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(54) POLYAMIDE MULTIFILAMENT, AND LACE KNIT AND STOCKINGS USING SAME

(57) Provided is a polyamide multifilament characterized by having a tensile strength at 15% elongation of 4.0 to 6.0 cN/dtex, a strength-elongation product of 10.0 or more, and a yarn unevenness (U%) of 1.2 or less. The present invention provides a high-strength polyamide multifilament with which it is possible to obtain stockings having high softness, durability, and transparency, and a lace knit in which patterns have a beautiful appearance.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a polyamide multifilament. More particularly, the present invention relates to a polyamide multifilament with which stockings excellent in terms of softness, durability, and sense of transparency can be provided and which, when used as a ground lace yarn, is capable of providing a knitted lace having excellent durability and having a pattern that looks attractive.

BACKGROUND ART

[0002] Polyamide fibers and polyester fibers, which are synthetic fibers, are in extensive use in clothing applications and industrial applications because of their excellent properties regarding mechanical and chemical properties. In particular, polyamide fibers are excellent in terms of the peculiar softness, high strength, colorability by dyeing, heat resistance, hygroscopicity, etc., and are hence in extensive use in general clothing applications including stockings, innerwear, and sportswear.

[0003] A consumer need regarding laces is patterns which look attractive. There has hence been a desire for durability on a conventional level and the sense of transparency of ground lace yarn. Consumer needs regarding stockings are comfortableness to wear and the sense of bare skin and there has hence been a desire for durability on a conventional level, softness, and sense of transparency. Namely, for replacement by polyamide fibers for clothing, it has been strongly desired to enhance fineness while maintaining the conventional strength.

[0004] In order to overcome these problems, various techniques for heightening the strength of polyamide fibers have been proposed. For example, Patent Document 1 proposes a knitted lace including a high-viscosity type nylon-6 filament having an elongation of 51-64% and a strength of 4.2-6.5 cN/dtex.

[0005] Patent Document 2 proposes a stocking including a polyamide filament having an elongation of 40-50% and a strength-elongation product of 9.1 or larger and about 9.8.

[0006] Patent Document 3 proposes a tire cord and a belt which each include polyamide-based fibers having an elongation of about 16-18%, a strength of 9.8 cN/dtex or higher, and a strength-elongation product of about 11.4-12.2 cN/dtex.

BACKGROUND ART DOCUMENT

PATENT DOCUMENT

[0007]

Patent Document 1: JP-A-2003-129331
Patent Document 2: WO 2016/76184
Patent Document 3: JP-A-63-159521

SUMMARY OF THE INVENTION

PROBLEMS THAT THE INVENTION IS TO SOLVE

[0008] However, the method described in Patent Document 1, although capable of obtaining a lace having a pattern which looks attractive, is disadvantageous in that the fiber modulus and the strength-elongation product are low and the knitted lace obtained therefrom has unsatisfactory product strength.

[0009] In the case where the method described in Patent Document 2 is used to produce a filament having a fineness suitable for covering yarns for single-covered elastic yarns, the fiber modulus and the strength-elongation product are low and the stockings obtained therefrom have unsatisfactory product strength.

[0010] In the case where the method described in Patent Document 3 is used in clothing applications, the modulus of the fibers is so high that the fibers are poor in high-order process passage capability in steps for producing a lace or stocking to suffer fiber breakage, fluffing, etc.

[0011] An object of the present invention, which overcomes those problems, is to provide a high-strength polyamide multifilament having a large strength-elongation product and a proper fiber modulus. More particularly, an object of the present invention is to provide: a knitted lace which has the enhanced sense of transparency of the ground lace yarn while retaining durability and can have a pattern that looks attractive; and a stocking having excellent sense of transparency and softness, since excellent high-order process passage capability, excellent product appearance quality, and a higher fineness can be obtained by using the polyamide multifilament having a large strength-elongation product and a proper fiber modulus.

MEANS FOR SOLVING THE PROBLEMS

[0012] In order to overcome those problems, the present invention employs the following configurations.

(1) A polyamide multifilament having a tensile strength at 15% elongation of 4.0-6.0 cN/dtex, a strength-elongation product of 10.0 or larger, and a yarn unevenness (U%) of 1.2 or less.
(2) The polyamide multifilament according to (1), having a single-filament fineness of 1.3-3.4 dtex.
(3) The polyamide multifilament according to (1) or (2), having an elongation of 30-50%.
(4) The polyamide multifilament according to any one of (1) to (3), having a sum of a content of crystals and a content of rigid amorphous components of 70-90%.
(5) A knitted lace produced using the polyamide multifilament according to any one of (1) to (4) as a ground lace yarn.
(6) A stocking partly comprising a covered yarn obtained using the polyamide multifilament according to any one of (1) to (4) as a covering yarn.

ADVANTAGE OF THE INVENTION

[0013] The polyamide multifilament of the present invention is a high-strength polyamide multifilament having a large strength-elongation product and a proper fiber modulus. Furthermore, since the polyamide multifilament of the present invention has excellent high-order process passage capability and excellent product appearance quality and is capable obtaining a higher fineness, a knitted lace which has the enhanced sense of transparency of the ground lace yarn while retaining durability and which can have a pattern that looks attractive and a stocking having excellent sense of transparency and softness can be obtained from the polyamide multifilament.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014]

Fig. 1 shows one embodiment of production devices which can be advantageously used in a method for producing a polyamide multifilament according to the present invention.
Fig. 2 is a diagrammatic sectional model diagram showing a spinneret and a heating cylinder which can be advantageously used in a method for producing a polyamide multifilament according to the present invention.

MODE FOR CARRYING OUT THE INVENTION

[0015] The present invention is explained in more detail below.

[0016] The polyamide multifilament of the present invention has a tensile strength at 15% elongation of 4.0-6.0 cN/dtex, a strength-elongation product of 10.0 or larger, and a yarn unevenness (U%) of 1.2 or less.

[0017] The polyamide which constitutes the polyamide multifilament of the present invention is a resin including a high-molecular-weight substance in which hydrocarbon groups are bonded to a main chain via amide bonds. The polyamide is excellent in terms of spinnability and mechanical property. The polyamide preferably is one mainly including polycaproamide (nylon-6) or polyhexamethyleneadipamide (nylon-66). More preferably is one mainly including polycaproamide (nylon-6) because of the unsusceptibility to gelation and satisfactory spinnability thereof. The term "mainly" means that in the case of polycaproamide, this polyamide contains at least 80% by mole ε-caprolactam as constituent units for constituting the polycaproamide, and that in the case of polyhexamethyleneadipamide, this polyamide contains at least 80% by mole hexamethylenediammonium adipate as constituent units for constituting the polyhexamethyleneadipamide. More preferably, the content of these constituent units is 90% by mole or higher. Other components are not particularly limited, and examples thereof include units of aminocarboxylic acids, dicarboxylic acids, diamines, and the like which are monomers for constituting polydodecanoamide, polyhexamethyleneadipamide, polyhexamethyleneazelamide, polyhexamethylenesebacamide, polyhexamethylenedodecanoamide, poly-m-xyleneadipamide, polyhexamethyleneterephthalamide, polyhexamethyleneisophthalamide, and the like.

[0018] From the standpoint of effectively producing the effects of the present invention, it is preferable that the polyamide contains none of various additives including delustering agents represented by titanium oxide. However, the polyamide may contain additives, e.g., a heat resistance improver, so long as the inclusion thereof does not impair the effects. Additives may be incorporated according to need so as to result in a content thereof in the range of 0.001-0.1 wt%.

