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(54) Moisture-absorbent composite fiber.

(57) Provided are composite fibers comprising a hydrophobic polyester (B) having a moisture absorbency at 20 °C, 65% RH of not more than 2% and having a total concentration of at least one metal selected from the group consisting of alkali metals and alkali earth metals of at least 500 ppm and a nylon-4 polymer (A) in an amount of 40 to 80% by weight based on the weight of the fiber. They are excellent for clothing use, since they have excellent moisture absorbency, give no clammy feeling upon absorption of moisture, and do not suffer delamination between the nylon-4 polymer and the hydrophobic polyester. Particularly excellent among them are sheath-core composite fibers comprising a core of the nylon-4 polymer (A) and a sheath of the hydrophobic polyester (B) and side-by-side composite fibers having a flat cross-section in which the nylon-4 polymer and the hydrophobic polyester are bimetal-wise laminated with each other.

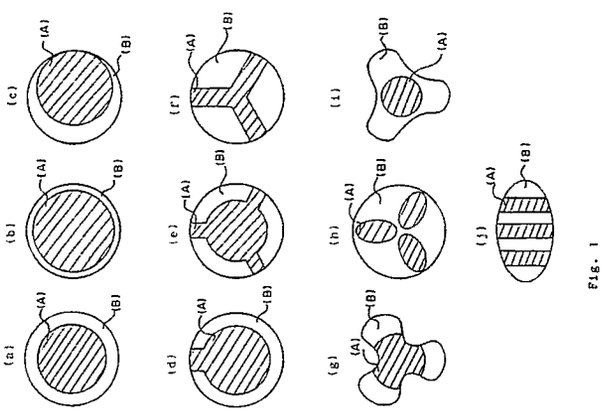

Fig. 1

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MOISTURE-ABSORBENT COMPOSITE FIBER

Field of the invention

The present invention relates to a synthetic fiber having excellent moisture-absorbency, and more specifically to a synthetic fiber having high moisture absorbency and giving, upon absorption of sweat, still agreeable feeling without clamminess.

Description of the prior art

Nylon-4 (polypyrrolidone) fiber has higher moisture absorbency than cotton and at the same time nearly the same excellent fiber properties as other thermoplastic fibers, has antistatic property, is well dyeble with disperse dyes, basic dyes, direct dyes, acidic dyes or the like, and hence is markedly suited for use in clothing, as well as for industrial uses.

However, nylon-4 fiber decreases it Young's modulus significantly upon absorption of water, whereby clothes comprising nylon-4 readily stick to the skin by absorption of sweat when the wearer perspires, thus giving him clammy feeling.

Japanese Patent Application Laid-open No. 12325/1975 discloses a technique for overcoming the above drawback of nylon-4 fiber, which comprises, in the spinning of nylon-4 fiber, melt spinning a blend of nylon-4 polymer chips with polyester polymer chips, thereby suppressing the decrease in Young's modulus of the obtained nylon-4 fiber upon absorption of water. The fiber obtained by this process, however, tends to split or delaminate between the two polymers, since nylon-4 polymer is not compatible with polyester polymer. The fiber then forms fibrils during the manufacturing process and/or the after-processes in which it is formed into fabric. The fibrils thus generated render the fiber difficult to process, or causes the fiber to become clammy again. Furthermore, the fiber obtained by this process does not produce a sufficient effect of eliminating clammy feeling since polyester polymer is present in individual filaments of the fiber in the form of finely divided discontinuous segments.

Japanese Patent Application Laid-open No. 215869/1985 discloses fibril-forming composite fibers comprising polyamide and polyester. This application describes a number of nylon polymers as the polyamide, including nylon-4. All the fibers described in the application, however, are strictly those for the purpose of producing fibrils, and, same as the fiber described in the afore-mentioned literature, create delamination between nylon-4 polymer and polyester polymer, thereby producing fibrils during their manufacturing process and/or processes for fabric formation, which worsen the processability. The thus fibrillated nylon-4 fibers will newly produce clammy feeling.

Fibers from nylon-4 polymer have another drawback of being readily decomposed to lower their strength and elongation by heat at ironing of fabrics made therefrom.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a nylon-4 fiber having excellent moisture absorbency, giving little clammy feeling upon absorption of moisture, hardly generating fibrils because of very rare delamination between polymers constituting the fiber and being hardly decomposed at high temperature conditions.

Another object of the present invention is to provide a nylon-4 fiber the individual filaments of which change their diameter by absorption/desorption of moisture, i.e. decrease the diameter by absorbing sweat and resume the original diameter by desorbing the moisture, being capable of giving clothing which can readily absorb and desorb moisture and is thus very comfortable.

The present invention provides a moisture-absorbent composite fiber comprising a hydrophobic polyester having a moisture absorbency at 20 °C, 65% RH of not more than 2% and having a total concentration of at least one metal selected from the group consisting of alkali metals and alkali earth metals (hereinafter simply referred to as "alkali metal-alkali earth metal concentration) of at least 500 ppm and a nylon-4 polymer having an alkali metal concentration of not more than 500 ppm, said nylon-4 polymer being contained in said fiber in an amount of 40 to 80% by weight based on the weight of the fiber.

The composite fiber of the present invention is preferably a sheath-core composite fiber comprising the nylon-4 polymer as core component and the hydrophobic polyester as sheath component, said sheath-core composite fiber more preferably having ring-shaped or bamboo-joint-like swells around the surface of individual filaments.

The composite fiber of the present invention preferably comprises filaments the diameter of which changes reversibly by absorption/desorption of moisture, while satisfying the conditions of $0.3 \leqq L_{100}/L_{65} \leqq 0.9$ and $1.1 \leqq L_0/L_{65} \leqq 2.5$, where L_{100}, L_{65} and L_0 represent the average maximum lengths of the cross-section of the filaments conditioned under conditions of 20°C and 100% RH, 20°C and 65% RH and 20°C and 0% RH, respectively.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same become better understood by reference to the following detailed description when considered in connection with the accompanying drawings, wherein:

FIGURE 1 shows cross-sectional views of fibers according to the present invention, the fibers being representative composite fibers;

FIGURES 2 and 3 show side views of fibers according to the present invention, the fibers having bamboo-joint like swells on their surface; and

FIGURE 4 shows cross-sectional views of a fiber according to the present invention, said fiber changing its filament diameter upon absorption or desorption of moisture; where (A) represents nylon-4 polymer and (B) hydrophobic polyester.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The nylon-4 polymer that constitutes the present invention includes, for example, those obtained by, as seen in U.S.P. 4,281,105, polymerizing 2-pyrrolidone in the presence of an alkaline polymerization catalyst and SO_2 and a polymerization accelerator of a quaternary ammonium sulfate or quaternary ammonium bisulfite, and may contain a delusterant, an antioxidant, a terminal stabilizer and the like.

Nylon-4 polymer however is difficult to melt spin, while readily decomposing during melt spinning from the terminals and at main chains of molecules thereof, because its melting point is close to decomposition temperature. Thus, in general, filament breakage occurs frequently during spinning or only nonuniform filaments with polymer blocks appearing thereon like bumps are obtained.

