterocyclic ring in which nitrogen atoms are arranged on an aromatic ring in the molecule. Examples of chemical structural backbones include: pyrrole, pyridine, carbazole, and quinoline, which have a one-nitrogen aromatic heterocyclic ring; imidazole, pyrazole, pyridazine, pyrazine, pyrimidine, naphthyridine, and phenanthroline, which have a two-nitrogen aromatic heterocyclic ring; triazine, benzotriazole, and naphthyridine, which have a three-nitrogen aromatic heterocyclic ring; and the like, and heteroatoms other than nitrogen may also be included, such as in benzothiazole and benzoxazole. As specific examples of the nitrogen-containing aromatic compound, benzotriazole compounds and triazine compounds known as ultraviolet light absorbers are preferable, and more specifically, examples include compounds such as 2-(3,5-di-t-amyl-2-hydroxyphenyl)benzotriazole, 2-(3-t-butyl-2-hydroxyphenyl)-5-chlorobenzotriazole, 2-(2-hydroxy-3,5-bisphenyl)benzotriazole, 2,4-di(2', 4'-dimethylphenyl)-6-(2"-hydroxy-4"-alkoxyphenyl)-1,3,5-triazine, and 2,2'-(1,4-phenylene)bis[4H-3,1-benzoxazin-4-one]. Examples of product names include: "Tinuvin"-P, "Tinuvin"-213, "Tinuvin"-234, "Tinuvin"-327, "Tinuvin"-328, "Tinuvin"-571, and "Tinuvin"-1577 manufactured by Ciba-Geigy; "Sumisorb" 250 manufactured by Sumitomo Chemical Co., Ltd.; "Cyasorb" UV-5411, UV-1164, and UV-3638 manufactured by American Cyanamid; "Adeka Stab" LA-31 manufactured by Asahi Denka Corporation; and the like.

In order to obtain a polyurethane elastic fiber simultaneously exhibiting high heat resistance, resistance to unsaturated fatty acids, and resistance to heavy metals during dyeing, as well as having high elastic recovery and high elongation, the content of nitrogen-containing aromatic compound must be no less than 0.05% by weight to no more than 2.0% by weight.

Among nitrogen-containing aromatic compounds, a group of compounds having a molecular weight of 300 or more is preferable from the perspective of suppressing loss through volatilization during spinning. Furthermore, from the perspective of improving heat resistance and spinnability during dyeing, it is more preferable that the compound have two or more nitrogen atoms in the aromatic ring, and this is assumed to facilitate the formation of a complex with a heavy metal and to demonstrate a chelating effect. Furthermore, in order to sufficiently exhibit this effect, the chemical structural backbone of the nitrogen-containing aromatic compound is preferably triazine. Note that it is preferable that testing be conducted in advance depending on the molecular weight of the nitrogen-containing aromatic compound which is actually to be used, as well as the number of effective nitrogen atoms in the aromatic ring, the application, and the like, and that an optimal value be appropriately determined.

Furthermore, 2,4-di(2',4'-dimethylphenyl)-6-(2"-hydroxy-4"-alkoxyphenyl)-1,3,5-triazine is preferred as the nitrogen-containing aromatic compound in order to obtain a polyurethane elastic fiber that has particularly high heat resistance during dyeing.

Furthermore, the compound used as the nitrogen-containing aromatic compound is preferably a liquid compound with a viscosity of no less than 100 cP to no more than 10,000 P at 20°C, from the perspective of accelerated dispersion and dissolution of the compound into the polyurethane, the imparting of desired properties to the produced polyurethane elastic fiber, the possibility of obtaining a polyurethane elastic fiber having an appropriate degree of transparency, the content of these compounds not decreasing even when heated or the like during the spinning process, and discoloration and yellowing of the polyurethane elastic fiber not occurring.

Furthermore, the polyurethane used in the present invention preferably contains a mixture of one or two or more terminal blocking agents. The terminal blocking agent is preferably: a monoamine such as dimethylamine, diisopropylamine, ethylmethylamine, diethylamine, methylpropylamine, isopropylmethylamine, diisopropylamine, butylmethylamine, isobutylmethylamine, isopentylmethylamine, dibutylamine, or diamylamine; a monool such as ethanol, propanol, butanol, isopropanol, allyl alcohol, or cyclopentanol; a monoisocyanate such as phenyl isocyanate; or the like.

Additionally, in the present invention, various stabilizers other than those mentioned above, such as hindered phenol-based, sulfur-based, and phosphorus-based antioxidants, hindered amine-based, triazole-based, benzophenone-based, benzoate-based, nickel-based, and salicylic-based antioxidants light stabilizers, antistatic agents, lubricants, molecular regulators such as peroxides, metal deactivators, organic and inorganic nucleating agents, neutralizing agents, fluorescent brightening agents, fillers, flame retardants, flame retardant aids, pigments, and the like may be contained in the polyurethane elastic fiber or polyurethane spinning solution within ranges that do not impede the effects of the present invention. For example, it is preferable that light resistant agents and antioxidants contain the following: 2,6-di-t-butyl-p-cresol (BHT) and benzophenone-based drugs, various hindered amine-based drugs, various pigments such as iron oxide and titanium oxide, inorganic substances such as zinc oxide, cerium oxide, magnesium oxide, and carbon black, fluorine-based or silicone-based resin powders, metal soaps such as magnesium stearate, disinfectants, deodorants, antibacterial agents containing silver, zinc, and these compounds, lubricants such as silicone and mineral oil, and various antistatic agents such as barium sulfate, cerium oxide, betaine, and phosphoric acid-based agents. It is also preferable to react these with a polymer. Furthermore, nitric oxide scavengers such as HN-130 and HN-150 manufactured by Japan Finechem Co., Inc., for example, are preferably used to further increase durability, particularly to light and various types of nitric oxides.

Furthermore, from the perspective of facilitating an increase in the spinning speed during the dry spinning process, fine particles of a metal oxide such as titanium dioxide, zinc oxide, or the like may be added to the spinning dope. Furthermore, from the perspective of improving heat resistance and functionality, inorganic materials and inorganic porous materials (for example, bamboo charcoal, charcoal, carbon black, porous mud, clay, diatomaceous earth, coconut shell activated carbon, coal-based activated carbon, zeolite, pearlite, and the like) may be added within a range that does not inhibit the effect of the present invention.

These additives may be added when preparing the spinning dope by mixing a polyurethane solution and the above modifiers, or may be added beforehand in the polyurethane solution or dispersion before mixing. The content of these additives is appropriately determined according to the purpose and the like.

In the polyurethane elastic fiber of the present invention, a content of no less than 0.002% by mass to no more than 5.0% by mass is preferable when an antioxidant is included. When the content of the antioxidant is within this range, the properties of the polyurethane elastic fiber are practically preferable. Particularly preferable antioxidants are hindered phenol compounds, and examples include phenol compounds generally known as antioxidants. For example, 3,5-di-t-butyl-4-hydroxy-toluene, n-octadecyl-β-(4'-hydroxy-3',5'-di-t-butylphenyl)propionate, tetrakis[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane, 1,3,5-trimethyl-2,4,6'-tris(3,5-di-t-butyl) -4-hydroxybenzyl)benzene, calcium (3,5-di-t-butyl-4-hydroxy-benzyl-monoethyl-phosphate), triethylene glycol-bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate], 3,9-bis[1,1-dimethyl-2-{β-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy}ethyl] 2,4,8,10-tetraoxaspiro[5,5]undecane, tocopherol, 2,2'-ethylidenebis(4,6-di-t-butylphenol), N,N'-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyl]hydrazine, 2,2'-oxamidobis[ethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, ethylene-1,2-bis(3,3-bis[3-t-butyl-4-hydroxyphenyl]butyrate), ethylene-1,2-bis(3-[3-t-butyl-4-hydroxyphenyl]butyrate), 1,1-bis(2-methyl-5-t-butyl-4-hydroxyphenyl)butane, 1,1,3-tris(2-methyl-

5-t-butyl-4-hydroxyphenyl)butane, 1,3,5-tris(3',5'-di-t-butyl-4'-hydroxybenzyl)-S-triazine - 2,4,6(1H,3H,5H)-trione, 1,3,5-tris(3'-t-butyl-4'-hydroxy-5-methylbenzyl)-S-triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6 (1H,3H,5H)-trione, and furthermore, high molecular weight hindered phenol compounds known as antioxidants for polyurethane elastic fibers are also suitably used.

