

(19)



(11)

EP 2 246 463 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
22.03.2017 Bulletin 2017/12

(51) Int Cl.:
D01F 6/76 ^(2006.01) **D01D 5/16** ^(2006.01)
D01D 5/096 ^(2006.01)

(21) Application number: **08870062.0**

(86) International application number:
PCT/JP2008/073521

(22) Date of filing: **25.12.2008**

(87) International publication number:
WO 2009/087901 (16.07.2009 Gazette 2009/29)

(54) **POLYPHENYLENE SULFIDE FIBER AND PROCESS FOR PRODUCING THE SAME**

POLYPHENYLENSULFIDFASER UND HERSTELLUNGSVERFAHREN DAFÜR

FIBRE DE POLY(SULFURE DE PHÉNYLÈNE) ET SON PROCÉDÉ DE FABRICATION

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT
RO SE SI SK TR**

(30) Priority: **09.01.2008 JP 2008002082**

(43) Date of publication of application:
03.11.2010 Bulletin 2010/44

(73) Proprietor: **Toray Industries, Inc.**
Tokyo 103-8666 (JP)

(72) Inventors:
• **HORIGUCHI, Hirotaka**
Okazaki-shi
Aichi 4440203 (JP)

• **OZAWA, Hiroaki**
Mishima-shi
Shizuoka 4118652 (JP)

(74) Representative: **Webster, Jeremy Mark et al**
Mewburn Ellis LLP
City Tower
40 Basinghall Street
London EC2V 5DE (GB)

(56) References cited:
EP-A2- 0 398 094 WO-A1-2006/097281
JP-A- 4 100 916 JP-A- 7 126 972
JP-A- 11 256 485 JP-A- 2001 192 953
JP-A- 2002 161 444 JP-A- 2003 117 319
JP-U- 3 114 389

EP 2 246 463 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[Technical field]

[0001] The invention relates to a polyphenylene sulfide fiber and a production method thereof. Specifically, it relates to a polyphenylene sulfide fiber with a large single-filament fineness that is suitable particularly for use as industrial material, and a production method thereof. More specifically, it relates to a polyphenylene sulfide fiber that can be produced with high production efficiency with little fluff, yarn break, etc. during the spinning process, and a production method thereof.

[Background art]

[0002] Polyphenylene sulfide has good properties including heat resistance, chemical resistance, fire retardance, and electrical insulation, and it is known to serve as high-performance engineering plastics for use in harsh environment. In the field of fiber materials, it has been in wider use due to its good material properties, and practically, it is currently used widely as material for multifilaments with a single-filament fineness of several dtex and monofilaments with a diameter of several hundred μm . These are used singly or in combination to provide final products, but multifilaments with an intermediate thickness are not manufactured. This is because it has been very difficult to produce polyphenylene sulfide fibers with a large single-filament fineness, and there are few disclosed techniques to produce multifilaments of such polyphenylene sulfide fibers with a large single-filament fineness.

[0003] Patent document 1 discloses basic matters relating to production of fibers of polyphenylene sulfide and describes that polyphenylene sulfide fibers can be produced by a melt-spinning process similar to the processes used for polyamide or polyester. The method proposed in Patent document 1, however, cannot produce high-tenacity, high-toughness polyphenylene sulfide fibers that are required in recent years. The use of a liquid refrigerant for strong cooling is proposed for production of thick yarns, but no practical processes that are actually used are shown. Furthermore, special equipment will be required to use such a refrigerant, making it difficult to apply this method to direct spinning and stretching.

[0004] Patent document 2 discloses a high-tenacity, high toughness polyphenylene sulfide fiber with a single-filament fineness of 50 denier or less that has moderate shrinkage properties and fluff-free properties as required for woven fabric production, and a production method thereof. These properties are achieved by controlling some fiber structure parameters in a specific range. For the technique described in Patent document 2, however, the maximum temperature of the atmosphere or the roller surface during stretching has to be in the relatively low range of 120 to 180°C in order to reduce the crystal size, leading to low dimensional stability, and furthermore, stable production of polyphenylene sulfide with a single-filament fineness of 10 dtex or more cannot be achieved actually by using the technique described in Patent document 2.

[Patent document 1]

Japanese Unexamined Patent Publication (Kokai) No. SHO 57-143518 (Claims)

[Patent document 2]

Japanese Unexamined Patent Publication (Kokai) No. HEI 4-100916 (Claims)

[Disclosure of the invention]

[Problems to be solved by the invention]

[0005] The present invention was achieved through a study that was carried out to solve the problems with the prior art described above. Thus it aims to provide a polyphenylene sulfide fiber with a large single-filament fineness that can be produced at low cost by the conventional direct spinning and stretching process without suffering fluff, yarn break, etc.

[0006] To achieve the aforementioned objective, the invention provides a polyphenylene sulfide fiber with a single-filament fineness of 10 to 50 dtex and a tenacity of 4.5 to 6 cN/dtex obtainable by melt spinning.

[0007] The polyphenylene sulfide fiber of the invention is expected to have excellent effect when the following requirements are met to give favorable conditions for it:

the fiber surface carries at least a surface active agent and an antioxidant;

the total weight of the surface-attached oil accounts for 0.5 to 2 wt% of the fiber weight, with the surface active agent accounting for 0.01 to 1 wt% and the antioxidant accounting for 0.002 to 0.1 wt%;

it is untwisted and has a total fineness of 100 to 1000 dtex and a filament count of 2 to 50;

the elongation is 15 to 25%, and the dry-heat shrinkage at 150°C is 2 to 10%; and

the fineness unevenness is 0.5 to 1%.

[0008] The invention also provides a production method for polyphenylene sulfide fibers with a single-filament fineness of 10 to 100 dtex and a tenacity of 4.5 to 6 cN/dtex wherein polyphenylene sulfide resin is melt-spun, processed with an aqueous emulsion lubricant, while being pulled, to cause the surface-attached oil to account for 0.1 to 1 wt%, and, without being wound up, stretched up to an overall draw ratio of 3.8 to 4.5.

[0009] Furthermore, the polyphenylene sulfide fiber production method of the invention is expected to have excellent effect when the following requirements are met to give favorable conditions for it:

a anhydrous lubricant is applied to the spun yarn up to a total percentage of surface-attached oil of 0.5 to 2 wt%; and the aqueous emulsion lubricant has an oil concentration of 15 to 40 wt%.

[Effect of the invention]

[0010] As described below, according to the invention, polyphenylene sulfide fibers with a large single-filament fineness that are high in tenacity, toughness, and quality, and useful as industrial material can be produced at low cost and with high production efficiency, and the fibers are as useful as the conventional ones with a small single-filament fineness when used, for instance, for production of woven fabrics.

[Brief description of the drawings]

[Figure 1]

[0011] Figure 1 shows a schematic diagram of the production method of the invention.

[Explanation of numerals]

[0012]

- 1: spinning orifice
- 2: insulation tube
- 3: cross flow type cooling chimney
- 4: cooling air
- 5: yarn
- 6: spinning duct
- 7: first lubrication roller
- 8: pulling roller
- 9: second lubrication roller
- 10: feed roller
- 11: first stretching roller
- 12: converging air guide
- 13: second stretching roller
- 14: third stretching roller
- 15: relaxation roller
- 16: entangled air guide
- 17: winder
- 18: fiber package

[Best mode for carrying out the invention]

[0013] The production method of the invention is described in detail below with reference to the schematic diagram given in Figure 1.

