



(11) **EP 3 951 037 A1**

(12) **EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 153(4) EPC

(43) Date of publication:  
**09.02.2022 Bulletin 2022/06**

(21) Application number: **20784550.4**

(22) Date of filing: **24.03.2020**

(51) International Patent Classification (IPC):  
**D03D 15/08** <sup>(2006.01)</sup> **A41D 7/00** <sup>(2006.01)</sup>  
**A41D 31/00** <sup>(2019.01)</sup> **A41D 31/10** <sup>(2019.01)</sup>  
**A41D 31/18** <sup>(2019.01)</sup> **D01F 6/70** <sup>(2006.01)</sup>  
**D02G 3/38** <sup>(2006.01)</sup> **D04B 1/18** <sup>(2006.01)</sup>  
**D04B 21/00** <sup>(2006.01)</sup> **D06M 15/643** <sup>(2006.01)</sup>  
**D06M 101/38** <sup>(2006.01)</sup>

(52) Cooperative Patent Classification (CPC):  
**A41D 7/00; A41D 31/00; A41D 31/10; A41D 31/18;**  
**D01F 6/70; D02G 3/38; D03D 15/56; D04B 1/18;**  
**D04B 21/00; D06M 15/643**

(86) International application number:  
**PCT/JP2020/012842**

(87) International publication number:  
**WO 2020/203434 (08.10.2020 Gazette 2020/41)**

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB**  
**GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO**  
**PL PT RO RS SE SI SK SM TR**  
Designated Extension States:  
**BA ME**  
Designated Validation States:  
**KH MA MD TN**

(30) Priority: **01.04.2019 JP 2019069827**

(71) Applicant: **Toray Industries, Inc.**  
**Tokyo, 103-8666 (JP)**

(72) Inventors:  
• **KIMURA Chika**  
**Otsu-shi, Shiga 520-2141 (JP)**  
• **TAKEDA Keiji**  
**Otsu-shi, Shiga 520-2141 (JP)**  
• **KASAHARA Keiko**  
**Osaka-shi, Osaka 530-8222 (JP)**

(74) Representative: **Dehns**  
**St. Bride's House**  
**10 Salisbury Square**  
**London EC4Y 8JD (GB)**

(54) **FIBROUS STRUCTURE CONTAINING ELASTIC POLYURETHANE YARN**

(57) The present invention relates to a fiber structure including an elastic polyurethane yarn. The elastic polyurethane yarn contains: 0.5 to 10 mass% of a cationic high-molecular-weight compound A having a number-average molecular weight of 2000 or more; and an inorganic chlorine deterioration inhibitor B. The mass ratio of the cationic high-molecular-weight compound A to the inorganic chlorine deterioration inhibitor B ranges from 0.3 to 3, and a silicone oil is applied to the elastic polyurethane yarn. The fiber structure is treated with water

repellent finishing. The fiber structure preferably includes an elastic polyurethane yarn whose ratio of fluorine (F) to carbon (C) on the elastic polyurethane yarn is 0.030 or more in an elemental mass concentration according to scanning electron microscope - energy dispersive X-ray spectroscopy (SEM-EDX). Thereby, it is possible to provide a fiber structure having high water repellency and keeping a low water retention rate when immersed in water for an extended time.

**EP 3 951 037 A1**

**Description**

## Technical Field

- 5 **[0001]** The present invention relates to a fiber structure including elastic polyurethane yarns, which has high water repellency and keeps a low water retention rate to resist being wetted when immersed in water.

## Background Art

- 10 **[0002]** Water and oil repellent agents containing fluorine-based compounds have been widely used to impart water repellency and oil repellency to clothing materials and industrial materials made from textiles.

- [0003]** However, such fluorine-based water and oil repellent agents are found to contain compounds that may affect the living environment and living organisms, such as perfluorooctanoate (hereinafter PFOA) and perfluorooctane sulfonate (hereinafter PFOS). Therefore, fluorine-based water and oil repellent agents free of these compounds are demanded for textiles.

- 15 **[0004]** It is considered that a small amount of PFOA as an impurity is mixed in the fluorine-based water repellent agents during the manufacturing process, but the mechanism is not clarified. Since fluorine-based water repellent agents containing a polyfluoroalkyl group with 8 or more carbon atoms are likely to generate PFOA when decomposed by some influence, they are being replaced with those containing a polyfluoroalkyl group with 6 or less carbon atoms that generate no PFOA by decomposition. Patent Document 1 proposes a water and oil repellent fabric obtained by applying a fluorine-based water repellent agent free of PFOA and a crosslinker to a fabric and subjecting it to heat treatment. Patent Document 2 proposes a fiber structure in which a fluorine-based water repellent compound having a PFOA and/or PFOS concentration of less than 5 ng/g is fixed to monofilament surfaces, on which a layer of the fluorine-based compound is further fixed to form a two-layer structure. Both of the above, however, have lower water repellent performance than the fluorine-based water repellent agents containing PFOA with 8 or more carbon atoms.

- 25 **[0005]** To improve water repellent performance, Patent Document 3 proposes a method of fixing a polymer containing a specific fluoroalkyl alcohol (meth)acrylic acid derivative in a part, a melamine resin, and a water-dispersible polyfunctional isocyanate crosslinker to fiber surfaces, through at least one of a sulfone group-containing compound or a polyphenol compound fixed to the fiber surfaces. This method achieves a low water retention rate, but the water repellent performance is lower than the fluorine-based water repellent agents containing PFOA with 8 or more carbon atoms when immersed in water for an extended time.

## Prior Art Documents

- 35 Patent Documents

**[0006]**

- 40 Patent Document 1: JP 2007-270374 A  
Patent Document 2: JP 2010-150693 A  
Patent Document 3: JP 2014-194098 A

## Disclosure of Invention

- 45 Problem to be Solved by the Invention

- [0007]** As described above, conventional techniques leave room for improvement of fiber structures suitable for water repellent finishing, and there have been demands for fiber structures having higher water repellency and lower water retention rate.

- 50 **[0008]** To solve the above conventional problem, the present invention provides a fiber structure having improved water repellency and keeping a low water retention rate when immersed in water for an extended time.

## Means for Solving Problem

- 55 **[0009]** A fiber structure of the present invention is a fiber structure including an elastic polyurethane yarn. The elastic polyurethane yarn contains: 0.5 to 10% by mass (mass%) of a cationic high-molecular-weight compound A having a number-average molecular weight of 2000 or more; and an inorganic chlorine deterioration inhibitor B. The mass ratio of the cationic high-molecular-weight compound A to the inorganic chlorine deterioration inhibitor B ranges from 0.3 to

3, and a silicone oil is applied to the elastic polyurethane yarn. The fiber structure is treated with water repellent finishing.

#### Effect of the Invention

**[0010]** The present invention can provide a fiber structure having high water repellency and keeping a low water retention rate when immersed in water for an extended time, with the following configurations: the elastic polyurethane yarn contains 0.5 to 10% by mass of a cationic high-molecular-weight compound A having a number-average molecular weight of 2000 or more, and an inorganic chlorine deterioration inhibitor B; the mass ratio of the cationic high-molecular-weight compound A to the inorganic chlorine deterioration inhibitor B ranges from 0.3 to 3; a silicone oil is applied to the elastic polyurethane yarn; and the fiber structure is treated with water repellent finishing. The fiber structure of the present invention is particularly advantageous as a fabric for a swimsuit.

