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(54) **Polyurethane elastic yarns and stretch fabrics**

Elastische Fäden aus Polyurethan und elastische Flächengebilde

Fils élastiques de polyuréthane et tissus élastiques

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- **PATENT ABSTRACTS OF JAPAN vol. 1996, no. 06, 28 June 1996 (1996-06-28) & JP 08 049145 A (TOYOBO CO LTD), 20 February 1996 (1996-02-20)**

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Description

[0001] The present invention relates to polyurethane elastic yarns and stretch fabrics, which can be set at low temperatures, and in particular, it relates to polyurethane elastic yarns and stretch fabrics, which are characterized in that products using the same can exhibit a sense of soft fit. More particularly, it relates to polyurethane elastic yarns and stretch fabrics, which can be set at low temperatures and can exhibit a sense of soft fit in combination with materials such as acrylic, wool, cotton, and silk fibers, for example, in pantyhose, cotton circular rib knitted fabrics, and wool fabrics, or in fabrics prepared only thereby.

[0002] Polyurethane fibers have been widely used for various applications by utilizing their feature that they have high elasticity (see eg WO 99/11 688, WO 95/23 883 and US-A-5 616 676). With the expansion of their application range, polyurethane fibers have become required to have additional characteristics. In particular, according to the recent fashion for stretch clothes, polyurethane fibers have been used in combination with various kinds of fibers. For example, polyurethane elastic yarns prepared by melt spinning are disclosed, which can be subjected to high-temperature high-pressure dyeing because of their improved resistance to wet heat and which can be woven or knitted in mixture with polyester fibers. Many other reports have been made on polyurethane elastic yarns intended to have improved heat resistance and elastic recovery. However, products using these polyurethane elastic yarns are not intended to have satisfactory setting properties at low temperatures and to exhibit a soft fit.

[0003] For union fabrics with nylon or acrylic fibers, or natural fibers, such as wool, cotton, or silk fibers, processing conditions should be made suitable for these partner materials, in which case the processing conditions are mild. Therefore, even conventional polyurethane elastic yarns can maintain their physical properties after processing, although they become difficult to have satisfactory setting properties. Contrary to this case, when processing conditions are made severe to confer satisfactory properties on the fibers (*i.e.*, processing temperature is raised), there occurs a problem that the feeling of partner materials to be mixed is deteriorated.

[0004] An object of the present invention is to provide polyurethane elastic yarns having low-temperature setting properties and exhibiting a soft fit. This object could be achieved by paying attention to crystalline regions composed mainly of urethane hard segments as the structure of basic fibers, inhibiting the growth of the said regions in directions perpendicular to the direction of the fiber axis, and disturbing their orientation to the direction of the fiber axis.

[0005] Thus, the present invention provides polyurethane elastic yarns meeting the following conditions:

(1) the angle corresponding to the half-height width of maximum peak intensity in an azimuthal scanning in the measurement of small-angle X-ray scattering is 60° or greater;
(2) the angle corresponding to the half-height width in the equatorial direction in the measurement of small-angle X-ray scattering is 2.5° or smaller;
(3) the temperature at the peak of maximum shrinkage stress in the measurement of thermal stress is 135°C or lower.

[0006] In preferred embodiments, the temperature at the peak of maximum shrinkage stress in the measurement of thermal stress may be 105°C or lower; the angle corresponding to the half-height width in the equatorial direction in the measurement of small-angle X-ray scattering may be in the range of from 0.8° to 1.5°; the percentage of setting with dry heat at 120°C (PSD120) may be 65% or higher and the percentage of setting with wet heat at 105°C (PSW105) may be 75% or higher; the maximum shrinkage stress in the measurement of thermal stress may be 10 mg/denier or smaller; the ratio in percentage of backward stress to forward stress at 150% elongation in the measurement of repeated stress at 300% elongation may be 20% or lower; or the above polyurethane elastic yarns may be prepared by melt spinning.

[0007] The present invention further provides stretch fabrics which are prepared by weaving or knitting of the above polyurethane elastic yarns in mixture with thermoplastic synthetic fibers, natural fibers, or regenerated fibers.

[0008] In preferred embodiments, the thermoplastic synthetic fibers may be polyester, polyamide, or acrylic fibers; the natural fibers may be cotton, wool, or silk fibers; or the regenerated fibers may be polynosic fibers.

[0009] The polyurethane elastic yarns of the present invention should meet the condition that the angle corresponding to the half-height width of maximum peak intensity in an azimuthal scanning in the measurement of small-angle X-ray scattering is 60° or greater. The phrase "angle corresponding to the half-height width of maximum peak intensity in an azimuthal scanning in the measurement of small-angle X-ray scattering" as used herein refers to an angle formed by the center of a photograph of diffraction images, which is obtained by azimuthal scanning measurement, and the half-height width of maximum peak intensity on the photograph. When the angle is smaller than 60°, crystalline regions composed mainly of urethane hard segments exhibit good orientation, so that stretching force becomes excess, making it difficult to obtain a soft fit of products in wear. In the present invention, the orientation of crystalline regions is disturbed on purpose to cause the strain deformation of polyurethane elastic yarns by relatively weak stress during the formation of strain in the direction of the fiber axis. Preferred angles are in the range of from 75° to 85°.