[0014] It is necessary for the polyphenylene sulfide fibers of the invention to have a single-filament fineness of 10 to 100 dtex, preferably 10 to 50 dtex, more preferably 15 to 45 dtex, and still more preferably 20 to 40 dtex. If the single-filament fineness is less than 10 dtex, the fibers will not significantly superior in properties than those of the conventional polyphenylene sulfide multifilaments. On the other hand, though it is possible to produce fibers above 100 dtex, sufficient cooling will not be achieved and the fibers will deteriorate in spinning performance or physical properties, or the spinning speed will have be extremely lowered to avoid this. Thus it is not preferable because the productivity will deteriorate in any case. It is also necessary for the polyphenylene sulfide fibers of the invention to have a tenacity of 4.5 to 6 cN/dtex, preferably 4.8 to 5.5 cN/dtex. It has been found that this range is essential for achieving spinning performance as high

as that seen in production of the conventional polyphenylene sulfide fibers with a single-filament fineness of several dtex (hereinafter, referred to as small single-filament fineness fibers), rather than for obtaining a product with required properties. If the tenacity is less than 4.5 cN/dtex, serious fluff will take place, and yarn break will frequently occur, not only making it almost impossible to wind up the fiber product, but also even to releasing the fibers from the fiber package.

This is a very peculiar phenomenon that does not take place in the conventional small single-filament fineness fibers. In the case of the conventional small single-filament fineness fibers, a yarn can be produced stably when the tenacity is, for instance, about 4.0 cN/dtex. When a polyamide or polyester yarn is produced, furthermore, deterioration in spinning performance will not take place in said low tenacity range, but high spinning performance can be achieved at a lower tenacity when the same feed material is used. Thus, it is preferable to reduce the tenacity by, for instance, decreasing the draw ratio if fluff and yarn break occurs frequently in a conventional melt-spinning process, whereas it has been found that for the polyphenylene sulfide fibers of the invention with a large single-filament fineness (hereinafter referred to as large single-filament fineness fibers), the spinning performance can be improved by raising the draw ratio to increase the tenacity. If the tenacity exceeds 6 cN/dtex, the fibers will break as it is stretched strongly as frequently seen in the common melt-spinning process. For the production of large single-filament fineness fibers of polyphenylene sulfide, therefore, the optimum tenacity occurs in a narrow high-tenacity range. To obtain large single-filament fineness fibers in such a tenacity range, it is preferred to perform stretching up to an overall draw ratio of 3.8 to 4.5 with the direct spinning and stretching method

[0015] To obtain the polyphenylene sulfide fibers of the invention, the yarn should preferably be treated with an aqueous emulsion lubricant to adjust the weight of the surface-attached oil to 0.1 to 1 wt% in terms of solid matter percentage. In general, the amount of oil attached on the surface of the fiber should preferably be relatively large in order to effectively depress fluff and yarn break during stretching and heat treatment. Japanese Unexamined Patent Publication (Kokai) No. 2001-262436, for instance, has disclosed that it is preferred to use an aqueous lubricant for polyphenylene sulfide and adjust the weight of the surface-attached oil to 1.0 to 3.0 wt% in terms of solid matter percentage and that whereas fibers can be produced with high spinning efficiency at a percent weight of the surface-attached oil of 1.5 to 2.5 wt% in the case of polyphenylene sulfide with a single-filament fineness of 4.5 dtex, significant fluff and yarn break will take place at a percent weight of the surface-attached oil of 0.6 wt%. In the case of polyphenylene sulfide fibers with a large single-filament fineness of the invention, the spinning performance will deteriorate, as in the case of polyamide, if the percent weight of the surface-attached oil is small. However, the spinning performance also deteriorates extremely and serious fluff and frequent yarn break occurs when an aqueous emulsion lubricant is added to the surface in excess of 1 wt% in terms of solid matter percentage, making it almost impossible not only to wind up the fiber product but also even to unwind the fiber from the fiber package 18. This tendency becomes noticeable as the single-filament fineness increases, and surprisingly, in the case of an increased single-filament fineness, the spinning performance increases with an increasing amount of the aqueous lubricant. Also surprisingly, when an anhydrous lubricant, instead of an aqueous lubricant, is added to the surface of unstretched polyphenylene sulfide fibers with a large single-filament fineness, the spinning performance improves, but both the fibers' tenacity and elongation decrease, with this tendency becoming more noticeable with an increasing single-filament fineness and with an increasing surface-attached anhydrous lubricant. It has been found that an aqueous emulsion lubricant should preferably be added to the surface up to 0.1 to 1 wt% in terms of solid matter percentage in order to obtain high-tenacity polyphenylene sulfide fibers with a single-filament fineness without a decrease in the spinning performance.

[0016] It is preferred that the anhydrous lubricant is added at the second stage up to a total surface-attached oil content of 0.5 to 2 wt%. This is particularly effective when polyphenylene sulfide fibers with a single-filament fineness so large that the solid content of the surface-attached aqueous lubricant has to be adjusted to less than 0.5 wt%. The optimum total amount of the surface-attached oil may be determined after considering the production conditions etc. The total amount of the surface-attached oil should be maximized to reduce the cost if high spinning performance and fluff quality can be maintained, and therefore, the total amount of the surface-attached oil will be 0.5 to 1 wt% in most cases. This will be particularly effective when the single-filament fineness is 50 dtex or less.

[0017] It is not clear what influence the physical properties and spinning performance has on the water in the polyphenylene sulfide fibers. But the saturation moisture content of the polyphenylene sulfide fiber is very small, and no significant difference in tenacity and elongation is detected between unstretched fibers with a surface-attached aqueous emulsion lubricant and unstretched fibers with a surface-attached anhydrous emulsion lubricant. Furthermore, the properties of the polyphenylene sulfide fibers largely change with the treatment temperature. These facts suggest that the heat exchange that occurs when the moisture attached on the single-filament surface evaporates through capillarity during stretching and heat treatment is playing an important role. Thus, there is a possibility that the polyphenylene sulfide fibers of the invention can be produced by supply moisture in the form of mist or steam before lubrication even when only an anhydrous lubricant is added without using an aqueous emulsion lubricant, though the use of an aqueous emulsion lubricant is more economical. The aqueous emulsion lubricant to be attached on the surface polyphenylene sulfide fibers with a single-filament fineness of 50 dtex or less, preferably 40 dtex or less, and more preferably 25 dtex or less, should preferably account for 0.5 to 1 wt% in terms of solid weight, more preferably 0.6 to 0.9 wt%, and still more preferably

0.7 to 0.8 wt%. If it is this range, high-tenacity fiber will be produced easily without a deterioration in spinning performance, but it is allowed to add an anhydrous lubricant of a generally known composition up to a total surface-attached weight of 2 wt% or less, more preferably 1.5 wt% or less, and still more preferably 1 wt% or less, after considering cost requirements. An aqueous emulsion alone can work sufficiently if the single-filament fineness is less than 25 dtex. If the single-filament fineness exceeds 50 dtex, on the other hand, the surface-attached solid content of the aqueous emulsion lubricant should preferably be 0.1 to 0.5 wt%, more preferably 0.1 to 0.3%, and still more preferably 0.1 to 0.2%. In this case, it is effective to further add an anhydrous lubricant so that the total surface-attached content is above 0.5 wt% and preferably 2 wt% or less, more preferably 1.5 wt% or less, and still more preferably 1 wt% or less. Moreover, the concentration of the aqueous emulsion lubricant should preferably be 15 to 40 wt%, more preferably 15 to 30 wt%, and still more preferably 18 to 22 wt%. Adjusting the concentration in this range serves to produce a highly stable aqueous emulsion lubricant at low cost, and it is also preferable because an appropriate amount of moisture can be added during lubrication of the polyphenylene sulfide fibers. It is preferred to attach a surface active agent and antioxidant over the fiber surface by adding them to the lubricant. With respect to their weight, the surface active agent and antioxidant components should preferably account for 0.01 to 1 wt% and 0.002 to 0.1 wt%, respectively, relative to the weight of the fiber. It is more preferable for the surface active agent and antioxidant components to account for 0.1 to 0.5 wt% and 0.003 to 0.05 wt%, respectively. Adjusting the surface-attached weights of these components to this range serves to mitigate the damage caused during stretching and heat treatment and maintain a high toughness and a small variation when stretched to a high degree.