#### Description of the Invention

**[0011]** To make fabrics such as swimwear fabrics water repellent, the present inventors have focused on elastic polyurethane yarns, which have not received much attention, and conducted various studies to improve the water repellency of the elastic polyurethane yarns themselves. As a result of the studies, specific elastic polyurethane yarns are found to be highly compatible with water repellent agents.

**[0012]** The elastic polyurethane yarn of the present invention contains: 0.5 to 10 mass% of a cationic high-molecular-weight compound A having a number-average molecular weight of 2000 or more; and an inorganic chlorine deterioration inhibitor B. The mass ratio of the cationic high-molecular-weight compound A to the inorganic chlorine deterioration inhibitor B ranges from 0.3 to 3, and a silicone oil is applied to the elastic polyurethane yarn. By treating a fiber structure including the elastic polyurethane yarn with water repellent finishing, it is possible to obtain a highly water and oil repellent fiber structure having high water repellency and a low water retention rate to resist being wetted when immersed in water for an extended time.

**[0013]** Any water repellent treatment finishing agent may be used in the present invention, but it is preferable to use a treatment agent that makes the ratio of fluorine (F) / carbon (C) (hereinafter, referred to as a F/C ratio) on the elastic polyurethane yarn satisfy 0.030 or more in the elemental mass concentration according to SEM-EDX. In the elemental mass concentration according to SEM-EDX, the F/C ratio of 0.030 or more on the elastic polyurethane fiber indicates that the adhesion amount of the fluorine-based water repellent agent is large, whereas the F/C ratio of less than 0.03 indicates that the adhesion amount of the fluorine-based water repellent agent is small, and wettability is not lowered sufficiently. The F/C ratio is further preferably 0.045 or more.

**[0014]** The water repellent finishing of the present invention preferably contains a water repellent agent and a crosslinker. As the crosslinker, melamine resin, a water-dispersible polyfunctional isocyanate crosslinker or the like is suitably used, and these may be mixed together. Examples of the melamine resin include trimethylolmelamine and hexamethylohexamine. The water-dispersible polyfunctional isocyanate crosslinker is not particularly limited as long as it is an organic compound containing two or more isocyanate functional groups in the molecule. Examples of the same includes tolylene diisocyanate, hexamethylene diisocyanate, diphenylmethane diisocyanate, hydrogenated diphenylmethane diisocyanate, triphenyl triisocyanate, xylene diisocyanate, and dichlohexylmethane diisocyanate. More preferably, the water-dispersible polyfunctional isocyanate crosslinker is a polyfunctional blocked isocyanate crosslinker obtained by reacting a trimethylolpropane tolylene diisocyanate adduct, a friserin tolylene diisocyanate adduct or the like, with a phenol that is a blocking compound (a compound that regenerates an isocyanate group when heated to 70 to 200°C together with an isocyanate adduct), diethyl malonate, methyl ethyl ketoxime, sodium bisulfite,  $\epsilon$ -caprolactam, etc.

**[0015]** It is preferred that the melamine resin is mixed in a proportion of 1 to 40 mass% based on the solid content of the water repellent agent, and the polyfunctional isocyanate crosslinker is mixed in a proportion of 1 to 10 mass% based on the solid content of the water repellent agent.

**[0016]** The fiber structure of the present invention includes the elastic polyurethane yarn in an amount of preferably 1 to 99 mass%, more preferably 10 to 90 mass%, further preferably 15 to 80 mass%, and particularly preferably 20 to 70 mass%, when the fiber structure is assumed to be 100 mass%. With this configuration, the fiber structure including the elastic polyurethane yarn can keep high water repellency and a low water retention rate as a whole. In the case of using the fiber structure as a fabric for a swimsuit, the fiber structure preferably includes the elastic polyurethane yarn in an amount of 5 to 70 mass%, more preferably 5 to 60 mass%, further preferably 5 to 50 mass%, and particularly preferably 5 to 40 mass%. With this configuration, the swimsuit including the elastic polyurethane yarn can keep high water repellency and a low water retention rate as a whole. As other fiber yarns, synthetic fiber yarns such as polyester yarns, nylon yarns, and polypropylene yarns can be appropriately used.

**[0017]** The water repellency of the fiber structure of the present invention is preferably grade 4 or higher, and more preferably grade 5 in the spray test according to JIS L 1092. The fiber structure having a water repellency of grade 4 or higher is suitable for, e.g., a swimsuit. The water retention rate of the fiber structure after 60 minutes is preferably 50

mass% or less, more preferably 40 mass% or less, and further preferably 30 mass% or less of the mass of the fiber structure.

**[0018]** The elastic polyurethane yarn may be either a bare yarn or a yarn covered with another synthetic fiber yarn. The covered yarn may be either a single covered yarn or a double covered yarn. The swimsuit is preferably constituted by a woven fabric or knitted fabric using an elastic polyurethane fiber yarn covered with another synthetic fiber yarn. Examples of the synthetic fiber yarn include, but are not particularly limited to, polyester synthetic fiber yarns typified by polyethylene terephthalate, polytrimethylene terephthalate, polybutylene terephthalate, and copolymerized polyester fiber yarns containing any of these as a main component; polyamide synthetic fiber yarns typified by nylon 6 and nylon 6,6; and polypropylene synthetic fiber yarns. Among them, polyamide synthetic fiber yarns and polyester synthetic fiber yarns are preferred. The polyamide fibers are preferable from the viewpoint of strength and processability with the elastic polyurethane yarn. The synthetic fibers may have any fiber form and any cross-sectional shape, but it is preferable to subject them to false twisting by a known method to impart crimps, in order to produce a highly stretchable woven fabric. To lower the water retention rate, it is preferable to use straight yarns to minimize spaces between yarns. It is more preferable to subject yarns to surface smoothing by a known method to reduce spaces therebetween.

**[0019]** The tearing strength of the fiber structure is preferably 8 N or more, more preferably 10 N or more, and further preferably 12 N or more according to JIS L 1096. With this configuration, it is possible to maintain a high tearing strength as a swimsuit. Moreover, the bursting strength of the fiber structure is preferably 200 kPa or more, more preferably 300 kPa or more, and further preferably 400 kPa or more according to JIS L 1096. With this configuration, it is possible to maintain a high bursting strength as a swimsuit.

**[0020]** The fiber structure is preferably at least one of a woven fabric or a knitted fabric. In many cases, swimsuits for top swimmers are made from woven fabrics, and swimsuits for general swimmers are made from knitted fabrics. The fiber structure of the present invention is suitable as a fabric for a swimsuit. When the fiber structure is used for a swimsuit, wettability in water is reduced during swimming. Particularly when it is used for a competition swimsuit, wettability of the swimsuit during a race is reduced and water resistance is also reduced.

**[0021]** The elastic polyurethane yarn of the present invention is mainly composed of polyurethane. First, the polyurethane will be described.

**[0022]** The polyurethane used in the present invention is not particularly limited as long as a polymer diol and a diisocyanate are used as starting materials. The synthesis method is also not particularly limited. For example, the polyurethane may be a polyurethane urea composed of a polymer diol, a diisocyanate and a low-molecular-weight diamine, or a polyurethane urethane composed of a polymer diol, a diisocyanate and a low-molecular-weight diol. Further, the polyurethane may be a polyurethane urea prepared using a compound having a hydroxyl group and an amino group in the molecule as a chain extender. It is also preferred that a polyfunctional glycol having trifunctionality or higher functionality, isocyanate and the like are used within a range that does not impair the effect of the present invention.