[0019] The polyamide multifilament of the present invention must have a 15% strength, a strength-elongation product, and a U% which are in the respective ranges shown above. The reasons for this is as follows. Increasing the fineness enhances the sense of transparency of the ground lace yarn to give a knitted lace having a pattern which looks attractive or give stockings having excellent sense of transparency and softness. However, product strength is reduced and durability becomes poor so that the products do not withstand practical use. For obtaining durability which enables the products to withstand practical use, it is necessary to heighten the strength-elongation product. Furthermore, for maintaining high-order process passage capability and product appearance quality, it is necessary to make the multifilament yarn to have proper values of 15% strength and U%.

[0020] The present inventors diligently made investigations and have discovered that for providing a knitted lace which is excellent in terms of high-order process passage capability, product appearance quality, and durability and which has the enhanced sense of transparency of the ground lace yarn and can have a pattern that looks attractive and for providing stockings having excellent sense of transparency and softness, it is essential to regulate the 15% strength, strength-elongation product, and U% to values within proper ranges.

[0021] The polyamide multifilament of the present invention must have a strength-elongation product of 10.0 or larger. Due to the strength-elongation product within that range, the stocking and the lace have durability which enables the stocking and the lace to withstand practical use. In case where the strength-elongation product thereof is less than 10.0, not only the stocking and the lace have such poor durability that the stocking and the lace do not withstand practical use but also the multifilament has impaired high-order process passage capability and filament breakages occur at a higher frequency in high-order processing steps. The strength-elongation product of the polyamide multifilament of the present invention is more preferably 10.3 or larger. The larger the strength-elongation product, the more the multifilament is preferred. However, an upper limit thereof in the present invention is about 11.0.

[0022] The polyamide multifilament of the present invention must have a tensile strength at 15% elongation (hereinafter referred to as "15% strength"), which is an index to yarn properties, of 4.0-6.0 cN/dtex. The 15% strength was determined by making a measurement in accordance with JIS L1013-2010, Tensile Strength and Elongation, drawing a tensile strength-elongation curve, dividing the tensile strength (cN) at 15% elongation by the fineness, and taking the resultant value as the 15% strength. The 15% strength is a value which roughly indicates the fiber modulus. In cases when the 15% strength is high, the tensile strength-elongation curve has a large inclination, showing that the fiber modulus is high. Meanwhile, in cases when the 15% strength is low, the tensile strength-elongation curve has a small inclination, showing that the fiber modulus is low.

[0023] Since the polyamide multifilament of the present invention has a 15% strength within that range, the stocking and the knitted lace not only have durability which enables the stocking and the knitted lace to withstand practical use but also have excellent softness. In case where the 15% strength thereof is less than 4.0 cN/dtex, the multifilament has a reduced strength-elongation product and the stocking and the knitted lace have such poor durability that the stocking and the knitted lace do not withstand practical use. In case where the 15% strength exceeds 6.0 cN/dtex, the multifilament not only has a reduced elongation to give stockings and knitted laces which are stiff in feeling and have reduced softness but also has impaired high-order process passage capability to suffer filament breakages at a higher frequency in high-order processing steps, resulting in reduced product appearance quality. The 15% strength thereof is preferably 4.5-5.5 cN/dtex.

[0024] The polyamide multifilament of the present invention preferably has an elongation of 30-50%. By regulating the elongation thereof so as to be within that range, the multifilament is rendered less apt to suffer filament breakages in high-order processing steps and is made to have satisfactory high-order process passage capability and product appearance quality. The multifilament shows excellent high-order process passage capability especially when used in high-speed knitting or weaving. In cases when the elongation thereof is 30% or higher, the multifilament shows satisfactory high-order process passage capability to be less apt to suffer filament breakages in high-order processing steps such as stocking production steps (the step of producing a covered yarn and the step of knitting a stocking) or knitted-lace production steps (warping step and weaving step). Furthermore, the stocking and the knitted lace give a satisfactory soft feeling. In cases when the elongation thereof is 50% or less, this multifilament has a sufficient strength-elongation product and the stocking and the knitted lace have durability which enables the stocking and the knitted lace to withstand practical use. In addition, the multifilament has improved high-order process passage capability to be less apt to suffer filament breakages in high-order processing steps, and has improved product appearance quality. The elongation thereof is more preferably 35-45%.

[0025] It is preferable that in the polyamide multifilament of the present invention, the sum of the content of crystals and the content of rigid amorphous components is 70-90%. The content of crystals and the content of rigid amorphous components are values calculated in the following manners.

[0026] The content of crystals (Xc) is determined by calculating the difference (ΔHm-ΔHc) between the quantity of heat of fusion and the quantity of heat of cold crystallization, which are determined by DSC, and calculating the content of crystals using equation (1). In equation (1), ΔHm0 is the quantity of heat of fusion of the crystalline polyamide, and the value thereof is 229.76 J/g.

[0027] The content of rigid amorphous components (Xra) is calculated from the content of crystals (Xc) and the content of movable amorphous components (Xma) using equation (2). The content of movable amorphous components (Xma) is calculated from a difference in specific heat (ΔCp) between before and after a glass transition observed on a temperature-heat flux reversible curve determined by temperature-modulated DSC (TMDSC). As the ΔCp is used a specific-heat gap between before and after the glass transition, the specific-heat gap being calculated from an extrapolated tangent which touches the temperature-heat flux reversible curve at around the glass transition. The content of movable amorphous components (Xma) is calculated using equation (3). In equation (3), ΔCp0 is a difference in specific heat between before and after the Tg of the amorphous polyamide, and the value thereof is 0.4745 J/g.

[0028] The content of rigid amorphous components was calculated from average values obtained from two measurements made by temperature-modulated DSC and DSC.

$$\text{Content of crystals: Xc } (\%) = (\Delta\text{Hm}-\Delta\text{Hc})/\Delta\text{Hm0}\times 100 \qquad (1)$$

$$\text{Content of rigid amorphous components: Xra } (\%) = 100-(\text{Xc}+\text{Xma}) \qquad (2)$$

$$\text{Content of movable amorphous components: Xma } (\%) = \Delta\text{Cp}/\Delta\text{Cp0}\times 100 \qquad (3)$$

[0029] The sum of the content of crystals and the content of rigid amorphous components is a value which roughly indicates the degree of orientation relaxation of the molecular chains of the polyamide polymer. In cases when the sum of the content of crystals and the content of rigid amorphous components is high, this indicates that the molecular chains have a small strain and the fibers are highly crystalline. In cases when the sum of the content of crystals and the content of rigid amorphous components is low, this indicates that the molecular chains are in a highly entangled state and the fibers are lowly crystalline. By regulating the sum of the content of crystals and the content of rigid amorphous components to 90% or less, the polyamide polymer is made to have a moderate molecular-chain strain amount and polyamide fibers not having too high crystallinity are obtained, thereby giving stockings and knitted laces which are excellent in terms of feeling and softness. By regulating the sum of the content of crystals and the content of rigid amorphous components to 70% or higher, the molecular chains of the polyamide polymer are made to have a moderate strain and, hence, polyamide fibers having excellent crystallinity are obtained, thereby giving stockings and knitted laces which have excellent durability. The sum thereof is more preferably 75-85%.

[0030] The polyamide multifilament of the present invention must have a U% of 1.2 or less. By regulating the U% thereof to a value within that range, the multifilament is made excellent in terms of product appearance quality. In case where the U% thereof exceeds 1.2, this multifilament is poor in product appearance quality to give knitted laces which upon dyeing come to have appearance failures, such as streaks formed by deep-dyed thick yarns. More preferably, the U% thereof is 1.0 or less in the case of stocking applications and is 1.0 or less in the case of knitted-lace applications. The smaller the U%, the more the multifilament is preferred. However, a lower limit thereof in the present invention is about 0.4.

[0031] The polyamide multifilament of the present invention preferably has a total fineness of 4.0-33.0 dtex from the standpoint of clothing applications. The total fineness thereof is more preferably 4.0-11.0 dtex in the case of stocking applications and 20.0-30.0 dtex in the case of lace applications.