[0018] The polyphenylene sulfide fibers of the invention should preferably have a total fineness of 100 to 1000 dtex, more preferably 200 to 900 dtex, and still more preferably 400 to 700 dtex. Production is possible if it is less than 100 dtex, but in the case, the fibers will frequently fail to have a desired tenacity. And this is not preferable because the efficiency will decrease if the total fineness is low when fibers are doubled or doubled-and-twisted to provide an intended product. On the other hand, it is possible to produce polyphenylene sulfide fibers with a total fineness exceeding 1000 dtex. In this case, however, the fibers may be simply doubled appropriately to provide an intended product, and it is not necessary to produce large-fineness fibers using large spinning equipment.

[0019] The filament count should preferably be 2 to 50, more preferably 10 to 40. If the filament count is 1, that is, in the case of a monofilament, there will be almost no uses for it in the single-filament fineness range proposed by the invention, and a higher productivity will be achieved more easily by producing multifilaments composed of two or more filaments, followed by fibrillating them. If the filament count exceeds 50, on the other hand, it will be difficult for the conventional direct spinning and stretching method to achieve cooling to an appropriate level required to produce fibers with a large single-filament fineness, depending of the size of the spinning equipment used. Furthermore, the polyphenylene sulfide fibers of the invention should preferably be twistless. Fibers with a large single-filament fineness can be used as multifilaments and in such cases, they may be twisted as required in a higher-degree processing step. Or, they may be fibrillated into monofilaments. Twisting is not preferable in this case because twisted fibers cannot be fibrillated. A twistless fiber package 18 can be produced with a generally known wind-up machine commonly used for direct spinning and stretching.

[0020] It is preferred that the elongation is 15 to 25%, more preferably 17 to 23%. If it is less than 15%, not only fluff and yarn break will frequently occur during the spinning process, but also the toughness will decrease, leading to deterioration in the high-degree processability. An elongation of much above 25% is not preferable because it will be difficult to achieve a tenacity that meets the requirements for the invention, but a polyphenylene sulfide that exceeds 25% can be produced by maximizing the rate of relaxation after stretching.

[0021] The 150°C dry-heat shrinkage should preferably be 2 to 10%, more preferably 2 to 6%, and still more preferably 2 to 4%. A polyphenylene sulfide with a large single-filament fineness of the invention has a relatively high tenacity, and therefore, it is difficult to achieve a 150°C dry-heat shrinkage of less than 2%. On the other hand, if a high-rigidity product is to be produced by performing high-temperature thermosetting during high-degree processing, it is preferred for the shrinkage rate to be higher, but a shrinkage rate above 10% necessitates lowering the temperature of the final stretching roller and using a high stretching tension. This will cause a deterioration in spinning performance and a decrease in toughness, leading to free shrinkage and complicated handling of the fiber, which is not preferable.

[0022] The fineness unevenness should preferably be 0.5 to 1%, more preferably 0.6 to 0.8%. It is difficult to achieve a fineness unevenness of 0.5% or less with a currently available technique. On the other hand, a fineness unevenness above 1% is not preferable because it will lead to a deterioration in spinnability or stretchability.

[0023] The polyphenylene sulfide fibers of the invention can be produced with the method described below.

[0024] Polyphenylene sulfide pellets with a melt flow rate (MFR) of 50 to 600 are dried at 140 to 180°C for 2 to 24 hours to remove foreign matters with a low boiling point, followed by melt-spinning. The melt flow rate (MFR) as referred to above is the parameter showing a polymer's melt flow measured by the ASTM D1238-82 method at a setting temperature of 316°C and a load of 5 kgf. A polyphenylene sulfide to be used for the invention should preferably be virtually linear, but it may contain trichlorobenzene (TCB) up to 0.1 wt%, or contain a small amount other additives.

[0025] An extruder-type spinning machine should preferably be used to melt pellets of the polyphenylene sulfide

polymer of the invention. The spinning temperature should be 300 to 320°C, and filtering through a 5 to 20 µm filter is carried out in the spinning pack. The filtered polymer is spun through the orifices in the spinning nozzle 1, allowed to pass through a slow cooling zone provided immediately below the nozzle, and cooled to solidify in a cool air stream. In said nozzle, the nozzle orifices are provided in a common zigzag or circular configuration, and the orifice diameter and orifice length are appropriately designed so that the pressure behind the nozzle is 70 to 150 kg/cm² and the spinning draft ratio, which is defined as the ratio between the lineal speed of the discharged material from the nozzle orifices and the take-up speed, is 20 to 50. The fineness unevenness will deteriorate as the spinning draft ratio exceeds 50. The pressure behind the nozzle should preferably be in the range of 90 to 110 kg/cm². The slow cooling zone is provided with the insulation tube 2 with a length of 5 to 10 cm, and the temperature is controlled so that the atmosphere temperature 10 cm immediately below the nozzle is 150 to 250°C. Said cooling is achieved by providing the cooling air stream 4 of 10 to 30°C at a speed of 30 to 40 m/min, preferable 35 m/min or more. The large single-filament fineness fibers of the invention require strong cooling, suggesting that the speed of the cool air stream should be as high as possible. However, the spinning tension will decrease largely as compared with conventional fibers with a small single-filament fineness. If the speed of the cool air stream is 40 m/min or more, the yarn 5 will tend to go away from the spinning duct 6, or come in contact with the spinning duct leading to deterioration in fiber physical properties or frequent occurrence of fluff, which is not desired. A transverse air blow type cooling chimney 3 may be used to give cool air in the perpendicular direction to the spun yarn, or a circular cooling chimney may be used to give cool air from the circumference toward the center of the spun yarn bundle or from the center toward the circumference. The use of a cross flow type cooling chimney is preferred.

[0026] Then, a lubricant is applied to the cooled and solidified yarn, and said yarn is taken up on a take-up roller 8 that rotates at an appropriate speed. Lubrication may be performed by a generally known method such as roller lubrication and guide lubrication. The lubricant used here may be either an aqueous emulsion lubricant or an anhydrous lubricant composed primarily of a smoothing agent, active agent, or emulsifier, but it is preferred that the first-step lubrication is performed with an aqueous emulsion lubricant by the first lubrication roller 7, followed by the second-step lubrication with an anhydrous lubricant by the second lubrication roller 9. The lubricant may be, for instance, an esterification product composed of polytetramethylene glycol with an average molecular weight of 600 to 6,000 in addition to a dibasic acid and a monovalent fatty acid, and may contain a polyether ester with an average molecular weight of 2,000 to 15,000. But this example does not place any limit, and other additives including pH adjustor, such as alkylamine-alkylene oxide addition product, ultraviolet absorber, and fluorine compound, may be added as required.

[0027] The practical smoothing agents include esters of divalent alcohol and higher fatty acid such as neopentyl glycol dilaurate and diethylene glycol dioleate; esters of trivalent alcohol and higher fatty acid such as glycerin trioleate, trimethylol propane trioleate; esters of tetra- or more valent alcohol and higher fatty acid such as pentaerythritol tetraoleate; esters of higher alcohol and dibasic acid such as dioctyl sebacate, dioleoyl adipate, and diisostearyl thiodipropionate; esters of higher alcohol and aromatic carboxylic acid such as dioleoyl phthalate, trioctyl trimellitate, and tetraoctyl pyromellitate; and esters of higher alcohol and higher fatty acid such as butyl stearate, isostearyl palmitate, oleyl laurate, and oleyl oleate.