**[0023]** Preferable examples of the polymer diol include polyether diol, polyester diol, and polycarbonate diol. Among these, a polyether diol is preferred particularly from the viewpoint of imparting flexibility and elongation to the yarn.

**[0024]** Preferable examples of the polyether diol include polyethylene oxide, polyethylene glycol, derivatives of polyethylene glycol, polypropylene glycol, polytetramethylene ether glycol (hereinafter, abbreviated as PTMG), copolymers of tetrahydrofuran (THF) and 3-methyltetrahydrofuran (modified PTMG), copolymers of THF and 2,3-dimethyl THF (modified PTMG), polyols having side chains on both sides as disclosed in, e.g., Japanese Patent No. 2615131, and random copolymers in which THF and ethylene oxide and/or propylene oxide are irregularly arranged. Such polyether diols may be used individually, or two or more kinds of these may be mixed or copolymerized.

**[0025]** From the viewpoint of imparting wear resistance and light stability to the elastic polyurethane yarn, polyester diols such as butylene adipate, polycaprolactone diol and polyester polyol having a side chain as disclosed in, e.g., JP S61-26612 A, and polycarbonate diols as disclosed in, e.g., JP H2-289516 A are favorably used.

**[0026]** Such polymer diols may be used individually, or two or more kinds of these may be mixed or copolymerized.

**[0027]** As the molecular weight of the polymer diol, the number-average molecular weight is preferably 1000 or more and 8000 or less, and more preferably 1500 or more and 6000 or less, from the viewpoint of imparting elongation, strength, heat resistance and the like to the yarn. The use of a polyol having a molecular weight of this range makes it possible to easily obtain an elastic yarn excellent in elongation, strength, elastic recovery, and heat resistance.

**[0028]** Next, as the diisocyanate, aromatic diisocyanates are particularly suitable for synthesizing a polyurethane with high heat resistance and high strength, examples of which include diphenylmethane diisocyanate (hereafter, abbreviated as MDI), tolylene diisocyanate, benzene 1,4-diisocyanate, xylylene diisocyanate, and 2,6-naphthalene diisocyanate. Further, preferable examples of alicyclic diisocyanates include methylenebis(cyclohexyl isocyanate), isophorone diisocyanate, methylcyclohexane 2,4-diisocyanate, methylcyclohexane 2,6-diisocyanate, cyclohexane 1,4-diisocyanate, hexahydroxylylene diisocyanate, hexahydroxylylene diisocyanate, and octahydro-1,5-naphthalene diisocyanate. Aliphatic diisocyanates are particularly effective to prevent yellowing of the elastic polyurethane yarn. Such diisocyanates may be used individually or in combinations of two or more kinds.

**[0029]** Next, the chain extender used in the synthesis of the polyurethane preferably contains at least one of a low-

molecular-weight diamine or a low-molecular-weight diol. The chain extender also may be a compound having a hydroxyl group and an amino group in the molecule such as ethanolamine.

**[0030]** Preferred examples of the low-molecular-weight diamine include ethylenediamine, 1,2-propanediamine, 1,3-propanediamine, hexamethylenediamine, p-phenylenediamine, p-xylylenediamine, m-xylylenediamine, p,p'-methylenedianiline, 1,3-cyclohexyldiamine, hexahydro metaphenylenediamine, 2-methylpentamethylenediamine, and bis(4-aminophenyl)phosphine oxide. It is preferable to use one or two or more of the above. Ethylenediamine is particularly preferred. The use of ethylenediamine makes it possible to easily obtain a yarn excellent in elongation, elastic recovery, and heat resistance. A triamine compound capable of forming a crosslinking structure with these chain extenders, such as diethylenetriamine, may be added within a range that does not impair the effect.

**[0031]** Typical examples of the low-molecular-weight diol include ethylene glycol, 1,3-propanediol, 1,4-butanediol, bishydroxyethoxybenzene, bishydroxyethylene terephthalate, and 1-methyl-1,2-ethanediol. It is preferable to use one or two or more of the above. Ethylene glycol, 1,3-propanediol, and 1,4-butanediol are particularly preferred. The use of the above makes it possible to obtain a yarn with further improved heat resistance as for polyurethane having diol extension and further improved strength.

**[0032]** As the molecular weight of the polyurethane in the present invention, the number-average molecular weight preferably ranges from 30000 to 150000, from the viewpoint of imparting high durability and strength to the fibers. The molecular weight is measured by GPC and converted by polystyrene.

**[0033]** One or a mixture of two or more kinds of end-capping agents are preferably used for the polyurethane. Preferable examples of the end-capping agent include monoamines such as dimethylamine, diisopropylamine, ethyl methylamine, diethylamine, methyl propylamine, isopropyl methylamine, diisopropylamine, butyl methylamine, isobutyl methylamine, isopentyl methylamine, dibutylamine and diamylamine, monools such as ethanol, propanol, butanol, isopropanol, allyl alcohol and cyclopentanol, and monoisocyanates such as phenylisocyanate.

**[0034]** In the present invention, when an elastic polyurethane yarn made from the polyurethane having the above basic composition contains 0.5 to 10 mass% of a cationic high-molecular-weight compound A having a number-average molecular weight of 2000 or more and an inorganic chlorine deterioration inhibitor B, and the A/B mass ratio ranges from 0.3 to 3, a large synergistic effect is produced, and an excellent effect of resisting chlorine deterioration and excellent water repellent property are exhibited.

**[0035]** The cationic high-molecular-weight compound used in the present invention is not particularly limited as long as it is a compound having an amino group in the structure. From the viewpoint of preventing chlorine deterioration and yellowing of the elastic polyurethane yarn, it is particularly preferable to use a compound having only a tertiary amino group in the molecule among primary to tertiary amino groups.

**[0036]** If the number-average molecular weight of the cationic high-molecular-weight compound is less than 2000, the water repellent property degrades due to falling off by rubbing with a guide or a knitting needle during formation of the elastic polyurethane yarn, or due to bleeding during processing such as dyeing in a bath. Therefore, the number-average molecular weight needs to be 2000 or more. In terms of solubility in the polyurethane spinning solution, the number-average molecular weight preferably ranges from 2000 to 10000. More preferably, it ranges from 2000 to 4000.

**[0037]** Containing the cationic high-molecular-weight compound can improve the water repellent property of the elastic polyurethane yarn. The content of the cationic high-molecular-weight compound is preferably more than 0.5 mass% and 10 mass% or less, and more preferably more than 0.5 mass% and 4 mass% or less with respect to the fiber mass, from the viewpoint of sufficiently producing this effect and not adversely affecting the physical properties of the fibers.

**[0038]** Moreover, the polyurethane yarn of the present invention is to contain the inorganic chlorine deterioration inhibitor, together with the cationic high-molecular-weight compound.

**[0039]** The inorganic chlorine deterioration inhibitor used in the present invention is preferably at least one of an oxide, a carbon oxide, a complex oxide or a solid solution of one or more elements selected from the group consisting of Zn, Mg, Ca and Al. From the viewpoint of durability against pool water and environment, carbon oxides  $\text{CaCO}_3$ ,  $\text{MgCO}_3$  and hydrotalcites composed of Mg and Al are particularly preferred.

**[0040]** The content of the inorganic chlorine deterioration inhibitor in the elastic polyurethane yarn in the present invention preferably ranges from 0.5 mass% to 10 mass%, from the viewpoint of durability against pool water and stability during production. The content thereof more preferably ranges from 1 mass% to 5 mass%.

