(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 589 689 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
28.02.2018 Bulletin 2018/09

(21) Application number: **11801135.2**

(22) Date of filing: **29.06.2011**

(51) Int Cl.:
D01F 2/08 *(2006.01)* ***D01D 5/06*** *(2006.01)*
D01F 2/00 *(2006.01)* ***D02G 1/00*** *(2006.01)*
D01G 1/04 *(2006.01)*

(86) International application number:
PCT/KR2011/004752

(87) International publication number:
WO 2012/002729 (05.01.2012 Gazette 2012/01)

(54) **DOPE FOR SPINNING LYOCELL, METHOD FOR PREPARING LYOCELL FILAMENT FIBER , AND METHOD FOR PREPARING A LYOCELL STAPLE FIBER USING SAME**

SPINNLÖSUNG ZUM SPINNEN EINER LYOZELLE, VERFAHREN ZUR HERSTELLUNG EINER LYOZELLENFILAMENTFASER UND VERFAHREN ZUR HERSTELLUNG EINER LYOZELLENSTAPELFASER DAMIT

DOPE POUR LE FILAGE DE FIBRE CELLULOSIQUE À HAUTE TÉNACITÉ, PROCÉDÉ POUR LA PRÉPARATION DE FIBRE DE FILAMENT CELLULOSIQUE À HAUTE TÉNACITÉ UTILISANT UN TEL DOPE, ET PROCÉDÉ POUR LA PRÉPARATION DE FIBRE COURTE DE FIBRE CELLULOSIQUE À HAUTE TÉNACITÉ

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

(30) Priority: **29.09.2010 KR 20100094505**
30.06.2010 KR 20100062577

(43) Date of publication of application:
08.05.2013 Bulletin 2013/19

(73) Proprietor: **Kolon Industries, Inc.**
Gwacheon-si, Gyeonggi-do 13837 (KR)

(72) Inventors:
- **KIM, Woo-Chul**
  Daegu 711-812 (KR)
- **LEE, Sang-Mok**
  Gumi-si
  Gyeongsangbuk-do 730-020 (KR)
- **JEONG, Jong-Cheol**
  Seoul 120-103 (KR)
- **JIN, Sang-Woo**
  Daegu 704-400 (KR)

(74) Representative: **Ter Meer Steinmeister & Partner Patentanwälte mbB**
Nymphenburger Straße 4
80335 München (DE)

(56) References cited:
EP-A1- 0 952 243
EP-A2- 1 433 881
EP-A2- 1 433 881
WO-A1-02/18682
WO-A1-97/35054
WO-A1-2009/118262
KR-A- 20090 025 977
US-A- 5 601 771
US-A- 5 958 320
US-A- 5 958 320
US-A- 6 042 769
US-A1- 2004 126 577
US-A1- 2008 173 419
US-A1- 2009 127 750

- **PEREPELKIN K E: "Lyocell fibres based on direct dissolution of cellulose in N-methylmorpholine N-oxide: Development and prospects", FIBRE CHEMISTRY, KLUWER ACADEMIC PUBLISHERS-PLENUM PUBLISHERS, NE, vol. 39, no. 2, 1 March 2007 (2007-03-01), pages 163-172, XP019526813, ISSN: 1573-8493, DOI: 10.1007/S10692-007-0032-9**
- **Axel Sczostak: "Cotton Linters: An Alternative Cellulosic Raw Material", MACROMOLECULAR SYMPOSIA., vol. 280, no. 1, 1 June 2009 (2009-06-01), pages 45-53, XP055373670, DE ISSN: 1022-1360, DOI: 10.1002/masy.200950606**

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).

EP 2 589 689 B1

Description

TECHNICAL FIELD

[0001] The present invention relates to a dope for spinning lyocell, a method for manufacturing lyocell filament fiber using the dope, and a method for manufacturing lyocell staple fiber using the dope. More particularly, the present invention relates to dope for spinning lyocell, a method for manufacturing lyocell filament fiber using the dope, and a method for manufacturing lyocell staple fiber using the dope, which may provide lyocell fiber that exhibits a low orientation degree and fibrillation degree, and high elongation, and thus may be applied for fiber for high grade clothing without conducting additional processes.

BACKGROUND OF THE ART

[0002] Fiber refers to a natural or artificial linear object that has flexibility and a thin shape, and has large ratio of length to thickness. The fiber may be divided into long fiber, semi-long fiber, and short fiber in terms of the shape, and natural fiber and artificial fiber in terms of the raw material.

[0003] Fiber has been closely related to human life, and natural fiber such as cotton, linen, wool, and silk has been used as a main ingredient for clothes. With the development of scientific technology since the Industrial Revolution, the application of fiber has been enlarged to industrial use as well as a material for clothes, and to satisfy the rapidly increasing demand of fiber, artificial fiber has been developed as a new fiber material.

[0004] Among the artificial fiber, regenerated fiber has excellent feel and wearability, and has much faster moisture absorption and discharge performance than cotton, and thus it has been used a lot as a material for clothes. Particularly, among the regenerated fiber, rayon fiber has excellent gloss and color formation property, may exhibit equivalent feel to natural fiber, and is recognized as a harmless material to a human body, and thus has been widely used in the past. However, the rayon fiber is easily shrunken and wrinkled, the manufacturing process is complicated, and a lot of chemicals are used in the process of dissolving wood pulp, and the like, thus causing environmental problems in operation or environmental pollution in the process of waste water treatment and the like.

[0005] Thus, studies have been progressed on fiber that is harmless to the environment and human body and has superior properties to the existing fiber, and recently, lyocell fiber manufactured from natural pulp and amine oxide hydrate has been introduced. The lyocell fiber has superior fiber properties such as tensile property and feel, and the like, compared to the existing regenerated fiber, does not generate pollutants in the manufacturing process, and the used amine oxide based solvent is recyclable and biodegraded when discarded, and thus it is used as an environmentally friendly fiber in various fields.

