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⑤④ **Process for producing aromatic polyester fiber.**

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GB-A- 1 499 513
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⑦③ Proprietor : **SUMITOMO CHEMICAL
COMPANY, LIMITED**
Kitahama 4-chome 5-33
Chuo-ku Osaka 541 (JP)
Proprietor : **JAPAN EXLAN COMPANY, LTD.**
2-8, Dojimahama-2-chome Kita-ku
Osaka-shi Osaka 530 (JP)

⑦② Inventor : **Sugimoto, Hiroaki**
13-5, Kawanishicho-1-chome
Takatsuki-shi (JP)
Inventor : **Hayatsu, Kazuo**
11-8, Kamihozumi-2-chome
Ibaraki-shi (JP)
Inventor : **Kobashi, Toshiyuki**
1-6, Saidajikami-3-chome
Okayama-shi (JP)
Inventor : **Takao, Seiji**
781-3, Kanada
Okayama-shi (JP)
Inventor : **Takagi, Jun**
615-1, Kanaokanishimachi
Okayama-shi (JP)

⑦④ Representative : **Henkel, Feiler, Hänzel &
Partner**
Möhlstrasse 37
D-8000 München 80 (DE)

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Description**FIELD OF THE INVENTION**

- 5 This invention relates to a process for producing an aromatic polyester fiber having high strength and high modulus of elasticity.

BACKGROUND OF THE INVENTION

- 10 It has been revealed in recent years that fibers of high strength and high modulus of elasticity can be produced by melt-spinning an aromatic polyester that exhibits anisotropy in its molten state. This process has various advantages in that no solvent is used and conventional spinning apparatuses can be used in the process. Although such a polyester forms a highly oriented and highly crystalline structure and exhibits excellent properties merely by melt-spinning, both the strength and the modulus of elasticity of the fiber can
- 15 be further improved when the fiber is heat-treated in the vicinity of its softening temperature.

For example, Japanese Patent Publication No. 20008/80 describes the method of carrying out a similar heat-treatment in an atmosphere of inert gas such as nitrogen. However, this heat-treatment may consume a long time and the use of such inert gas cannot be economically desirable.

SUMMARY OF THE INVENTION

It is an object of the invention to provide a process for producing fibers of an aromatic polyester which exhibits anisotropy in the molten state, wherein the heat-treatment of spun fibers can be accomplished economically or at low costs.

- 25 The above object of the invention can be achieved by using a dehumidified oxygen-containing atmosphere for the heat-treatment of melt-spun fibers of an aromatic polyester exhibiting anisotropy in the molten state.

DETAILED DESCRIPTION OF THE INVENTION

- 30 The polyester which exhibits anisotropy in its molten state referred to in this invention means one which has a property of allowing the transmission of light at a temperature region in which it is flowable when the powder sample of the polyester is placed on a heating sample stage positioned between two polarizing plates crossed at an angle of 90° and the temperature of the sample is increased. Such polyesters are those
- 35 formed of aromatic dicarboxylic acids, aromatic diols and/or aromatic hydroxycarboxylic acid, and the derivatives thereof, disclosed in Japanese Patent Application Kokoku (Post-Exam. Publn.) Nos. 18016/81 and 20008/80, and optionally include copolymers of these with alicyclic dicarboxylic acids, alicyclic diols, aliphatic diols, and the derivatives thereof.

- From EP-A-0 072 155 there are known melt-processable aromatic polyesters capable of forming an
- 40 anisotropic melt phase at elevated temperature which after their processing are subjected to a thermal treatment in an oxygen-containing atmosphere.

Also from GB-A-1 499 513 it is known to melt spun aromatic copolyester fibers and to thermally treat the fibers as spun in an oxygen-containing atmosphere.

- Examples of the aromatic dicarboxylic acids include terephthalic acid, isophthalic acid, 4, 4'-dicarboxydiphenyl, 2, 6-dicarboxynaphthalene, 1, 2-bis(4-carboxyphenoxy)ethane, and the nuclear-substituted
- 45 products thereof with an alkyl, aryl, alkoxy, or halogen group.