**[0041]** From the viewpoint of achieving both of durability against pool water and water repellent property, the mass ratio (A)/(B) of the cationic high-molecular-weight compound (A) to the inorganic chlorine deterioration inhibitor (B) in the elastic polyurethane yarn ranges from 0.3 to 3, and more preferably 0.5 to 2.

**[0042]** The inorganic chlorine deterioration inhibitor, which is blended in the spinning solution and spun, is preferably fine powder with an average particle diameter of 2  $\mu\text{m}$  or less, and more preferably fine powder with an average particle diameter of 1  $\mu\text{m}$  or less, from the viewpoint of spinning stability. Further, if the average primary particle diameter is smaller than 0.01  $\mu\text{m}$ , the cohesive force increases, which makes the particles difficult to be uniformly mixed in the spinning solution. Therefore, the average primary particle diameter is preferably 0.01  $\mu\text{m}$  or more from the viewpoint of dispersibility. As the average particle diameter, a 50% particle diameter is measured by the laser diffracted light scattering

method. The measuring device is, e.g., a laser diffraction/scattering particle size distribution analyzer LA-950S2 manufactured by HORIBA, Ltd.

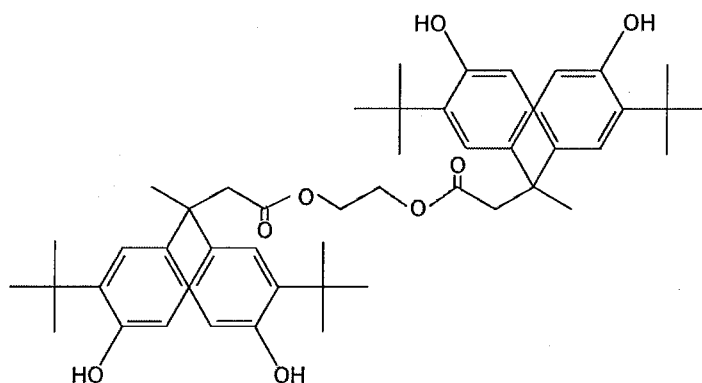
**[0043]** To finely pulverize the inorganic chlorine deterioration inhibitor, it is preferable to employ a method that includes: mixing the inorganic chlorine deterioration inhibitor with a solvent such as N,N-dimethylacetamide (hereafter, abbreviated as DMAc), dimethylformamide (hereafter, abbreviated as DMF), dimethylsulfoxide (hereafter, abbreviated as DMSO), N-methylpyrrolidone (hereafter, abbreviated as NMP) or a solvent containing any of these as a main component, and other additives such as a thickener to prepare a slurry; and crushing the slurry by, e.g., a vertical or horizontal mill.

**[0044]** Further, for the purpose of improving the dispersibility of the inorganic chlorine deterioration inhibitor into the yarn and stabilizing the spinning, it is also preferable to use an inorganic chlorine deterioration inhibitor that has been surface-treated with, e.g., an organic substance such as a fatty acid, a fatty acid ester, a phosphoric acid ester or a polyol organic substance, a silane coupling agent, a titanate coupling agent, water glass, a fatty acid metal salt, or a mixture of these.

**[0045]** Moreover, it is preferred that the elastic polyurethane yarn of the present invention contains a partially hindered phenol compound, from the viewpoint of improving durability against pool water. The partially hindered phenol compound preferably contains at least two partially hindered hydroxyphenyl groups and has a skeleton selected from bisester and alkylidene. It is more desirable that the alkyl group present in the ring position adjacent to the hydroxyl group in the hydroxyphenyl group is a tertiary butyl group, and it is further desirable that the equivalent of the hydroxyl group is 600 or less.

**[0046]** A preferable example of such a partially hindered phenol compound is ethylene-1,2-bis(3,3-bis[3-t-butyl-4-hydroxyphenyl]butyrate) having a structure in which a partially hindered hydroxyphenyl group is covalently bonded to a bisester skeleton (Chemical Formula 1 below).

[Chemical Formula 1]



**[0047]** Containing the partially hindered phenol compound can increase the effect of resisting chlorine deterioration. The content of the partially hindered phenol compound is preferably 0.15 to 4 mass%, and more preferably 0.5 to 3.5 mass% with respect to the elastic polyurethane yarn, from the viewpoint of sufficiently producing this effect and not adversely affecting the physical properties of the fibers.

**[0048]** As a treatment agent for the elastic polyurethane yarn in the present invention, a specific amount of silicone, ranging from 0.5 mass% to 20 mass%, is applied to the elastic fibers in the form of, e.g., an oil. The silicone is typically used to reduce the tension fluctuation during unwinding of the elastic polyurethane yarn in the manufacture of fabrics so that fine elastic fibers can be prevented from breaking due to the tension fluctuation during unwinding. In the present case, the silicone greatly contributes to an improvement in the water repellent property. The content of the silicone in the treatment agent is 0.5 to 10 mass%, preferably 1 to 6 mass% in dry mass. Thus, the affinity with the water repellent treatment agent can be improved. For example, an oil containing silicone can reduce the surface energy of a fabric and remarkably improve spreadability of a water repellent finishing agent when it is applied to the fabric surface.

**[0049]** Examples of the silicone include polydimethylsiloxane having dimethylsiloxane units, polydialkylsiloxanes having dimethylsiloxane units and dialkylsiloxane units containing an alkyl group with 2 to 4 carbon atoms, and polysiloxanes having dimethylsiloxane units and methylphenylsiloxane units, and these silicone oils are preferably used. Further, it is preferred that the silicone has a viscosity at 25°C of  $5 \times 10^{-6}$  to  $50 \times 10^{-6}$  m<sup>2</sup>/s, from the viewpoint of handleability and reduction of running friction with guides or the like. The viscosity can be measured by the method specified in JIS-K2283: "Crude petroleum and petroleum products - Determination of kinematic viscosity and calculation of viscosity index from kinematic viscosity".

**[0050]** The silicone oil is preferably mixed with a paraffinic hydrocarbon such as a mineral oil, an antistatic agent, a

dispersant, a metal soap, etc. The paraffinic hydrocarbon such as a mineral oil preferably has a viscosity at 25°C of  $5 \times 10^{-6}$  to  $50 \times 10^{-6}$  m<sup>2</sup>/s, from the viewpoint of handleability and reduction of running friction with guides or the like. Preferable examples of the antistatic agent include anionic surfactants such as alkyl sulfate, fatty acid soap, alkyl sulfonate, and alkyl phosphate. Preferable examples of the dispersant include silicone resin, polyether-modified silicone, carbinol-modified silicone, carboxyl-modified silicone, amino-modified silicone, amide-modified silicone, carboxamide-modified silicone, mercapto-modified silicone, and organic carboxylic acid, and these may be used individually or as a mixture. Preferable examples of the metal soap include magnesium stearate (hereafter, abbreviated as St-Mg) and calcium stearate, and the average particle diameter is preferably 0.1 to 1.0 µm from the viewpoint of improving handleability and dispersibility.

**[0051]** The silicone oil used in the present invention preferably contains components that are typically used in treatment agents for synthetic fibers, including a binder, an ultraviolet absorber, an antioxidant, a preservative, and a wettability modifier, as needed. The contents of the paraffinic hydrocarbon such as a mineral oil, metal soap, antistatic agent, dispersant, etc., are appropriately determined depending on the intended purpose.