[0032] The polyamide multifilament of the present invention preferably has a single-filament fineness of 1.3-3.4 dtex. In cases when the single-filament fineness thereof is in that range, this polyamide multifilament gives stockings and laces which are excellent in terms of durability and softness. The single-filament fineness thereof is more preferably 1.6-3.2 dtex.

[0033] The polyamide multifilament of the present invention preferably has a sulfuric acid relative viscosity of 2.5-4.0. The sulfuric acid relative viscosity thereof is more preferably 3.2-3.8. In cases when the sulfuric acid relative viscosity thereof is 2.5-4.0, this polyamide multifilament gives stockings and knitted laces which have durability that enables the stockings and knitted laces to withstand practical use. Furthermore, these products have satisfactory appearance quality.

[0034] The polyamide multifilament of the present invention is not particularly limited in cross-sectional shape thereof. For example, the filaments may have a circular cross-section, a flat cross-section, a lens-shaped cross-section, a trifoliate cross-section, a multilobar cross-section, an irregular cross-section having three to eight protrusions and the same number of recesses, a hollow cross-section, or any of other known irregular cross-sections.

[0035] One example of methods for producing the high-strength polyamide multifilament of the present invention is explained in detail. Fig. 1 shows one embodiment of production devices operated by a direct spinning drawing method which are advantageously usable in a method for producing a high-strength polyamide multifilament according to the present invention.

[0036] The polyamide multifilament of the present invention may be produced in the following manner. A polyamide resin is melted, and the polyamide polymer is weighed and transported by a gear pump and finally extruded through ejection holes formed in a spinneret 1, thereby forming filaments. The filaments ejected from the spinneret 1 are passed through the following parts shown in Fig. 1: a gas feeder 2, which ejects steam in order to inhibit the spinneret from being fouled with the lapse of time; a multilayered heating cylinder 3 disposed for gradual cooling so as to entirely surround the ejected filaments; and a cooler 4. Thus, the filaments are cooled to room temperature and solidified. Thereafter, an oil is applied to the filaments with an oiling device 5 and the filaments are collected to form a multifilament, which is entangled with a fluid entangling nozzle device 6 and passed through a take-up roller 7 and a drawing roller 8. During this passing, the multifilament is drawn in accordance with the ratio between the peripheral speed of the take-up roller 7 and that of the drawing roller 8. Furthermore, the yarn is heat-treated with the heat of the drawing roller 8 and is wound up with a winding device 9.

[0037] In the production of a polyamide multifilament according to the present invention, it is preferable that the polyamide resin has a sulfuric acid relative viscosity of 2.5-4.0. By regulating the sulfuric acid relative viscosity thereof to a value within that range, a high-strength polyamide multifilament having a large strength-elongation product is obtained.

[0038] The temperature for melting is preferably higher by 20-95°C than the melting point of the polyamide.

[0039] In the production of a polyamide multifilament according to the present invention, the heating cylinder 3 must have been disposed over the cooler 4 so as to entirely surround the filaments. By disposing the heating cylinder over the cooler 4 and regulating the temperature of the atmosphere within the heating cylinder so as to be in the range of 100-300°C, the polyamide polymer ejected from the spinneret 1 can be caused to undergo orientation relaxation without thermally deteriorating. As a result of the orientation relaxation due to gradual cooling from the spinneret surface to the cooling, a multifilament having a high 15% strength and a large strength-elongation product is obtained. In case where the heating cylinder is omitted, the orientation relaxation due to gradual cooling from the spinneret surface to the cooling is insufficient and it tends to be difficult to obtain fibers which satisfy both the 15% strength and the strength-elongation product.

[0040] In the production of a high-strength polyamide multifilament according to the present invention, the heating cylinder must have a multilayer configuration. Patent Document 3 proposes a heating cylinder for keeping the temperature of the atmosphere just under the spinneret at 250-450°C for the purpose of gradual cooling. Although the proposed heating cylinder is effective in an industrial low-fineness region, use thereof for multifilaments for clothing in a high-fineness region, such as the polyamide multifilament of the present invention, is disadvantageous in that since the temperature distribution in the heating cylinder is constant, the thermal convection is prone to be disordered to affect the solidification of the filaments and this is a factor which impairs the U%. A heating cylinder having a multilayer configuration is hence disposed and temperatures are set so as to decline in stages from the uppermost layer to the lowermost layer. Thus, thermal convection from the uppermost layer to the lowermost layer is purposely formed to produce a descending air flow in the same direction as the flow accompanying the filaments. As a result, the thermal convection within the heating cylinder is inhibited from being disordered and filament oscillation is reduced, thereby obtaining a multifilament having a small value of U%.

[0041] The length L of the multilayered heating cylinder, although depending on the fineness of the filaments, is preferably 40-100 mm. It is preferable that the multilayered heating cylinder is configured of two or more layers, and the single-layer length L1 of the multilayered heating cylinder is preferably in the range of 10-25 mm.

[0042] The atmosphere in the multilayered heating cylinder has temperatures in the range of 100-300°C, and it is necessary to form a gentle temperature gradient over the layers. For example, in the case where the length L of the multilayered heating cylinder is 75 mm and the single-layer length L1 is 25 mm, it is necessary that the upper layer have an atmosphere temperature of 250-300°C, the middle layer have an atmosphere temperature of 200-250°C, and the lower layer have an atmosphere temperature of 100-200°C.

[0043] Due to this configuration, an atmosphere-temperature profile for from the spinneret to the cooling can be controlled in stages over the range of 100-300°C, thereby yielding a high-strength polyamide multifilament having satisfactory 15% strength, strength-elongation product, and U%.

[0044] In the production of a polyamide multifilament according to the present invention, use can be made of any of methods in which the cooler 4 is a cooler which ejects cooling/rectifying air A from certain directions, or an annular cooler which ejects cooling/rectifying air A from the peripheral side toward the center, or an annular cooler which ejects cooling/rectifying air from the center side toward the periphery, or the like. The vertical distance LS (hereinafter referred to as "cooling initiation distance") from the lower surface of the spinneret to the upper end of the cooling-air ejection part of the cooler 4 is preferably in the range of 159-219 mm from the standpoints of inhibiting filament oscillation and inhibiting the U% from increasing, and is more preferably 169-189 mm. With respect to the velocity of the cooling air being ejected from the cooling-air ejection surface, it is preferable that the velocity thereof is in the range of 20.0-40.0 (m/min) in terms of average for the zone ranging from the upper end to the lower end of the cooling-air ejection part, from the standpoints of U% and strength-elongation product.

[0045] In the production of a polyamide multifilament according to the present invention, the position of the oiling device 5, that is, the vertical distance Lg (hereinafter referred to as "oiling position") from the lower surface of the spinneret to the position of the oiling nozzle of the oiling device 5 in Fig. 1, is preferably 800-1,500 (mm), more preferably 1,000-1,300 (mm), although the distance Lg depends on the single-filament fineness and the efficiency of the cooling of the filaments by the cooler. In cases when the distance Lg is 800 (mm) or longer, the temperature of the filaments declines to a temperature suitable for the oiling. In cases when the distance Lg is 1,500 mm or less, the filament oscillation due to the descending air flow is small and a multifilament having a small value of U% is obtained. In addition, in cases when the distance Lg is 1,500 mm or less, the distance from the solidification point to the oiling position is short, resulting in a diminished accompanying flow and a reduced spinning tension and hence in reduced spinning orientation. Consequently, a high-strength multifilament which has excellent drawability and is hence high in strength-elongation product and 15% strength is obtained. In cases when the distance Lg is 800 (mm) or longer, the bending of the filaments in the zone ranging from the spinneret to the oiling guide is appropriate and the filaments are less apt to be affected by fretting on the guide, thereby inhibiting the strength-elongation product and the 15% strength from decreasing.