- Examples of the aromatic diols include hydroquinone, resorcin, 4, 4'-dihydroxydiphenyl, 4, 4'-dihydroxybenzophenone, 4, 4'-dihydroxydiphenylmethane, 4, 4'-dihydroxydiphenylethane, 2, 2-bis(4-hydroxyphenyl)-propane, 4, 4'-dihydroxydiphenyl ether, 4, 4'-dihydroxydiphenyl sulfone, 4,
- 50 4'-dihydroxydiphenyl sulfide, 2, 6-dihydroxynaphthalene, 1, 5-dihydroxynaphthalene, and the nuclear-substituted products thereof with an alkyl, aryl, alkoxy, and halogen group.

Examples of the aromatic hydroxycarboxylic acids include p-hydroxybenzoic acid, m-hydroxybenzoic acid, 2-hydroxynaphthalene-6-carboxylic acid, 1-hydroxynaphthalene-5-carboxylic acid, and the nuclear-substituted products thereof with an alkyl, aryl, alkoxy, and halogen group.

- 55 Examples of alicyclic dicarboxylic acids include trans-1, 4-dicarboxycyclohexane, cis-1, 4-dicarboxycyclohexane and the substituted products thereof with an alkyl, aryl, and halogen group.

Examples of the alicyclic and aliphatic diols include trans-1, 4-dihydroxycyclohexane, cis-1, 4-dihydroxycyclohexane, ethylene glycol, 1, 4-butanediol, and xylylene diol.

Among the combinations of the aforesaid materials, there may be mentioned as examples of a preferable aromatic polyester to be used in this invention :

(1) a copolyester comprising 40 to 70% by mole of p-hydroxybenzoic acid residue, 15 to 30% by mole of an above-mentioned aromatic dicarboxylic acid residue, and 15 to 30% by mole of an aromatic diol residue ;

(2) a copolyester formed of terephthalic acid and/or isophthalic acid and chlorohydroquinone, phenylhydroquinone and/or hydroquinone ; and

(3) a copolyester comprising 20 to 80% by mole of p-hydroxybenzoic acid residue and 20 to 80% by mole of 2-hydroxynaphthalene-6-carboxylic acid residue.

To attain the polyesters to be used in this invention by using these starting materials, they are subjected to polycondensation as they are or after being esterified by an aliphatic or aromatic monocarboxylic acid or the derivative thereof, or an aliphatic alcohol, a phenol, or the derivative thereof.

The polycondensation can be carried out by using a known method including mass polymerization, solution polymerization and suspension polymerization. It may be conducted at a temperature of 150 to 360°C under normal pressure or a reduced pressure of 1330 to 13,3 Pa (10 to 0.1 Torr) optionally in the presence of polymerization catalyst such as a Sb, Ti and Ge compound, a stabilizer such as a phosphorus compound, and fillers such as TiO₂, CaCO₃, and talc, added thereto. The polymer thus obtained is heat-treated, as it is or in a pulverized form, in an inert gas or under reduced pressure to give a sample material for spinning. It is also be used after once granulated through an extruder.

The melt spinning apparatus to be used for the aromatic polyester according to this invention may be of any desired type so long as it is provided with a melting section comprising a screw or a plunger equipped with a heat control device, a metering section such as a gear pump, and a spinning head including a spinneret.

Suitable temperature for spinning in this invention is 280 to 420°C, more preferably 300 to 400°C. Temperatures lower than the above-mentioned temperature region will result in too large load on the apparatus or insufficiency of uniform melting of the sample, whereas temperatures higher than the region will cause fiber breakage due to decomposition and foaming.

Although a conventional spinning nozzle can be used as it is, preferable spinneret include those having a hole diameter (d) of 0.3 mm or less and the ratio (l/d) of the hole length (l) to the hole diameter of 0.8 or more. Further, the breakage of single filaments and spiral extrusion can be prevented and effects of promoting orientation and suppressing foam generation in fibers can be exhibited by controlling the spinning pressure at the spinneret section at 294,312 PG (3 kg/cm²G) or more.

The fibers obtained by melt spinning as mentioned above are then taken up or drawn down as they are or after adhering a textile oil thereto. The velocity of taking up or drawing down is 10 to 10,000 m/minute, 100 to 2,000 m/minute being preferable from the viewpoint of productivity and stable spinning. The diameter and the cross sectional shape of the fiber to be obtained can be selected as desired according to intended uses. A diameter of 0,055 to 1,11 tex (0.5 to 10 deniers) is preferable from the viewpoint of physical properties.