For the purpose of preventing the above troubles, it is preferred that the intrinsic viscosity $[\eta]$ and ratio, $\overline{M}_W/\overline{M}_N$ of weight average molecular weight $\overline{M}_W$ to number average molecular weight $\overline{M}_N$ after spinning of the nylon-4 polymer constituting the composite fiber be 0.8 to 1.8 g/dl and 1.5 to 3.5, respectively. To this end, it is preferred to use a nylon-4 polymer having an $[\eta]$ and $\overline{M}_W/\overline{M}_N$ before spinning of 4 to 7 g/dl and 1 .5 to 4, respectively. It is further effective for preventing thermal decomposition during spinning to use, as described in more detail hereinlater, a nylon-4 polymer having an alkali metal concentration of not more than 500 ppm.

In the present invention, the intrinsic viscosity $[\eta]$ is, both for nylon-4 polymer and polyester, obtained by measurement at 30°C of viscosities of specimen solutions in a mixed solvent of phenol/tetrachloroethane = 1/1. The $[\eta]$ of nylon-4 polymer contained in a composite fiber (i.e. after spinning) is determined on a specimen polymer obtained from the fiber by removing the constituting polyester with a 20 g/l aqueous NaOH solution at 95°C. The molecular weight is obtained by GPC on a 0.01% specimen solution in hexafluoroisopropanol with a standard of polymethyl methacrylate, a higher ratio of weight average molecular weight $[\overline{M}_W]$ to number average molecular weight $[\overline{M}_N]$ indicating a sharper molecular weight distribution.

If the $[\eta]$ of the nylon-4 polymer constituting the fiber in question is less than 0.8 g/dl, the fiber will be of low strength and elongation, while with an $[\eta]$ exceeding 1.8 g/dl the fiber often contains bump-like unmelted polymer blocks to become non-uniform. If the $\overline{M}_W/\overline{M}_N$ exceeds 3.5, even at an optimum spinning temperature, unmelted polymer will stay in bump form in the fiber or low-molecular-weight fractions will vigorously decompose during spinning to generategas, which disturbs spinning stability. On the other hand, if the $\overline{M}_W/\overline{M}_N$ is less than 1 .5, a slight fluctuation of spinneret temperature will affect the spinnability, whereby uniform fiber is difficult to obtain.

Nylon-4 polymers are in most cases obtained using a polymerization catalyst of an alkali metal hydroxide represented by KOH. In particular for such nylon-4 polymers having a polymerization degree as used in the present invention, the use of an alkali metal hydroxide as polymerization catalyst can be said to be a must. The present inventors have found that the alkali metal present in this polymerization catalyst will accelerate depolymerization of the nylon-4 polymer during spinning and further, when clothes using the obtained nylon-4 fiber are ironed, accelerate thermal decomposition of the nylon-4 polymer to decrease the strength and elongation of the fiber. The present inventors have also found that the thermal decompositon

of nylon-4 polymer during spinning and when ironed can be significantly suppressed by keeping the alkali metal concentration below 500 ppm.

Commercially available nylon-4 polymers generally contain an alkali metal from the polymerization catalyst used in an amount exceeding 1,000 ppm. In the present invention it therefore is preferred to decrease the alkali metal concentration in the nylon-4 polymer pellets used below 500 ppm prior to the spinning thereof, by hot water washing or like means. The hot water washing may naturally be conducted after spinning, i.e. on fiber as long as it can assure an alkali metal concentration in nylon-4 of 500 ppm or below. More preferred alkali metal concentration is 350 ppm or below. The alkali metal concentration and alkali metal-alkali earth metal concentration herein mean those excluding alkali metal compounds and alkali earth metal compounds that are present in the polymer in the form of insoluble and inert particles, such as calcium carbonate particles.

It is also recommendable for eliminating the above-described troubles at spinning or ironing of nylon-4 polymer to, as seen in Japanese Patent Publication No. 33279/1979, use a copolymer nylon-4 obtained by copolymerizing caprolactam with 2-pyrrolidone to lower the melting point. The obtained copolymer will then have a larger difference between melting point and thermal decomposition temperature, thereby being more readily melt spinnable. In this case the ratio of caprolactam copolymerized is preferably 25 to 75% by weight. With the ratio of less than 25% by weight the melting point decreases only a litte, while with the ratio exceeding 75% by weight the obtained nylon-4 polymer has not so high moisture absorbency. With a copolymerization ratio of 65% or so, the nylon-4 polymer has a melting point of 200 °C, showing a large decrease from that of pure nylon-4, 267 °C, and still exhibits a well maintained moisture absorbency, which is preferred. Such a copolymer nylon-4 further has a feature that clothes utilizing the fiber therefrom show only a markedly small dimensional change when washed repeatedly.

The nylon-4 polymer used in the present invention is a water-insoluble crystalline polymer and has a moisture absorbency at 20 °C, 65% RH of 8.5 to 9%, which is higher than that of cotton, 7 to 8%. The polymer further has a very high moisture absorbency at 20 °C, 85% RH of 14% and that at 20 °C, 100% RH of 37%. Thus, the nylon-4 polymer is a very unique polymer, no other polymers having such a high moisture absorbency. Fibers of the nylon-4 polymer are, however, of low Young's modulus like conventional polyamide fibers, in particular when wet, and hence give clammy feeling when used singly. These fibers cannot be said to be fully comfortable in spite of their high moisture absorbency. The present invention therefore utilizes the technique of composite spinning with a hydrophobic polyester having high Young's modulus to overcome this drawback.

The hydrophobic polyester herein means a polyester having a moisture absorbency at 20 °C, 65% RH of not more than 2% and includes polyesters obtained from a principal acid component of terephthalic acid and a principal glycol component of at least one member selected from the group consisting of ethylene glycol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol and hexamethylene glycol, among which ethylene glycol and tetramethylene glycol are preferred. In these polyesters part of terephthalic acid that is the acid component may be replaced by other bifunctional carboxylic acids. Examples of the other carboxylic acids are bifunctional aromatic dicarboxylic acids such as isophthalic acid, sodium 5-sulfoisophthalic acid, naphthalenedicarboxylic acid, diphenyldicarboxylic acid, diphenoxyethanedicarboxylic acid, β -oxyethoxybenzoic acid and p-oxybenzoic acid; bifunctional aliphatic dicarboxylic acids such as sebacic acid, adipic acid and oxalic acid; and bifunctional alicyclic dicarboxylic acids such as 1,4-cyclohexanedicarboxylic acid. Part of the glycol component of the polyester may also be replaced by other glycol components. Examples of the other glycol components are, besides the above-mentioned glycols other than the principal glycol component, aliphatic, alicyclic and aromatic diols such as neopentyl glycol, 3-methylpentanediol, cyclohexane-1,4-dimethanol, nonanediol, 2-methyloctanediol, bisphenol A and bisphenol S.