[0010] The polyurethane elastic yarns of the present invention should have, in addition to the above feature, a structure such that the angle corresponding to the half-height width in the equatorial direction in the measurement of small-angle X-ray scattering is 2.5° to smaller. The phrase "angle corresponding to the half-height width in the equatorial direction in the measurement of small-angle X-ray scattering" refers to the vertical angle of an isosceles triangle formed by the half-height width in the equatorial direction on a photograph of diffraction images and the center of camera distance. When the angle is greater than 2.5°, the growth of crystalline regions, particularly in directions perpendicular to the direction of the fiber axis, becomes insufficient, so that the resulting yarns have lowered strength elongation, causing problems from an viewpoint of practical use. Preferred angles are in the range of from 0.8° to 2.5°, more preferably from 0.8° to 1.5°. When the angle is smaller than 0.8°, the spread of crystalline regions composed mainly of urethane hard segments, particularly in directions perpendicular to the direction of the fiber axis, becomes wide, so that stretching force becomes excess, making it difficult to obtain a soft fit of products in wear.

[0011] The polyurethane elastic yarns of the present invention should further meet the condition that the temperature at the peak of maximum shrinkage stress in the measurement of thermal stress is 135°C or lower. When the temperature is higher than 135°C, products obtained in combination with other materials such as acrylic, wool, cotton, and silk fibers cannot satisfactorily be set under the processing conditions suitable for these other materials, making it difficult to attain the desired advantageous effects of the present invention. Therefore, the temperature at the peak of maximum shrinkage stress is desirable, if as low as possible, preferably 130°C or lower, more preferably 115°C or lower, and still more preferably 100°C or lower.

[0012] The polyurethane elastic yarns of the present invention may desirably have the maximum shrinkage stress of 10 mg/denier or smaller in the measurement of thermal stress. When the maximum shrinkage stress is higher than 10 mg/denier, shrinkage force after setting becomes high, so that products obtained in combination with other materials such as acrylic, wool, cotton, and silk fibers cannot satisfactorily be set under the processing conditions suitable for these other materials. The maximum shrinkage stress in the measurement of thermal stress is more preferably 7 mg/denier or lower.

[0013] The polyurethane elastic yarns of the present invention may desirably have the percentage of setting with dry heat at 120°C (PSD120) of 65% or higher and the percentage of setting with wet heat at 105°C (PSW105) of 75% or higher. This is because a combination of polyurethane elastic yarns having these characteristics and other materials such as acrylic, wool, cotton, and silk fibers makes it possible to obtain satisfactorily setting properties under the processing conditions suitable for these other materials. In other words, when PSD120 is lower than 65%, heat setting properties in dry heat treatments such as presetting steps in the post-processing stage become poor, making it impossible to obtain a desired soft fit. When PSW105 is lower than 75%, heat resistance in wet heat treatments such as dyeing steps becomes good, which is inconvenient for the purpose of obtaining a soft fit. Preferably, PSD120 is 70% or higher and PSW105 is 80% or higher.

[0014] The polyurethane polymers as the raw materials of the polyurethane elastic yarns of the present invention may desirably have the molar ratio of isocyanate groups to hydroxyl groups (NCO/OH ratio) of 1 or lower. This means that the polyurethane elastic yarns of the present invention contain substantially no cross-links such as allophanate bonds. When the NCO/OH ratio is higher than 1, allophanate cross-links are formed by the reaction of excess isocyanate groups with urethane groups. The presence of such cross-links deteriorates heat setting properties and improves the stretchability.of polyurethane elastic yarns, making it difficult to obtain a soft fit.

[0015] For the polyurethane elastic yarns of the present invention, the ratio in percentage of backward stress to forward stress at 150% elongation in the measurement by repeated stressing at 300% elongation is preferably 20% or lower. When the ratio in percentage is higher than 20%, the polyurethane elastic yarns will have increased stretchability, making it difficult to obtain a soft fit. More preferred ratios in percentage are 10% or lower.

[0016] As described above, the polyurethane elastic yarns of the present invention can be set at low temperatures and can exhibit a sense of soft fit, and, particularly when combined with other materials to produce various fabrics, can keep the feelings and functions of both materials.

[0017] The following will illustrate the preparation of polyurethane elastic yarns according to the present invention with specific examples.

[0018] The polyurethane polymers used in the polyurethane elastic yarns of the present invention can be prepared from polyols, organic polyisocyanates, and low molecular weight diols as chain extenders. The preparation may preferably be carried out so that the NCO/OH ratio becomes 1 or lower and the polymers obtained have terminal hydroxyl groups in principle. Specific methods of preparation may include, but are not limited to, pre-polymer methods and one-shot methods. In the polymers obtained, there may exist urea bonds in part to such an extent that the advantageous effects of the present invention will not be deteriorated.

[0019] The polyols for use in the preparation of polyurethane polymers used in the polyurethane elastic yarns of the present invention may include, but are not limited to, polyether polyols such as polytetramethylene ether glycol; polyester polyols such as polybutylene adipate; polycaprolactone polyols; polyester polycarbonate polyols such as reaction products of polyester glycols such as polycaprolactons with alkylene carbonates; reaction products of the reaction

mixtures (which are obtained by reacting ethylene carbonate with polyhydric alcohols such as ethylene glycol, propylene glycol, butylene glycol, and neopentyl glycol) with organic carboxylic acids such as adipic acid, azelaic acid, and sebacic acid; and polycarbonate polyols obtained by the interesterification of polyhydroxyl compounds such as 1,4-butanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, and 1,8-octanediol with aryl carbonates such as diphenyl carbonate. These polyols may be used alone or in mixture of two or more.