**[0052]** Further, the silicone oil is preferably blended with a stabilizer, a thermal conductivity improver, and a pigment, within a range that does not impair the effect of the present invention.

**[0053]** The elastic polyurethane yarn of the present invention may contain various stabilizers, a pigment and the like, as needed. For example, as a light resistance agent, an antioxidant and the like, the elastic polyurethane yarn may contain the following: a sterically hindered phenol-based chemical agent typified by BHT or "SUMILIZER" (registered trademark) GA-80 manufactured by Sumitomo Chemical Co., Ltd., a benzotriazole- or benzophenone-based chemical agent such as "Tinuvin" (registered trademark) manufactured by Ciba-Geigy Corporation, a phosphorus-based chemical agent such as "SUMILIZER" P-16 manufactured by Sumitomo Chemical Co., Ltd., various hindered amine-based chemical agents, an inorganic pigment such as titanium oxide or carbon black, a fluorine- or silicone-based resin powder based on vinylidene polyfluoride or the like, a metal soap such as magnesium stearate, a germicide containing silver, zinc or any of these compounds, a deodorant, a lubricant such as silicone or mineral oil, barium sulfate, cerium oxide, an antistatic agent such as betaine, a phosphoric acid compound or phosphoric acid ester compound. These may be reacted with polymer to remain present. To further increase durability, especially against light and nitrogen oxides, it is preferred that the elastic polyurethane yarn also contains a nitrogen oxide scavenger such as HN-150 manufactured by Nippon Hydrazine Co., Ltd., or "Hostanox" (registered trademark) SE10 manufactured by Clariant Corporation, a thermo-oxidation stabilizer such as "SUMIUSER" GA-80 manufactured by Sumitomo Chemical Co., Ltd., and a light stabilizer such as "SUMISORB" (registered trademark) 300#622 manufactured by Sumitomo Chemical Co., Ltd.

**[0054]** Next, the method for producing the elastic polyurethane yarn of the present invention will be described in detail.

**[0055]** The production method of the polyurethane may be either melt polymerization or solution polymerization, or another method. However, solution polymerization is more preferred. In the solution polymerization, foreign substances such as gel are less generated in the polyurethane, spinning is easy, and an elastic polyurethane yarn of low fineness is easily obtained. Obviously, solution polymerization is advantageous in that the operation of preparing a solution can be omitted.

**[0056]** A polyurethane particularly suitable for the present invention is synthesized using PTMG having a molecular weight of 1500 to 6000 as a polymer diol, MDI as a diisocyanate, and at least one of ethylenediamine, 1,2-propanediamine, 1,3-propanediamine or hexamethylenediamine as a chain extender.

**[0057]** The polyurethane is obtained, for example, by synthesizing the above raw materials in a solvent such as DMAc, DMF, DMSO, NMP, or a solvent containing any of these as a main component. For example, particularly suitable methods which may be employed are: a one-shot method of throwing the raw materials into such a solvent to dissolve, and heating and reacting them to form a polyurethane; and a method of first melting and reacting a polymer diol and a diisocyanate, then dissolving the reaction product in a solvent and reacting it with the chain extender to form a polyurethane.

**[0058]** In the case of using a diol as a chain extender, it is preferable to adjust the melting point of the polyurethane on the high temperature side to a range from 200°C to 260°C, from the viewpoint of obtaining a polyurethane having excellent heat resistance. A typical method of achieving this adjustment is to control the type and ratio of the polymer diol, MDI, and diol. In the case that the polymer diol has a low molecular weight, increasing the relative proportion of MDI can yield a polyurethane having a high melting point on the high temperature side. Similarly, in the case that the diol has a low molecular weight, reducing the relative proportion of the polymer diol can yield a polyurethane having a high melting point on the high temperature side.

**[0059]** In the case that the polymer diol has a molecular weight of 1800 or more, the polymerization preferably takes place with a ratio of (the number of moles of MDI) / (the number of moles of polymer diol) = 1.5 or more in order to make the melting point on the high temperature side 200°C or higher.

**[0060]** One or a mixture of two or more kinds of catalysts such as an amine catalyst and an organometallic catalyst are preferably used for the synthesis of the polyurethane.

**[0061]** Examples of the amine catalyst include N,N-dimethyl cyclohexylamine, N,N-dimethyl benzylamine, triethylamine, N-methylmorpholine, N-ethylmorpholine, N,N,N',N'-tetramethyl ethylenediamine, N,N,N',N'-tetramethyl-1,3-pro-

panediamine, N,N,N',N'-tetramethyl hexanediamine, bis-2-dimethylaminoethyl ether, N,N,N',N',N'-pentamethyl diethylenetriamine, tetramethylguanidine, triethylenediamine, N,N'-dimethylpiperazine, N-methyl-N'-dimethylaminoethyl-piperazine, N-(2-dimethylaminoethyl)morpholine, 1-methylimidazole, 1,2-dimethylimidazole, N,N-dimethylaminoethanol, N,N,N'-trimethylaminoethyl ethanolamine, N-methyl-N'-(2-hydroxyethyl)piperazine, 2,4,6-tris(dimethylaminomethyl)phenol, N,N-dimethylaminoethanol, and triethanolamine.

**[0062]** Examples of the organometallic catalyst include tin octanoate, dibutyltin dilaurate, and lead dibutyl octanoate.

**[0063]** Typically, the concentration of the polyurethane in the polyurethane solution thus obtained preferably ranges from 30 mass% to 80 mass%.

**[0064]** In the present invention, the polyurethane solution contains the cationic high-molecular-weight compound having a number-average molecular weight of 2000 or more and the inorganic chlorine deterioration inhibitor to improve durability against chlorine in pool water and the water repellent property. As a method for incorporating the cationic high-molecular-weight compound into the spinning solution, it may be solely mixed with the spinning solution, or it may be mixed with the inorganic chlorine deterioration inhibitor beforehand. As a method for evenly dispersing the cationic high-molecular-weight compound and the inorganic chlorine deterioration inhibitor in the polyurethane spinning solution before spinning, it is preferred that they are added to a polyurethane spinning solution containing N,N-dimethylformamide or N,N-dimethylacetamide as a solvent, and then stirred and mixed evenly. Specifically, it is preferred that the cationic high-molecular-weight compound and the inorganic chlorine deterioration inhibitor are dissolved or dispersed in a solvent such as N,N-dimethylformamide or N,N-dimethylacetamide beforehand, and the solution or dispersion is mixed with the polyurethane spinning solution. Here, the solvent for the cationic high-molecular-weight compound and the inorganic chlorine deterioration inhibitor to be added is preferably the same as the solvent for the polyurethane solution, from the viewpoint of adding them evenly in the polyurethane solution. The chemical agents such as a light resistance agent and an antioxidant and the pigment described above may be added simultaneously with the cationic high-molecular-weight compound and the inorganic chlorine deterioration inhibitor. Any method can be adopted to add the cationic high-molecular-weight compound and the inorganic chlorine deterioration inhibitor into the polyurethane solution. Various typical methods may be adopted, including a method using a static mixer, a method using stirring, a method using a homomixer, and a method using a biaxial extruder.

**[0065]** To improve durability against chlorine in pool water, the elastic polyurethane yarn preferably contains a partially hindered phenol compound having at least one partially hindered hydroxyphenyl group and having a molecular weight of 300 or more, in an amount of, e.g., 0.15 mass% or more and 4.0 mass% or less. Any method can be adopted to incorporate the partially hindered phenol compound into the spinning solution, and it may be solely mixed with the spinning solution, or it may be mixed with the above solution or dispersion beforehand.