[0028] The practical surface active agents include a reaction product of monocarboxylic acid and/or dicarboxylic acid with an esterification product of a polyhydric alcohol-alkylene oxide addition product in which the number of moles of the alkylene oxide added is 10 to 40. Said esterification products include stearate and maleate of hydrogenated castor oil EO (25) or hydrogenated castor oil ethylene oxide EO (25), and ethylene oxide EO (20) distearate.

[0029] The practical antioxidants include phenolic antioxidant, phosphoric acid antioxidant, amine antioxidant, hindered phenol antioxidant, and sulfur antioxidant, which may be used singly or in combination. It should be noted that the antioxidants are included in the surface active agents.

[0030] The take-up roller 8 may be of overhung type, Nelson type, or separate roller type, any of which will work sufficiently. Its temperature is commonly room temperature, with water circulated inside said roller to adjust the temperature to 20 to 40°C. The take-up speed is 400 to 1000 m/min, preferably 500 to 800 m/min. If said pulling speed, i.e. the spinning speed, is less than 400 m/min, the quantity of production per unit time will decrease, and polyphenylene sulfide fibers will not be produced efficiently. Furthermore, it will be difficult to set a practical draw ratio to allow stable production of polyphenylene sulfide fibers in the required tenacity range for the invention. If it exceeds 1000 m/min, on the other hand, an excessively large amount of the polymer will be discharged from the nozzle, and it will be difficult to achieve sufficient cooling with a conventional spinning technique, leading to a deterioration in spinning performance. It will be necessary to cool the polyphenylene sulfide yarn to below the glass transition point before continuing the process.

[0031] To ensure stable quality and spinning performance, the spun yarn may be pulled by the feed roller 10, instead of being wound up, and subjected to prestretching between the take-up roller and the feed roller, followed by winding up with the multistage drawing technique as used for polyamide and polyester, or winding up with the unique multistage drawing technique suitable for production of polyphenylene sulfide fibers as proposed in Japanese Unexamined Patent Publication (Kokai) No. 2001-262436, the latter being preferable when the spinning speed is low.

[0032] In the case of the same multistage drawing technique as for polyamide etc., polyphenylene sulfide fibers are

stretched and heat-treated as described below. Prestretching is carried out up to 2 to 10%, preferably 4 to 8%. It is preferred that the temperature of the feed roller 10 is controlled at 70 to 110°C. Then, the first-stage stretching is performed between said feed roller and the first stretching roller 11. The first stretching roller is heated up to 80 to 120°C. To produce the polyphenylene sulfide fibers of the invention, it is preferred that the first-stage draw ratio should be as high as possible, i.e. up to about 3.3 to 3.8, as long as single-filament remain unbroken. After the first-stage stretching, the yarn is subjected to the second-stage stretching by the second stretching roller 13. The second stretching roller is maintained in the range of 180 to 250°C. The second-stage draw ratio should preferably be adjusted to 1.05 to 1.3. Here, a converging air guide 12 should preferably be provided between the first stretching roller and the second stretching roller to bundle the threads, which serves to prevent the spun yarn to break. A third stretching roller 14 may be provided as needed to perform a third-stage stretching. In this case, the temperature of the third stretching roller is adjusted to 180 to 250°C, and should commonly be higher than the tem of the second stretching roller. Commonly, the second-stage draw ratio is divided to calculate the third-stage draw ratio so that the second-stage draw ratio is higher than the third-stage draw. The overall draw ratio should preferably be 3.8 to 4.5, more preferably 3.9 to 4.4, and still more preferably 4.0 to 4.3. The overall draw ratio should be strictly maintained in such a narrow range to obtain large single-filament fineness polyphenylene sulfide fibers free of significant fluff and yarn break for the invention, and the use of a draw ratio out of this range alone will lead to an unspinnable state. In particular, if the temperature of the second stretching roller is as high as 200°C or more, the orientation should be maximized to increase the tenacity before contact with the high temperature roller. After the second-stage stretching or the third-stage stretching, the yarn is heat-treated for relaxation before the relaxation roller 15. The relaxation roller is not heated or maintained at 150°C or below. The relaxation rate should preferably be 2 to 10%, more preferably 4 to 8%. All rollers from said first stretching roller to the relaxation roller should preferably be of Nelson type.

[0033] If the spinning speed is very low and spinning cannot be performed under said conditions, polyphenylene sulfide fibers are stretched and heat-treated as described below. Specifically, said prestretching ratio and the first-stage draw ratio are adjusted to 1.2 to 1.6 and 2.5 to 3.5, respectively, while all other conditions remain the same as above. Other useful conditions are that the first-stage draw ratio and the second-stage draw ratio are adjusted to 1.2 to 1.6 and 2.5 to 3.5, respectively, while the third-stage draw ratio is adjusted so that the overall draw ratio comes in the range of 3.8 to 4.5. In this case, it is preferred that the first stretching roller, the second stretching roller, and the third stretching roller are adjusted to the temperature range of 70 to 110°C, 80 to 120°C, and 180 to 250°C, respectively.

[0034] If the polyphenylene sulfide yarn produced is to be used in an unfibrillated state, it is preferred that the yarn is fluid-treated for intermingling before winding up. For entangled, entangled air guide 16 is used for fluid treatment at an appropriate fluid flow rate and winding tension. It is preferred that the number of entangled is 5 to 20 per meter.

[0035] The polyphenylene sulfide fibers of the invention are obtained according to the method described above. With the direct spinning and stretching method, the polyphenylene sulfide fibers of the invention can be subjected to simultaneous multi-thread stretching at a spinning speed of 2000 m/min or more and with a high stretchability during the spinning process. The process is almost completely free of yarn break, fluff due to breakage of single-filament, and unsmooth releasing of the fiber due to fluff. Thus the yarn can be processed smoothly during subsequent higher-degree processes as compared with conventional small single-filament fineness polyphenylene sulfide fibers. The polyphenylene sulfide fibers of the invention can serve for uses where the good properties and rigidity of polyphenylene sulfide are required, particularly as industrial material.

[Examples]

[0036] The invention is described in detail below with reference to Examples. The definitions of different characteristics and the measuring methods used for the invention are as described below.

(1) Total fineness: The corrected fineness was determined with the method according to JIS L1013 (1999) 8.3.1 A with a predetermined load 0.045 cN/dtex to provide the value of the total fineness.

(2) Filament count: Calculations were made with the method according to JIS L1013 (1999) 8.4.

(3) Single-filament fineness: Calculations were made by dividing the aforementioned total fineness by the aforementioned filament count.

(4) Percent weight of surface-attached oil: The weight of the extract with diethyl ether is measured with method according to JIS L1013 (1999) 8.27 b) to provide the weight of the surface-attached oil. The weight of the oil attached on the surface of an unstretched yarn after being subjected to the first-stage lubrication is measured to provide the weight of the surface-attached aqueous lubricant. The total weight of the surface-attached oil was determined from measurements with a wound-up, stretched yarn. The weight of the surface-attached surface active agent and anti-oxidant was determined from the composition and the weight of the surface-attached lubricant at first stage and the second stage.

(5) Tenacity and elongation: Measurements were made under the constant rate extension conditions as specified

for the standard test according to JIS L1013 8.5.1. A Tensilon tester, UCT-100 supplied by Orientec Co., Ltd., was used with a specimen length of 25 cm and a tensile speed of 30 cm/min. The elongation was determined from the elongation at the point on the S-S curve where the maximum force was shown.

(6) 150°C dry-heat shrinkage: Measurements were made using a drying machine heated at 150°C with the method according to JIS L1013 (1999) 8.18.2 b).