[0046] In the production of a polyamide multifilament according to the present invention, the spinning speed is preferably such that the take-up roller 7 is rotated at 1,000-2,000 m/min, which is in a low-speed range. Thus, draft draw unevenness can be diminished and the filaments can be evenly cooled, making it possible to obtain a U% as small as 1.2 or less. In cases when the speed thereof is 2,000 m/min or less, spinning orientation is inhibited and the gradually cooling effect of the heating cylinder is heightened, thereby enhancing the strain relaxation of the molecular chains. As a result, a high-strength multifilament having a high 15% strength and a large strength-elongation product is obtained.

[0047] It is preferable that the drawing roller 8 is used as a heating roller to conduct a heat treatment so that the heat-setting length is 500-1,200 mm and the heat treatment temperature is 120-180°C. This is because a proper heat treatment makes it possible to design the heat shrinkage of the multifilament. In cases when the heat-setting length is 500 mm or larger, the fibers undergo sufficient crystallization, resulting in an increased 15% strength, thereby yielding products having excellent durability. In cases when the heat-setting length is 1,200 mm or less, crystallization in the fibers is prevented from proceeding excessively and a high-strength polyamide multifilament having a 15% strength in a proper range and having excellent process passage capability in high-order processing steps is obtained, the multifilament giving products having a soft feeling.

[0048] A polyamide multifilament according to the present invention can be produced by disposing a heating cylinder over the cooler 4, regulating the atmosphere within the heating cylinder so as to have temperatures in the range of 100-300°C, configuring the heating cylinder as a multilayer type heating cylinder, thereby forming a temperature gradient in the heating cylinder and purposely forming a descending air flow in the same direction as the flow accompanying the filaments, and regulating the oiling position to 800-1,500 mm from the spinneret surface, the spinning speed to 1,000-2,000 m/min, and the heat-setting length after drawing to 500-1,200 mm.

[0049] By employing such conditions for the direct spinning drawing method, a high-strength polyamide multifilament having a large strength-elongation product of 10.0 cN/dtex or larger, a 15% strength of 4.0-6.0 cN/dtex, and a U% of 1.2 or less is obtained.

[0050] The polyamide multifilament of the present invention as such may be fed as a ground yarn to a lace knitting machine to knit a lace fabric by an ordinary method. The lace fabric may be one of any of ordinary knit stitches, such as an embroidery lace, raschel lace, leaver lace, etc.

[0051] The polyamide multifilament of the present invention may be used as the covering yarn of a covered yarn. The covered yarn may be a single-covered yarn obtained by single-winding the covering yarn around an elastic fiber, such as an elastic polyurethane fiber or an elastic polyamide elastomer fiber, as a core yarn or a double-covered yarn obtained by double-winding the covering yarn around the core yarn.

[0052] The polyamide multifilament of the present invention may be used in stockings which partly include the covered yarn. As a knitting machine for knitting the stockings, an ordinary hosiery machine can be used without limitations. A knitting machine having two or four yarn feeders may be used by an ordinary method in which the covered yarn of the present invention is fed to knit the stocking.

[0053] With respect to conditions for dyeing after the knitting, succeeding post-processing, and final setting, these steps may be conducted by known methods. Usable dyes include acid dyes and reactive dyes, and the dyeing is not limited in color, etc.

EXAMPLES

[0054] The present invention is explained in more detail below by reference to Examples.

A. Strength, Elongation, Strength-elongation Product, 15% Strength

[0055] A fiber sample is examined in accordance with JIS L1013-2010, Tensile Strength and Elongation, to draw a tensile strength-elongation curve. The test conditions included a constant-rate extension type tester, a chuck-to-chuck distance of 50 cm, and a stretching speed of 50 cm/min. In the case where the tensile strength at break was lower than the maximum strength, the maximum tensile strength and the corresponding elongation were measured.
[0056] The strength and the strength-elongation product were determined using the following equations.

$$\text{Elongation} = \text{elongation at break (\%)}$$

$$\text{Strength} = [\text{tensile strength at break (cN)}]/[\text{fineness (dtex)}]$$

$$\text{Strength-elongation product} = \{\text{strength (cN/dtex)}\}\times\{\text{elongation (\%)} + 100\}/100$$

$$15\%\ \text{strength} = [\text{tensile strength at 15\% elongation (cN)}]/[\text{fineness (dtex)}]$$

B. Total Fineness, Single-filament Fineness

[0057] A fiber sample was set on a sizing reel having a circumference of 1.125 m, and the sizing reel was rotated to make 500 turns to produce a loop-like hank. The hank was dried in a hot-air drying oven (105±2°C × 60 min) and weighed with a balance. The measured weight was multiplied by an official moisture regain, and the fineness was calculated from the resultant value. The official moisture regain was assumed to be 4.5%.

C. Sulfuric Acid Relative Viscosity (ηr)

[0058] A polyamide chip sample or fiber sample in an amount of 0.25 g was dissolved in sulfuric acid having a concentration of 98% by mass, so that the sample amount was 1 g per 100 mL of the sulfuric acid. Using an Ostwald viscometer, the solution was examined for a flow time (T1) at 25°C. Subsequently, the sulfuric acid alone having a concentration of 98% by mass was examined for flow time (T2). The ratio of T1 to T2, i.e., T1/T2, was taken as the sulfuric acid relative viscosity.

D. Yarn Unevenness (U%)

[0059] Using USTER TESTER IV, manufactured by Zellweger Uster AG, a fiber sample was examined under the conditions of: sample length, 500 m; test yarn speed V, 100 m/min; twister, type S at 30,000 /min; and 1/2 Inert.

E. Content of Crystals, Content of Rigid Amorphous Components

[0060] Xc is determined by calculating the difference (ΔHm-ΔHc) between the quantity of heat of fusion and the quantity of heat of cold crystallization, which are determined by DSC, and calculating the Xc using equation (1). In equation (1), ΔHm0 is the quantity of heat of fusion of the crystalline polyamide, and the value thereof is 229.76 J/g.
[0061] The content of rigid amorphous components (Xra) is calculated from the content of crystals (Xc) and the content of movable amorphous components (Xma) using equation (2). The content of movable amorphous components (Xma) is calculated from a difference in specific heat (ΔCp) between before and after a glass transition observed on a temperature-heat flux reversible curve determined by temperature-modulated DSC (TMDSC). As the ΔCp is used a specific-heat gap between before and after the glass transition, the specific-heat gap being calculated from an extrapolated tangent which touches the temperature-heat flux reversible curve at around the glass transition. The content of movable amorphous components (Xma) is calculated using equation (3). In equation (3), ΔCp0 is a difference in specific heat between before and after the Tg of the amorphous polyamide, and the value thereof is 0.4745 J/g°C.
[0062] The content of rigid amorphous components was calculated from average values obtained from two measurements made by temperature-modulated DSC and DSC.

$$\text{Content of crystals: Xc (\%)} = (\Delta Hm - \Delta Hc)/\Delta Hm0 \times 100 \qquad (1)$$

$$\text{Content of rigid amorphous components: Xra (\%)} = 100 - (Xc + Xma) \qquad (2)$$

Content of movable amorphous components:

$$\text{Content of movable amorphous components: Xma (\%)} = \Delta Cp/\Delta Cp0 \times 100 \qquad (3)$$

[0063] The ordinary DSC and temperature-modulated DSC were conducted under the following measuring conditions.

(a) Ordinary DSC

[0064] Using Q1000, manufactured by TA Instruments, data processing was conducted with Universal Analysis 2000. A measurement was made in a nitrogen stream (50 mL/min) under the conditions of a temperature range of 0-300°C, a heating rate of 10 °C/min, and a sample weight of about 5 mg (the calorimetric data were normalized with respect to the weight of the sample which had undergone the examination).

[0065] Details of the above-described DSC are described in the following [Document 1].