[0020] The polyols may usually have a number-average molecular weight of about 500 to 6000, preferably 1000 to 5000, and more preferably 1000 to 3000. When the number-average molecular weight is smaller than 500, the elastic yarns obtained have a tendency to exhibit unsatisfactory elongation. In contrast, when the number-average molecular weight is higher than 6000, the elastic yarns obtained have a tendency to exhibit unsatisfactory mechanical strength, such as tenacity and elastic recovery.

[0021] The organic polyisocyanates for use in the preparation of polyurethane polymers used in the polyurethane elastic yarns of the present invention may include, but are not limited to, aromatic diisocyanates such as 4,4'-diphenylmethane diisocyanate, 1,5-naphthalene diisocyanate, 1,4-phenylene diisocyanate, 2,4-trilene diisocyanate, and 2,6-trilene diisocyanate; aralkyl diisocyanates such as m-xylylene diisocyanate and p-xylylene diisocyanate; aliphatic diisocyanates such as hexamethylene diisocyanate; and alicyclic diisocyanates such as 1,4-cyclohexane diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, and isophorone diisocyanate. These organic polyisocyanates may be used alone or in mixture of two or more.

[0022] The low molecular weight diols as chain extenders for use in the preparation of polyurethane polymers used in the polyurethane elastic yarns of the present invention may include, but are not limited to, ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanediol, 1,4-bis-(hydroxyethoxy)benzene, 1,3-bis(hydroxyethoxy) benzene, 1,2-bis(hydroxyethoxy)benzene, cyclohexanedimethanol, bis(2-hydroxyethyl) terephthalate, bis(2-hydroxyethyl) isophthalate, and bis(2-hydroxyethyl) phthalate.

[0023] In the preparation of polyurethane polymers used in the polyurethane elastic yarns of the present invention, there may be added catalysts, activators, lubricants, ultraviolet light absorbers, light-proofing agents, antioxidants, antistatic agents, antifungal agents, and other ordinary additives to such an extent that the advantageous effects of the present invention will not be deteriorated.

[0024] The above polyurethane polymers, which have optionally been mixed with the above additives, are extruded from a spinneret, desirably melt spinning from the following point of view. That is, an objective of the present invention is to allow polyurethane elastic yarns to have a specific structure by paying attention to crystalline regions composed mainly of urethane hard segments, inhibiting the growth of the said regions in directions perpendicular to the direction of the fiber axis, and disturbing their orientation to the direction of the fiber axis, whereby the polyurethane elastic yarns can be set at low temperatures and can exhibit a soft fit. In addition, melt spinning has the advantage that finer monofilaments can be obtained with high uniformity, which is also desirable from the viewpoints of working conditions and costs.

[0025] The spinning apparatus and spinning conditions for use in the preparation of the polyurethane elastic yarns of the present invention may widely vary with the composition of polyurethane polymers, the fineness of fibers to be prepared, and other factors; polyurethane polymers in usual cases may preferably be fed to an extrusion spinning apparatus and spun at a spinning temperature of 180°C to 240°C at a winding speed of 1000 m/min. or lower, particularly 600 m/min. or lower. In addition, to allow polyurethane elastic yarns to have a specific structure by paying attention to crystalline regions composed mainly of urethane hard segments, inhibiting the growth of the said regions in directions perpendicular to the direction of the fiber axis, and disturbing their orientation to the direction of the fiber axis, whereby the polyurethane elastic yarns can be set at low temperatures and can exhibit a soft fit, the ambient temperature from quenching in the spinning chimney to winding is desirable, if as low as possible; in particular, it is the most important to set the temperature of quenching air at 20°C or lower and the temperature of filaments when wound at 20°C or lower, desirably both in the range of from 0°C to 10°C.

[0026] The monofilament fineness of the polyurethane elastic yarns of the present invention is not particularly limited, but may suitably be selected for their applications. In general, their monofilament fineness is preferably about 5 to 100 deniers. The polyurethane elastic yarns of the present invention may be in the form of either monofilaments or multifilaments. For multifilaments, the number of filaments and the total denier number are both not particularly limited, but may suitably be selected. The section of the polyurethane elastic yarns is also not particularly limited, but can have any shape, for example, round, square, rectangular, triangular, oval, flat, or dumbbell shape. The polyurethane elastic yarns may further be either solid or hollow fibers.

[0027] The following will describe partner materials to be woven or knitted in mixture with the above polyurethane elastic yarns.

[0028] For the materials to be woven or knitted in mixture, any of thermoplastic synthetic fibers, natural fibers, and regenerated fibers can be used. For the thermoplastic synthetic fibers, it is desirable to use any of polyester fibers, polyamide fibers, and acrylic fibers; for the natural fibers, any of cotton, wool, and silk fibers; and for the regenerated fibers, polynosic fibers. These thermoplastic synthetic fibers, natural fibers, and regenerated fibers may be used alone

or in mixture of two or more.

[0029] Particularly preferred are weaving and knitting of the above polyurethane elastic yarns in mixture with wool, silk, acrylic, or any other fibers, which require low temperatures of 150°C or lower at the heat setting in the dyeing processing.