(7) Number of entangled: The number of entangled portions with a length 1 mm or more was measured with the water entanglement method, and the measurement was converted into the number per meter. Measurements were made for 10 yarn specimens and the average was taken.

[0037] The water immersion bath had a length of 70 cm, width of 15 cm, and depth of 5 cm, and partition plates were provided at the positions 10 cm from the ends in the length direction. The bath was filled with pure water, and yarn specimens were immersed, followed by counting the entangled portions. Pure water was replaced for each test run to eliminate the influence of the lubricant and other impurities.

(8) Fineness unevenness: An Uster tester (Monitor C supplied by Zellweger Uster AG) was used to determine the half value. The INEAT mode was used to make measurements over a length of 125 m at a yarn speed of 25 m/min.

(9) Yarn break during spinning: The number of yarn breaks that took place before the total weight of the spun fiber package reached 300 kg.

(10) Fluff during spinning: A laser type fluff detector was installed 5 mm away from a roller provided between the heat treatment roller for stretching and relaxation and the wind-up machine to count the number of fuzz fibers detected before the total weight of the spun fiber package reached 300 kg. The measurement was converted into the number of fuzz fibers per 10,000 km.

(11) Yarn releasing properties: From six fiber packages (30 kg), yarns were unwound at a rate of 300 m/min, and the frequency that the unwinding motion stopped due to fuzz fibers was counted.

(12) Fluff in doubled-and-twisted yarn: Three spun threads were bundled, and twisted with a twisting machine to produce a twisted yarn with a twist count of 5 per 10 cm, followed by observing the twisted yarn for fluff.

[Example 1]

[0038] A polyphenylene sulfide polymer product with a MFR of 200 supplied by Toray Industries, Inc. was melted in an extruder type spinning machine at a polymer temperature of 315°C under a vacuum of 1.33 kPa, and the molten polymer was filtered in the spinning pack through a metal filter with 5 μm pores, and then spun through a spinning nozzle containing 19 orifices with a 0.50 mm diameter in a single line configuration. The discharge rate to be used was calculated from a wind-up speed required for the resulting fiber to have a fineness of 440 dtex, and the measuring pump was adjusted accordingly. A heating tube with a length of 100 mm was provided immediately below the nozzle, and the yarn was cooled gradually, and solidified in a 25°C, 38 m/min cool air stream in a cross flow type cooling chimney. Then an aqueous emulsion lubricant (aqueous lubricant 20) containing a smoothing agent and other additives is supplied on a lubrication roller rotating at 10 rpm, and the spun yarn was taken up on a spun yarn take-up roller rotating at 558 m/min. Said aqueous emulsion lubricant (aqueous lubricant 20) was composed primarily of a polyether ester smoothing agent produced from adipic acid and oleic acid with a polytetramethylene glycol product supplied by Takemoto Oil & Fat Co., Ltd., containing an antioxidant IRGANOX 245 supplied by Ciba Japan K.K., an extreme pressure agent composed of lauryl (EO) 2 phosphate K salt or lauryl alcohol PO·EO addition product, and a surface active agent such as hydrogenated castor oil EO 25, and emulsified with 80 wt% pure water. In the lubricant, the surface active agent and the antioxidant account for 42.3 wt% and 0.96 wt%, respectively.

[0039] Subsequently, an anhydrous lubricant of similar components to above, comprising a lubricant composed of a 43.4 wt% surface active agent and a 1.42 wt% antioxidant diluted with a 14 wt% mineral oil is supplied to the yarn from two opposite directions on a lubrication roller rotating at 8 rpm, followed by stretching and heat treatment to provide polyphenylene sulfide fibers produced with the direct spinning and stretching method.

[0040] First, the yarn was stretched by 6% between the take-up roller and the feed roller, and then subjected to the first-stage stretching between the feed roller and the first stretching roller and the second-stage stretching between the first stretching roller and the second stretching roller. Subsequently, it was heat-treated for 5% relaxation between the second stretching roller and the relaxation roller, entangled in entangled air guide, and wound up on a winder. The roller surface temperature was adjusted to room temperature, 80°C, 110°C, 235°C, and 150°C for the take-up roller, feed roller, first stretching roller, second stretching roller, and relaxation roller, respectively. The rotating speeds of the first stretching roller and the second stretching roller were adjusted so that the first-stage draw ratio and the overall draw ratio would be 3.70 and 4.30, respectively.

[0041] Properties and evaluation results of the resulting polyphenylene sulfide fibers are shown in Table 1. A high-tenacity yarn was produced at a high draw ratio with an appropriate lubrication method using an appropriate weight of

surface-attached oil, serving to prevent significant yarn break and fluff during spinning, and unsmooth unwinding due to fluff. Thus, it was possible to obtain a fiber package useful as material, for instance, for fabrics that would have to meet stringent quality requirements. It was also possible to produce fluff-free, doubled-and-twisted yarns.

[Examples 2 and 3]

[0042] In Example 2, a spinning nozzle with eight discharge orifices with a diameter of 0.70 mm arranged in a single line configuration was used at a pulling speed of 512 m/min. The rotating speeds of the other rollers were changed accordingly, and the rotating speed of the second-stage lubrication roller was adjusted to 12 rpm. Except for these, the same procedure as in Example 1 was carried out to produce a polyphenylene sulfide fiber. In Example 3, a spinning nozzle with five discharge orifices with a diameter of 0.75 mm arranged in a single line configuration was used at a pulling speed of 512 m/min. The rotating speeds of the other rollers were changed accordingly, and the rotating speed of the second-stage lubrication roller was adjusted to 15 rpm. Except for these, the same procedure as in Example 1 was carried out to produce a polyphenylene sulfide fiber. Properties and evaluation results of the resulting polyphenylene sulfide fibers are shown in Table 1. As compared with Example 1, the fibers were slightly inferior with respect to the yarn break during spinning, fluff during spinning, and unsmooth yarn releasing properties, and the tenacity and elongation decreased with an increasing single-filament fineness, but satisfactory evaluation results were obtained.

[Example 4]

[0043] Except that the pulling speed was adjusted to 628 m/min and that the rollers' rotating speeds were changed accordingly, the same procedure as in Example 1 was carried out to produce a polyphenylene sulfide fiber. Properties and evaluation results of the resulting polyphenylene sulfide fibers are shown in Table 1. As compared with Example 1, the fibers were slightly inferior with respect to yarn break during spinning and fluff during spinning, but satisfactory evaluation results were obtained.

[Example 5]

[0044] The measuring pump was adjusted to allow the total fineness to be 220 dtex. A spinning nozzle with ten discharge orifices with a diameter of 0.50 mm arranged in a single line configuration was used, and the rotating speed of the first-stage lubrication roller and the rotating speed of the second-stage lubrication roller were adjusted to 15 rpm and 5 rpm, respectively. Except for these, the same procedure as in Example 1 was carried out to produce a polyphenylene sulfide fiber. Properties and evaluation results of the resulting polyphenylene sulfide fibers are shown in Table 1. As compared with Example 1, the fibers were slightly inferior with respect to yarn break during spinning and fluff during spinning, but satisfactory evaluation results were obtained.

[Example 6]

[0045] The rotating speed of the first-stage lubrication roller was adjusted to 25 rpm, and the second-stage lubrication roller was not performed. Except for these, the same procedure as in Example 1 was carried out to produce a polyphenylene sulfide fiber. Properties and evaluation results of the resulting polyphenylene sulfide fibers are shown in Table 1. As compared with Example 1, the fibers were slightly inferior with respect to fluff during spinning, but satisfactory evaluation results were obtained.