These polyesters can be produced by any optional process. For example, polyethylene terephthalate can readily be obtained by conducting a first-stage reaction of forming glycol ester of terephthalic acid and/or low-polymerization-degree products thereof by subjecting terephthalic acid and ethylene glycol to direct esterification reaction, subjecting a lower alkyl ester of terepthalic acid such as dimethyl terephthalate and ethylene glycol to transesterification reaction or reacting terephthalic acid with ethylene oxide; and then conducting a second-stage reaction of polycondensing the product thus obtained to a desired polymerization degree by heating under reduced pressure.

In order that the composite fiber of the present invention can exhibit excellent physical properties as well as high moisture absorbency, it is preferred that the hydrophobic polyester have at least 80% of dicarboxylic acid component of terephthalic acid or ester-forming derivatives thereof, and have the glycol component of ethylene glycol.

If the moisture absorbency at 20 °C, 65% RH of the polyester used exceeds 2%, it tends to be clammy

upon absorption of sweat, whereby the effect of reducing clammy feeling of nylon-4 polymer is not produced.

The hydrophobic polyester used in the present invention must contain at least one metal selected from the group consisting of alkali metals and alkali earth metals in an alkali metal-alkali earth metal concentration of at least 500 ppm. The alkali metal and alkali earth metal herein include sodium, potassium, calcium, magnesium and like metals. These metals may be incorporated as pure metals, in the form of compounds or as atoms constituting the copolymerization components, such as sodium sulfoisophthalate. Where they are added in the form of compounds, preferred compounds are carboxylates. The present inventors have, when studying how to produce composite fibers comprising nylon-4 polymer and polyester, found that there is a very low adhesiveness between the two polymers and the individual filaments delaminate during fiber manufacturing process, in processes for formation into fabrics and in after-processes of the fabrics, thereby decreasing the processability and the physical properties. The present inventors have also found that this delamination between nylon-4 polymer and polyester can be prevented by incorporation of an alkali metal or an alkali earth metal into the polyester. The effect of improving the adhesiveness is not so large with the alkali metal-alkali earth metal concentration in the polyester of less than 500 ppm. On the other hand, if the concentration exceeds 5,000 ppm, the physical properties of the obtained fiber will sometimes decrease, high adhesiveness being secured though. More preferably, the alkali metal-alkali earth metal concentration is at least 1,000 ppm.

In the present invention, when the polyester used comprises copolymerization units from isophthalic acid, the spinning temperature can be lowered and, consequently, the thermal decomposition during spinning of nylon-4 polymer can be suppressed. Isophthalic acid is preferably copolymerized in an amount of 4 to 12 mol%. With the copolymerization ratio of less than 4 mol%, the melting point of the resulting copolymer polyester decreases only a little; while with the ratio exceeding 12 mol% the physical property of the obtained fiber decreases. Copolymerization of 0.45 to 3 mol% of an alkali metal salt of sulfoisophthalic acid, which assures the above-described incorporation of the alkali metal in the specified amount, causes substantially no delamination between nylon-4 polymer and the polyester to occur, whereby the obtained fiber will exhibit its full characteristics as composite fiber. To summarize, the preferred polyester is polyethylene terephthalate or polybutylene terephthalate comprising 4 to 12 mol% of copolymerization units from isophthalic acid and 0.45 to 3 mol% of units from an alkali metal salt of sulfoisophthalic acid.

The degree of polymerization of the polyester is, as expressed by intrinsic viscosity, preferably at least 0.45 g/dl for the purpose of obtaining a composite fiber with desired characteristics, and preferably not more than 0.80 g/dl in view of melt viscosity at spinning. It will be difficult to conduct composite spinning with nylon-4 polymer if the intrinsic viscosity of the polyester exceeds 0.80 g/dl.

The term "composite fiber" as referred to in the present invention means a fiber consisting of 2 or more components and having any cross-sectional shape including side-by-side, multilayered, sheath-core and others. The sheath-core herein includes those of one-core, multi-core and eccentric-core. The cross-sectional shapes of representative sheath-core composite fibers are shown in FIGURE 1, with the exception of (f) and (j) that are not called sheath-core. The nylon-4 polymer used is contained in the composite fiber preferably in an amount of 40 to 80% by weight. If the amount is less than 40% by weight, the resulting fiber will have as low a moisture absorbency as those of conventional nylon-6 and nylon-6,6 fibers. On the other hand, if the content exceeds 80% by weight, contribution of high Young's modulus of the counterpart polyester will be small and the fiber will be of low Young's modulus and give a clammy feeling particularly when wet. The content of the nylon-4 polymer is more preferably 50 to 70% by weight.

Particularly effective for the purpose of reducing clammy feeling inherent to nylon-4 polymer are composite fibers with the nylon-4 polymer as core component and the hydrophobic polyester as sheath component. In these fibers moisture is absorbed into the core, and the polyester present on the surface does not contain moisture and is dry, whereby clothes made therefrom give no clammy feeling at all and thus are very agreeable.

Among these sheath-core composite fibers, in particular those having a plurality of bamboo-joint like swells extending circumferentially around the surface of each individual filament gives almost no clammy feeling and is preferred. For developing the swells of this type, the sheath-core composite fibers are preferably of one-core type in which the sheath component completely wraps the core component, as shown in FIGURE 1 (a) and (i). The presence of such swells on the fiber surface is very effective in reducing clammy feeling and giving a "dry-touch" feeling of clothes made from the fiber, since it reduces the area of contact between the wearer's skin and the clothes when wet.

The joint-like swell herein means a fiber structure having a diameter ratio L'/L of 1.1 to 2.0, wherein L' and L represent the average diameter of the projected swells or ring-shaped parts measured in a direction perpendicular to the fiber axis and the average diameter of the cross-sections of non-swollen or regular

parts, respectively, of individual filaments and can be determined by observing the side surface of the filament with a conventional optical microscope or scanning electron microscope. FIGURE 2 shows diagrammatical views of representative examples having this structure. As shown in this FIGURE, the joint-like swells in the present invention are generally present on the surface of each filament in the form of rings which extend circumferentially around the surface. Where the core is highly eccentric, the joint-like swells sometimes appear only on one side of each filament surface, as shown in FIGURE 2 (c).

An L'/L of not more than 1.1 cannot give a sufficient dry touch. On the other hand, if the L'/L exceeds 2.0, the resulting fiber will be of insufficient strength, which is not preferred. It is therefore preferred for the purpose of realizing the bulky and "dry-touch" hand together with sufficent strength, that is characteristic of the present invention, that the L'/L be 1.1 to 2.0, more preferably 1.2 to 1.6. Functional tests conducted by the present inventors have revealed that presence of the above joint-like swells in a density of at least 1 and not more than 50 pieces per 1 mm of filament length gives the bulky and dry-touch feeling to clothes made from the fiber. With the density of less than 1 piece/mm of the joint-like swells the clothes do not give excellent bulky and dry-touch feeling, while the density exceeding 50 pieces/mm causes the clothes to exhibit a stiff touch. More preferably the density is 5 to 20 pieces/mm.