[Document 1]

[0066] Wunderlich B., Thermal Analysis of Polymeric Materials, Appendix 1 (The ATHAS Data Bank), Springer (2005)

(b) Temperature-modulated DSC

[0067] Using Q1000, manufactured by TA Instruments, data processing was conducted with Universal Analysis 2000. A measurement was made in a nitrogen stream (50 mL/min) under the conditions of a temperature range of 0-200°C, a heating rate of 2 °C/min, and a sample weight of about 5 mg (the calorimetric data were normalized with respect to the weight of the sample which had undergone the examination).

[0068] This technique is a method in which the temperature is evenly elevated to examine the sample while repeatedly conducting heating and cooling with certain period and amplitude. All the DSC signals (total heat flow) can be separated into ones attributable to reversible components (reversing heat flow) such as glass transition and ones attributable to irreversible components (nonreversing heat flow) such as enthalpy relaxation, curing reaction, solvent elimination, etc. It is, however, noted that a crystal shows a melting peak for both reversible components and irreversible components.

[0069] Details of the temperature-modulated DSC are described in [Document 1] shown above.

F. Evaluation of Lace

(a) Softness

[0070] A lace product was evaluated for relative softness by inspectors (five persons) rich in experiences in evaluating feeling. The grades respectively evaluated by the inspectors were averaged, and the average was rounded off to the nearest whole number. Grades 5, 4, 3, and 1-2 on average were indicated by S, A, B, and C, respectively.

5: highly excellent
4: slightly excellent
3: fair
2: slightly poor
1: poor

[0071] S and A were regarded as acceptable in terms of softness.

(b) Durability

[0072] Bursting strength was evaluated in the following manner. Arbitrarily selected three portions were examined for bursting strength by the bursting strength test method according to JIS L1096-2010, Mullen type method (method A), and an average value of the measured values was evaluated in the following four grades.

S: 130 kPa or higher
A: 100 kPa or higher but less than 130 kPa
B: 90 kPa or higher but less than 100 kPa
C: less than 90 kPa

[0073] S and A were regarded as acceptable in terms of durability.

(c) Appearance Quality

[0074] A lace product was evaluated for relative degree of uneven dyeing by inspectors (five persons). The grades respectively evaluated by the inspectors were averaged, and the average was rounded off to the nearest whole number. Grades 5, 4, 3, and 1-2 on average were indicated by S, A, B, and C, respectively.

5: highly excellent
4: slightly excellent
3: fair
2: slightly poor
1: poor
S and A were regarded as acceptable in terms of appearance quality.

(d) Process Passage Capability

[0075] Suitability for knitting: The number of yarn breakages which occurred during knitting per roll of lace fabric (80 m) was shown according to the following criteria.

S: 0 or more and less than 5 yarn breakages
A: 5 or more and less than 10 yarn breakages
B: 10 or more and less than 20 yarn breakages
C: 20 or more and less than 30 yarn breakages
S and A were regarded as acceptable in terms of process passage capability.

G. Evaluation of Stocking

(a) Softness

[0076] A stocking product in the state of being worn by a human leg form was evaluated for relative softness of the leg portion by inspectors (five persons) rich in experiences in evaluating feeling. The grades respectively evaluated by the inspectors were averaged, and the average was rounded off to the nearest whole number. Grades 5, 4, 3, and 1-2 on average were indicated by S, A, B, and C, respectively.

5: highly excellent
4: slightly excellent
3: fair
2: slightly poor
1: poor
S and A were regarded as acceptable in terms of softness.

(b) Durability

[0077] A stocking product was put, with the right side out, on a human leg form so that the garter part lay in a position 60 cm apart from the heel toward the thigh. On the back of the thigh of the leg form, a circular mark according to a measuring frame is put so that the center of the mark lay in a position 52.5 cm apart from the heel toward the thigh. In fixing the product to the measuring frame, the product was fixed so that the circular mark thus put was positioned properly with respect to the frame. Thus, the product was examined for bursting strength in the same state as the state of being worn. The bursting strength was used as an index to durability.

[0078] Bursting strength was evaluated in the following manner. Arbitrarily selected three portions were examined for bursting strength by the bursting strength test method according to JIS L1096-2010, Mullen type method (method A), and an average value of the measured values was evaluated in the following four grades.

S: 117.7 kPa or higher
A: 98.1 kPa or higher but less than 117.7 kPa
B: 88.3 kPa or higher but less than 98.1 kPa
C: less than 88.3 kPa

[0079] S and A were regarded as acceptable in terms of durability.

(c) Appearance Quality

[0080] A stocking product was evaluated for relative degree of uneven dyeing by inspectors (five persons). The grades respectively evaluated by the inspectors were averaged, and the average was rounded off to the nearest whole number. Grades 5, 4, 3, and 1-2 on average were indicated by S, A, B, and C, respectively.

5: highly excellent
4: slightly excellent
3: fair
2: slightly poor
1: poor

[0081] S and A were regarded as acceptable in terms of appearance quality.

(d) Process Passage Capability

[0082] A hosiery machine was continuously operated for 1 hour at a rotational speed of 400 rpm to knit stockings, and the number of machine stops due to yarn breakages during the knitting was evaluated according to the following criteria.

S: less than 2 yarn breakages
A: 2 or more and less than 4 yarn breakages
B: 4 or more and less than 6 yarn breakages
C: 6 or more yarn breakages

[0083] S and A were regarded as acceptable in terms of process passage capability.

[Example 1]

(Production of Polyamide Multifilament)

[0084] Nylon-6 chips having a sulfuric acid relative viscosity (ηr) of 3.3 and a melting point of 225°C, as a polyamide, were dried in an ordinary method so as to result in a moisture content of 0.03% by mass or less. The nylon-6 chips thus obtained were melted at a spinning temperature (melting temperature) of 290°C and ejected from a spinneret. The spinneret used had forty-two holes, which were round and had a diameter of 0.25, and was for producing six yarns per spinneret.

[0085] The spinning was conducted using a spinning machine (direct spinning drawing machine) having the configuration shown in Fig. 1. As the heating cylinder was used a two-layer heating cylinder having a heating cylinder length L of 50 mm and single-layer lengths L1 and L2 of 25 mm each. Temperatures were set so that the atmosphere in the upper layer of the heating cylinder had a temperature of 300°C and the atmosphere in the lower layer of the heating cylinder had a temperature of 150°C.

[0086] The filaments ejected from the spinneret are gradually cooled at ambient temperatures of 150-300°C in the two-layer heating cylinder and passed through an annular cooler having a cooling initiation distance LS of 169 mm and supplying 18°C cool air. Thus, the filaments are cooled to room temperature and solidified. Thereafter, the filaments were collected, while being oiled at an oiling position Lg of 1,300 mm, in terms of distance from the spinneret surface, thereby forming a multifilament. The multifilament was entangled with a fluid entangling nozzle device. The multifilament was then passed through the take-up roller, which had a speed (spinning speed) of 1,500 m/min, and the drawing roller, which had a heat-setting length of 600 mm and had been heated to 155°C, drawn thereby at a draw ratio of 2.8, and wound up. Thus, a nylon-6 multifilament having a fineness of 22.0 dtex and including seven filaments was obtained.

[0087] The nylon-6 multifilament obtained was evaluated, and the results thereof are shown in Table 1.

(Production of Knitted Lace)

[0088] Next, the multifilament was warped and set as a back yarn for a 28-G raschel lace ground yarn so as to have a runner length of 21.0 cm and also as a front yarn for the ground yarn so as to have a runner length of 100.0 cm, and then knitted together with patterning yarns of 235-330 dtex. The resultant fabric was subjected to scouring, dyeing, and finish setting, thereby obtaining a knitted lace for innerwear use. The lace product obtained was evaluated, and the results thereof are shown in Table 1.