[Table 1]

		Example 1						Example 2						Example 3						Example 4						Example 5						Example 6					
		m/min						m/min						m/min						m/min						m/min						m/min					
fiber production method	spinning speed	558						512						512						628						558						558					
	feed roll speed	592						542						542						666						592						592					
	first stretching roll speed	2189						2007						2007						2463						2189						2189					
	second stretching roll speed	2400						2200						2200						2700						2400						2400					
	relaxation roll speed	2280						2090						2090						2565						2280						2280					
	second stretching roll temperature	235						235						235						235						235						235					
	first-stage draw ratio	3.70						3.70						3.70						3.70						3.70						3.70					
	overall magnification	4.3						4.3						4.3						4.3						4.3						4.3					
	relaxation rate	0.95						0.95						0.95						0.95						0.95						0.95					
	first-stage lubrication oil type	aqueous (20)						aqueous (20)						aqueous (20)						aqueous (20)						aqueous (20)						aqueous (20)					
	second-stage lubrication oil type	anhydrous						anhydrous						anhydrous						anhydrous						anhydrous						anhydrous					
fiber properties	total fineness	440						440						440						440						220						440					
	filament count	19						8						5						19						10						19					
	single-filament fineness	23						55						88						23						22						23					
	% weight of surface-attached aqueous lubricant	0.22						0.15						0.10						0.20						0.22						0.22					
	% weight of surface-attached oil	0.97						1.15						1.40						0.96						0.97						0.97					
	% weight of surface-attached surface active agent	0.42						0.50						0.61						0.41						0.42						0.31					
	% weight of surface-attached antioxidant	0.012						0.016						0.019						0.013						0.012						0.007					
	tenacity	5.07						5.02						4.72						5.38						5.02						5.22					
	elongation	22.5						22.2						20.3						23.9						24.1						22.0					
	150°C dry-heat shrinkage	3.0						3.1						3.4						3.1						2.9						3.1					
	number of entangled	10						10						10						10						10						10					
evaluation results	fineness unevenness	0.67						0.88						0.97						0.53						0.55						0.69					
	yarn break during spinning	0						0						1						2						1						0					
	fluff during spinning	7						31						135						62						22						14					
	yarn releasing properties	0						0						2						0						0						0					
fluff in doubled-and-twisted yarn		none						none						none						none						none						none					

[Examples 7 and 8]

[0046] Except that the overall draw ratio was changed and that the production conditions, such as spinning speed, described in Table 2 were used, the same procedure as in Example 6 was carried out to produce a polyphenylene sulfide fiber. Properties and evaluation results of the resulting polyphenylene sulfide fibers are shown in Table 2. As compared with Example 6, the fibers were slightly inferior with respect to yarn break during spinning, fluff during spinning, and yarn releasing properties, but satisfactory evaluation results were obtained.

[Example 9]

[0047] A spinning nozzle with 30 discharge orifices with a diameter of 0.35 mm arranged in a double zigzag line configuration was used. The production conditions described in Table 2 were used so that the spinning speed, first-stage draw ratio, and overall draw ratio would be 690 m/min, 3.50, and 4.20, respectively, and the rotating speed of the first-stage lubrication roller was changed to 35 rpm. Except for these, the same procedure as in Example 6 was carried out to produce a polyphenylene sulfide fiber. Properties and evaluation results of the resulting polyphenylene sulfide fibers are shown in Table 2. Though fluff during spinning increased, satisfactory evaluation results were obtained.

[Example 10]

[0048] Except that the amount of the antioxidant in the aqueous emulsion lubricant used for the first-stage lubrication was halved, and that the anhydrous lubricant for the second-stage lubrication did not contain an antioxidant, the same procedure as in Example 1 was carried out to produce a polyphenylene sulfide fiber. Properties and evaluation results of the resulting polyphenylene sulfide fibers are shown in Table 2. As compared with Example 1, the tenacity and elongation decreased, and the fibers were slightly inferior with respect to the yarn break during spinning, fluff during spinning, and yarn releasing properties, because the lubricant did not contain an antioxidant, but as a whole, satisfactory evaluation results were obtained.

[Example 11]

[0049] Except that the rotating speed of the first-stage lubrication roller was adjusted to 15 rpm, the same procedure as in Example 6 was carried out to produce a polyphenylene sulfide fiber. Properties and evaluation results of the resulting polyphenylene sulfide fibers are shown in Table 2. As compared with Example 6, the fibers were inferior with respect to the tenacity, elongation, yarn break during spinning, fluff during spinning, and yarn releasing properties, but as a whole, satisfactory evaluation results were obtained.

5
10
15
20
25
30
35
40
45
50
55

5
10
15
20
25
30
35
40
45
50
55

[Comparative examples 1 and 2]

[0050] The overall draw ratio was changed and the production conditions, such as spinning speed, described in Table 2 were used. And the rotating speed of the first-stage lubrication roller was adjusted to 30 rpm. Except for these, the same procedure as in Example 6 was carried out to produce a polyphenylene sulfide fiber. Results are shown in Table 3. In Comparative example 1, the tenacity was low, and yarn break frequently occurred during spinning, only making it possible to take a polyphenylene sulfide fiber sample enough for measurement of fiber properties. Fluff was detected constantly during spinning by the laser type fluff detector. In Comparative example 2, the overall draw ratio was too high even to take a fiber sample.

[Comparative examples 3 and 4]

[0051] Except that the rotating speed of the first-stage lubrication roller was adjusted to 35 rpm and 50 rpm in Comparative examples 3 and 4, respectively, the same procedure as in Example 6 was carried out to produce a polyphenylene sulfide fiber. Results are shown in Table 3.

[0052] In Comparative example 3, a large amount of oil was attached on the surface to cause serious yarn break during spinning, fluff during spinning, and deterioration of yarn releasing properties. The serious fluff taking place during spinning led to serious fluff in doubled-and-twisted yarns.

[0053] In Comparative example 4, the amount of oil attached on the surface was equivalent to that for the conventional polyphenylene sulfide fibers with a small single-filament fineness. But that surface-attached oil amount was too large for the large single-filament fineness fibers of the invention, leading to frequent yarn break. Even the sampling of fibers was performed.

[Comparative example 5]

[0054] A spinning nozzle with 24 discharge orifices with a diameter of 0.40 mm arranged in a zigzag configuration was used, and the rotating speed of the first-stage lubrication roller was changed to 45 rpm. Except for these, the same procedure as in Example 6 was carried out to produce a polyphenylene sulfide fiber. Results are shown in Table 3.

[0055] The fibers were apparently inferior with respect to yarn break during spinning and fluff during spinning, but they were not so serious such as in Comparative example 4. There was no significant deterioration in yarn releasing properties, or fluff in doubled-and-twisted yarns.

[Comparative example 6]

[0056] Emulsion with 90 wt% pure water was performed to prepare an aqueous emulsion lubricant (aqueous lubricant 10) to be used for the first-stage lubrication. Except for this, the same procedure as in Example 1 was carried out to produce a polyphenylene sulfide fiber. Results are shown in Table 3. The amount of the surface-attached aqueous lubricant was smaller while the amount of the surface-attached water was larger. Accordingly, yarn break frequently occurred during spinning, only making it possible to take a polyphenylene sulfide fiber sample enough for measurement of fiber properties.