**[0066]** The polyurethane yarn of the present invention can be obtained by subjecting the spinning solution prepared as described above to dry spinning, wet spinning or melt spinning, followed by winding, for example. Among them, dry spinning is preferred because it enables stable spinning in any fineness from thin to thick.

**[0067]** The elastic polyurethane yarn of the present invention may have any fineness and any cross-sectional shape. For example, the cross-sectional shape of the yarn may be circular or elliptical.

**[0068]** The dry spinning method is also not specifically limited, and suitable spinning conditions are to be selected depending on the desired characteristics, spinning equipment, etc.

**[0069]** The spinning speed is preferably 250 m/min or greater from the viewpoint of improving the strength of the elastic polyurethane yarn to be obtained.

**[0070]** The knitted fabric including the elastic polyurethane yarn may be any of a circular knitted fabric, a weft knitted fabric, or a warp knitted fabric (e.g., a tricot knitted fabric, a raschel knitted fabric). The knitted structure may be pile stitch, flat stitch, plain stitch, rib stitch, smooth stitch (interlock stitch), rib stitch, pearl stitch, denbigh stitch, double denbigh stitch, cord stitch, half stitch, back half stitch, atlas stitch, double atlas stitch, chain stitch, inlay stitch, or any combination of the above.

**[0071]** The woven fabric including the elastic polyurethane yarn and other fibers is woven by a general method. Examples of the woven fabric structure include plain weave, twill weave, sateen weave, variegated plain weave, variegated twill weave, variegated sateen weave, fancy weave, brocade, single texture, double texture, multiple texture, warp pile weave, weft pile weave, interweave, and any combination of the above. The woven fabric may be either a one-way stretch fabric in which the polyurethane yarn is used for warp or weft, or a two-way stretch fabric in which the polyurethane yarn is used for both warp and weft.

**[0072]** The fabric including the elastic polyurethane yarn and other fibers is scoured, relaxed, and set under normal conditions. The fabric is usually dyed with a dye and conditions that are suitable for other fibers mixed at a high ratio in the fabric. The dye may be a disperse dye, an acid dye, a metal complexed dye, or a conventional dye. The fabric may be subjected to a fixing treatment for dye fixing, an antibiotic treatment, a softening treatment, etc., as needed.

**[0073]** The following describes the water repellent finishing method of the present invention. The water repellent finishing of the present invention is preferably imparted by dry heat treatment. The dry heat treatment may be performed by applying a treatment liquid containing a water repellent agent to a fiber structure with a device such as a mangle,



followed by drying and heat treatment. As a device for applying the treatment liquid containing a water repellent agent to a fiber structure, a device that can uniformly apply the liquid to the fiber structure is preferred, and a normal mangle is suitable as a liquid applying device. The treatment liquid also can be applied by a foam processing machine, or a method such as printing, inkjet, spraying or coating method. The drying temperature is preferably 80°C to 150°C. The treatment time is preferably 15 seconds to 5 minutes, more preferably 30 seconds to 3 minutes at 100°C to 140°C. The heat treatment temperature after drying is preferably 80 to 200°C. The treatment time is preferably 15 seconds to 8 minutes, more preferably 30 seconds to 5 minutes at 130°C to 190°C. When the treatment temperature is low, the reaction will not occur sufficiently, which lowers water repellency.

## Examples

**[0074]** Hereinafter, the present invention will be described further specifically by way of examples. However, the present invention is not limited to the following examples. Further, in the following examples, the weight ratio simply expressed by % indicates mass%.

**[0075]** Various characteristics of woven fabrics were measured in the following manner.

### (Elemental Mass Concentration)

**[0076]** The elemental mass concentration was measured according to SEM-EDX under the conditions below, using elastic polyurethane yarns that appeared on the surface of a dismantled fiber structure or elastic polyurethane fibers taken out from unraveled yarns. The F/C ratio was calculated from the obtained elemental mass concentration. A SEM (S-3400N manufactured by Hitachi, Ltd.) and an EDX detector (EMAX x-act manufactured by HORIBA, Ltd.) were used as the measuring devices.

### <Measurement Conditions>

#### **[0077]**

Acceleration voltage: 5 kV

Resolution: 1024 × 768

Probe current: 50 mA

Live time: 120 sec

Vacuum: 30 Pa

Process time: mode: 4

WD: 10 mm

Spectral range: 0 to 20 keV

Magnification: 2000 times

Number of channels: 2K

### (Water Repellency)

**[0078]** The water repellency was evaluated and classified according to the spray method specified in JIS L 1092: "Testing methods for water resistance of textiles" (1998).

### (Water Retention Rate)

**[0079]** A circle of diameter 11.2 cm was drawn in the middle of each fiber structure that was cut in 20 cm long and 20 cm wide, and the fiber structure was stretched to extend the circled area by 80%, to which a specimen holding frame for a water repellency test (JIS L 1092) was attached. After the spray test (JIS L 1092), the fiber structure was removed from the holding frame and air-dried in an environment of 20°C × 53% RH. Ten pieces of the same fiber structure were prepared, and each was weighed as a "weight before treatment".

**[0080]** 30 L of water (water temperature: 25 to 29°C) was filled in a washing machine (JIS C 9606), into which the 10 pieces of the fiber structure were immersed. They were rotated for a predetermined period of time (10 minutes, 60 minutes, 120 minutes) under "strong conditions" and taken out from water one by one. They were inclined about 15 degrees in a spread state for 10 seconds to remove water droplets from the fiber structure, and each was weighed as a "weight after treatment" to measure the water retention rate by Formula below.

$$\text{Water retention rate (\%)} = ((\text{Weight after treatment} - \text{Weight before treatment}) / \text{Weight before treatment}) \times 100$$

#### <Tearing Strength>

**[0081]** The tearing strength was evaluated according to the pendulum method specified in JIS L 1096: "Testing methods for woven and knitted fabrics" (1999).

#### <Bursting Strength>

**[0082]** The bursting strength was evaluated according to the Mullen method specified in JIS L 1096: "Testing methods for woven and knitted fabrics" (1999).

#### <Elongation Rate>

**[0083]** The elongation rate was measured according to the cut strip method specified in JIS L 1096 A: "Testing methods for woven and knitted fabrics" (1999). A test piece was 5 cm wide, and a clamp interval was 20 cm. An initial load was set at a load corresponding to a gravity applied to 1 m (length) of the test piece. A tensile speed was set at 20 cm/min. An elongation rate (%) under a load of 17.7 N (1.8 kg) was measured. The elongation rate represents stretchability.

#### <Stress at 30% Elongation>

**[0084]** The stress (N) at 30% elongation during measurement of the elongation rate in warp and weft directions was measured, and the value obtained was converted into per centimeter and expressed by N/cm. The stress at 30% elongation can be a criterion for evaluating the compression (wearing pressure) function of the sample.

#### (Preparation of Yarn A)

**[0085]** PTMG having a number-average molecular weight of 1800 and MDI were placed in a container at a molar ratio of MDI/PTMG = 1.58/1 and reacted at 90°C, and the resulting reaction product was dissolved in N,N-dimethylacetamide (DMAc). Next, a DMAc solution containing ethylenediamine and diethylamine was added to the solution in which the reaction product was dissolved to prepare a polyurethane urea solution having a solid content of 35 mass% in polymer.