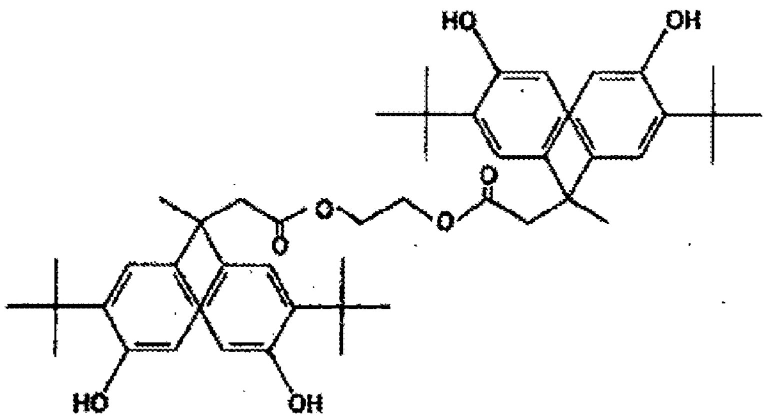
Preferable specific examples of the hindered phenol compound having such a high molecular weight include an addition polymer of divinylbenzene and cresol, an addition polymer isobutylene adduct of dicyclopentadiene and cresol, and a polymer of chloromethylstyrene and a compound such as cresol, ethylphenol, and t-butylphenol. Here, divinylbenzene and chloromethylstyrene may be p- or m-. Furthermore, cresol, ethylphenol, and t-butylphenol may be o-, m-, or p-.

Among these, from the perspective of stabilizing the viscosity of the raw material spinning solution of the polyurethane elastic fiber, suppressing the loss through volatilization during spinning, and obtaining favorable spinning properties, it is preferable that the compound have a molecular weight of 300 or more. Furthermore, in order to efficiently exhibit high spinning speed, heat resistance during dyeing, resistance to unsaturated fatty acids, and resistance to heavy metals, one or a combination of polymers having a repeating number of 6 to 12, which is an adduct of 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazin-2,4,6(1H,3H,5H)-trione, triethylene glycol-bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate], ethylene-1,2-bis(3,3-bis[3-t-butyl-4-hydroxyphenyl]butylate), divinylbenzene, and p-cresol, is preferably used. Of these, 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione is particularly preferable. Furthermore, when a triazine compound is selected as compound (a) and compound (c), a particularly high synergistic effect may be obtained in terms of heat resistance during dyeing. Of these, it is particularly preferable that the compound (a) be 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione and the compound (c) be 2,4-di(2',4'-dimethylphenyl)-6-(2"-hydroxy-4"-alkoxyphenyl)-1,3,5-triazine.

Furthermore, from the perspective of heat resistance, combined durability, light resistance, and suppression of the reduction of various types of durability such as yellowing due to oxidation and the like, a partially hindered phenol compound is preferably included in the polyurethane elastic fiber of the present invention. The partially hindered phenol compound is preferably a compound containing at least two partially hindered hydroxyphenyl groups and having a backbone selected from bis-esters and alkylidenes. Here, the alkyl group present at the ring position adjacent to the hydroxyl group in the hydroxyphenyl group is preferably a tertiary butyl group, and the equivalent of the hydroxyl group is more preferably 600 or less.

Furthermore, a partially hindered phenol compound is also preferable as the phenol compound in the present invention. For example, ethylene-1,2-bis(3,3-bis[3-t-butyl-4-hydroxyphenyl]butyrate) (chemical formula 1 below) having a structure in which a partially hindered hydroxyphenyl group is covalently bonded to a bis-ester backbone is preferable as the partially hindered phenol compound.

[Formula 4]



Inclusion the foregoing partially hindered phenol compound can enhance the effect of suppression of the deterioration of characteristics. Furthermore, this type of hindered phenol compound acts to specifically suppress the molecular weight of the polyurethane constituting the polyurethane elastic fiber and is effective when washing and bleaching are performed at a high frequency, such as for underwear. From the perspective of ensuring that this effect is sufficient and not adversely affecting the physical properties of the fiber, the partially hindered phenol compound is preferably contained in an amount of 0.15 to 4% by mass and more preferably in an amount of 0.5 to 3.5% by mass relative to the urethane elastic fiber, and rupture strength/elongation, combined durability, yellowing resistance, and in some cases, light resistance, are ensured. A more preferable content of the antioxidant is in the range of no less than 0.2% by mass to no more than 3.0% by mass, and further preferably in the range of no less than 0.5% by mass to no more than 2.0% by mass.

Furthermore, the content of the antioxidant in the polyurethane elastic fiber is preferably in the range of no less than 0.1% by mass to no more than 5.0% by mass. When the content of the antioxidant in the polyurethane elastic fiber is within this range, it becomes possible to easily control the content of the antioxidant contained in the polyurethane elastic fiber that is ultimately produced to the desired content of the antioxidant described above. The content of the antioxidant in the polyurethane elastic fiber is more preferably in the range of no less than 0.2% by mass to no more than 3.0% by mass, and further preferably in the range of no less than 0.5% by mass to no more than 2.0% by mass.

More specifically, a hindered phenol compound having a molecular weight of 1,000 or more which is known as an antioxidant agent for a polyurethane elastic fiber is preferably used as the contained antioxidant. There are no particular restrictions with regard to the hindered phenol compound other than a relatively high molecular weight of 1,000 or more. Preferable specific examples of the hindered phenol compound having such a high molecular weight include an addition polymer of divinylbenzene and cresol, an addition polymer isobutylene adduct of dicyclopentadiene and cresol, and a polymer of chloromethylstyrene and a compound such as cresol, ethylphenol, or t-butylphenol. Here, divinylbenzene and chloromethylstyrene may be p- or m-. Furthermore, cresol, ethylphenol, and t-butylphenol may be o-, m-, or p-.

Of these, a hindered phenol compound of a polymer derived from cresol is preferable from the perspective of stabilizing the viscosity of the raw material spinning solution of the polyurethane elastic fiber and obtaining good spinnability. Furthermore, in order to efficiently exhibit a high spinning speed, heat resistance during dyeing, resistance to unsaturated fatty acids, and resistance to heavy metals, it is preferable to include a certain amount of the high molecular weight hindered phenol compound; however, from the perspective of obtaining better basic properties as a polyurethane elastic fiber, it is preferable that this not be too much.

In the polyurethane elastic fiber of the present invention, the content of a degradation product of the antioxidant described above is preferably regulated to 1.0% by mass or less. When the content of the degradation product of the antioxidant is within this range, properties of the polyurethane elastic fiber that are practically favorable, particularly favorable rupture strength/elongation, resistance to discoloration, and durability are ensured. A preferred content of degradation products of the antioxidant is in the range of 1.0% by mass or less, and more preferably in the range of 0.5% by mass or less.