[0030] The polyurethane elastic yarns of the present invention are woven or knitted in mixture with these partner materials. More specifically, in the case of weaving in mixture, thermoplastic synthetic fibers, natural fibers, or regenerated fibers are desirably arranged as warps, and the polyurethane elastic yarns as wefts.

[0031] For warp-knitted union fabrics, a desirable method involves arrangement of polyurethane elastic yarns in a rear reed and partner materials in a front reed. For circular-knitted union fabrics, a desirable method involves plated-stitching of polyurethane elastic yarns onto partner materials.

[0032] The stretch fabrics obtained in this way are then dyed by an ordinary process comprising gray fabric preparation, relaxation and scouring, presetting, dyeing, drying, feeling treatment, and finish setting. It is important to select processing temperature conditions suitable for partner materials to be woven or knitted in mixture with polyurethane elastic yarns. In particular, dyeing at a solution temperature of 100°C or lower in the same manner as carried out for wool, silk, acrylic, or any other fibers, and dry heat setting at low temperatures of 150°C or lower are suitable for the expression of a soft feeling.

Examples

[0033] The present invention will be further illustrated by the following examples; however, the present invention is not limited to these examples. Various measurements were carried out according to the following methods.

(Small angle X-ray scattering measurement)

[0034] Yarns were skeined, of which about 1800 yarns were reeled out and then bound at their both ends into a bundle, and this was used as a sample for measurement. Using a RAD-RC X-ray generator, photographs were taken by a point focusing camera at a camera distance of 350 mm for an exposure time of 30 minutes. An X-ray source used was CuKα line (through a Ni filter, wavelength of 1.5418 angstrom) with a power of 40.0 kV.

(Method of thermal stress measurement)

[0035] Using an SSC-5220 apparatus available from Seiko Instruments Inc., a yarn having a length of 2 cm was loaded with an initial tension of 5 mg per denier, and then measured at a programming rate of 20°C/min.

(Method of repeated stress measurement)

[0036] As defined in JIS-L1013, a yarn was left in a temperature-and-humidity controlled room at 20°C and 65% RH, and then measured with a tensile tester (Autograph DSS-500 available from Shimadzu Corporation) by drawing from the yarn length of 5 cm up to 300% elongation at a speed of 50 cm/min., and then immediately drawing back at a speed of 50 cm/min.

(Method of PSD measurement)

[0037] A polyurethane elastic yarn having an initial length of 22.5 cm (*L1*) was treated with dry heat at 120°C for 1 minute under 100% elongation, and then measured for yarn length (*L2*) after left shrinking and cooling at room temperature for 10 minutes. The value of PSD (%) was determined by the following equation.

$$PSD\ (\%) = (L2 - L1)/L1 \times 100$$

(Method of PSW measurement)

[0038] A polyurethane elastic yarn having an initial length of 9.5 cm (*L3*) was heated from 40°C to 105°C over 60 minutes under 100% elongation, and then measured for yarn length (*L4*) after left shrinking and cooling at room temperature for 10 minutes. The value of PSW (%) was determined by the following equation.

$$PSW\ (\%) = (L4 - L3)/L3 \times 100$$

Example 1

[0039] A polyurethane polymer having a Shore A hardness of 90, composed of polybutylene adipate polyol/diphenylmethane diisocyanate/1,4-butanediol, and substantially having an NCO/OH ratio of 1 or lower, was fed to a spinning machine with a single screw extruder, and melt spinning was carried out at a spinning temperature of 220°C, using a spinning nozzle having a nozzle diameter of 0.28 mmϕ and a nozzle length of 0.56 mm, *i e.*, L/D = 2.0, at a winding speed of 500 m/min., to give a monofilament having a fineness of 20 denier. At that time, the ambient temperature from the quench temperature in a spinning chimney to a winding device was controlled at 10°C. The contact temperature of the monofilament when wound was 11°C.

[0040] The polyurethane elastic yarn obtained had a breaking load of 27 g (1.5 g/denier) and a percentage elongation at breakage of 410%. The yarn characteristics are shown in Table 1. This yarn was used to produce a bare plain-knitted union fabric with an acrylic filament. The knitted fabric was subjected to relaxation in hot water at 95°C for 1 minute, followed by air drying, and then subjected to finish setting at 120°C for 50 seconds. The finished fabric exhibited good setting properties. The finished fabric was examined in a sensory test by ten panelists, and evaluated to have a soft fit by nine of the ten panelists and a soft feeling by eight of the ten panelists.

Example 2

[0041] A pellet-shaped polyurethane polymer composed of polytetramethylene glycol-polybutylene adipate copolymer polyol (3/7)/diphenylmethane diisocyanate/1,4-butanediol, and substantially having an NCO/OH ratio of 1 or lower, was fed to a spinning machine with a single screw extruder, and melt spinning was carried out at a spinning temperature of 215°C, using a spinning nozzle having a nozzle diameter of 0.28 mmϕ and a nozzle length of 0.56 mm, *i.e.*, L/D = 2.0, at a winding speed of 550 m/min., to give a monofilament having a fineness of 20 denier. At that time, the ambient temperature from the quench temperature in a spinning chimney to a winding device was controlled at 10°C. The contact temperature of the monofilament when wound was 11°C.