[Table 3]

fiber production method		Comparative example 1	Comparative example 2	Comparative example 3	Comparative example 4	Comparative example 5	Comparative example 6
fiber properties	spinning speed	m/min	632	500	558	558	558
	feed roll speed	m/min	669	530	592	592	592
	first stretching roll speed	m/min	2477	1961	2189	2189	2189
	second stretching roll speed	m/min	2400	2400	2400	2400	2400
	relaxation roll speed	m/min	2280	2280	2280	2280	2280
	second stretching roll temperature	°C	235	235	235	235	235
	first-stage draw ratio	-	3.70	3.70	3.70	3.70	3.70
	overall magnification	-	3.8	4.8	4.3	4.3	4.3
	relaxation rate	-	0.95	0.95	0.95	0.95	0.95
	first-stage lubrication oil type	aqueous (20)	aqueous (20)	aqueous (20)	aqueous (20)	aqueous (20)	aqueous (10)
	second-stage lubrication oil type	none	none	none	none	none	anhydrous
	total fineness	dtex	440	sampling impossible	440	440	440
	filament count	number	19		19	24	19
	single-filament fineness	dtex	23		23	18	23
evaluation results	% weight of surface-attached aqueous lubricant		0.81		1.08	1.39	0.09
	% weight of surface-attached oil	wt%	0.81		1.08	1.39	0.85
	% weight of surface-attached surface active agent	wt%	0.34		0.46	0.59	0.37
	% weight of surface-attached antioxidant	wt%	0.008		0.010	0.013	0.012
	tenacity	cN/dtex	4.38		5.13	4.97	5.17
	elongation	%	27.2		22.1	21.3	21.7
	150°C dry-heat shrinkage	%	2.5		2.9	3.0	3.1
	number of entangled	number /m	10		10	10	10
	fineness unevenness	%	0.91		0.75	0.69	0.69
	yarn break during spinning	number /300kg	evaluation impossible		evaluation impossible	6	evaluation impossible
	fluff during spinning	number /10000km				548	
	yarn releasing properties	number /30kg				0	
	fluff in doubled-and-twisted yarn	-				none	

[Comparative example 7]

[0057] A anhydrous lubricant was used for the first-stage lubrication. It had a composition similar to that in Example 1, but the surface active agent and antioxidant components accounted for 31 wt% and 0.4 wt%, respectively, in the composition of the lubricant that is free of mineral oil. Actually, it was diluted with 75 wt% mineral oil. The rotating speed of the lubrication roller was 25 rpm, and the second-stage lubrication was not performed. Except for these, the same procedure as in Example 1 was carried out to produce a polyphenylene sulfide fiber. Results are shown in Table 4. The resulting fibers had good properties without significant yarn break during spinning, fluff during spinning, or deterioration of yarn releasing properties, but suffered a large decrease in tenacity and elongation.

[Comparative example 8]

[0058] A spinning nozzle with 12 discharge orifices with a diameter of 0.60 mm arranged in a single line configuration was used, and the pulling speed was adjusted to 512 m/min. The production conditions, including roller speed, were as described in Table 2. Except for these, the same procedure as in Example 7 was carried out to produce a polyphenylene sulfide fiber. Results are shown in Table 4. The resulting fibers had good properties without significant yarn break during spinning, fluff during spinning, or deterioration of yarn releasing properties, but suffered a still larger decrease in tenacity and elongation.

[Comparative example 9]

[0059] A spinning nozzle with 4 discharge orifices with a diameter of 0.80 mm arranged in a single line configuration was used, and the rotating speed of the first-stage lubrication roller and the rotating speed of the second-stage lubrication roller were adjusted to 15 rpm and 20 rpm, respectively. Except for these, the same procedure as in Example 2 was carried out to produce a polyphenylene sulfide fiber. Results are shown in Table 4. The fibers suffered a decrease in tenacity and elongation, and they were inferior with respect to yarn break during spinning, fluff during spinning, and deterioration of yarn releasing properties.

[Reference examples 1 to 3]

[0060] Conventional polyphenylene sulfide fibers with a small single-filament fineness were spun in these Reference examples under the production conditions shown in Table 4. In Reference example 1, the aqueous emulsion lubricant used for the first-stage lubrication in Example 1 was supplied at a roller rotating speed of 25 rpm, while in Reference examples 2 and 3, the anhydrous lubricant used for the first-stage lubrication in Comparative example 7 was supplied at a roller rotating speed of 17 rpm and 25 rpm, respectively. The process in Reference example 1 produced yarns with good properties though failing to meet the requirements of the invention. Similar results are obtained in both Reference examples 2 and 3, and deterioration in properties did not occur when a anhydrous lubricant was used in very large amounts.

5
10
15
20
25
30
35
40
45
50
55

5
10
15
20
25
30
35
40
45
50
55

[Industrial applicability]

[0061] According to the invention, a polyphenylene sulfide fiber with a large single-filament fineness can be produced with the conventional direct spinning and stretching method without using special equipment at a high spinnability equivalent to that for small single-filament fineness fibers.

[0062] Thus, the technique provided by the invention will make a very large contribution to industrial material manufacturing, particularly in the fields where polyphenylene sulfide fibers with higher rigidity than the conventional products are required.

Claims

1. A polyphenylene sulfide fiber with a single-filament fineness of 10 to 100 dtex and a tenacity of 4.5 to 6 cN/dtex obtainable by melt-spinning.
2. A polyphenylene sulfide fiber as claimed in Claim 1 wherein the fiber surface carries at least a surface active agent and an antioxidant.
3. A polyphenylene sulfide fiber as claimed in either Claim 1 or 2 wherein the total weight of the surface-attached oil accounts for 0.5 to 2 wt% of the fiber weight, with the surface active agent accounting for 0.01 to 1 wt% and the antioxidant accounting for 0.002 to 0.1 wt%,
4. A polyphenylene sulfide fiber as claimed in any of Claims 1 to 3 that is untwisted and has a total fineness of 100 to 1000 dtex and a filament count of 2 to 50.
5. A polyphenylene sulfide fiber as claimed in any of Claims 1 to 4 wherein the elongation is 15 to 25%, and the dry-heat shrinkage at 150°C is 2 to 10%.
6. A polyphenylene sulfide fiber as claimed in any of Claims 1 to 5 wherein the fineness unevenness is 0.5 to 1%.
7. A production method for polyphenylene sulfide fibers with a single-filament fineness of 10 to 100 dtex and a tenacity of 4.5 to 6 cN/dtex wherein polyphenylene sulfide resin is melt-spun, processed with an aqueous emulsion lubricant, while being pulled, to cause the surface-attached oil to account for 0.1 to 1 wt%, and, without being wound up, stretched up to an overall draw ratio of 3.8 to 4.5.
8. A production method for polyphenylene sulfide fibers as claimed in Claim 7 wherein an anhydrous lubricant is applied to the spun yarn up to a total percentage of surface-attached oil of 0.5 to 2 wt%.
9. A production method for polyphenylene sulfide fibers as claimed in either Claim 7 or 8 wherein the aqueous emulsion lubricant has an oil concentration of 15 to 40 wt%.