In the polyurethane elastic fiber of the present invention, a content of no less than 0.2% by mass to no more than 5.0% by mass is preferable when a tertiary amine compound is included. When the content of the tertiary amine compound is within this range, properties of the polyurethane elastic fiber that are practically preferable, as well as spinnability, dyeability, durability, and resistance to yellowing are improved.

The tertiary amine compound used in the present invention is not particularly limited so long as it is a compound which has an amino group in the structure, but from the perspective of resistance to chlorine degradation and resistance to yellowing of the urethane elastic fiber, a compound having only tertiary amino groups in the molecule from among primary to tertiary amino groups is particularly preferable.

When the number average molecular weight of the tertiary amine compound is less than 2,000, water repellency deteriorates due to shedding as a result of friction with the guide or the knitting needle during knitting of the polyurethane elastic fiber or due to outflow during processing in a bath such as dyeing. Therefore, the number average molecular weight must be 2,000 or more. In view of solubility in the polyurethane spinning dope, the number average molecular weight is preferably in a range of 2,000 to 10,000. More preferably, it is in the range of 2,000 to 4,000.

Inclusion of the tertiary amine compound can enhance the performance of the polyurethane elastic fiber, particularly the performance in terms of preventing yellowing. From the perspective of ensuring that this effect is sufficient and of not adversely affecting the physical properties of the fiber, the tertiary amine compound is preferably contained in an amount of no less than 0.2% by mass to no more than 5.0% by mass and more preferably in an amount of no less than 0.5% by mass to no more than 4.0% by mass relative to the mass of the fiber. A more preferable content of the tertiary amine compound is in the range of no less than 0.5% by mass to no more than 3.0% by mass, and further preferably in the range of no less than 0.5% by mass to no more than 2.0% by mass.

More specifically, the contained tertiary amine compound may be a linear polymer compound with a number average molecular weight of 2,000 or more that is produced by a reaction of t-butyl diethanolamine and methylene-bis-(4-cyclohexyl isocyanate), polyethyleneimine, a polymer compound having a branched structure containing a primary amino group, a secondary amino group, and a tertiary amino group in the molecular backbone, or the like.

In the polyurethane elastic fiber of the present invention, the content of a degradation product of the tertiary amine compound described above is preferably regulated to 1.0% by mass or less. When the content of the degradation product of the tertiary amine compound is within this range, properties of the polyurethane elastic fiber that are practically favorable, and a particularly favorable wound body shape, combined durability, and resistance to yellowing are ensured. A more preferable content of the degradation product of the tertiary amine compound is in the range of 1.0% by mass or less, and further preferably in the range of 0.5% by mass or less.

Furthermore, in the polyurethane elastic fiber of the present invention, a content of no less than 0.002% by mass to no more than 2.0% by mass is preferable when a crosslinked structure regulator is included. The crosslinked structure regulator is an agent that is added after the polyurethane polymerization terminator is added and the polymerization is completed. When the content of the crosslinked structure regulator is within this range, properties of the polyurethane elastic fiber that are practically favorable, and a particularly favorable rupture strength/elongation, permanent strain rate, and resistance to yellowing are ensured. A more preferable content of the crosslinked structure regulator is in the range of no less than 0.02% by mass to no more than 1.5% by mass, and further preferably in the range of no less than 0.2% by mass to no more than 1.0% by mass.

Examples of the contained crosslinked structure regulator include monoamines and/or diamines. More specifically, examples of monoamines include dimethylamine, diethylamine, cyclohexylamine, and the like, and examples of diamines include ethylenediamine, 1,2-propanediamine, 1,3-propanediamine, hexamethylenediamine, p-phenylenediamine, p-xylylenediamine, m-xylylenediamine, 1,3-cyclohexyldiamine, hexahydrometaphenylenediamine, 2-methylpentamethylenediamine, and the like. Combined use of a monoamine and a diamine is particularly preferable.

It is effective to do so. In terms of the index, it is preferable to blend a polyurethane having no peaks or shoulders in the detection intensity curve in a region wherein the number average molecular weight based on gel permeation chromatography (GPC) is no less than 20,000 to no more than 120,000 and the molecular weight based on GPC is 30,000 or less. In view of rupture strength/elongation of the polyurethane elastic fiber, the number average molecular weight is preferably in the range of no less than 30,000 to no more than 100,000. More preferably, it is in the range of no less than 40,000 to no more than 80,000. Note that the detection intensity curve is a differential molecular weight distribution curve (the horizontal axis is a molecular weight, and the vertical axis is a value wherein a concentration fraction is differentiated by a logarithmic value of the molecular weight), and the shoulder is a shoulder peak.

Note that in terms of the molecular weight of the polyurethane elastic fiber of the present invention, when a tertiary amine compound with a number average molecular weight in a range of 2,000 to 10,000 or an antioxidant with molecular weight of 1,000 or more, which is preferably used, is mixed in, the number average molecular weight is preferably in the range of no less than 10,000 to no more than 50,000. Note that the molecular weight is measured by GPC and converted using polystyrene.

Next, the method for producing the polyurethane elastic fiber of the present invention will be described in detail.

In the present invention, it is preferable to first prepare a polyurethane solution. The method for producing the polyurethane solution and the polyurethane which is the solute in the solution may be either of a melt polymerization method or a solution polymerization method, or may be any other method. However, a more preferred method is solution polymerization. In the case of a solution polymerization method, the generation of foreign matter such as gel and the like in the polyurethane is minimal, and therefore, spinning is easy, and it is easy to produce a polyurethane elastic fiber having low linear density. Furthermore, in the case of solution polymerization, there is an advantage in that an operation to obtain a solution can be omitted.

An article may be formed comprising a polyurethane elastic fiber according to any of the embodiments of the present invention described herein. Specific examples of articles formed may include a fiber, a fabric, a film, and combinations thereof. Examples of the fabric may include a knit, a woven, and a non-woven.

The polyurethane elastic fiber of the present invention may be used in various applications. Specific examples include pantyhose, bras, slips, camisoles, bodysuits, underwear, girdles, tightening strings for socks and pants, swimwear, training wear, yoga wear, mountaineering wear, work clothes, fire-resistant suits, clothing such as men’s and women’s suits produced in combination with natural stable fibers, wet suits, leak-prevention tightening members for sanitary products such as disposable diapers, artificial skin, artificial blood vessels, artificial hearts, electrical insulation materials, wiping cloths, copier cleaners, gaskets, tightening members for safety clothing, tightening members for laboratory coats, tightening members for waterproof materials, tightening members for bandages and gloves, and the like. That is, the polyurethane elastic fiber may be suitably used in areas where elastic stretching force is required.

[Examples]

(Examples 1 to 18 and Comparative Examples 1 to 10)

The production and evaluation of polyurethane elastic fibers and elastic fibers to which the nitrogen-containing aromatic compound has been added will be described below in regard to Examples 1 to 18 and Comparative Examples 1 to 10 illustrated in Tables 1 to 4.

[Comparative Example 1]

In Comparative Example 1, which is conventional art, 87.5 mol of dehydrated tetrahydrofuran and 4.0 mol of dehydrated 3-methyl-tetrahydrofuran were placed in a reactor with a stirrer. A polymerization reaction was performed for 8 hours under a nitrogen seal in the presence of a catalyst (a mixture of 70% by weight perchloric acid and 30% by weight acetic anhydride) at a temperature of 10°C, and a copolymerized tetramethylene ether diol with a number average molecular weight of 3,500 (including 4.0% by mole of structural unit (a) derived from 3-methyl-tetrahydrofuran) obtained by means of a copolymerization method of neutralization with an aqueous sodium hydroxide solution in a reaction termination solution was used as a polyalkylene ether diol.