[0042] The polyurethane elastic yarn obtained had a breaking load of 32 g (1.6 g/denier) and a percentage elongation at breakage of 430%. The yarn characteristics are shown in Table 1. This yarn was used to produce a bare plain-knitted union fabric with an acrylic filament. The knitted fabric was subjected to relaxation in hot water at 95°C for 1 minute, followed by air drying, and then subjected to finish setting at 120°C for 50 seconds. The finished fabric exhibited good setting properties. The finished fabric was examined in a sensory test by ten panelists for its fit and feeling, and evaluated to have a soft fit by eight of the ten panelists and a soft feeling by eight of the ten panelists.

Example 3

[0043] A spinning dope obtained by the addition of butanol as a terminal blocker to a solution of polytetramethylene glycol/diphenylmethane diisocyanate/ethylene glycol in dimethylacetamide was extruded from a spinning nozzle having a nozzle diameter of 0.28 mmϕ and a nozzle length of 0.56 mm, *i.e.*, L/D = 2.0, into a spinning chimney under a flow of air heated at 220°C, and dry spinning was carried out at a winding speed of 650 m/min., to give a monofilament having a fineness of 20 denier.

[0044] The polyurethane elastic yarn obtained had a breaking load of 28 g (1.4 g/denier) and a percentage elongation at breakage of 410%. The yarn characteristics are shown in Table 1. This yarn was used to produce a bare plain-knitted union fabric with an acrylic filament. The knitted fabric was subjected to relaxation in hot water at 95°C for 1 minute, followed by air drying, and then subjected to finish setting at 120°C for 50 seconds. The finished fabric exhibited good setting properties. The finished fabric was examined in a sensory test by ten panelists for its fit and feeling, and evaluated to have a soft fit by seven of the ten panelists and a soft feeling by seven of the ten panelists, and therefore considered as having a soft fit and a soft feeling.

Example 4

[0045] A bare plain-knitted union fabric was prepared from a polyurethane elastic yarn having a fineness of 30 denier as described in Example 1 and a silk-like promix fiber (trademark "CHINON" owned by Toyobo) having a fineness of 75 denier. The knitted fabric was subjected to relaxation and scouring at 90°C for 40 seconds, presetting at 140°C for 30 seconds, dyeing at 98°C for 40 minutes, dewatering and drying at 120°C, and then finish setting at 140°C for 30 seconds. The finished fabric exhibited good setting properties without causing yellow discoloration. The finished fabric was examined in a sensory test by ten panelists for its fit and feeling, and evaluated to have a soft fit by nine of the ten panelists and a soft feeling by eight of the ten panelists.

Example 5

[0046] A twist-covered composite yarn (commonly called "ply yarn") was prepared from a polyurethane elastic yarn having a fineness of 40 denier as described in Example 1 and two wool yarn each having a yarn count of 1/60. Using this yarn as a weft and a two-folded wool yarn having a yarn count of 2/60 as a warp, a stretch wool fabric was prepared. The fabric was subjected to scouring with a Perclene solvent at 80°C for 30 seconds, drying pretreatment at 130°C for 30 seconds, dyeing at 98°C for 45 minutes, drying, shearing, decatizing, shrinking, felting post-treatment with dry heat at 130°C for 30 seconds, and textile finishing with steam wet heat at 105°C for 10 minutes. The finished fabric exhibited good setting properties with a stretch in the weft direction. The finished wool fabric was examined in a sensory test by ten panelists for its fit and feeling, and evaluated to have a soft fit by nine of the ten panelists and a soft feeling by eight of the ten panelists.

Comparative Example 1

[0047] A polyurethane polymer having a Shore A hardness of 90, composed of polybutylene adipate polyol/diphenylmethane diisocyanate/1,4-butanediol, and substantially having an NCO/OH ratio of 1 or lower, was fed to a spinning machine with a single screw extruder, and melt spinning was carried out at a spinning temperature of 220°C, using a spinning nozzle having a nozzle diameter of 0.28 mmϕ and a nozzle length of 0.56 mm, *i.e.*, L/D = 2.0, at a winding speed of 500 m/min., to give a monofilament having a fineness of 20 denier. The quench temperature was set at 30°C, while the ambient temperature to a winding device was not controlled. At that time, the contact temperature of the monofilament when wound was 40°C.

[0048] The polyurethane elastic yarn obtained had a breaking load of 27 g (1.5 g/denier) and a percentage elongation at breakage of 440%. The yarn characteristics are shown in Table 1. This yarn was used to produce a bare plain-knitted union fabric with an acrylic filament. The knitted fabric was subjected to relaxation in hot water at 95°C for 1 minute, followed by air drying, and then subjected to finish setting at 120°C for 50 seconds. The finished fabric exhibited relatively good setting properties. The finished fabric was examined in a sensory test by ten panelists, and evaluated to have a soft fit by two of the ten panelists and a soft feeling by three of the ten panelists, and therefore considered as having neither a soft fit nor a soft feeling.