[Example 2]

[0089] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the ejected filaments were gradually cooled at ambient temperatures of 100-300°C in the heating cylinder by setting the temperature of the atmosphere in the upper layer of the heating cylinder at 300°C and the temperature of the atmosphere in the lower layer of the heating cylinder at 100°C and that the speed of the take-up roller was changed to 1,700 m/min and the draw ratio was changed to 2.7. The results of the evaluation are shown in Table 1.

[Example 3]

[0090] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the ejected filaments were gradually cooled at ambient temperatures of 200-300°C in the heating cylinder by setting the temperature of the atmosphere in the upper layer of the heating cylinder at 300°C and the temperature of the atmosphere in the lower layer of the heating cylinder at 200°C and that the draw ratio was changed to 3.0. The results of the evaluation are shown in Table 1.

[Example 4]

[0091] A nylon-66 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that nylon-66 chips having a sulfuric acid relative viscosity (ηr) of 3.2 and a melting point of 265°C were used as a polyamide. The results of the evaluation are shown in Table 1.

[Comparative Example 1]

[0092] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that a single-layer heating cylinder having a length L of 50 mm was used and the temperature of the atmosphere therein was set at 300°C and that the draw ratio was changed to 3.2. The results of the evaluation are shown in Table 1.

[0093] Because of the use of the single-layer heating cylinder, the temperature of the atmosphere in the heating cylinder was constant and the thermal convection within the heating cylinder was disordered, resulting in an impaired U%. In addition, since the set temperature of the atmosphere in the heating cylinder was 300°C, which was close to the spinning temperature, the orientation relaxation due to gradual cooling from the spinneret surface to the cooling was insufficient, resulting in too high a 15% strength. Because of this, the knitted lace was poor in process passage capability, appearance quality, and softness.

[Comparative Example 2]

[0094] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the ejected filaments were gradually cooled at ambient temperatures of 100-200°C in the heating cylinder by setting the temperature of the atmosphere in the upper layer of the heating cylinder at 200°C and the temperature of the atmosphere in the lower layer of the heating cylinder at 100°C and that the speed of the take-up roller was changed to 1,700 m/min. The results of the evaluation are shown in Table 1.

[0095] Since the set temperatures of the atmosphere in the heating cylinder were 100-200°C, which were lower by

90°C than the spinning temperature, the orientation relaxation due to gradual cooling from the spinneret surface to the cooling was insufficient, resulting in too small a strength-elongation product and too low a 15% strength. Because of this, the knitted lace had poor durability.

[Comparative Example 3]

[0096] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that no heating cylinder was disposed. The results of the evaluation are shown in Table 1.

[0097] Since no heating cylinder had been disposed, the orientation relaxation due to gradual cooling from the spinneret surface to the cooling was insufficient, resulting in too small a strength-elongation product and too low a 15% strength. Because of this, the knitted lace had poor durability.

Table 1

		Example 1	Example 2	Example 3	Example 4	Comparative Example 1	Comparative Example 2	Comparative Example 3
Polymer	polyamide	N6	N6	N6	N66	N6	N6	N6
Spinning conditions	Heating cylinder	included	included	included	included	included	included	not included
	Temperature of atmosphere in upper layer of heating cylinder (°C)	300	300	300	300	300	200	-
	Temperature of atmosphere in middle layer of heating cylinder (°C)	225	200	250	225	300	150	-
	Temperature of atmosphere in lower layer of heating cylinder (°C)	150	100	200	150	300	100	-
	Spinning speed (m/min)	1,500	1,700	1,500	1,500	1,500	1,700	1,500
	Draw ratio	2.8	2.7	3.0	2.8	3.2	2.8	2.8
Yarn properties	Total fineness (dtex)	22	22	22	22	22	22	22
	Single-filament fineness (dtex)	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Elongation (%)	42.0	43.0	38.3	41	36.0	39.0	36.0
	Strength (cN/dtex)	7.4	7.0	7.6	7.3	7.9	6.7	6.7
	Strenght-elongation product (cN/dtex)	10.5	10.0	10.5	10.3	10.7	9.3	9.1
	U%	0.60	0.40	1.20	0.60	1.60	0.35	0.60
	15% strength (cN/dtex)	4.5	4.2	5.0	4.5	6.1	3.4	3.4
	Content of crystals (%)	29	25	30	28	33	19	23
	Content of rigid amorphous components (%)	55	53	55	53	58	45	50
	Sum of content of crystals and content of rigid amorphous components (%)	84	78	86	81	91	64	73
Evaluation of lace	Softness	S	S	S	S	C	S	S
	Durability	S	A	S	S	S	C	C
	Appearance quality	S	S	A	S	C	S	S
	Process passage capability	S	S	S	S	C	S	S

[Example 5]

[0098] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the oiling position Lg was changed to 800 mm and the draw ratio was changed to 3.0. The results of the evaluation are shown in Table 2.

[Example 6]

[0099] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the oiling position Lg was changed to 1,500 mm and the draw ratio was changed to 2.7. The results of the evaluation are shown in Table 2.

[Comparative Example 4]

[0100] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the oiling position Lg was changed to 600 mm and the draw ratio was changed to 3.2. The results of the evaluation are shown in Table 2.

[0101] Since the filaments in the state of having a temperature which was still above room temperature were oiled, the multifilament had an impaired U%. In addition, the bending of the filaments in the zone ranging from the spinneret surface to the oiling guide was large and, hence, the filaments were affected by fretting on the oiling guide, resulting in too small a strength-elongation product and too low a 15% strength. Because of this, the knitted lace was poor in process passage capability, durability, and appearance quality.

[Comparative Example 5]

[0102] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the oiling position Lg was changed to 3,000 mm and the draw ratio was changed to 2.7. The results of the evaluation are shown in Table 2.

[0103] The descending air flow considerably affected the filament oscillation, resulting in an impaired U%. In addition, the accompanying flow heightened the spinning tension and hence enhanced the spinning orientation, resulting in too low a 15% strength and too small a strength-elongation product. Because of this, the knitted lace was poor in appearance quality and durability.

[Example 7]

[0104] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the speed of the take-up roller (spinning speed) was changed to 1,000 m/min and the draw ratio was changed to 3.8. The results of the evaluation are shown in Table 2.

[Example 8]

[0105] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the speed of the take-up roller (spinning speed) was changed to 2,000 m/min and the draw ratio was changed to 2.3. The results of the evaluation are shown in Table 2.

[Comparative Example 6]

[0106] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the speed of the take-up roller (spinning speed) was changed to 800 m/min and the draw ratio was changed to 4.5. The results of the evaluation are shown in Table 2.

[0107] Since the spinning speed was too low, the spinning tension was reduced to enhance the filament oscillation, resulting in an impaired U%. In addition, the gradually cooling effect of the heating cylinder was heightened to cause the strain relaxation of the polyamide molecular chains to proceed excessively, resulting in too high a 15% strength. Because of this, the knitted lace was poor in process passage capability, appearance quality, and softness.

[Comparative Example 7]

[0108] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that the speed of the take-up roller (spinning speed) was changed to 2,500 m/min and the draw ratio was changed to 1.9. The results of the evaluation are shown in Table 2.

[0109] Since the spinning speed was too high, the strain rate was heightened to increase unevenness in the strain rate, resulting in enhanced draft draw unevenness and an impaired U%. In addition, the gradually cooling effect of the heating cylinder was lowered to render the strain relaxation of the polyamide molecular chains insufficient, resulting in too low a 15% strength and too small a strength-elongation product. Because of this, the knitted lace was poor in appearance quality and durability.

[Example 9]

[0110] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that a drawing roller having a different diameter was used to regulate the heat-setting length to 1,200 mm. The results of the evaluation are shown in Table 2.

[Comparative Example 8]

[0111] A nylon-6 multifilament having a fineness of 22 dtex and including seven filaments and a knitted lace were obtained in the same manner as in Example 1, except that a drawing roller having a different diameter was used to regulate the heat-setting length to 1,800 mm. The results of the evaluation are shown in Table 2.