4,4'-MDI was placed in a container so as to constitute 1.97 mol with respect to 1 mole of this copolymerized tetramethylene ether diol and reacted at 90°C, and the obtained reaction product was sufficiently stirred and dissolved in N,N-dimethylacetamide (DMAc) to obtain a solution. Next, a DMAc solution containing 60% by mole of ethylenediamine (EDA) and 40% by mole of 1,2-propanediamine (1,2-PDA) as a chain extender was added to a solution in which the reaction product was dissolved, and a DMAc solution containing diethylamine as a terminal sequestering agent was also added to prepare a polyurethane urea solution with a polymer solid content of 25% by weight.

The resulting solution had a viscosity of approximately 2,400 poise at 40°C. The polymer had an intrinsic viscosity of 0.90 when measured at 25°C at a solution concentration of 0.5 g/100 mL in DMAc.

The polyurethane urea solution was discharged from a spinneret into an inert gas (nitrogen gas) at a high temperature (350°C) using four filaments, dried by passing through the high temperature gas, passed through an air jet-type twisting machine so that the yarn was twisted during drying, fused with four filaments, and wound at a speed of 540 m/minute. Four filaments were then fused to produce a polyurethane urea fiber of 44 dtex. The glass transition point (Tg) was -74°C. Note that the urethane group concentration of the polyurethane urea constituting the polyurethane urea fiber was 0.49 mol/kg, and the effective terminal amine concentration was 18 meq/kg.

Next, one-to-one (mass ratio) mixture of a polyurethane ("Methachlor" (registered trademark) 2462 manufactured by DuPont) produced by reacting t-butyl diethanolamine and methylene-bis-(4-cyclohexyl isocyanate) and a condensation polymer of p-cresol and divinylbenzene ("Methachlor" (registered trademark) 2390 manufactured by DuPont) was used as an antioxidant, and a DMAc solution (35% by mass) of this mixture was prepared to produce an additive solution (B).

The foregoing solution PUUX1, the additive solution (B), and the nitrogen-containing aromatic compound (C) were uniformly mixed at 99% by mass, 1.0% by mass, and 0.2% by mass, respectively, and were made to be the spinning solution (D).

Using the spinning dope obtained in this manner, dry spinning was carried out at a dry nitrogen temperature of 300°C or higher so that DMAc and floating ethylene diamine in the spinning solution were 1/100 or lower of the content of the spinning dope. At this time, the 22 dtex/3 fil multifilament polyurethane elastic fiber was spun with the speed ratio of the godet roller and the winder set to 1:1.20, and the treatment agent (oil agent) described below was supplied to the roller by the oiling roller before winding. The polyurethane elastic fiber was wound using a surface drive winder via a traverse guide providing a winding width of 38 mm to a cylindrical paper tube with a winding speed of 600 m/min and a length of 58 mm, and a dry spun polyurethane elastic fiber was obtained as a 500 g wound body. The obtained polyurethane elastic fiber was a spliced yarn made by splicing three filaments together. The rotational speed of the oiling roller was adjusted so that the amount of treatment agent applied was a predetermined amount relative to the yarn. Furthermore, the amount of treatment agent added was measured using n-hexane as an extraction solvent in accordance with JIS-L1073 (synthetic fiber filament yarn testing method). The composition of the treatment agent used herein is a mixture of 80 parts by mass of polydimethylsiloxane having a viscosity of $1\times10^{-5}$ $m^2/s$ at 25°C, 15 parts by mass of mineral oil having a viscosity of $1.2\times10^{-5}$ $m^2/s$ at 25°C, and 5 parts by mass of magnesium distearate having an average particle diameter of 0.5 μm.

[Example 1]

The 44 dtex polyurethane urea fiber was produced in exactly the same way, except that 2-methyl-tetrahydrofuran was used in place of the 3-methyl-tetrahydrofuran in Comparative Example 1. The glass transition point (Tg) was -70°C. Note that the urethane group concentration of the polyurethane urea constituting the polyurethane urea fiber was 0.49 mol/kg, and the effective terminal amine concentration was 20 meq/kg.

[Examples 2 to 5]

As shown in Table 1, only the concentration of 2-methyl-tetrahydrofuran in the copolyether polyol was changed, and a 44 dtex polyurethane urea fiber was produced using the same method as Example 1.

[Comparative Examples 2 to 5]

As shown in Table 1, only the concentration of 3-alkyl-tetrahydrofuran in the copolyether polyol was changed, and a 44 dtex polyurethane urea fiber was produced using the same method as Example 1.

[Examples 6 to 10]

As shown in Table 2, based on Example 2, only the content of the nitrogen-containing aromatic compound in the polyurethane elastic fiber was changed, and a 44 dtex polyurethane urea fiber was produced using the same method as Example 1.

[Comparative Examples 6 to 10]

As shown in Table 2, based on Comparative Example 4, only the content of the nitrogen-containing aromatic compound in the polyurethane elastic fiber was changed, and a 44 dtex polyurethane urea fiber was produced using the same method as Example 2.

[Examples 11 to 13]

As shown in Table 3, based on Example 7, only the concentration of a secondary hydroxyl group in the copolyether polyol was changed, and a 44 dtex polyurethane urea fiber was produced using the same method as Example 1.

[Examples 14 to 16]

As shown in Table 4, based on Example 7, only the number average molecular weight of the copolyether polyol was changed, and a 44 dtex polyurethane urea fiber was produced using the same method as Example1.

[Examples 17 and 18]

As shown in Table 4, based on Example 7, only the bio-conversion rate was changed, and a 44 dtex polyurethane urea fiber was produced using the same method as Example 1.

As can be seen from Table 1, mechanical properties such as stress at 200% elongation recovery show the same effect when the copolymer molar concentration of the 2-methyl-tetrahydrofuran is half of the copolymer molar concentration of the 3-methyl-tetrahydrofuran.

As can be seen from Table 2, heat resistance is maximized when the amount of the nitrogen-containing aromatic compound in the 2-methyl-tetrahydrofuran system is around 0.6. This does not occur in the 3-methyl-tetrahydrofuran system, in which it only attenuates. Note that the concentration of 2-tetrahydrofuran adopted in the copolyether polyol was 8, and the concentration of 3-tetrahydrofuran adopted in the copolyether polyol was 16. This is because mechanical properties such as stress at the time of 200% elongation recovery show similar values.

As can be seen from Table 3, the concentration of the secondary hydroxyl group in the 2-methyl-tetrahydrofuran system affects both recovery stress and durability.

As can be seen from Table 4, the number average molecular weight of the copolyether polyol in the 2-methyl-tetrahydrofuran system affects both recovery stress and durability.

Furthermore, in Example 17, in order to make the raw material 2-MeTHF, which is a raw material of the ($CH_2CH_2CH_2CHR^2$-O) structural unit, a component derived from a carbon neutral biomass resource that is suitable for thermal recycling, 2-MeTHF synthesized via D-xylol and furfural derived from hemicellulose was used. Furthermore, in Example 18, THF synthesized via D-xylol and furfural derived from hemicellulose was similarly used as the raw material for the ($CH_2CH_2CH_2CH_2$-O) structural unit. As a result, performance was shown that was equal to or better than Example 7 using raw materials of petrochemical origin.

Note that in Tables 1 to 4, the content percentage is a value relative to 100 parts by mass of polymer solid content in the spinning dope.

Next, the dry spun polyurethane elastic fiber (hereinafter referred to as the sample yarn) obtained above was subjected to the following evaluations.

<Rupture Elongation, Rupture Strength, Permanent Strain Rate, Stress Relaxation Rate>

The rupture elongation, rupture strength, permanent strain rate, and stress relaxation rate were measured by subjecting the polyurethane elastic fiber to tensile tests using an Instron model 5564 tensile tester.