Comparative Example 2

[0049] A polyurethane polymer having a Shore A hardness of 90, composed of polytetramethylene glycol-polybutylene adipate copolymer polyol (3/7)/diphenylmethane diisocyanate/1,4-butanediol, and having an NCO/OH ratio of 1.1, was fed to a spinning machine with a single screw extruder, and melt spinning was carried out at a spinning temperature of 220°C, using a spinning nozzle having a nozzle diameter of 0.28 mmϕ and a nozzle length of 0.56 mm, *i.e.*, L/D = 2.0, at a winding speed of 500 m/min., to give a monofilament having a fineness of 20 denier. At that time, the ambient temperature from the quench temperature in a spinning chimney was controlled at 30°C. The contact temperature of the monofilament when wound was 30°C.

[0050] The polyurethane elastic yarn obtained was wound up, and subjected to aging under a low dew point atmosphere (dew point = -30°C) at 80°C for 24 hours and further aging at 25°C and a relative humidity of 60% for 7 days. This yarn had a breaking load of 32 g (1.6 g/denier) and a percentage elongation at breakage of 480%. The yarn characteristics are shown in Table 1. This yarn was used to produce a bare plain-knitted union fabric with an acrylic filament. The knitted fabric was subjected to relaxation in hot water at 95°C for 1 minute, followed by air drying, and then subjected to finish setting at 120°C for 50 seconds. The finished fabric exhibited poor setting properties. The finished fabric was examined in a sensory test by ten panelists, and evaluated to have a soft fit by zero of the ten panelists and a soft feeling by zero of the ten panelists, and therefore considered as having neither a soft fit nor a soft feeling.

Comparative Example 3

[0051] A polyurethane polymer having a Shore A hardness of 90, composed of polybutylene adipate polyol/diphenylmethane diisocyanate/1,4-butanediol, and substantially having an NCO/OH ratio of 1 or lower, was fed to a spinning machine with a single screw extruder, and melt spinning was carried . out at a spinning temperature of 220°C, using a spinning nozzle having a nozzle diameter of 0.28 mmϕ and a nozzle length of 0.56 mm, *i.e.*, L/D = 2.0, at a winding speed of 500 m/min., to give a monofilament having a fineness of 20 denier. At that time, the ambient temperature from the quench temperature in a spinning chimney was controlled at -3°C. The contact temperature of the monofilament when wound was -1°C.

[0052] The polyurethane elastic yarn obtained had a breaking load of 20 g (1.0 g/denier) and a percentage elongation

at breakage of 250%. The yarn characteristics are shown in Table 1. This yarn was used to try producing a bare plain-knitted union fabric with an acrylic filament; however, it was not able to produce a knitted fabric because of a lack of its strength elongation, particularly its elongation.

Comparative Example 4

[0053] A spinning dope containing polybutylene adipate polyol/diphenylmethane diisocyanate/ethylene diamine in dimethylacetamide was extruded from a spinning nozzle having a nozzle diameter of 0.28 mmϕ and a nozzle length of 0.56 mm, *i.e.*, L/D = 2.0, into a spinning chimney under a flow of air heated at 220°C, and dry spinning was carried out at a winding speed of 500 m/min., to give a monofilament having a fineness of 20 denier.

[0054] The polyurethane elastic yarn obtained had a breaking load of 24 g (1.2 g/denier) and a percentage elongation at breakage of 470%. The yarn characteristics are shown in Table 1. This yarn was used to produce a bare plain-knitted union fabric with an acrylic filament. The knitted fabric was subjected to relaxation in hot water at 95°C for 1 minute, followed by air drying, and then subjected to finish setting at 190°C for 50 seconds. The finished fabric exhibited poor setting properties. The finished fabric was examined in a sensory test by ten panelists for its fit and feeling, and evaluated to have a soft fit by zero of the ten panelists and a soft feeling by zero of the ten panelists, and therefore considered as having neither a soft fit nor a soft feeling.

Comparative Example 5

[0055] A bare plain-knitted union fabric was prepared from a polyurethane elastic yarn having a fineness of 30 denier as described in Comparative Example 1 and a silk-like promix fiber (trademark "CHINON" owned by Toyobo) having a fineness of 75 denier. The knitted fabric was subjected to relaxation and scouring at 90°C for 40 seconds, presetting at 160°C for 30 seconds, dyeing at 98°C for 40 minutes, dewatering and drying at 120°C, and then finish setting at 160°C for 30 seconds. The finished fabric exhibited good setting properties, but the promix fiber caused yellow discoloration by heat. The finished fabric was examined in a sensory test by ten panelists for its fit and feeling, and evaluated to have a soft fit by two of the ten panelists and a soft feeling by three of the ten panelists, and considered as having neither a soft fit nor a soft feeling by the remaining five panelists.

Comparative Example 6

[0056] A twist-covered composite yarn (commonly called "ply yarn") was prepared from a polyurethane elastic yarn having a fineness of 40 denier as described in Comparative Example 1 and two wool yarn each having a yarn count of 1/60. Using this yarn as a weft and a two-folded wool yarn having a yarn count of 2/60 as a warp, a stretch wool fabric was prepared. The fabric was subjected to scouring with a Perclene solvent at 80°C for 30 seconds, drying pretreatment at 150°C for 30 seconds, dyeing at 98°C for 45 minutes, drying, shearing, decatizing, shrinking, felting post-treatment with dry heat at 160°C for 30 seconds, and textile finishing with steam wet heat at 115°C for 10 minutes. The finished fabric exhibited good setting properties with a stretch in the weft direction. The finished wool fabric was examined in a sensory test by ten panelists for its fit and feeling, and evaluated to have a soft fit by two of the ten panelists and a soft feeling by three of the ten panelists, and considered as having neither a soft fit nor a soft feeling by the remaining five panelists.