The thus obtained fiber is heat-treated in an atmosphere. This atmosphere contains oxygen and has been dehumidified.

The oxygen-containing atmosphere has an oxidizing action or the like, which will result in slight crosslinkage between main chains of the polymer to increase its molecular weight and will decompose and remove the remaining monomer and oligomer which hinder the heat-treated fiber from exhibiting improved properties. If the atmosphere contains much water vapor, no sufficient improvement of the fiber in strength and in elastic modulus will be achieved conceivably because of the main-chain scission resulting from hydrolysis.

The content of water vapor in the dehumidified oxygen-containing atmosphere is generally up to 0.3%, preferably up to 0.1%, particularly preferably up to 0.05%, by volume. Higher brightness and lower saturations intensities of color, in addition to the improved strength and elastic modulus, are given to the fiber when the atmosphere is dehumidified than when it is not dehumidified as in the prior art heat-treatment.

The dehumidification of oxygen-containing atmospheric gas can be accomplished by ; the contact thereof with a moisture absorbent or drying agent such as a molecular sieve, calcium chloride, silica gel, phosphorus pentoxide, or sulfuric acid ; cooling the gas with a refrigerant such as liquid nitrogen, liquid ammonia, or LPG ; adiabatic compression of the gas ; or combination of these means.

In the thus dehumidified oxygen-containing atmosphere, the fiber is heat-treated at a temperature of 220 to 440°C, preferably 280 to 360°C, for a period of several minutes to scores of hours.

The oxygen-containing atmosphere may comprise any of nitrogen, argon, helium, and the like, besides oxygen. Suitable oxygen concentrations in the atmosphere are from 1 to 100% by volume.

The fiber obtained by melt-spinning of an aromatic polyester exhibiting anisotropy in the molten state

can be brought into contact with the oxygen-containing atmosphere, for example, in the following way : The fiber wound up around a bobbin is brought as such into contact with the atmosphere or the fiber is continuously moved in a stream of the atmospheric gas. In this case, tension may be applied to the fiber so far as it does not break the fiber ; however, it is unnecessary to apply such high tension as to stretch the fiber.

5 By applying the above described technique of the present invention, it is possible to provide higher strengths and higher elastic moduli to fibers formed by melt-spinning of an aromatic polyester exhibiting anisotropy in the molten state. The heat-treatment of the fibers in a dehumidified oxygen-containing atmosphere produces the additional effect of making the brightness of fibers higher than that of similar fibers heat-treated according to the prior art.

10 The fiber thus obtained shows no phenomenon of fusion and can be used in a wide field of applications including tire cords, ropes, cables, the tension member of FRP (fiber reinforced plastic), FRTP (fiber reinforced thermoplastic), FRC (fiber reinforced concrete) and FRM (fiber reinforced metal), speaker cones, ballistic applications, space suits, and submarine working clothes.

15 EXAMPLE

Some embodiments of this invention will be described below to make this invention more clearly understood. However, these are merely for the sake of illustration and the essentials of this invention are not limited thereby. The characteristic values shown in the Examples were measured and calculated in the following manner.

(1) Flow temperature of polymer

20 A Flow Tester CFT- 500® (mfd. by Shimadzu Corp.) was used with a nozzle having a diameter of 1 mm and a length of 10 mm. An organic polymer sample was kept under a pressure of 9810 kPa (100 kg/cm² and heated to increase its temperature at a rate of 4°C/min. The flow temperature was defined as the temperature at which the sample flowing through the nozzle shows an apparent viscosity 9600 Pas of (96000 poises).

(2) Optical anisotropy

A sample was placed on a heating stage and observed with the naked eye under polarized light while the temperature of the sample was increased at a rate of 25°C/min.

30 (3) Tensile test

The test was conducted by using a Tensilon® Type II (a trade name, mfd. by Toyo Baldwin Co. Ltd.) with a specimen gap of 20 mm and a stretching velocity of 2 mm/min. The number of specimens was 24. The result of determination was expressed in terms of the mean value excluding the maximum and the minimum measured value.

35 (4) Color of fiber

A sample fiber was measured for brightness L and saturations a_L (the larger positive figure indicates the denser red) and b_L (the larger positive figure indicates the denser yellow) by using a colorimetric color-difference meter supplied by Nippon Denshoku Co., Ltd.