A sample with a test length of 5 cm (L1) was subjected to 300% elongation five times at a tensile rate of 50 cm/minute. At this time,

the stress at 200% elongation was defined as (G+200),

and the stress at 300% elongation was defined as (G1).

Next, the sample length was maintained for 30 seconds at 300% elongation. The stress after being maintained for 30 seconds was defined as (G2).

Next, the sample elongation was recovered,

the stress at 200% elongation recovery was defined as (G-200),
and the length of the sample when the stress became 0 was defined as (L2).
This operation of 300% elongation, maintenance, and recovery was repeated, and in a 6th elongation, the sample was elongated until it broke. The stress at the time of rupture was defined as (G3), and the sample length at the time of rupture was defined as (L3). The above characteristics are calculated below using the following formula.

Rupture strength (cN) = (G3)

20 or more: ◎, 17 or more and less than 20: ○, 14 or more and less than 17: △, less than 14: ×

Rupture elongation (%) = 100×((L3)-(L1))/(L1)

480 or more: ◎, 460 or more and less than 480: ○, 430 or more and less than 460: △, less than 430: ×

Stress at 200% elongation (cN) = (G+200)

1.2 or more and less than 1.4: ◎, 1.4 or more and less than 1.5: ○, 1.5 or more and less than 1.6: △, over 1.6: ×

Stress at 200% elongation recovery = (G-200),

1.2 or more: ◎, 1.0 or more and less than 1.2: ○, 0.8 or more and less than 1.0: △, less than 0.8: ×

Permanent strain rate (%) = 100x((L2)-(L1))/(L1)

Less than 20: ◎, 20 or more and less than 22: ○, 22 or more and less than 24: △, 24 or more: ×

Stress relaxation rate (%) = 100×((G1)-(G2))/(G1)

Less than 25: ◎, 25 or more and less than 28: ○, 28 or more and less than 31: △, 31 or more: ×.

<Heat Resistance>

A two-way half tricot having a machine well number of 9/inch and a machine course number of 18/inch composed of 85% by weight of nylon filament (24 dtex, 7 filaments) and 15% by weight of polyurethane elastic fiber (44 dtex) was produced by a conventional knitting method to obtain a raw knitted fabric.

The obtained raw knitted fabric was preset under conditions of 3% elongation for 60 seconds at 170°C, and 0.1 mL of Agent 1 was applied, followed by an application of 0.1 mL of Agent 2 (at approximately the same time and within 1 minute). Next, the fabric was submitted to dry heat treatment (after dry heat treatment for 60 seconds at 175°C, the fabric was extracted once, and after radiating to room temperature, dry heat treatment was then performed for 60 seconds at 180°C). Then, the fabric was subjected to a bending tester with a maximum elongation of 20% alternately in both the vertical and horizontal directions, twice/second. Note that a mineral oil-based spinning oil for nylon containing 1% oleic acid was used as Agent 1. Furthermore, an aqueous solution of copper acetate (copper concentration of 100 ppm) was used as Agent 2. The raw knitted fabric coated with Agent 1 and Agent 2 in this manner was a model reproduction of a slight amount of a mechanical oil (containing a metal) and a spinning oil for nylon during knitting coating a nylon-based stretch raw knitted fabric at a stage before dyeing. The amount of Agent 1 coating 0.9 g of the raw knitted fabric was 3.0 mg and the amount of Agent 2 coating 0.9 g of the raw knitted fabric was 3.0 mg.

The obtained stretch fabric was dyed using a conventional method.

The degree of damage to the polyurethane tissue in the obtained dyed stretch fabric was observed visually with the naked eye or under magnification, and a determination was made using the following criteria. Note that the determination was performed by five people and that the mode (the determination appearing most frequently) was used. Furthermore, when the determination was divided into two people, two people, and one person, the determination was defined as "△."

◎: No damage, and the knitting structure was homogenous.

○: No damage.

Δ: Sagging and depressions were observed in the fabric, and when observed under magnification, the polyurethane elastic fiber was brittle.

×: There were holes in the fabric.

<Light Resistance, Yellowing, and Combined Durability>

Characteristics after the following exposure treatments (A), (B), and (C) were determined according to the following.

- Light Resistance

The following exposure treatment (A) was performed while the sample yarn was elongated to 100%, and the subsequent rupture strength retention rate was found.

- Yellowing

Yellowing was evaluated using the degree of yellowing (hereinafter abbreviated as Δb) following exposure treatments (A) and (B). During each exposure treatment, the degree of yellowing was calculated as follows.

Δb = b value after exposure treatment - b value before exposure treatment

The measurement sample form and measurement of yellowing were as follows.

The sample yarn was wound onto a 5×5 cm sample plate with minimal load and in close contact to the extent that the color of the sample plate did not affect the sample, and this was made to be the sample.

The front surface of the sample and a common-use standard white surface (4.3.4 of JIS Z 8722) were tightly covered with a homogeneous, flat, transparent glass plate of approximately 1 mm. The b value was measured according to JIS L 1013 Method C (Hunter's method) using a Hunter color difference meter and calculated based on the following formula. The number of measurements was 5, and the average of the measurements was used.

$b=7.0(Y-0.847Z)/Y^{1/2}$

(However, X, Y, and Z were calculated according to JIS Z 8701)

- Combined durability

The following exposure treatments (A), (B), and (C) were performed while the sample yarn was elongated to 100%, and the subsequent rupture strength retention rate was found.

Each exposure treatment was performed as follows.

(A) Ultraviolet (UV) exposure treatment

The sample was subjected to exposure treatment for 25 hours at a temperature of 63°C and a relative humidity of 60% using a carbon arc type weather meter manufactured by Suga Test Instruments Co., Ltd.

(B) Nitrogen oxide (NOx) exposure treatment

The sample was subjected to exposure treatment with 10 ppm NO2 gas for 20 hours at a temperature of 40°C and a relative humidity of 60% using a sealed container (Scott tester) with a rotating sample stand.

(C) Chlorine bleach (Cl2) exposure treatment

After exposing the sample to a 500 ppm aqueous solution of "Kao Haiter" manufactured by Kao Corporation in a constant temperature bath for 40°C for 30 minutes, a cycle of 10-minute water washing was repeated eight times.

The determination criteria were as follows.

- Light Resistance

80% or more: ◎, 60% or more and less than 80%: ○, 40% or more and less than 60%: △, less than 40%: ×

- Yellowing

3 or less: ◎, 3 or more and 6 or less: ○, 6 or more and 10 or less: △, 10 or more: ×

- Combined durability

60% or more: ◎, 40% or more and less than 60%: ○, 20% or more and less than 40%:

△, less than 20%: ×

<Molecular Weight>

Molecular weight measurement by GPC was carried out under the following conditions.

Column: 2 SHODEX KF-806M columns manufactured by Showa Denko K.K.