TABLE 1

		Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Small-angle X-ray scattering	Angle corresponding to the half-height width of maximum peak intensity in an azimuthal scanning (degrees)	77.5	75.0	79.8	55.0	56.0	80.0	58.0
	Angle corresponding to the half-height width in the equatorial direction (degrees)	1.13	1.14	2.00	1.12	1.11	3.00	1.10
Thermal stress	Temperature at the peak of maximum shrinkage stress (°C)	95	96	114	120	139	–	140
	Maximum shrinkage stress (mg/denier)	100	110	177	120	210	–	205
PSD120 (%)		77.0	76.0	45.1	64.0	40.4	–	20.4
PSW105 (%)		84.9	82.0	62.6	72.5	52.1	–	42.5
(Backward stress at 150% elongation / forward stress at 150% elongation) x 100 (at 300% elongation) (%)		6.5	7.0	16.0	8.2	9.2	–	21.0

[0057] According to the present invention, polyurethane elastic yarns and stretch fabrics, which can be set at low temperatures and can exhibit a sense of soft fit, and which, particularly when combined with other materials to produce various fabrics, can keep the feelings and functions of both materials.

Claims

1. A polyurethane elastic yarn meeting the following conditions:

   (1) the angle corresponding to the half-height width of maximum peak intensity in an azimuthal scanning in the measurement of small-angle X-ray scattering is 60° or greater;
   (2) the angle corresponding to the half-height width in the equatorial direction in the measurement of small-angle X-ray scattering is 2.5° or smaller;
   (3) the temperature at the peak of maximum shrinkage stress in the measurement of thermal stress is 135°C or lower.

2. The polyurethane elastic yarn according to claim 1, wherein the temperature at the peak of maximum shrinkage stress in the measurement of thermal stress is 105°C or lower.

3. The polyurethane elastic yarn according to claim 1 or 2, wherein the angle corresponding to the half-height width in the equatorial direction in the measurement of small-angle X-ray scattering is in the range of from 0.8° to 1.5°.

4. The polyurethane elastic yarn according to any of claims 1 to 3, wherein the percentage of setting with dry heat at 120°C (PSD120) is 65% or higher and the percentage of setting with wet heat at 105°C (PSW105) is 75% or higher.

5. The polyurethane elastic yarn according to any of claims 1 to 4, wherein the maximum shrinkage stress in the measurement of thermal stress is 10 mg/denier or smaller.

6. The polyurethane elastic yarn according to any of claims 1 to 5, wherein the ratio in percentage of backward stress to forward stress at 150% elongation in the measurement of repeated stress at 300% elongation is 20% or lower.

7. The polyurethane elastic yarn according to any of claims 1 to 6, which is prepared by melt spinning.

8. A stretch fabric which is prepared by mixed weaving or knitting of a polyurethane elastic yarn according to any of claims 1 to 7 and a thermoplastic synthetic fiber.

9. The stretch fabric according to claim 8, wherein the thermoplastic synthetic fiber is a polyester, polyamide, or acrylic fiber.

10. A stretch fabric which is prepared by mixed weaving or knitting of a polyurethane elastic yarn according to any of claims 1 to 7 and a natural fiber.

11. The stretch fabric according to claim 10, wherein the natural fiber is a cotton, wool, or silk fiber.

12. A stretch fabric which is prepared by mixed weaving or knitting of a polyurethane elastic yarn according to any of claims 1 to 7 and a regenerated fiber.

13. The stretch fabric according to claim 12, wherein the regenerated fiber is a polynosic fiber.

14. A method of producing the polyurethane elastic yarn according to any of claims 1 to 7, wherein the temperature of the quenching air is set at 20°C or lower and the temperature of the filaments when wound is 20°C or lower.

Patentansprüche

1. Elastisches Polyurethangarn, das die folgenden Bedingungen erfüllt:

(1) der Winkel, welcher der Halbwertsbreite der maximalen Peakintensität bei einer Azimutalabtastung bei der Messung der Röntgenkleinwinkelstreuung entspricht, beträgt 60° oder mehr;
(2) der Winkel, welcher der Halbwertsbreite in Äquatorialrichtung bei der Messung der Röntgenkleinwinkelstreuung entspricht, beträgt 2,5° oder weniger;
(3) die Temperatur im Scheitelwert der maximalen Schrumpfspannung bei der Messung der Wärmespannung beträgt 135°C oder weniger.

2. Elastisches Polyurethangarn nach Anspruch 1, wobei die Temperatur im Scheitelwert der maximalen Schrumpfspannung bei der Messung der Wärmespannung 105°C oder weniger beträgt.

3. Elastisches Polyurethangarn nach Anspruch 1 oder 2, wobei der Winkel, welcher der Halbwertsbreite in Äquatorialrichtung bei der Messung der Röntgenkleinwinkelstreuung entspricht, im Bereich von 0,8° bis 1,5° liegt.

4. Elastisches Polyurethangarn nach einem der Ansprüche 1 bis 3, wobei die prozentuale Fixierung bei trockener Wärme bei 120°C (PSD120) 65% oder mehr und die prozentuale Fixierung bei feuchter Wärme bei 105°C (PSW105) 75% oder mehr beträgt.