In the present invention, the ratio of the sum of the widths of the joint-like swells to the total filament length is preferably not more than 25%. This is explained below with reference to FIGURE 3. From a photomicrograph or electron photomicrograph, there are determined the width, W_1, i.e. size in the direction of fiber length of a swell at its base is determined, that of a second swell, W_2, and in the same way upto W_n of the n-th swell, the n pieces of swells being present in a filament length, L_0 (usually 1 mm). Then, the ratio of the sum of the n widths to L_0:

$$\frac{(W_1 + W_2 + W_3 + \cdots\cdots + W_n)}{L_0} \times 100$$

is preferably not more than 25%. If the ratio exceeds 25%, the dry-touch feeling will decrease. The ratio is more preferably not more than 15%.

There are no restrictions with respect to the width (i.e. W_1 , W_2, W_3, ... or W_n shown in FIGURE 3 (a) and (b)), but it is preferably 1 to 10μ m, more preferably 4 to 7μ m.

The above sheath-core composite fiber having a multiplicity of joint-like swells can be produced by for example preparing a sheath-core composite fiber comprising a core of nylon-4 polymer and a sheath of hydrophobic polyester and having a hot water shrinkage (hereinafter referred to as "WSR") of at least 9% and then shrinking the obtained sheath-core composite fiber by hot water treatment. In this case if WSR is less than 9, the desired joint-like structure will be difficult to develop. The WSR is preferably at least 12%, which gives, in addition to the desired joint-like structure, crimps to the composite fiber so that fabrics made from the resulting fiber will exhibit a soft and bulky hand like that of fabrics from textured yarn.

The WSR value depends on the ratio of nylon-4 polymer and polyester and heat drawing temperature and heat treating temperature at fiber manufacturing process. For the purpose of assuring a WSR of at least 9%, the content of nylon-4 polymer is at least 40% by weight based on the weight of the fiber and the heat drawing and heat treating temperatures are set a little low, for example at not higher than 160 $^\circ$ C.

The mechanism of the development of joint-like structure by hot water treatment is not clear, but is considered to be due to the following. Nylon-4 polymer has a markedly high wet shrinkage (WSR = 40 to 50%) and is not compatible with polyester, and hence when the sheath-core composite fiber of the present invention is hot water treated, the sheath polyester cannot withstand the shrinking force produced by the core nylon-4 polymer, whereby delamination occurs partially at their interface and the sheath polyester eventually generates yields to form joint-like swells. Where the composite fiber has a WSR of at least 12%, the sheath polyester further, after having formed yields, shrinks, thereby causing the entire composite fiber to crimp.

The joint-like swells thus generated on a fiber has another feature of increasing the rate of absorption/desorption of moisture of the fiber. This is because of cracks formed in the sheath polyester when the joint-like swells generate by its yielding. The cracks formed at the swollen parts permit moisture to readily pass therethrough, thus increasing the rate of absorption/desorption of moisture. Ordinary sheath-core composite fibers having no such joint-like swells are of low rate of absorption/desorption of moisture and hence cannot be necessarily said to be very agreeable, while they have satisfactory equilibrium moisture absorbency.

There seem to be applicable also other methods for increasing the rate of absorption/desorption of

moisture, such as eccentric-core sheath-core type, multilayered type, side-by-side bimetal type and the like. In all of these types, however, nylon-4 polymer is exposed on the surface and tends to cause the fibers to give clammy feeling when they absorb moisture or water.

With the composite fiber having joint-like swells according to the present invention, cracks generate on the joint parts and still nylon-4 polymer is not exposed on the surface. The fiber therefore has high rate of absorption/ desorption of moisture and gives no clammy feeling when wet with moisture or water, and it desorbs moisture without causing the wearer's skin to be deprived of much heat, whereby he does not feel cold. The fiber thus gives very comfortable feeling.

In the present invention, the WSR is determined according to JIS L1013, 7.15(1) HOT WATER SHRINKAGE, Method B as follows. A specimen fiber is loaded with an initial load of 0.05 g/d, and a length of 500 mm is accurately measured on the specimen and marked at its both ends. The initial load is replaced by a load of 0.5 mg/d and then the specimen is immersed in hot water at 98 °C for 30 minutes. After the immersion, the specimen is air-dried without the load and then loaded with the initial load and measured for the length (ℓ) between the marks. The WSR (%) is:

$$WSR\ (\%) = \frac{500 - \ell}{500} \times 100$$

where ℓ = the length between the 2 marks after the immersion in mm.

The hot water treatment herein can be conducted by any process such as immersion in boiling water, ordinary relaxation process, alkali etching or dyeing process, and is conducted at a temperature of preferably 70 to 140 °C for a period, depending on the process employed, of preferably 1 minute to about 2 hours.

The present inventors have also found that a composite fiber having a flat cross-sectional shape of bimetal of nylon-4 polymer and hydrophobic polyester, the laminated line constituting the maximum length line of the flat section, changes its diameter reversibly with the moisture absorption. Then, clothes made from such a fiber are provided with a moisture conditioning function to suppress both stuffy feeling between the clothes and the skin and a chill felt upon excess dissipation of sweat. When the humidity inside the clothes increases, this composite fiber absorbs the moisture and desorbs it outward, thereby suppressing stuffy feeling. Further when the water content inside the clothes becomes markedly high because of profuse perspiration, the composite fiber decreases its diameter and increase the moisture permeability of the clothes so that the moisture accumulating inside them can effectively permeate outward, whereby the stuffy feeling is again suppressed. On the other hand, when the perspiration stops and the moisture inside the clothes starts decreasing, the composite fiber gradually desorbs moisture and resumes its original diameter to prevent the skin temperature from decreasing rapidly on account of excess evaporation.

It is preferred for the purpose of exhibiting the moisture conditioning function that prevents stuffy feeling and assures comfortable wear, that the composite fiber change its diameter by absorption/desorption of moisture satisfying the conditions of $0.3 \leqq L_{100}/L_{65} \leqq 0.9$ and $1.1 \leqq L_0/L_{65} \leqq 2.5$, where L_{100}, L_{65} and L_0 are average maximum lengths of the cross-section of the composite fiber conditioned at 20 °C under saturated vapor pressure and under 65% RH and bone-dried, respectively. While the fiber diameter decreases to a extent by moisture absorption, it particularly is preferred that $0.3 \leqq L_{100}/L_{65} < 0.7$. If $L_{100}/L_{65} > 0.9$, that means the fiber diameter decreases only to a small extent, the water having rapidly accumulated in a large amount inside the clothes will not effectively permeate therethrough outward. With $L_{100}/L_{65} < 0.3$, it is difficult to fully prevent delamination of the two layers of the composite fiber even when the constituting polyester contain an amount of an alkali metal and the like to prevent the delamination between nylon-4 polymer. Then, the desired reversible change of fiber diameter is also difficult to realize. With respect to the diameter change upon moisture desorption, it is preferred that $1.1 \leqq L_0/L_{65} \leqq 2.5$. If $L_0/L_{65} < 1.1$, the composite fiber will exhibit little conditioning function. On the other hand, when $L_0/L_{65} > 2.5$, delamination of the two layers tends to occur.