[0112] The thermal crystallization of the fibers proceeded excessively, resulting in too high a 15% strength. Because of this, the knitted lace was poor in process passage capability and softness.

Table 2

		Example 5	Example 6	Example 7	Example 8	Example 9	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Polymer	polyamide	N6	N6	N6	N6	N6	N6	N6	N6	N6	N6
Spinning conditions	Heating cylinder	included	included	included	included	included	included	included	included	included	included
	Lg: oiling position (mm)	800	1,500	1,300	1,300	1,300	600	3,000	1,300	1,300	1,300
	Spinning speed (m/min)	1,500	1,500	1,000	2,000	1,500	1,500	1,500	800	2,500	1,500
	Heat-setting length (mm)	600	600	600	600	1,200	600	600	600	600	1,800
	Draw ratio	3.0	2.7	3.8	2.3	2.8	3.2	2.7	4.5	1.9	2.8

(continued)

		Example 5	Example 6	Example 7	Example 8	Example 9	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Yarn properties	Total fineness (dtex)	22	22	22	22	22	22	22	22	22	22
	Single-filament fineness (dtex)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Elongation (%)	41	44	41	42	32	39	42	39	43	27
	Strength (cN/dtex)	7.3	7.0	7.3	7.2	7.8	6.9	6.6	7.5	6.5	8.2
	Strength-elongation product (cN/dtex)	10.3	10.1	10.3	10.2	10.3	9.6	9.4	10.4	9.3	10.4
	U%	0.80	1.10	0.80	0.60	0.60	1.30	1.80	1.40	1.50	0.60
	15% strength (cN/dtex)	5.6	4.1	5.6	4.5	5.5	3.9	3.5	6.1	3.6	6.4
	Content of crystals (%)	32	27	32	29	29	25	23	30	25	30
	Content of rigid amorphous components (%)	56	53	56	55	55	50	50	55	50	61
	Sum of content of crystals and content of rigid amorphous components (%)	88	80	88	84	84	75	73	85	75	91

(continued)

		Example 5	Example 6	Example 7	Example 8	Example 9	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
Evaluation of lace	Softness	A	S	A	S	S	S	S	C	S	C
	Durability	S	A	S	S	S	C	C	S	C	S
	Appearance quality	S	A	S	S	S	C	C	C	C	S
	Process passage capability	A	S	A	S	S	C	S	C	S	C

[Example 10]

(Production of Polyamide Multifilament)

[0113] Nylon-6 chips having a sulfuric acid relative viscosity (ηr) of 3.3 and a melting point of 225°C, as a polyamide, were dried in an ordinary method so as to result in a moisture content of 0.03% by mass or less. The nylon-6 chips thus obtained were melted at a spinning temperature (melting temperature) of 290°C and ejected from a spinneret. The spinneret used had thirty holes, which were round and had a diameter of 0.20, and was for producing six yarns per spinneret.

[0114] The spinning was conducted using a spinning machine having the configuration shown in Fig. 1. As the heating cylinder was used a two-layer heating cylinder having a heating cylinder length L of 50 mm and single-layer lengths L1 and L2 of 25 mm each. Temperatures were set so that the atmosphere in the upper layer of the heating cylinder had a temperature of 300°C and the atmosphere in the lower layer of the heating cylinder had a temperature of 150°C.

[0115] The filaments ejected from the spinneret are gradually cooled at ambient temperatures of 150-300°C in the two-layer heating cylinder and passed through an annular cooler having a cooling initiation distance LS of 169 mm and supplying 18°C cool air. Thus, the filaments are cooled to room temperature and solidified. Thereafter, the filaments were collected, while being oiled at an oiling position Lg of 1,300 mm, in terms of distance from the spinneret surface, thereby forming a multifilament. The multifilament was entangled with a fluid entangling nozzle device. The multifilament was then passed through the take-up roller, which had a speed (spinning speed) of 1,500 m/min, and the drawing roller, which had a heat-setting length of 600 mm and had been heated to 155°C, drawn thereby at a draw ratio of 2.6, and wound up. Thus, a nylon-6 multifilament having a fineness of 8.0 dtex and including five filaments was obtained.

[0116] The nylon-6 multifilament obtained was evaluated, and the results thereof are shown in Table 3.

(Production of Stocking)

[0117] Next, the multifilament was used as a covering yarn for a covered yarn, and an elastic polyurethane yarn having a fineness of 22 dtex was used as a core yarn. The draft ratio was set at 3.0, and the core yarn was single-covered with the covering yarn, with the number of twists being 2,400 t/m (S and Z directions). Thus, a single-covered elastic yarn (SCY) was produced.

[0118] The SCY obtained was used in knitting with a hosiery machine. The resultant knitted fabric was subjected to scouring, dyeing, and 120°C 30-second final setting to obtain a pantyhose product. The leg portion of the pantyhose product was evaluated, and the results thereof are shown in Table 3.

[Comparative Example 9]

[0119] A nylon-6 multifilament having a fineness of 8 dtex and including five filaments and a pantyhose product were obtained in the same manner as in Example 10, except that no heating cylinder was disposed. The results of the evaluation are shown in Table 3.

[0120] Since no heating cylinder had been disposed, the orientation relaxation due to gradual cooling from the spinneret surface to the cooling was insufficient, resulting in too small a strength-elongation product and too low a 15% strength. Because of this, the pantyhose product had poor durability.

[Comparative Example 10]

[0121] A nylon-6 multifilament having a fineness of 8 dtex and including five filaments and a pantyhose product were obtained in the same manner as in Example 10, except that no heating cylinder was disposed and that the speed of the take-up roller (spinning speed) was changed to 2,500 m/min and the draw ratio was changed to 1.5. The results of the evaluation are shown in Table 3.

[0122] Since the spinning speed was too high, the strain rate was heightened to increase unevenness in strain rate, resulting in enhanced draft draw unevenness and an impaired U%. In addition, since no heating cylinder had been disposed, the strain relaxation due to gradual cooling from the spinneret surface to the cooling was insufficient, resulting in too low a 15% strength and too small a strength-elongation product. Because of this, the pantyhose product was poor in appearance quality and durability.

[Comparative Example 11]

[0123] A nylon-6 multifilament having a fineness of 8 dtex and including five filaments and a pantyhose product were obtained in the same manner as in Example 10, except that a single-layer heating cylinder having a length L of 50 mm was used and the temperature of the atmosphere therein was set at 300°C and that the oiling position Lg was changed to 3,000 mm, the speed of the take-up roller (spinning speed) was changed to 600 m/min, and the draw ratio was changed to 4.5. The results of the evaluation are shown in Table 3.

[0124] Because of the use of the single-layer heating cylinder, the temperature of the atmosphere in the heating cylinder was constant and the thermal convection within the heating cylinder was disordered. Furthermore, due to the low oiling position (long distance from the spinneret to the oiling) and the low spinning rate, the filament oscillation was enhanced, resulting in an impaired U%. Moreover, the low-spinning speed heightened the gradually cooling effect of the heating cylinder to cause the strain relaxation of the polyamide molecular chains to proceed excessively, and the increased heat-setting length caused the crystallization of the fibers to proceed excessively, resulting in too high a 15% strength. Because of this, the pantyhose product was poor in process passage capability, appearance quality, and softness.