5. Elastisches Polyurethangarn nach einem der Ansprüche 1 bis 4, wobei die maximale Schrumpfspannung bei der Messung der Wärmespannung 10 mg/Denier oder weniger beträgt.

6. Elastisches Polyurethangarn nach einem der Ansprüche 1 bis 5, wobei das prozentuale Verhältnis der Rückwärtsspannung zur Vorwärtsspannung bei 150% Dehnung bei der Messung der Dauerbeanspruchung bei 300% Dehnung 20% oder weniger beträgt.

7. Elastisches Polyurethangarn nach einem der Ansprüche 1 bis 6, das durch Schmelzspinnen hergestellt wird.

8. Stretch-Gewebe, das durch gemischtes Weben oder Wirken eines elastischen Polyurethangarns nach einem der Ansprüche 1 bis 7 und einer thermoplastischen Synthesefaser hergestellt wird.

9. Stretch-Gewebe nach Anspruch 8, wobei die thermoplastische Synthesefaser eine Polyester-, Polyamid- oder Acrylfaser ist.

10. Stretch-Gewebe, das durch gemischtes Weben oder Wirken eines elastischen Polyurethangarns nach einem der Ansprüche 1 bis 7 und einer Naturfaser hergestellt wird.

11. Stretch-Gewebe nach Anspruch 10, wobei die Naturfaser Baumwoll-, Woll- oder Seidenfaser ist.

12. Stretch-Gewebe, das durch gemischtes Weben oder Wirken eines elastischen Polyurethangarns nach einem der Ansprüche 1 bis 7 und einer Regeneratfaser hergestellt wird.

13. Stretch-Gewebe nach Anspruch 12, wobei die Regeneratfaser eine polynosische Faser ist.

14. Verfahren zur Herstellung des elastischen Polyurethangarns nach einem der Ansprüche 1 bis 7, wobei die Temperatur der Abschreckluft auf 20°C oder weniger eingestellt wird und die Temperatur der Elementarfäden im aufgewickelten Zustand 20°C oder weniger beträgt.

Revendications

1. Fil élastique de polyuréthanne répondant aux conditions suivantes :

(1) l'angle correspondant à la largeur à mi-hauteur de l'intensité de pic maximale obtenu lors d'un balayage azimutal dans la mesure de la diffusion de rayons X aux petits angles est de 60° ou plus;
(2) l'angle correspondant à la largeur à mi-hauteur dans la direction équatoriale dans la mesure de la diffusion de rayons X aux petits angles est de 2,5° ou moins;
(3) la température au pic de la tension de retrait maximale dans la mesure de la contrainte thermique est de 135°C ou moins.

2. Fil élastique de polyuréthanne suivant la revendication 1, dans lequel la température au pic de la tension de retrait maximale dans la mesure de la contrainte thermique est de 105°C ou moins.

3. Fil élastique de polyuréthanne suivant l'un ou l'autre des revendications 1 et 2, dans lequel l'angle correspondant à la largeur à mi-hauteur dans la direction équatoriale dans la mesure de la diffusion de rayons X aux petits angles se situe dans la plage de 0,8° à 1,5°.

4. Fil élastique de polyuréthanne suivant l'une quelconque des revendications 1 à 3, dans lequel le pourcentage de prise à la chaleur sèche à 120°C (PSD120) est de 65% ou plus et le pourcentage de prise à la chaleur humide à 105°C (PSW 105) est de 75% ou plus.

5. Fil élastique de polyuréthanne suivant l'une quelconque des revendications 1 à 4, dans lequel la tension de retrait maximale dans la mesure de la contrainte thermique est de 10 mg/denier ou moins.

6. Fil élastique de polyuréthanne suivant l'une quelconque des revendications 1 à 5, dans lequel le rapport en pourcentage d'une contrainte en arrière à une contrainte en avant à 150% d'allongement dans la mesure d'une contrainte répétée à 300% d'allongement est de 20% ou moins.

7. Fil élastique de polyuréthanne suivant l'une quelconque des revendications 1 à 6, qui est préparé par filage à chaud.

8. Tissu frisé qui est préparé par un tissage ou tricotage mixte d'un fil élastique de polyuréthanne suivant l'une quelconque des revendications 1 à 7 et d'une fibre synthétique thermoplastique.

9. Tissu frisé suivant la revendication 8, dans lequel la fibre synthétique thermoplastique est une fibre de polyester, de polyamide ou acrylique.

10. Tissu frisé qui est préparé par un tissage ou tricotage mixte d'un fil élastique de polyuréthanne suivant l'une quelconque des revendications 1 à 7 et d'une fibre naturelle.

11. Tissu frisé suivant la revendication 10, dans lequel la fibre naturelle est une fibre de coton, de laine ou de soie.

12. Tissu frisé qui est préparé par un tissage ou tricotage mixte d'un fil élastique de polyuréthanne suivant l'une quelconque des revendications 1 à 7 et d'une fibre régénérée.

13. Tissu frisé suivant la revendication 12, dans lequel la fibre régénérée est une fibre polynosique.

14. Procédé de production d'un fil élastique de polyuréthanne suivant l'une quelconque des revendications 1 à 7, dans lequel la température de l'air de refroidissement est fixée à 20°C ou moins et la température des filaments lorsque enroulés est de 20°C ou moins.