The mechanism of the reversible diameter change of the composite fiber of this type by absorption/desorption of moisture is considered to be as follows. The nylon-4, which is moisture-absorbing component, repeats inflation and deflation by absorption/desorption of moisture, while hydrophobic polyester keeps its volume almost constant against humidity change. Then, a composite fiber obtained by lamination of the two resins to form a flat fiber cross-section in which the interface constitutes the maximum length line of the cross-section, will warp upon absorption of moisture to change its apparent diameter, and resume original flat cross-sectional shape upon desorption of moisture. The maximum length of the cross-sections of the conditioned fibers can be measured by observing the cross-sections using a conventional

optical microscope. It is preferred that the degree of flattening of the flat bimetal-laminated composite fiber, i.e. ratio of the width of the lamination plane, or the maximum length of the cross-section, to the height, or thickness, measured in a direction perpendicular to the lamination plane be 3 to 10.

Further in the present invention, incorporation of fine particles, such as colloidal silica and aluminum oxide, having a diameter of not more than 1μ m into the polyester component, followed by alkali etching to roughen or make micro-crators on the fiber surface can provide a fiber giving dry-touch and less clammy feeling or one having still higher rate of absorption/desorption of moisture.

Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

EXAMPLES

Examples and Comparative Examples

Various nylon-4 chips having different intrinsic viscosities and $\overline{M}_W/\overline{M}_N$'s were prepared by polymerizing 2-pyrrolidone with a catalyst of potassium hydroxide. They were hot-water washed under various conditions to give chips having different residual potassium concentrations as shown in the column of "Raw material nylon-4" in Tables 1 and 3. The thus obtained nylon-4 chips were combined with the various raw material polyesters shown in Tables 1 and 3 and each of the combination was melt spun. The obtained composite fibers as spun were drawn to give filament yarns of 75 deniers/24 filaments. The thus obtained composite fibers were of composite ratios (ratio by weight of nylon-4 to polyester) and cross-sectional shapes as shown in Tables 2 and 4. Also Tables 2 and 4 show the intrinsic viscosities and $\overline{M}_W/\overline{M}_N$'s of the nylon-4 polymers contained in the obtained composite fibers and the Young's moduli and the moisture absorptions and rates of moisture absorption at 20 ° C, 65% RH of the composite fibers.

Round knits were prepared from these composite fibers, relaxation treated in boiling water to remove finishing agent, while some (Examples 10 and 11) were further alkali-etched in a 4% aqueous sodium hydroxide solution. The thus treated round knits were tested for clammy feeling upon absorption of moisture in the following manner. Each specimen round knit made wet by immersion in water for 10 minutes and dewatered was air-dried under conditions of 20 ° C and 65% RH until its water content decreased to a level 10% higher than its equilibrium moisture content at 20 ° C x 65% RH. Then the specimen was tested by touching with the hand. The results of evaluation for clamminess are shown in Tables 2 and 4.

Tables 3 and 4 also show the cases where nylon-6 was used instead of nylon-4 (Comparative Examples 1 and 7), a homofil fiber of nylon-6 was spun and tested (Comparative Example 2), homofil fiber of polyethylene terephthalate was tested (Comparative Example 3) and homofil fiber of nylon-4 was tested (Comparative Example 6).

In the Examples above, the composite fiber of Example 2, after drawing, had a hot water shrinkage (WSR) of 15%, and gave, by treatment of the round knit prepared from this fiber in boiling water, a fiber having 7.8 pieces/mm of joint-like swells with an L'/L, described hereinbefore, of 1.4 and having a ratio of the sum of swell widths to the fiber length of 5.3%. The composite fiber of Example 13 had a hot water shrinkage (WSR) of 16.5% and gave, by treatment of the round knit prepared from this fiber in boiling water, a fiber having 40 pieces/mm of joint-like swells with an L'/L of 1.4 and having a ratio of the sum of swell widths to the fiber length of 18%. These fibers having joint-like swells gave excellent dry-touch feeling particularly when wet.

On the other hand, the composite fiber of Comparative Example 9 had a hot water shrinkage (WSR) of 19% and gave, by treatment of the round knit prepared from this fiber in boiling water, a fiber having 51 pieces/mm of joint-like swells with an L'/L of 2.1 and having a ratio of the sum of swell widths to the fiber length of 26%. This fiber had higher number and ratio of joint-like swells than the composite fibers of Examples 2 and 13, and therefore gave inferior dry-touch feeling and stiffer hand and had formed fibrils with projections of the core polymer from bursted parts of the sheath.

The composite fibers of Examples 7 and 8 and Comparative Example 7 were all flat bimetal fibers having a degree of flattening of 5. The composite fibers of Examples 7 and 8 had L_{100}/L_{65} 's of 0.6 and 0.4 respectively and L_0/L_{65} 's of 2.0 and 1.4 respectively, and both changed their diameter by moisture absorption. The knits prepared from them were both effective for evaporating and dissipating sweat from the skin surface and, after having dissipated moisture to an appropriate extent, the fibers resumed to their original fiber diameters, thereby reducing moisture permeability and maintaining the surface temperatures of the wearers. On the other hand, the composite fiber of Comparative Example 7 had, although this was a flat bimetal composite fiber, an L_{100}/L_{65} and L_0/L_{65} of both 1.0 and thus did not substantially change its fiber

diameter upon absorption of moisture.

In Examples 10 and 11, where, as mentioned before, alkali etching had been conducted (temperature of alkali bath: 95°C, amount alkali-etched: 20% by weight of polyester component), the finished composite fibers had a finely roughened surface structure and gave still higher dry feeling. Furthermore, alkali etching had made the sheath component thinner, thereby enhancing the rate of moisture absorption; in particular the composite fiber of Example 11 had a microporous sheath and hence still higher rate of moisture absorption and was thus more comfortable.

Example 6 used as nylon-4 polymer a caprolactam-copolymerized nylon-4 (contents of caprolactam: 60% by weight). The composite fiber obtained in this Example gave clothes which, besides being markedly comfortable, had another feature of exhibiting very high dimensional stability even by repeated washing.