40 For the measurement, the sample fiber was wound around an acrylic resin plate (40 mm × 40 mm × 2 mm) without leaving any gap between turns of the fiber.

Referential Example

45 Into a polymerization vessel having a comb-type stirrer, were placed 7.20 kg (40 moles) of p-acetoxybenzoic acid, 2.49 kg (15 moles) of terephthalic acid, 0.83 kg (5 moles) of isophthalic acid, and 5.45 kg (20.2 moles) of 4, 4'-diacetoxydiphenyl, and the resulting mixture was brought to elevated temperature with stirring under a nitrogen gas atmosphere and polymerized at 330°C for 3 hours. During the period, acetic acid formed was removed and the polymerization was carried out with powerful stirring. Thereafter, the system was gradually cooled and the polymer formed was taken out at 200°C from the system. The yield of polymer was 10.88 kg, 97.8% of theoretical yield. The polymer was pulverized in a hammer mill to give particles of 2.5 mm or less. The polymer powder was then treated in a rotary kiln in nitrogen atmosphere at 280°C for 5 hours. The resulting product gave a "flowing temperature" of 326°C and showed optical anisotropy at a temperature of 350°C or higher.

55 The polymer obtained above was melt-spun by using a 30 mm extruder. The spinneret used had a hole diameter of 0.07 mm, a hole length of 0.14 mm and a number of holes of 300. The spinning temperature at the spinneret was 355°C.

These spun multifilaments of 0,333 tex (3.0 d) were wound up at a speed of 348 m/min.

Example 1

A 200 g portion of the multifilaments prepared in Referential Example was rewound around a hollow cylindrical aluminum bobbin of 15 mm outer diameter having a large number of 5-mm diametric perforations. These rewound multifilaments were placed each in a 280°C oven, then its temperature was raised over 4 hours upto 320°C, and after 3-hour heating at this temperature, the multifilaments were taken out. The atmospheric gas used for this heat-treatment was prepared by mixing air with nitrogen gas and passing the mixture through a metal pipe of 2 m length and 3 cm inner diameter packed with a molecular sieve 4A. The content of water vapor in this gas mixture was 450 ppm, as measured at 27°C with a dew-point hygrometer (water content analyzer). Table 1 shows tensile strengths, elastic moduli, and color properties of heat-treated fiber as stated above, where the oxygen concentration in the atmospheric gas mixture was varied.

Comparative Example 1

The procedure of Example 1 was followed but using a nitrogen gas of 99.9 vol% purity in which the water vapor content was 6 ppm at 27°C, in place of the gas mixture. Results are shown in Table 1. This heat-treated fiber, as compared with those of Example 1, exhibits low elastic modulus and low brightness.

Comparative Example 2

The procedure of Example 1 was followed except that the gas mixture of Example 1 was replaced with air (oxygen concentration 21.1 vol%, water vapor content 2.3 vol% at 27°C) and with dehumidified air (water vapor content 0.88 vol% at 27°C) prepared by passing the above air through a pipe of 25 cm length and 3 cm inner diameter packed with silica gel. As shown in Table 1, these heat-treated multifilaments are inferior to those of Example 1 in tensile strength as well as in colorlessness.

Table 1 Properties of heat-treated fiber

| Example | Atmospheric gas for heat-treatment | | Properties of heat-treated fiber | | | | |
|--------------------------|---------------------------------------|---------------------------------|---------------------------------------|---------------------------------------|-----------------|------------------------------|------------------------------|
| | Oxygen conc. (Vol%) | Water vapor content (ppm) | Tensile strength 9/1/9/ex (g/d) | Elastic modulus 9/1/9/tex (g/d) | Brightness L | Saturation a _L | Saturation b _L |
| As spun fiber | --- | --- | 52,2 (5.8) | 3870 (430) | 71 | 0.4 | 20.2 |
| Comparative Example 1 | 0 | 6 | 234 (26.0) | 8037 (893) | 64 | 2.2 | 18.2 |
| Example 1 | 1.2 | 450 | 232,2 (25.8) | 9180 (1020) | 69 | 2.2 | 22.0 |
| " | 2.7 | " | 236,7 (26.3) | 9360 (1040) | 67 | 2.5 | 20.7 |
| " | 10.8 | " | 233,1 (25.9) | 9360 (1040) | 67 | 2.2 | 21.2 |
| " | 21.1 | " | 235,8 (26.2) | 9450 (1050) | 70 | 2.7 | 23.1 |
| " | 35.2 | " | 233,1 (25.9) | 9180 (1020) | 67 | 3.1 | 22.0 |
| Comparative Example 2 | 21.1 | 8800 | 214,2 (23.8) | 7270 (1030) | 62 | 6.7 | 21.1 |
| " | 21.1 | 23000 | 172,8 (19.2) | 8820 (980) | 59 | 8.0 | 21.5 |