Solvent: N,N-dimethylacetamide 1 mL/min

Temperature: 40°C

Detector: Differential refractometer (RI detector)

<Bio-Conversion Rate>

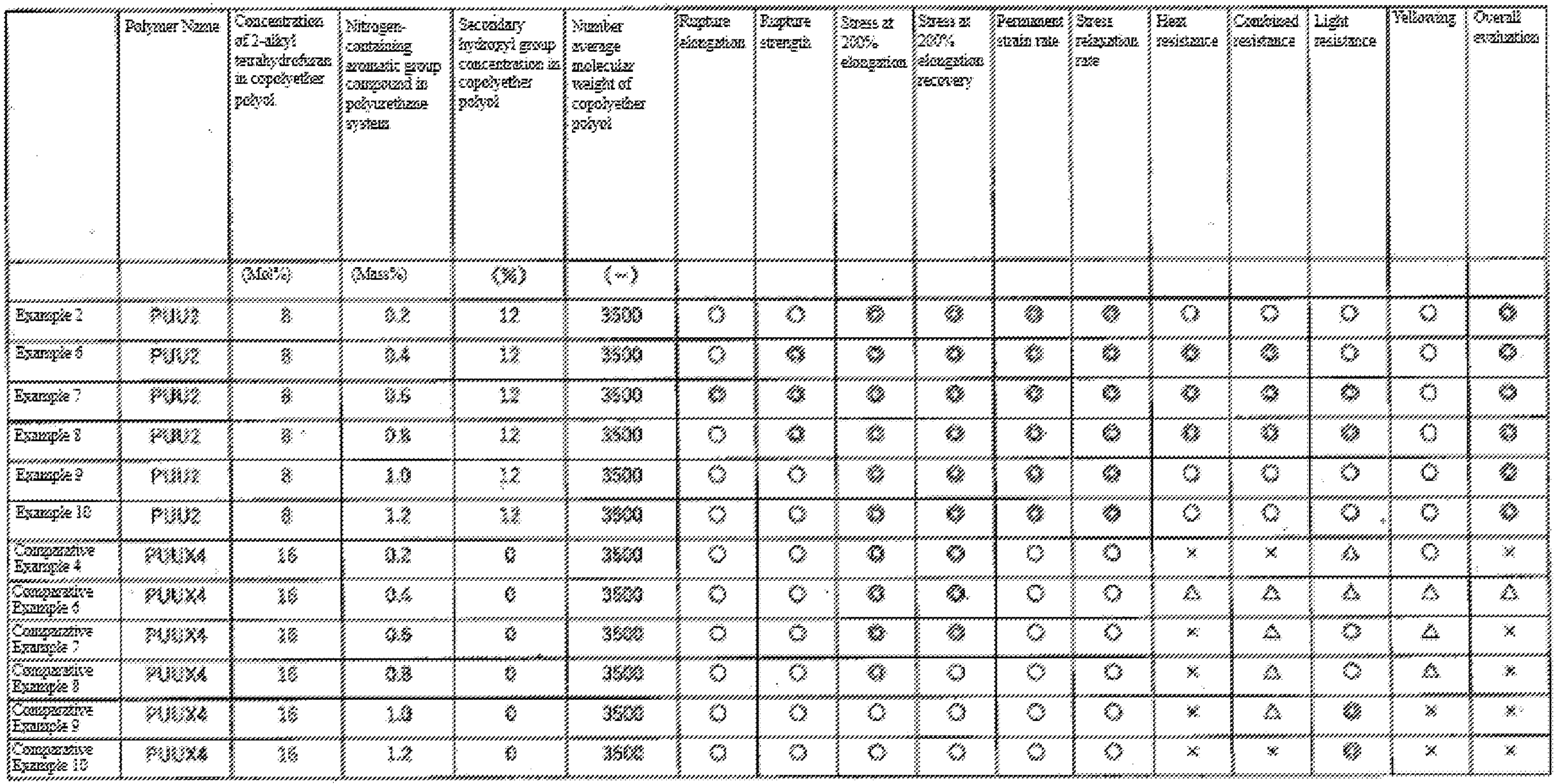
The bio-conversion rate (% by mass) was measured using ISO 16620-2, which is a radiocarbon (carbon 14) concentration measurement identification method.

[Table 1]

[Table 1]

| | Polymer Name | Concentration of 2-alkyl tetrahydrofuran in copolyether polyol | Nitrogen-containing aromatic group compound in polyurethane system | Secondary hydroxyl group concentration in copolyether polyol | Number average molecular weight of copolyether polyol | Rupture elongation | Rupture strength | Stress at 200% elongation | Stress at 200% elongation recovery | Permanent strain rate | Stress relaxation rate | Heat resistance | Combined durability | Light resistance | Yellowing | Overall evaluation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | (Mol%) | (Mass%) | (%) | (−) | | | | | | | | | | | |
| Example 1 | PUU1 | 4 | 0.2 | 12 | 3500 | ○ | ○ | ○ | ○ | ○ | ○ | △ | △ | ○ | ○ | ○ |
| Example 2 | PUU2 | 8 | 0.2 | 12 | 3500 | ○ | ○ | ◎ | ◎ | ◎ | ◎ | ○ | ○ | ○ | ○ | ◎ |
| Example 3 | PUU3 | 12 | 0.2 | 12 | 3500 | ○ | ○ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ○ | ○ | ◎ |
| Example 4 | PUU4 | 16 | 0.2 | 12 | 3500 | ○ | ○ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ◎ | ○ | ◎ |
| Example 5 | PUU5 | 32 | 0.2 | 12 | 3500 | ○ | ○ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ◎ | ○ | ◎ |
| Comparative Example 1 | PUUX1 | 4 | 0.2 | 0 | 3500 | △ | △ | △ | △ | △ | △ | △ | × | × | ○ | × |
| Comparative Example 2 | PUUX2 | 8 | 0.2 | 0 | 3500 | △ | △ | △ | △ | △ | △ | × | × | △ | ○ | × |
| Comparative Example 3 | PUUX3 | 12 | 0.2 | 0 | 3500 | ○ | ○ | ○ | ○ | △ | ○ | × | × | △ | ○ | × |
| Comparative Example 4 | PUUX4 | 16 | 0.2 | 0 | 3500 | ○ | ○ | ◎ | ◎ | ○ | ○ | × | × | △ | ○ | × |
| Comparative Example 5 | PUUX5 | 32 | 0.2 | 0 | 3500 | ○ | ○ | ◎ | ◎ | ◎ | ◎ | × | × | △ | ○ | × |

[Table 2]



[Table 2]