In Comparative Example 12, a composite fiber was spun into fiber without having been fully removed of alkali metal contained in nylon-4 by hot water washing (600 ppm remain). The obtained fiber was of not fully satisfactory strength because of thermal decomposition of the nylon-4 polymer duringspinning. When a clothing article made this fiber was subjected to 10 repetitions of washing and ironing at 170°C, the strength and elongation of the original fiber, 2.2 g/d and 25% respectively, decreased to 1.5 g/d and 20% respectively. This is attributable to thermal decomposition of the nylon-4 polymer by ironing heat. In contrast, in all other Examples and Comparative Examples in which the alkali (potassium) concentration in nylon-4 polymer had been suppressed down below 500 ppm, decreases in the fiber strength and elongation were hardly observed. Here the potassium concentrations in nylon-4 polymers showed almost no change after fiber spinning and formation into fabric, and remained about the same as those in raw material nylon-4's as shown in Tables 1 and 3.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

Table 1

Example	Raw material nylon-4				Raw material polyester			
	Intrinsic viscosity (g/dl)	Mw/Mn	Potassium concentration (ppm)	Moisture absorption at 20°C, 65% RH (%)	Polymer	Conc. of alkali metal or alkali earth metal (ppm)	Moisture absorption at 20°C, 65% RH (%)	Intrinsic viscosity (g/dl)
1	6.2	2.5	10	7	Polyethylene terephthalate containing calcium acetate	550	0.4	0.68
2	4.5	3.2	300	〃	Polyethylene terephthalate copolymerized with 0.5 mol% of sodium sulfoisophthalate	550	0.5	0.60
3	5.5	2.0	20	〃	Polyethylene terephthalate copolymerized with 8 mol% of isophthalic acid and 1.75 mol% of sodium sulfoisophthalate	2,000	0.5	0.47
4	〃	〃	〃	〃	〃	〃	〃	〃
5	〃	〃	〃	〃	〃	〃	〃	〃
6	〃	〃	〃	〃	〃	〃	〃	〃
7	6.2	2.5	10	〃	Polyethylene terephthalate copolymerized with 4 mol% of isophthalic acid and 2.5 mol% of sodium sulfoisophthalate	2,850	〃	0.46
8	〃	〃	〃	〃	Polyethylene terephthalate copolymerized with 8 mol% of isophthalic acid and 2.5 mol% of sodium sulfoisophthalate	〃	〃	0.46
9	4.5	3.2	300	〃	〃	〃	〃	〃
10	〃	〃	〃	〃	Copolymer polyethylene terephthalate of Example 8 incorporating 3 wt% of silica having an average diameter of 50 mμ	〃	〃	〃
11	〃	〃	100	〃	Copolymer polyethylene terephthalate of Example 8 incorporating 2 wt% of alumina having an average diameter of 0.5μ	〃	〃	〃
12	〃	〃	5	〃	Polyethylene terephthalate containing sodium acetate	600	0.4	0.68
13	〃	〃	〃	〃	Polyethylene terephthalate containing sodium acetate	〃	〃	〃
14	〃	〃	〃	〃	Polyethylene terephthalate containing calcium acetate	4500	〃	〃
15	5.0	3.0	30	6.2	Polyethylene terephthalate copolymerized with 5 mol% of isophthalic acid and 0.5 mol% of sodium sulfoisophthalate	550	0.5	0.56
16	4.3 (Nylon-4 copolymerized with caprolactam, copolymerization ratio: 60 wt%)	2.5	20	6.0	Polyethylene terephthalate copolymerized with 8 mol% of isophthalic acid and 1.75 mol% of sodium sulfoisophthalate	2000	0.5	0.47

Table 2

Example	Composite ratio by weight of Nylon-4/ polyester	Cross-sectional shape of fiber	Properties of composite fiber						
			Nylon-4		Young's modulus (g/ denier)	Moisture absorption at 20°C 65% RH	Absorption rate (%/5 min)	Clamminess	Overall evaluation
			Intrinsic viscosity (g/dl)	$\overline{Mw}/\overline{Mn}$					
1	50/50	FIG. 1(a)	1.10	2.2	35	3.7	0.9	no	Very agreeable as clothing.
2	70/30	FIG. 1(b)	0.9	2.6	28	6.4	1.3	〃	〃
3	50/50	FIG. 1(a)	1.70	1.7	33	3.8	0.85	〃	〃
4	〃	FIG. 1(c)	1.25	〃	35	4.5	3.8	little	〃
5	〃	FIG. 1(f)	〃	〃	〃	3.9	3.5	〃	〃
6	〃	FIG. 1(d)	〃	〃	〃	4.0	3.0	〃	〃
7	〃	FIG. 4(b)	1.10	2.2	30	3.8	3.5	〃	Very agreeable as clothing, having moisture-conditioning function while changing the fiber diameter by absorption/desorption of moisture.
8	40/60	〃	〃	2.2	〃	3.3	0.8	〃	〃
9	50/50	FIG. 1(j)	1.20	2.6	〃	3.9	3.5	〃	Very agreeable as clothing.
10	〃	FIG. 1(a)	〃	〃	35	5.1	1.5	no	〃
11	〃	〃	〃	〃	〃	〃	2.0	〃	〃
12	〃	FIG. 1(h)	1.10	〃	30	3.7	1.2	little	〃
13	70/30	FIG. 1(b)	1.15	〃	33	6.4	1.5	no	〃
14	50/50	FIG. 1(a)	1.0	〃	35	3.7	0.9	little	〃
15	〃	FIG. 1(a)	1.7	2.5	50	3.3	0.8	〃	〃
16	50/50	FIG. 1(a)	1.25	2.2	40	3.1	0.8	little	〃

Table 3

Comparative Example	Raw material nylon-4				Raw material polyester			
	Intrinsic viscosity (g/dl)	Mw/Mn	Potassium concentration (ppm)	Moisture absorption at 20°C, 65% RH (%)	Polymer	alkali metal-alkali earth metal concentration (ppm)	Moisture absorption at 20°C, 65% RH (%)	Intrinsic viscosity (g/dl)
1	nylon-6 was used			3.5	Polyethylene terephthalate	0	0.4	0.68
2	〃			3.5	Not used	—	—	—
3	Not used			—	Polyethylene terephthalate	0	0.4	0.68
4	6.2	2.5	10	7	Polyethylene terephthalate	0	0.5	0.68
5	〃	〃	〃	〃	〃	〃	〃	0.68
6	〃	〃	〃	〃	Not used	—	—	—
7	nylon-6 was used			3.5	Polyethylene terephthalate	0	0.4	0.68
8	5.5	2.0	20	7	Polyethylene terephthalate copolymerized with 8 mol% of isophthalic acid and 2.5 mol% of sodium sulfoisophthalate and containing calcium acetate	2850	0.5	0.46
9	4.5	3.2	5	〃	Polyethylene terephthalate	0	0.4	0.68
10	6.2	2.5	10	〃	〃	〃	〃	〃
11	5.5	2.0	20	〃	Polyethylene terephthalate containing calcium acetate	300	0.4	〃
12	〃	〃	600	〃	Polyethylene terephthalate copolymerized with 8 mol% of isophthalic acid and 1.75 mol% of soduim sulfoisophthalate and containing calcium acetate	2000	0.5	0.47