**[0086]** A condensation polymer of p-cresol and divinylbenzene ("Methacrol" (registered trademark) 2390 manufactured by DuPont), as an antioxidant, and 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenyl ("Cyasorb" (registered trademark) 1164 manufactured by Cytech Inc.), as an ultraviolet absorber, were mixed at a ratio (mass ratio) of 3/2 to prepare a DMAc solution (concentration: 35 mass%) as an additive solution (35 mass%).

**[0087]** The polyurethane urea solution and the additive solution were mixed at a ratio of 98 mass% and 2 mass% to prepare a polymer solution (X1).

**[0088]** As a cationic high-molecular-weight compound, a cationic high-molecular-weight compound having a number-average molecular weight of 2600 was prepared by reacting t-butyldiethanolamine with methylene-bis- (4-cyclohexyl isocyanate). The cationic high-molecular-weight compound thus obtained was dissolved in DMAc to prepare a solution (A1) with a concentration of 35 mass%.

**[0089]** Calcium carbonate HakuenkaA (CaCO<sub>3</sub>, average primary particle diameter: 1.0 μm) manufactured by Shiraishi Kogyo Kaisha, Ltd., was used as a chlorine deterioration inhibitor to prepare a 35 mass% DMAc dispersion. For this preparation, a horizontal mill DYNO-MIL KDL manufactured by Willy A. Bachofen AG was used, and 85% zirconia beads were filled therein to finely and evenly disperse them at a flow rate of 80 g/min to prepare a DMAc dispersion B1 of synthetic carbonate (35 mass%).

**[0090]** As a partially hindered phenol compound, ethylene-1,2-bis(3,3-bis[3-t-butyl-4-hydroxyphenyl]butyrate ("Hos-tanox" (registered trademark) 03 manufactured by Clariant Corporation) was dissolved in DMAc to prepare a solution (C1) with a concentration of 35 mass%.

**[0091]** The polymer solutions X1, A1, B1 and C1 were mixed at a ratio of 97 mass%, 1 mass%, 3 mass% and 1 mass%, respectively, to prepare a spinning solution Y1. The spinning solution Y1 was dry-spun at a winding speed of 580 m/min to produce an elastic polyurethane yarn (78 decitex) (Z1). A silicone oil as a treatment agent was applied thereto while winding. As the silicone oil, a treatment agent (oil) containing 96% of silicone (polydimethylsiloxane), 3% of St-Mg and 1% of dispersant was applied in an amount of 6% in dry weight.

**[0092]** The elastic polyurethane yarn obtained in the above-described manner was covered with a nylon 66 yarn. The

nylon 66 yarn used was 33 decitex, 10 filaments. The covering was 1400 T/m, single covering. Thus, a yarn A was obtained.

(Preparation of Yarn B)

- 5 **[0093]** A yarn B was produced in the same manner as the yarn A except that an elastic polyurethane yarn was produced in 55 decitex.

(Preparation of Yarn C)

- 10 **[0094]** A yarn C was produced in the same manner as the yarn A except that an elastic polyurethane yarn was produced in 44 decitex and covered with a nylon 66 yarn of 33 decitex, 10 filaments.

(Preparation of Yarn D)

- 15 **[0095]** An elastic polyurethane yarn of 78 decitex (Type 176E, manufactured by TORAY OPELONTEX CO., LTD.) was covered with a nylon 66 yarn of 33 decitex, 10 filaments, to produce a yarn D.

(Preparation of Yarn E)

- 20 **[0096]** An elastic polyurethane yarn of 55 decitex (Type 254E, manufactured by TORAY OPELONTEX CO., LTD.) was covered with a nylon 66 yarn of 33 decitex, 10 filaments, to produce a yarn E.

(Preparation of Yarn F)

- 25 **[0097]** An elastic polyurethane yarn of 44 decitex (Type 254T, manufactured by TORAY OPELONTEX CO., LTD.) was covered with a nylon 66 yarn of 33 decitex, 48 filaments, to produce a yarn F.

(Example 1)

- 30 **[0098]** The yarn A was used as a warp yarn, and the yarn B and the yarn C were used as weft yarns to produce a plain woven fabric. The obtained woven fabric was 66% of nylon and 34% of polyurethane. The woven fabric was subjected to scouring, intermediate setting, dyeing, and drying according to ordinary methods. The obtained woven fabric was immersed in a water repellent preparation below, squeezed with a pickup of 50%, and then dried in a pin  
35 tenter set at a temperature of 130°C. Then, the woven fabric was subjected to dry heat treatment for 1 minute in the pin tenter at 170°C to obtain a processed woven fabric (fiber structure) of Example 1. Regarding the finished density of the woven fabric, the warp density was 185 yarns/2.54 cm, the weft density was 201 yarns/2.54 cm, and the mass per unit area was 146 g/m<sup>2</sup>. The obtained processed fabric was a highly water repellent fiber structure having a high water repellent degree and a low water retention rate.

- 40
- FX-ML (fluorine-based water repellent agent manufactured by Kyokenkasei): 100 g/L
  - BECKAMINE M-3 (melamine resin manufactured by DIC Corporation): 3 g/L
  - BECKAMINE ACX (catalyst manufactured by DIC Corporation): 2 g/L
  - Super Fresh JB7200 (water-dispersible polyfunctional isocyanate crosslinker manufactured by Kyokenkasei): 5 g/L

45 (Example 2)

- [0099]** A processed woven fabric (fiber structure) of Example 2 was obtained in the same manner as in Example 1, except that the yarn A and the yarn B were used as a warp yarn and a weft yarn, respectively, and the woven fabric was constituted by 66% of nylon and 34% of polyurethane. Regarding the finished density of the woven fabric, the warp  
50 density was 184 yarns/2.54 cm, the weft density was 178 yarns/2.54 cm, and the mass per unit area was 129 g/m<sup>2</sup>. The obtained processed fabric was a highly water repellent fiber structure having a high water repellent degree and a low water retention rate.

(Comparative Example 1)

- 55 **[0100]** A processed woven fabric (fiber structure) of Comparative Example 1 was obtained in the same manner as in Example 1, except that the yarn D was used as a warp yarn, and the yarn E and the yarn F were used as weft yarns, and the woven fabric was constituted by 66% of nylon and 34% of polyurethane. The obtained processed fabric had a

high water repellent degree but also a high water retention rate, which was unsatisfactory.

(Comparative Example 2)

**[0101]** A processed woven fabric (fiber structure) of Comparative Example 2 was obtained in the same manner as in Example 1, except that the yarn D was used as a warp yarn, and the yarn E was used as a weft yarn, and the woven fabric was constituted by 66% of nylon and 34% of polyurethane. The obtained processed fabric had high a water repellent degree but also a high water retention rate, which was unsatisfactory. Table 1 summarizes the results.

[Table 1]

		Example 1	Example 2	Comparative Example 1	Comparative Example 2
	Mass (g/m <sup>2</sup> )	146	129	136	126
	Tearing strength (N)				
	Warp	15.4	16.3	18.4	18.9
	Weft	15.8	12.9	19.0	15.2
	Bursting strength (kPa)	490	518	615	600
	SEM-EDX analysis value (F/C ratio)	0.059	0.045	0.023	0.029
	Elongation rate (%)				
	Warp direction	55.1	38.7	54.7	43.4
	Weft direction	31.8	34.4	37.6	33.7
	Stress at 30% elongation (N/cm)				
	Warp direction	1.61	2.57	1.27	2.14
	Weft direction	3.27	3.00	2.61	3.00
	Water repellency (grade)	5	5	5	5
	Water retention rate (%)				
	After 10 minutes	3.7	6.9	8.1	8.3
	After 60 minutes	10.2	12.1	63.3	35.1
	After 120 minutes	17.3	29.0	70.3	51.5

**[0102]** Table 1 shows that the fiber structures of Examples 1 and 2 were high in water repellency and low in water retention rate, particularly they were low in water retention to resist being wetted when immersed in water for an extended time.