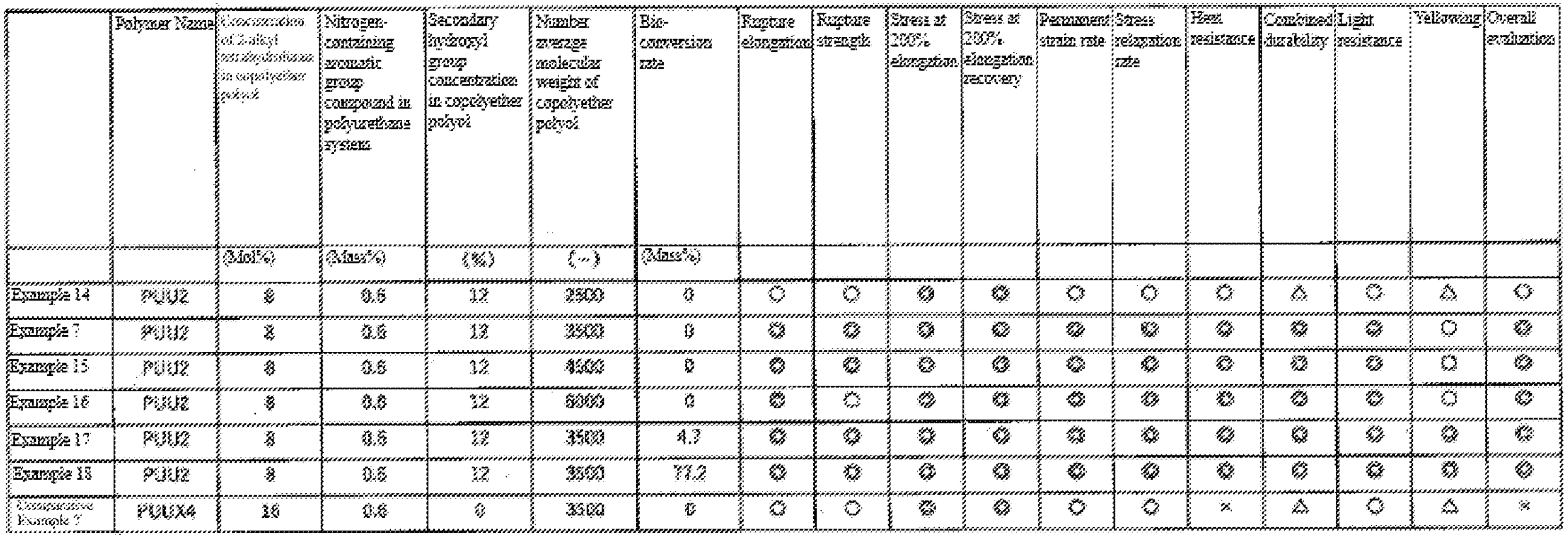
| | Polymer Name | Concentration of 2-alkyl tetrahydrofuran in copolyether polyol | Nitrogen-containing aromatic group compound in polyurethane system | Secondary hydroxyl group concentration in copolyether polyol | Number average molecular weight of copolyether polyol | Rupture elongation | Rupture strength | Stress at 200% elongation | Stress at 200% elongation recovery | Permanent strain rate | Stress relaxation rate | Heat resistance | Combined resistance | Light resistance | Yellowing | Overall evaluation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | (Mol%) | (Mass%) | (%) | (--) | | | | | | | | | | | |
| Example 2 | PUU2 | 8 | 0.2 | 12 | 3500 | ○ | ○ | ◎ | ◎ | ◎ | ◎ | ○ | ○ | ○ | ○ | ◎ |
| Example 6 | PUU2 | 8 | 0.4 | 12 | 3500 | ○ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ○ | ◎ |
| Example 7 | PUU2 | 8 | 0.6 | 12 | 3500 | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ◎ |
| Example 8 | PUU2 | 8 | 0.8 | 12 | 3500 | ○ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ◎ |
| Example 9 | PUU2 | 8 | 1.0 | 12 | 3500 | ○ | ○ | ◎ | ◎ | ◎ | ◎ | ○ | ○ | ○ | ○ | ◎ |
| Example 10 | PUU2 | 8 | 1.2 | 12 | 3500 | ○ | ○ | ◎ | ◎ | ◎ | ◎ | ○ | ○ | ○ | ○ | ◎ |
| Comparative Example 4 | PUUX4 | 16 | 0.2 | 0 | 3500 | ○ | ○ | ◎ | ◎ | ○ | ○ | × | × | △ | ○ | × |
| Comparative Example 6 | PUUX4 | 16 | 0.4 | 0 | 3500 | ○ | ○ | ◎ | ◎ | ○ | ○ | △ | △ | △ | △ | △ |
| Comparative Example 7 | PUUX4 | 16 | 0.6 | 0 | 3500 | ○ | ○ | ◎ | ◎ | ○ | ○ | × | △ | ○ | △ | × |
| Comparative Example 8 | PUUX4 | 16 | 0.8 | 0 | 3500 | ○ | ○ | ◎ | ○ | ○ | ○ | × | △ | ○ | △ | × |
| Comparative Example 9 | PUUX4 | 16 | 1.0 | 0 | 3500 | ○ | ○ | ○ | ○ | ○ | ○ | × | △ | ◎ | × | × |
| Comparative Example 10 | PUUX4 | 16 | 1.2 | 0 | 3500 | ○ | ○ | ○ | ○ | ○ | ○ | × | × | ◎ | × | × |

[Table 3]

[Table 3]

|  | Polymer Name | Concentration of 2-alkyl tetrahydrofuran in copolyether polyol | Nitrogen-containing aromatic group compound in polyurethane system | Secondary hydroxyl group concentration in copolyether polyol | Number average molecular weight of copolyether polyol | Rupture elongation | Rupture strength | Stress at 200% elongation | Stress at 200% elongation recovery | Permanent strain rate | Stress relaxation rate | Heat resistance | Combined durability | Light resistance | Yellowing | Overall evaluation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | (Mol%) | (Mass%) | (%) | (−) |  |  |  |  |  |  |  |  |  |  |  |
| Example 11 | PUU11 | 8 | 0.6 | 8 | 3500 | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Example 7 | PUU2 | 8 | 0.6 | 12 | 3500 | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ◎ |
| Example 12 | PUU12 | 8 | 0.6 | 15 | 3500 | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ |
| Example 13 | PUU13 | 8 | 0.6 | 20 | 3500 | ○ | ○ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ◎ |
| Comparative Example 7 | PUUX4 | 16 | 0.6 | 0 | 3500 | ○ | ○ | ◎ | ◎ | ○ | ○ | × | △ | ○ | △ | × |

[Table 4]



[Table 4]

| | Polymer Name | Concentration of 2-alkyl tetrahydrofuran in copolyether polyol | Nitrogen-containing aromatic group compound in polyurethane system | Secondary hydroxyl group concentration in copolyether polyol | Number average molecular weight of copolyether polyol | Bio-conversion rate | Rupture elongation | Rupture strength | Stress at 200% elongation | Stress at 200% elongation recovery | Permanent strain rate | Stress relaxation rate | Heat resistance | Combined durability | Light resistance | Yellowing | Overall evaluation |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | (Mol%) | (Mass%) | (%) | (−) | (Mass%) | | | | | | | | | | | |
| Example 14 | PUU2 | 8 | 0.6 | 12 | 2500 | 0 | ○ | ○ | ◎ | ◎ | ○ | ○ | ○ | △ | ○ | △ | ○ |
| Example 7 | PUU2 | 8 | 0.6 | 12 | 3500 | 0 | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ◎ |
| Example 15 | PUU2 | 8 | 0.6 | 12 | 4500 | 0 | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ◎ |
| Example 16 | PUU2 | 8 | 0.6 | 12 | 6000 | 0 | ◎ | ○ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ○ | ◎ |
| Example 17 | PUU2 | 8 | 0.6 | 12 | 3500 | 4.7 | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ |
| Example 18 | PUU2 | 8 | 0.6 | 12 | 3500 | 77.2 | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ | ◎ |
| Comparative Example 7 | PUUX4 | 18 | 0.6 | 0 | 3500 | 0 | ○ | ○ | ◎ | ◎ | ○ | ○ | × | △ | ○ | △ | × |

The values for the tensile strength at the time of breakage, elongation at the time of breakage, residual strain rate, and thermal softening point of the polyurethane resin measured by the following method using the same polyurethane urea solution provided for spinning in Examples 1 to 5 and Comparative Examples 1 to 5 are shown in Table 5.

A polyurethane resin solution was applied at a thickness of 1.0 mm to a glass plate that had been subjected to a mold release treatment, dried for 3 hours in an air-circulating dryer at 70°C, and then peeled from the glass plate to produce a film with a thickness of approximately 0.2 mm.

[2] Method for measuring film strength and elongation

After the film obtained above was allowed to stand for one day in a room adjusted to a temperature of 25°C and a relative humidity of 65%, tensile strength at the time of breakage and elongation at the time of breakage were measured in accordance with JIS K 6251. The larger these values, the better the properties as an elastic fiber. Note that the thickness of parallel portions of the dumbbell-shaped test piece was 200 μm, the width of the parallel portions was 5 mm, and the initial gauge length was 20 mm.

[3] Method for measuring residual strain rate

A strip-shaped test piece of 100 mm in length x 5 mm in width was cut out from the film obtained above, and gauge lines were applied so that the gauge length was 50 mm. This test piece was set in the chuck of an Instron model tensile testing machine (Autograph manufactured by Shimadzu Corporation), and after elongating until the distance between the gauge lines reached 300% at a constant speed of 500 mm/minute under an atmosphere of 25°C, an operation was performed immediately to return to the test piece to the distance between the chuck before elongation at the same speed.