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Table 4

Comparative Example	Composite ratio by weight of nylon-4/ polyester	Cross-sectional shape of fiber	Properties of composite fiber						
			Nylon-4		Young's modulus (g/ denier)	Moisture absorption at 20°C, 65% RH	Absorption rate (%/5 min)	Clamminess	Overall evaluation
			Intrinsic viscosity (g/dl)	$\bar{M}w/\bar{M}n$					
1	50/ 50	FIG. 1(a)	—	—	35	2.4	0.5	no	Less agreeable, having low absorption and rate of absorption.
2	100/ 0	Circular, homofil	—	—	10	3.5	2.7	severe	Too clammy, not suited for clothing use.
3	0/100	〃	—	—	80	0.4	0.25	no	Substantially no absorptive capacity, less agreeable as clothing.
4	50/ 50	FIG. 1(f)	0.8	2.2	40	3.7	0.9	no	Splitted by delamination and formed fibrils. Many troubles occurred during spinning of fiber and at stages of processing the fiber into fabric.
5	85/ 15	FIG. 1(b)	1.10	2.2	20	7.0	3.9	severe	〃
6	100/ 0	Circular, homofil	1.60	2.2	10	8.9	4.1	very severe	Too clammy, not suited for clothing use.
7	50/ 50	FIG. 4(b)	—	—	30	2.4	0.5	no	Frequent fiber breakage occurred due to thermal decomposition at spinning.
8	30/ 70	FIG. 1(j)	1.10	1.7	50	2.8	0.7	little	〃
9	80/ 20	FIG. 1(a)	1.15	2.6	24	7.0	1.8	medium	Delaminated markedly and formed fibrils; a little clammy.
10	50/50	〃	1.10	2.2	35	3.7	0.9	no	Delaminated markedly. The sheath bursted at dyeing with the cores projecting out from the bursted points and formed fibrils.
11	〃	〃	1.25	1.7	〃	〃	〃	〃	〃
12	50/50	FIG. 1(a)	0.7	1.7	20	3.8	0.85	no	The strength and elongation significantly decreased when ironed, due to thermal decompostion.

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Claims

1. A moisture-absorbent composite fiber comprising a hydrophobic polyester (B) having a moisture absorbency at 20 °C, 65% RH of not more than 2% and having a total concentration of at least one metal selected from the group consisting of alkali metals and alkali earth metals of at least 500 ppm and a nylon-4 polymer (A) having an alkali metal concentration of not more than 500 ppm, said nylon-4 polymer (A) being contained in said fiber in an amount of 40 to 80% by weight based on the weight of said fiber.

2. A moisture-absorbent composite fiber according to Claim 1, wherein said nylon-4 polymer (A) has an intrinsic viscosity (η) of 0.8 to 1.8 g/dl and a ratio of weight average molecular weight to number average molecular weight of 1.5 to 3.5.

3. A moisture-absorbent composite fiber according to Claim 1, said composite fiber being a sheath-core composite fiber comprising a core of said nylon-4 polymer (A) and a sheath of said hydrophobic polyester (B).

4. A moisture-absorbent composite fiber according to Claim 3, said composite fiber having a multiplicity of bamboo-joint-like swells on the surface thereof.

5. A moisture-absorbent composite fiber according to Claim 1, said composite fiber changing its diameter reversibly by absorption/desorption of moisture, while satisfying the conditions of $0.3 \leqq L_{100}/L_{65} \leqq 0.9$ and $1.1 \leqq L_0/L_{65} \leqq 2.5$, where L_{100}, L_{65} and L_0 represent the average maximum lengths of the cross-section of said composite fiber conditioned under conditions of 20 °C and 100% RH, 20 °C and 65% RH and 20 °C and 0% RH, respectively.

6. A moisture-absorbent composite fiber according to Claim 1, wherein said hydrophobic polyester (B) is a polyethylene terephthalate or polybutylene terephthalate copolymerized with 4 to 12 mol% of isophthalic acid and 0.45 to 3 mol% of an alkali metal salt of sulfoisophthalic acid.

7. A moisture-absorbent composite fiber according to Claim 1, wherein said nylon-4 polymer (A) is nylon-4 or a copolymer of 2-pyrrolidone with caprolactam in a copolymerization ratio of caprolactam of 25 to 75% by weight.