Table 3

		Example 10	Comparative Example 9	Comparative Example 10	Comparative Example 11
Polymer	polyamide	N6	N6	N6	N6
Spinning conditions	Heating cylinder	included	not included	not included	included
	Temperature of atmosphere in upper layer of heating cylinder (°C)	300	-	-	300
	Temperature of atmosphere in middle layer of heating cylinder (°C)	225	-	-	300
	Temperature of atmosphere in lower layer of heating cylinder (°C)	150	-	-	300
	Lg: oiling position (mm)	1,300	1,300	1,300	3,000
	Spinning speed (m/min)	1,500	1,500	2,500	600
	Heat-setting length (mm)	600	600	600	2,400
	Draw ratio	2.6	2.6	1.5	4.5
Yarn properties	Total fineness (dtex)	8	8	8	8
	Single-filament fineness (dtex)	1.6	1.6	1.6	1.6
	Elongation (%)	44	40	38	28
	Strength (cN/dtex)	7.3	6.4	6.1	8.3
	Strength-elongation product (cN/dtex)	10.5	9.0	8.4	10.6
	U%	0.80	0.80	1.50	1.30
	15% strength (cN/dtex)	4.4	3.8	3.4	6.5
	Content of crystals (%)	29	23	20	32
	Content of rigid amorphous components (%)	55	50	40	63
	Sum of content of crystals and content of rigid amorphous components (%)	84	73	60	95

(continued)

		Example 10	Comparative Example 9	Comparative Example 10	Comparative Example 11
Evaluation of pantyhose	Softness	S	S	S	C
	Durability	S	C	C	S
	Appearance quality	S	S	C	B
	Process passage capability	S	S	S	C

DESCRIPTION OF REFERENCE NUMERALS AND SIGNS

[0125]

1: Spinneret
2: Gas ejector
3: Heating cylinder
4: Cooler
5: Oiling device
6: Fluid entangling nozzle device
7: Take-up roller
8: Drawing roller
9: Winding device
L: Length of multilayered heating cylinder
L1: Single-layer length of multilayered heating cylinder
LS: Cooling initiation distance
Lg: Oiling position

Claims

1. A polyamide multifilament having a tensile strength at 15% elongation of 4.0-6.0 cN/dtex, a strength-elongation product of 10.0 or larger, and a yarn unevenness (U%) of 1.2 or less.

2. The polyamide multifilament according to claim 1, having a single-filament fineness of 1.3-3.4 dtex.

3. The polyamide multifilament according to claim 1 or 2, having an elongation of 30-50%.

4. The polyamide multifilament according to any one of claims 1 to 3, having a sum of a content of crystals and a content of rigid amorphous components of 70-90%.

5. A knitted lace produced using the polyamide multifilament according to any one of claims 1 to 4 as a ground lace yarn.

6. A stocking partly comprising a covered yarn obtained using the polyamide multifilament according to any one of claims 1 to 4 as a covering yarn.

Fig. 1

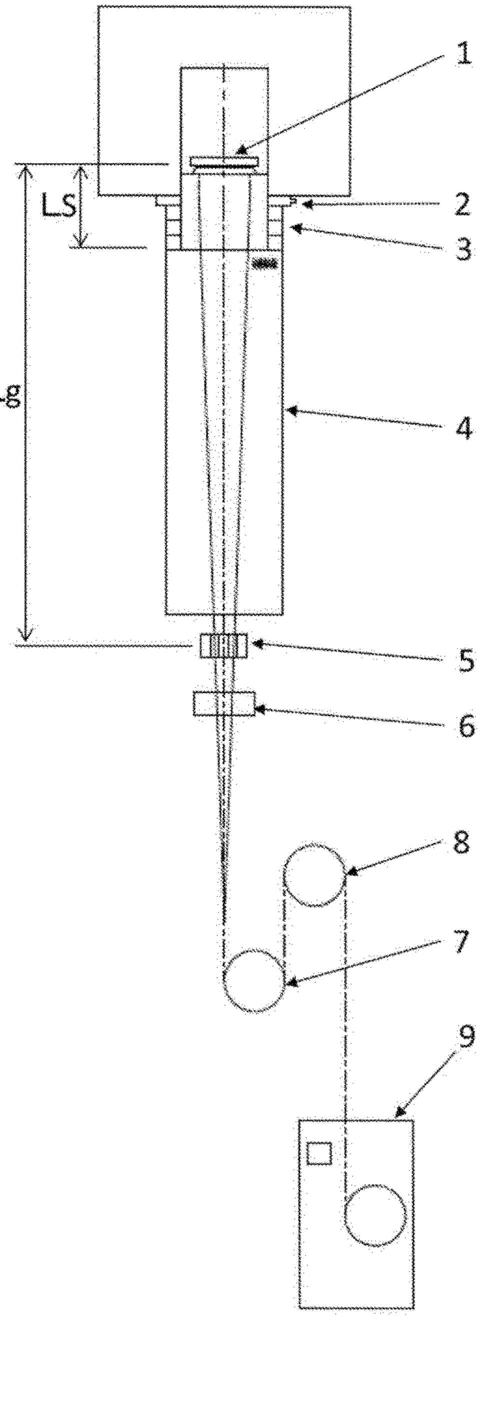
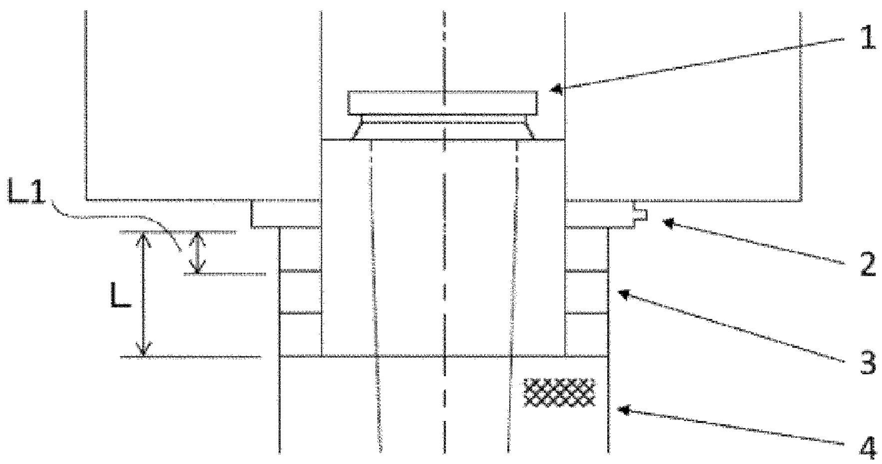


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/025223

A. CLASSIFICATION OF SUBJECT MATTER
D01F6/60(2006.01)i, *A41B11/14*(2006.01)i, *D02G3/38*(2006.01)i, *D02G3/44*(2006.01)i, *D04B21/12*(2006.01)i

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)
D01F1/00-6/96, 9/00-9/04, D01D1/00-13/02, A41B11/14, D02G3/38, D02G3/44, D04B21/12

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2017
Kokai Jitsuyo Shinan Koho	1971-2017	Toroku Jitsuyo Shinan Koho	1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Japio-GPG/FX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/104278 A1 (Toray Industries, Inc.), 30 June 2016 (30.06.2016), entire text & TW 201632665 A	1-6
A	JP 2001-20128 A (Unitika Ltd.), 23 January 2001 (23.01.2001), entire text (Family: none)	1-6
A	JP 61-124622 A (Toyobo Co., Ltd.), 12 June 1986 (12.06.1986), entire text (Family: none)	1-6

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02 October 2017 (02.10.17)	10 October 2017 (10.10.17)

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INTERNATIONAL SEARCH REPORT

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PCT/JP2017/025223

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 51-2528 B1 (Toray Industries, Inc.), 27 January 1976 (27.01.1976), entire text (Family: none)	1-6
A	WO 2016/076184 A1 (Toray Industries, Inc.), 19 May 2016 (19.05.2016), entire text & KR 10-2017-0083021 A & CN 107075741 A & TW 201636466 A	1-6

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REFERENCES CITED IN THE DESCRIPTION

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- JP 2003129331 A **[0007]**
- WO 201676184 A **[0007]**
- JP 63159521 A **[0007]**

Non-patent literature cited in the description

- **WUNDERLICH B.** Thermal Analysis of Polymeric Materials. Springer, 2005 **[0066]**