#### Industrial Applicability

**[0103]** The fiber structure including the elastic polyurethane yarn of the present invention can be applied to various stretch foundations of sports clothing, swimwear, girdles, brassieres, intimate products and underwear, sock cuffs, tights, pantyhose, waistbands, body suits, spats, stretch sportswear, stretch outerwear, bandages, supporters, medical wear, stretch liners, and disposable diapers, for example. The fiber structure is particularly suitable as a fabric for a swimsuit used in pools. A swimsuit obtained therefrom can be excellent in water repellency and water retention rate.

#### Claims

1. A fiber structure comprising an elastic polyurethane yarn, wherein the elastic polyurethane yarn comprises:

0.5 to 10% by mass of a cationic high-molecular-weight compound A having a number-average molecular weight of 2000 or more; and  
 an inorganic chlorine deterioration inhibitor B,  
 a mass ratio of the cationic high-molecular-weight compound A to the inorganic chlorine deterioration inhibitor

B ranges from 0.3 to 3,  
a silicone oil is applied to the elastic polyurethane yarn, and  
the fiber structure is treated with water repellent finishing.

- 5     **2.** The fiber structure according to claim 1, wherein the fiber structure comprises an elastic polyurethane yarn whose ratio of fluorine (F) to carbon (C) on the elastic polyurethane yarn is 0.030 or more in an elemental mass concentration according to scanning electron microscope - energy dispersive X-ray spectroscopy (SEM-EDX).
- 10    **3.** The fiber structure according to claim 1 or 2, wherein the fiber structure comprises 1 to 99% by mass of the elastic polyurethane yarn.
- 4.** The fiber structure according to any of claims 1 to 3, wherein the fiber structure has a water repellency of grade 4 or higher in the spray test according to JIS L 1092.
- 15    **5.** The fiber structure according to any of claims 1 to 4, wherein the fiber structure has a water retention rate after 60 minutes of 50% by mass or less of the mass of the fiber structure.
- 6.** The fiber structure according to any of claims 1 to 5, wherein the elastic polyurethane yarn is covered with another synthetic fiber yarn.
- 20    **7.** The fiber structure according to any of claims 1 to 6, wherein the fiber structure comprises a polyamide fiber yarn or a polyester fiber yarn.
- 8.** The fiber structure according to any of claims 1 to 7, wherein the fiber structure has a tearing strength of 8 N or more according to JIS L 1096.
- 25    **9.** The fiber structure according to any of claims 1 to 8, wherein the fiber structure has a bursting strength of 200 kPa or more according to JIS L 1096.
- 30    **10.** The fiber structure according to any of claims 1 to 9, wherein the fiber structure is at least one of a woven fabric or a knitted fabric.
- 11.** The fiber structure according to any of claims 1 to 10, wherein the fiber structure is a fabric for a swimsuit.
- 35    **12.** The fiber structure according to any of claims 1 to 11, wherein the inorganic chlorine deterioration inhibitor B is an oxide, a carbon oxide, a complex oxide or a solid solution of at least one element selected from the group consisting of Zn, Mg, Ca and Al.
- 40    **13.** The fiber structure according to any of claims 1 to 12, wherein the cationic high-molecular-weight compound A is a compound having a tertiary amino group and having neither a primary amino group nor a secondary amino group in its molecular structure.
- 14.** The fiber structure according to any of claims 1 to 13, wherein the elastic polyurethane yarn further comprises 0.3 to 4% by mass of a partially hindered phenol-based antioxidant.
- 45    **15.** The fiber structure according to any of claims 1 to 14, wherein the silicone oil comprises 50% by mass or more of at least one silicone selected from the group consisting of dimethyl silicone and a modified silicone.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/012842

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. D03D15/08 (2006.01)i, A41D7/00 (2006.01)i, A41D31/00 (2019.01)i, A41D31/10 (2019.01)i, A41D31/18 (2019.01)i, D01F6/70 (2006.01)i, D02G3/38 (2006.01)i, D04B1/18 (2006.01)i, D04B21/00 (2006.01)i, D06M15/643 (2006.01)i, D06M101/38 (2006.01)n  
 FI: D03D15/08, A41D7/00Z, A41D31/00502B, A41D31/00502C, A41D31/00503F, A41D31/00503G, A41D31/00503K, A41D31/10, A41D31/18, D01F6/70Z, D02G3/38, D04B1/18, D04B21/00B, D06M15/643, D06M101:38

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)

Int.Cl. A41D5/00-11/00, A41D15/00-17/04, A41D31/00-31/32, D02G1/00-3/48, D02J1/00-13/00, D03D1/00-27/18, D04B1/00-39/08, D06M13/00-15/715

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	1971-2020
Registered utility model specifications of Japan	1996-2020
Published registered utility model applications of Japan	1994-2020

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 JSTPlus/JMEDPlus/JST7580 (JDreamIII)

## 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.) 12.07.2012 (2012-07-12), claims, paragraphs [0002], [0043], [0141]	1-15
Y	JP 2000-064121 A (ASAHI KASEI KOGYO CO., LTD.) 29.02.2000 (2000-02-29), paragraphs [0001], [0033], [0034], examples	1-15
Y	JP 2002-294563 A (TORAY INDUSTRIES, INC.) 09.10.2002 (2002-10-09), paragraphs [0001], [0022], [0024], examples	1-15
Y	JP 2014-194098 A (TORAY INDUSTRIES, INC.) 09.10.2014 (2014-10-09), claims, examples	4

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

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"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
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  
 02.06.2020

Date of mailing of the international search report  
 23.06.2020

Name and mailing address of the ISA/  
 Japan Patent Office  
 3-4-3, Kasumigaseki, Chiyoda-ku,  
 Tokyo 100-8915, Japan

Authorized officer  
  
 Telephone No.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/012842

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2006-097194 A (OPELONTEX CO., LTD.) 13.04.2006 (2006-04-13), claims, paragraphs [0026], [0038], examples	14
Y	JP 2006-342448 A (OPELONTEX CO., LTD.) 21.12.2006 (2006-12-21), claims, paragraphs [0001], [0049], [0098], examples	1-15
A	JP 60-252747 A (TOYOBO CO., LTD.) 13.12.1985 (1985-12-13)	1-15

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

PCT/JP2020/012842

JP 2012-132130 A 12.07.2012 (Family: none)

JP 2000-064121 A 29.02.2000 EP 1123994 A1  
paragraphs [0001], [0046], [0047],  
[0062]-[0081]  
US 6406788 B1

JP 2002-294563 A 09.10.2002 (Family: none)

JP 2014-194098 A 09.10.2014 (Family: none)

JP 2006-097194 A 13.04.2006 (Family: none)

JP 2006-342448 A 21.12.2006 (Family: none)

JP 60-252747 A 13.12.1985 (Family: none)



**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- JP 2007270374 A [0006]
- JP 2010150693 A [0006]
- JP 2014194098 A [0006]
- JP 2615131 B [0024]
- JP 61026612 A [0025]
- JP H2289516 A [0025]