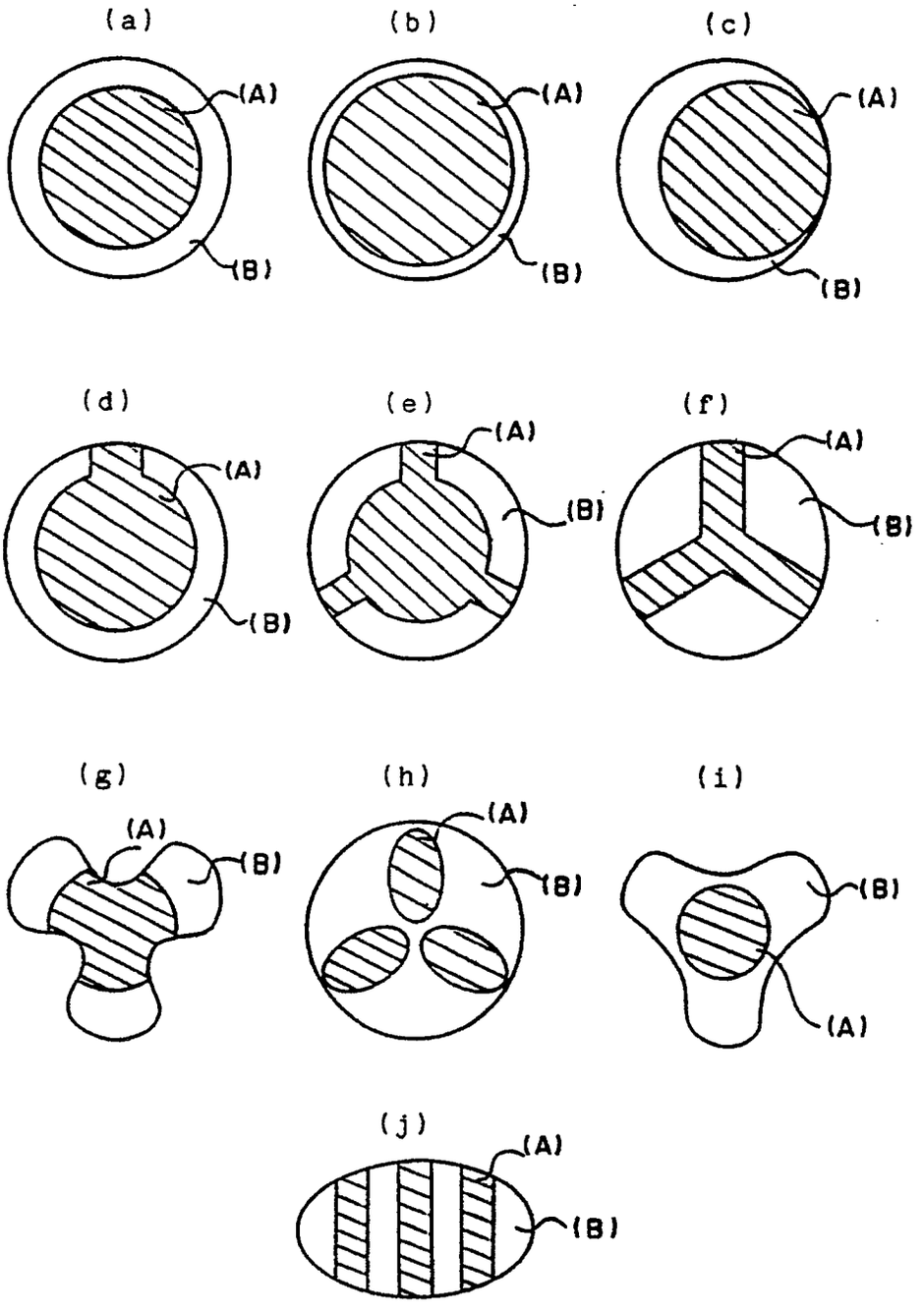

Fig. 1

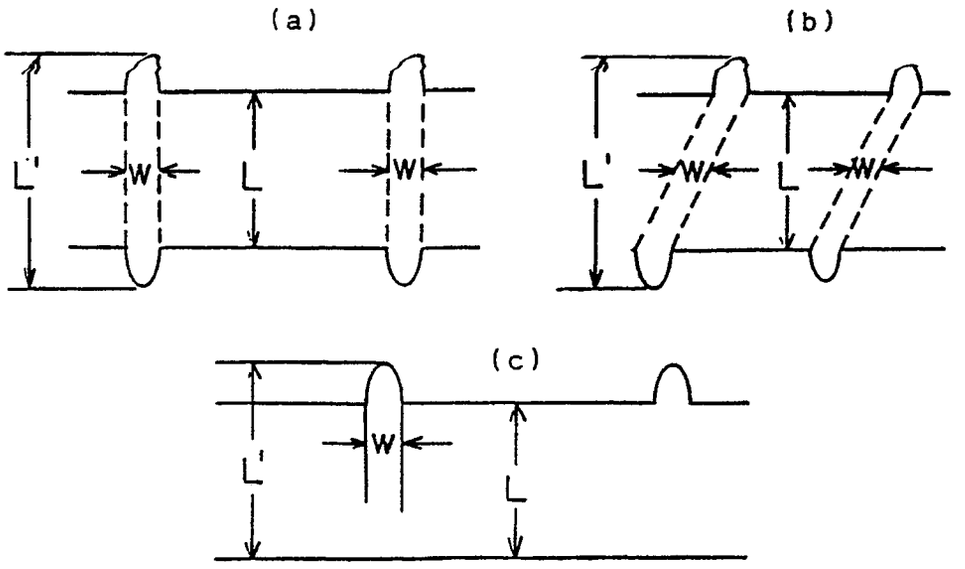

Fig. 2

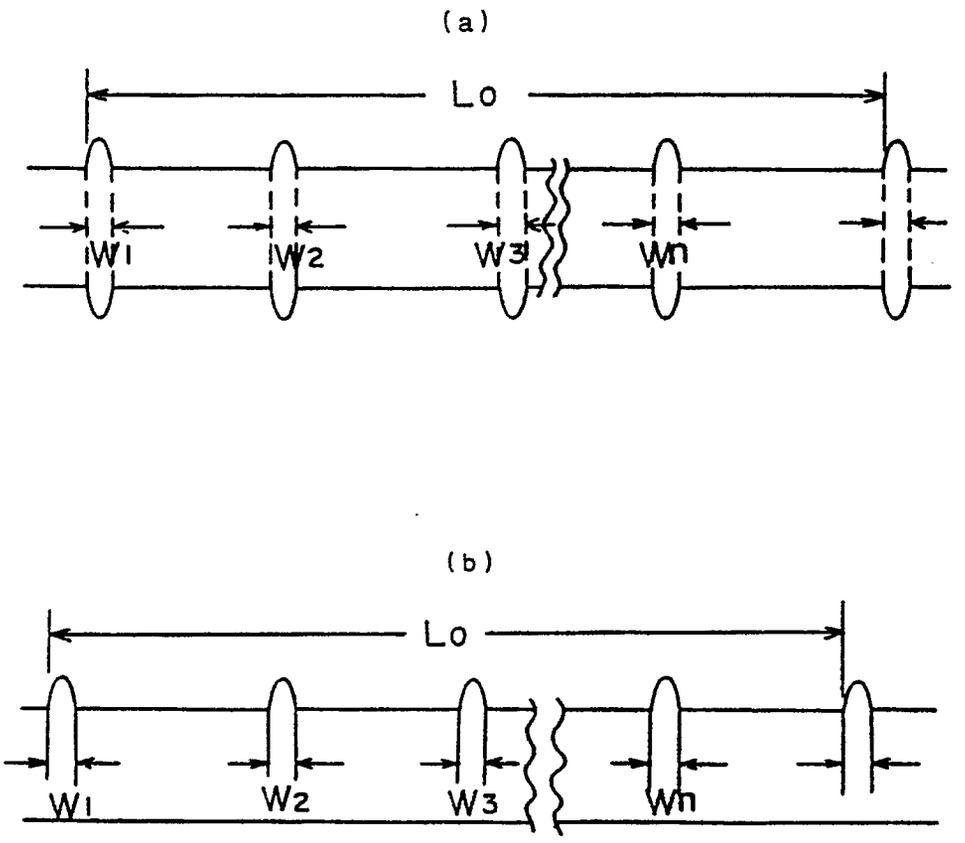

Fig. 3

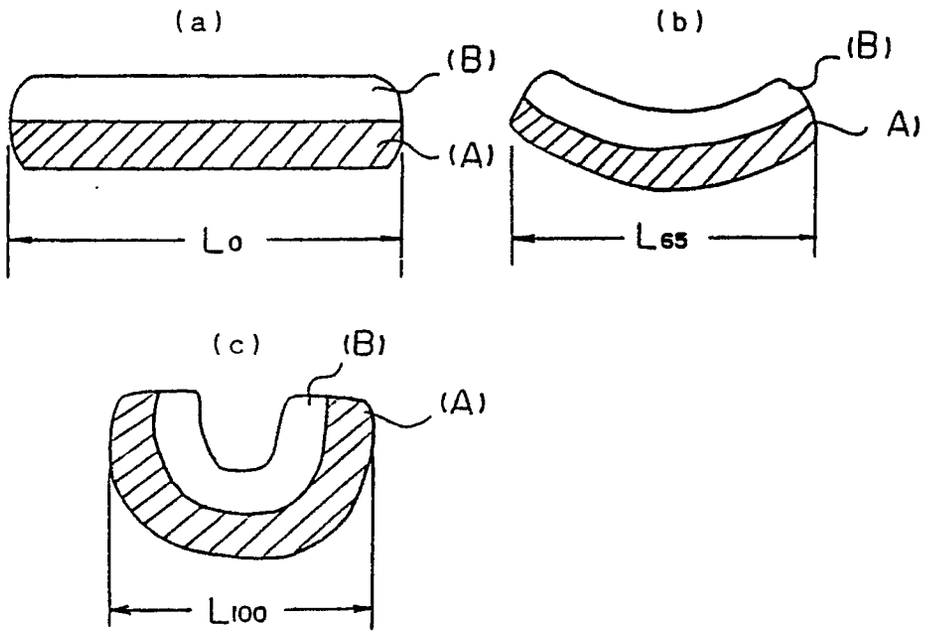

Fig. 4