Patentansprüche

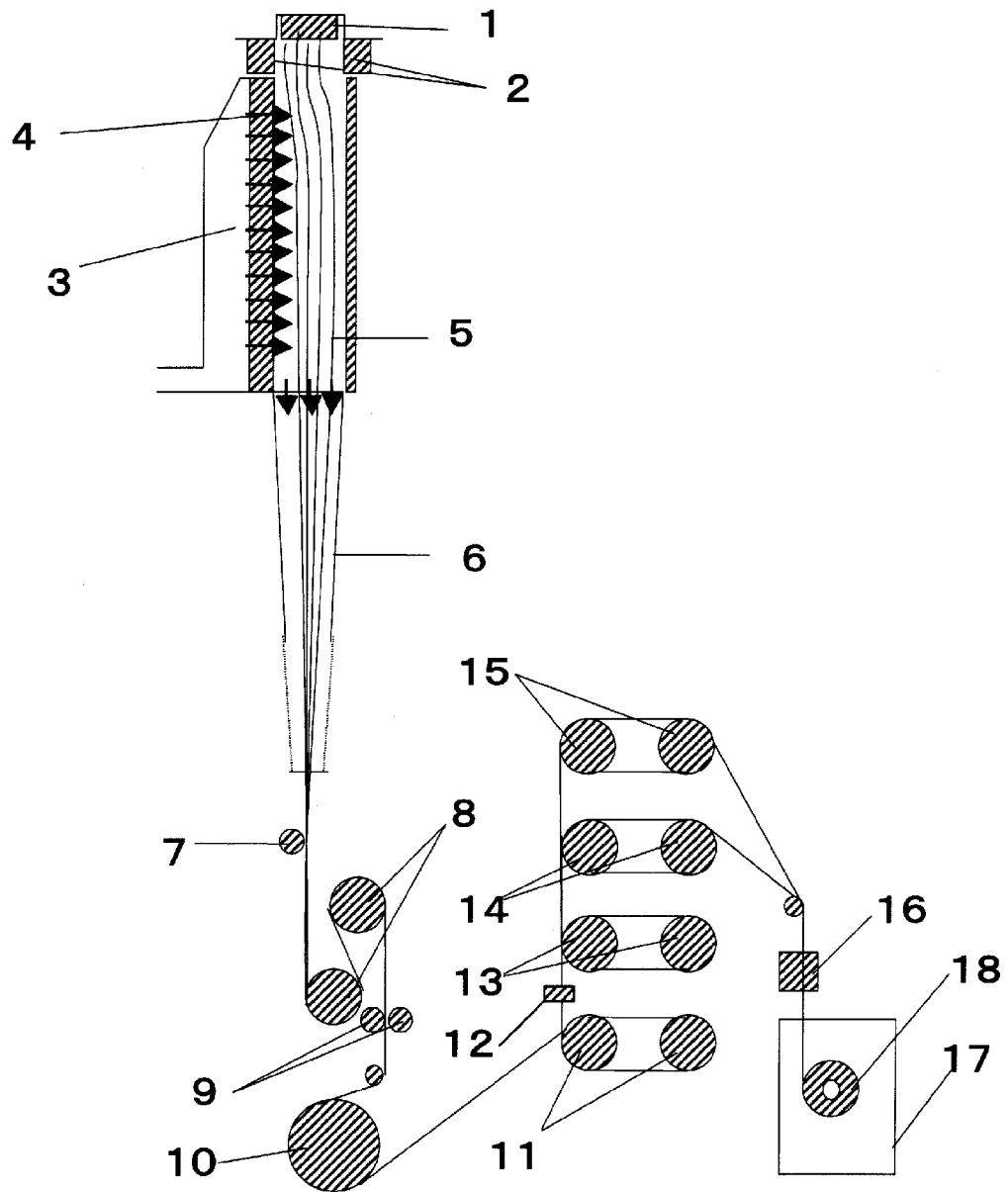
1. Polyphenylensulfidfaser mit einer Einzelfilamentfeinheit von 10 bis 100 dtex und einer Zugfestigkeit von 4,5 bis 6 cN/dtex, die durch Schmelzspinnen erhalten werden kann.
2. Polyphenylensulfidfaser nach Anspruch 1, wobei die Faseroberfläche zumindest ein oberflächenaktives Mittel und ein Antioxidans umfasst.
3. Polyphenylensulfidfaser nach Anspruch 1 oder 2, wobei das Gesamtgewicht des an der Oberfläche gebundenen Öls 0,5 bis 2 Gew.-% des Fasergewichts beträgt, wobei das oberflächenaktive Mittel 0,01 bis 1 Gew.-% beträgt und das Antioxidans 0,002 bis 0,1 Gew.-% beträgt.
4. Polyphenylensulfidfaser nach einem der Ansprüche 1 bis 3, die unverdrillt ist und eine Gesamteinheit von 100 bis 1000 dtex und eine Filamentanzahl von 2 bis 50 aufweist.
5. Polyphenylensulfidfaser nach einem der Ansprüche 1 bis 4, wobei die Dehnung 15 bis 25 % und die Schrumpfung

bei 150 °C Trockenhitze 2 bis 10 % betragen.

6. Polyphenylensulfidfaser nach einem der Ansprüche 1 bis 5, wobei die Feinheitungleichheit 0,5 bis 1 % beträgt.
7. Herstellungsverfahren für Polyphenylensulfidfasern mit einer Einzelfilamentfeinheit von 10 bis 100 dtex und einer Zugfestigkeit von 4,5 bis 6 cN/dtex, bei dem Polyphenylensulfidharz schmelzgesponnen wird, mit einem wässrigen Emulsionsgleitmittel verarbeitet wird, während es gezogen wird, um zu bewirken, dass das an die Oberfläche gebundene Öl 0,1 bis 1 Gew.-% ausmacht, und auf ein Gesamt-Reckverhältnis von 3,8 bis 4,5 gereckt wird, ohne dabei aufgewickelt zu werden.
8. Herstellungsverfahren für Polyphenylensulfidfasern nach Anspruch 7, wobei ein wasserfreies Gleitmittel auf das gesponnene Garn bis zu einem Gesamtprozentsatz von an die Oberfläche gebundenem Öl von 0,5 bis 2 Gew.-% aufgebracht wird.
9. Herstellungsverfahren für Polyphenylensulfidfasern nach Anspruch 7 oder 8, wobei das wässrige Emulsionsgleitmittel eine Ölkonzentration von 15 bis 40 Gew.-% aufweist.

Revendications

1. Fibre de polysulfure de phénylène ayant une finesse monofilamentaire de 10 à 100 dtex et une ténacité de 4,5 à 6 cN/dtex pouvant être obtenue par filage par fusion.
2. Fibre de polysulfure de phénylène selon la revendication 1, dans laquelle la surface fibreuse porte au moins un agent tensio-actif et un antioxydant.
3. Fibre de polysulfure de phénylène selon la revendication 1 ou 2, dans laquelle le poids total de l'huile liée à la surface représente 0,5 à 2 % en poids du poids de fibre, l'agent tensio-actif représentant 0,01 à 1 % en poids et l'antioxydant représentant 0,002 à 0,1 % en poids.
4. Fibre de polysulfure de phénylène selon l'une quelconque des revendications 1 à 3, qui est non tordue et a une finesse totale de 100 à 1 000 dtex et un nombre de filaments de 2 à 50.
5. Fibre de polysulfure de phénylène selon l'une quelconque des revendications 1 à 4, dans laquelle l'allongement est de 15 à 25 %, et le rétrécissement au séchage à 150°C est de 2 à 10 %.
6. Fibre de polysulfure de phénylène selon l'une quelconque des revendications 1 à 5, dans laquelle l'irrégularité de finesse est de 0,5 à 1 %.
7. Procédé de production de fibres de polysulfure de phénylène ayant une finesse monofilamentaire de 10 à 100 dtex et une ténacité de 4,5 à 6 cN/dtex, dans laquelle une résine de polysulfure de phénylène est filée à l'état fondu, traitée à l'aide d'un lubrifiant en émulsion aqueuse, tout en étant tirée, pour amener à ce que l'huile liée à la surface représente 0,1 à 1 % en poids et, sans être enroulée, étirée jusqu'à un rapport de tirage global de 3,8 à 4.5.
8. Procédé de production de fibres de polysulfure de phénylène selon la revendication 7, dans lequel un lubrifiant anhydre est appliqué sur le fil filé jusqu'à un pourcentage total en huile liée à la surface de 0,5 à 2 % en poids.
9. Procédé de production de fibres de polysulfure de phénylène selon l'une quelconque des revendications 7 ou 8, dans lequel le lubrifiant en émulsion aqueuse a une concentration en huile de 15 à 40 % en poids.



REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- JP SHO57143518 A [0004]
- JP HEI4100916 A [0004]
- JP 2001262436 A [0015] [0031]