Claims

- 5 1. A process for producing fibers of an aromatic polyester exhibiting anisotropy in the molten state by heat-treatment of melt-spun fibers of said aromatic polyester in an oxygen-containing atmosphere, characterized in that the oxygen-containing atmosphere is dehumidified.
2. The process of claim 1, wherein air is used as the oxygen-containing atmosphere.
3. The process of claim 1 or 2, wherein the content of water vapor in the dehumidified oxygen-containing
10 atmosphere is up to 0.3% by volume.
4. The process of claim 3, wherein the content of water vapor in the dehumidified oxygen-containing atmosphere is up to 0.1% by volume, and the fiber is heat-treated at a temperature of 220°C to 440°C.
5. The process of claim 4, wherein air is used as the oxygen-containing atmosphere and the aromatic polyester is a copolyester comprising 40 to 70% by mole of p-hydroxybenzoic acid residue, 15 to 30% by
15 mole of an aromatic dicarboxylic acid residue, and 15 to 30% by mole of an aromatic diol residue.

Ansprüche

- 20 1. Verfahren zur Herstellung von Fasern eines aromatischen Polyesters mit Anisotropie im Schmelzustand durch Wärmebehandeln der durch Schmelzspinnen erhaltenen Fasern des aromatischen Polyesters in einer sauerstoffhaltigen Atmosphäre, dadurch gekennzeichnet, daß die sauerstoffhaltige Atmosphäre entfeuchtet ist.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß als sauerstoffhaltige Atmosphäre Luft
25 benutzt wird.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Gehalt an Wasserdampf in der entfeuchteten sauerstoffhaltigen Atmosphäre bis zu 0,3 Vol.-% beträgt.
4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß der Gehalt an Wasserdampf in der entfeuchteten sauerstoffhaltigen Atmosphäre bis zu 0,1 Vol.-% beträgt und daß die Faser bei einer Temperatur
30 von 220 - 440°C wärmebehandelt wird.
5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß als sauerstoffhaltige Atmosphäre Luft benutzt wird und daß es sich bei dem aromatischen Polyester um einen Mischpolyester aus 40-70 Mol-% p-Hydroxybenzoesäureresten, 15-30 Mol-% an aromatischen Dicarbonsäureresten und 15 - 30 Mol-% an aromatischen Diolresten handelt.

Revendications

- 40 1. Procédé de production de fibres d'un polyester aromatique présentant une anisotropie à l'état fondu par traitement thermique de fibres filées à l'état fondu dudit polyester aromatique dans une atmosphère contenant de l'oxygène, caractérisé en ce que l'atmosphère contenant de l'oxygène est déshumidifiée.
2. Procédé selon la revendication 1, dans lequel de l'air est utilisé comme atmosphère contenant de l'oxygène.
3. Procédé selon l'une ou l'autre des revendications 1 et 2, dans lequel la teneur en vapeur d'eau de
45 l'atmosphère contenant de l'oxygène déshumidifiée va jusqu'à 0,3% en volume.
4. Procédé selon la revendication 3, dans lequel la teneur en vapeur d'eau de l'atmosphère contenant de l'oxygène déshumidifiée va jusqu'à 0,1% en volume, et les fibres sont traitées thermiquement à une température de 220°C à 440°C.
5. Procédé selon la revendication 4, dans lequel de l'air est utilisé comme atmosphère contenant de
50 l'oxygène, et le polyester aromatique est un copolyester comprenant de 40 à 70% en moles de reste acide p-hydroxybenzoïque, de 15 à 30% en moles de reste acide dicarboxylique aromatique et de 15 à 30% en moles de reste diol aromatique.