The distance between the gauge lines after the above operation (D1) was measured, and the residual strain rate (%) was determined based on the following formula using this value and the distance between the gauge lines before the test (D0=50 mm).

$$\text{Residual strain rate (\%)} = \{(D1-D0)/D0\}\times 100$$

[4] Method for measuring thermal softening point

A test piece of 10 mm in length x 10 mm in width was cut out from the film obtained above, the sample was heated from room temperature to 300°C at a speed of 5°C/minute in accordance with JIS K 7196, and the thermal softening point was measured. A TMA/SS6100 (manufactured by SII) was used for the measurement.

The higher the thermal softening point, the better the heat resistance of the polyurethane resin.

[Table 5]

[Table 5]

| | Polymer Name | Concentration of 2-alkyl tetrahydrofuran in copolyether polyol | Nitrogen-containing aromatic group compound in polyurethane system | Secondary hydroxyl group concentration in copolyether polyol | Number average molecular weight of copolyether polyol | Elongation at time of breakage | Tensile strength at time of breakage | Permanent strain rate | Thermal softening point |
|---|---|---|---|---|---|---|---|---|---|
| | | (Mol%) | (Mass%) | (%) | (−) | (%) | (MPa) | (%) | (°C) |
| Example 1 | PUU1 | 4 | 0.2 | 12 | 3500 | 880 | 66 | 31 | 210 |
| Example 2 | PUU2 | 8 | 0.2 | 12 | 3500 | 900 | 68 | 28 | 208 |
| Example 3 | PUU3 | 12 | 0.2 | 12 | 3500 | 930 | 69 | 25 | 208 |
| Example 4 | PUU4 | 16 | 0.2 | 12 | 3500 | 1020 | 70 | 25 | 208 |
| Example 5 | PUU5 | 32 | 0.2 | 12 | 3500 | 1180 | 70 | 25 | 208 |
| Comparative Example 1 | PUUX1 | 4 | 0.2 | 0 | 3500 | 700 | 60 | 31 | 211 |
| Comparative Example 2 | PUUX2 | 8 | 0.2 | 0 | 3500 | 730 | 63 | 30 | 207 |
| Comparative Example 3 | PUUX3 | 12 | 0.2 | 0 | 3500 | 800 | 63 | 28 | 203 |
| Comparative Example 4 | PUUX4 | 16 | 0.2 | 0 | 3500 | 850 | 64 | 28 | 202 |
| Comparative Example 5 | PUUX5 | 32 | 0.2 | 0 | 3500 | 970 | 64 | 27 | 196 |

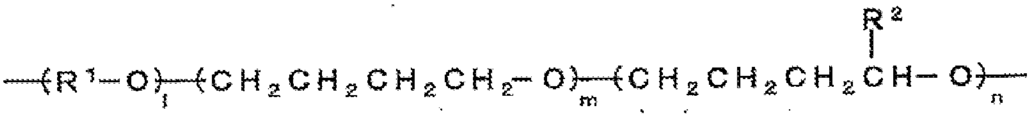
# CLAIMS

1. A polyurethane elastic fiber comprising a polyurethane having a polyether structure in its backbone and a nitrogen-containing aromatic compound, wherein

the polyether structure is represented by the following general formula (1),

and the polyurethane elastic fiber contains no less than 0.05% by mass to no more than 2.0% by mass of the nitrogen-containing aromatic compound

[Formula 1]



$$-(R^1-O)_l-(CH_2CH_2CH_2CH_2-O)_m-(CH_2CH_2CH_2\overset{\overset{R^2}{|}}{C}H-O)_n- \quad (1)$$

(1)

($R^1$ is an alkylene group having 2 to 6 carbon atoms, $R^2$ is an alkyl group having 1 to 2 carbon atoms,

and l, m, and n satisfy $4 \leq n/(l+m+n) \times 100 \leq 50$ ).

2. The polyurethane elastic fiber according to claim 1, wherein l, m, and n in the foregoing general formula (1) satisfy $6 \leq n/(l+m+n) \times 100 \leq 16$.

3. The polyurethane elastic fiber according to claim 1 or 2, wherein the polyurethane elastic fiber contains no less than 0.2% by mass to no more than 0.8% by mass of the nitrogen-containing aromatic compound.

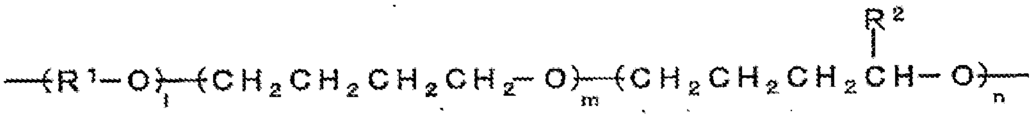
4. The polyurethane elastic fiber according to claim 1 or 2, wherein, when n’ is defined as the number of $-(CH_2CH_2CH_2CHR^2-O)n-$ in the foregoing general formula (1) at terminals of the polyurethane, $5 \leq n'/(l+m+n) \times 100 \leq 30$ is satisfied.

5. The polyurethane elastic fiber according to claim 1 or 2, wherein the number average molecular weight of the moiety of the foregoing general formula (1) is no less than 3,000 to no more than 30,000.

6. The polyurethane elastic fiber according to claim 1 or 2, wherein the bio-conversion rate by carbon isotope ratio measurement established in ISO 16620-2 is 3% or more in a carbon mass ratio.

7. An article comprising a polyurethane elastic fiber having a polyether structure in its backbone and a nitrogen-containing aromatic compound, wherein

the polyether structure is represented by the following general formula (1),
and the polyurethane elastic fiber contains no less than 0.05% by mass to no more than 2.0% by mass of the nitrogen-containing aromatic compound
[Formula 1]



$$-\!\left(R^1-O\right)_l\!-\!\left(CH_2CH_2CH_2CH_2-O\right)_m\!-\!\left(CH_2CH_2CH_2\overset{R^2}{\overset{|}{C}}H-O\right)_n\!- \quad (1)$$

($R^1$ is an alkylene group having 2 to 6 carbon atoms, $R^2$ is an alkyl group having 1 to 2 carbon atoms,

and l, m, and n satisfy $4 \leq n/(l+m+n) \times 100 \leq 50$ ).

8. The article of claim 7, wherein the article is selected from the group consisting of a fiber, a fabric, a film, and combinations thereof.

9. The article of claim 8, wherein the fabric is selected from a knit, a woven, and a nonwoven.

# INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2023/061811

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C08G18/48 C08G18/08 C08G18/32 C08G18/66 C08G18/75
C08G18/76 C08L65/00 D01F6/70

ADD.

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)

C08K D01F C09J C08G C08L

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

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

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| Y | column 1, line 7 - line 14; claims 1-20<br>column 6, line 20 - column 7, line 4;<br>example 1; table I<br>----- | 1-9 |
| X | CN 111 534 883 A (ZHENGZHOU ZHONGYUAN SPANDEX ENGINEERING TECH CO LTD)<br>14 August 2020 (2020-08-14) | 1-9 |
| Y | paragraph [0001]; claims 1-10<br>paragraph [0048] - paragraph [0079]; examples<br>paragraph [0040] - paragraph [0047]<br>paragraphs [0007], [0019], [0029]<br>-----<br>-/-- | 1-9 |

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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| | |
|---|---|
| Date of the actual completion of the international search<br>19 January 2024 | Date of mailing of the international search report<br>05/02/2024 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Paulus, Florian |

1

C(Continuation). **DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| Y | paragraph [0001]; claim 19<br>paragraph [0062] - paragraph [0087];<br>examples; tables 1-4<br>paragraph [0015]<br>paragraph [0036] | 1-9 |

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1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2023/061811

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