[0006] However, lyocell fiber has disadvantages in that excessive fibrils are formed on the surface due to high orientation degree and weak binding force between fibrils, and thereby, the fiber surface feel and final product quality are degraded. In addition, to remove fibril from lyocell, an additional process such as acid cellulose treatment is required, thus rendering the manufacturing process complicated, increasing manufacturing cost, decreasing fabric weight in the process of fibril removal, or degrading fiber properties.

[0007] Accordingly, there is a demand for development of a method for providing high quality fiber that has a low orientation degree and fibrillation degree while maintaining the properties of environmentally friendly lyocell fiber, by a simple process without an additional process for fibril removal.

[0008] WO 2009/118262 A1 refers to solvent-spun cellulosic mouldings from a solution predominantly containing cellulose in a solvent.

[0009] KR20090025977 is directed to cellulose filament fibers including a cross-linking unit between cellulose molecules, wherein the cross-linking unit includes an aromatic group selected from a group consisting of aryl, alkylaryl or arylalkyl, heteroaryl and heteroarylalkyl and one selected from the group consisting of hydrogen, halogen, thiol, hydroxy, allyl, alkyl.

[0010] EP 1 433 881 A2 is directed to a lyocell multi-filament for a tire cord and a method of producing the same.

[0011] Axel Sczostak "Cotton Liners: An Alternative Cellulosic Raw Material", Macromolecular Symposia, vol. 280, no.1, June 2009, p. 45-53 gives an overview of cotton and cotton linters.

[0012] US 2008/0173419 A1 describes a method of making regenerated cellulose microfibers including forming segmented fibers with multiple longitudinally extending segments of slightly different composition.

DETAILED DESCRIPTION OF THE INVENTION

TECHNICAL OBJECTIVES

[0013] The present invention provides a dope for spinning lyocell that may provide lyocell fiber that exhibits a low

orientation degree and fibrillation degree, and high elongation, and thus may be applied for fiber for high grade clothing without conducting additional processes.

[0014] The present invention also provides a method for manufacturing lyocell filament fiber using the dope for spinning lyocell.

[0015] The present invention also provides lyocell filament fiber manufactured from the dope for spinning lyocell.

[0016] The present invention also provides a method for manufacturing lyocell staple fiber that exhibits a low orientation degree and fibrillation degree, and high elongation, and thus may be applied for fiber for high grade clothing without conducting additional processes.

TECHNICAL SOLUTIONS

[0017] The present invention provides dope for spinning lyocell including cotton linter pulp that comprises 99 wt% or more of alpha-cellulose, water, and N-methylmorpholine-N-oxide (NMMO).

[0018] The present invention also provides a method for manufacturing lyocell filament fiber including: discharging the spinning dope from a spinner; passing the discharged dope through a coagulation bath to coagulate it into filament; washing the filament that has passed through the coagulation bath; and drying the washed filament.

[0019] The present invention also provides lyocell filament fiber manufactured from the spinning dope.

[0020] The present invention also provides a method for manufacturing lyocell staple fiber, including: discharging spinning dope including cotton linter pulp that comprises 99 wt% or more of alpha-cellulose, and an aqueous solution of N-methylmorpholine-N-oxide (NMMO) from a spinner; passing the discharged dope through a coagulation bath to coagulate it into filament; washing the filament that has passed through the coagulation bath; drying the washed filament; crimping the dried filament; and cutting the crimped filament.

[0021] Hereinafter, dope for spinning lyocell, a method for manufacturing lyocell filament fiber, lyocell filament fiber, and a method for manufacturing lyocell staple fiber according to specific embodiments of the invention will be explained in detail.

[0022] According to one embodiment, there is provided dope for spinning lyocell including cotton linter pulp, water, and N-methylmorpholine-N-oxide (NMMO).

[0023] During the studies for solving problems of lyocell fiber in that it has high orientation degree and excessive fibrils are formed on the surface of fiber, the inventors confirmed through experiments that if dope for spinning lyocell including cotton linter pulp is applied to a specific manufacturing method as described below, lyocell fiber having a low orientation degree and fibrillation degree may be provided, and completed the invention. If the dope for spinning lyocell is used, the amount of fibrils formed on the surface of lyocell fiber or fibrillation degree becomes very low, and thus surface feel of the fiber and quality of the final product may be improved, and an additional post process may be dispensed with thus simplifying the manufacturing process and reducing manufacturing cost. Further, since lyocell fiber obtained using the dope for spinning lyocell may have a low initial modulus, it may be applied for fiber for high grade clothing such as lining of a suit, underwear, and the like.

[0024] In general, a side having a long fiber length, primarily separated from cotton seed is referred to as lint, and a side having a short fiber length, secondarily separated, is referred to as linter. The linter commonly has a fiber length of 3 to 5 mm, and it may be obtained from annual cotton, and thus is favorable for supply and demand of raw material.

[0025] As described below, since the cotton linter pulp includes a high content of alpha-cellulose, namely 99 wt% or more of alpha-cellulose, it may exhibit a low fibrillation degree, and since it contains a trace amount of impurities, it may be used for fabric for high grade clothing.

[0026] The dope for spinning lyocell may include 6 to 16 wt% of cotton linter pulp. If the content of the cotton linter pulp is less than 6 wt%, fiber properties may not be achieved, and if it is greater than 16 wt%, it may be difficult to dissolve in an aqueous solution.

[0027] The dope for spinning lyocell may include 84 to 94 wt% of an aqueous solution of N-methylmorpholine-N-oxide as a solvent ingredient. If the content of the N-methylmorpholine-N-oxide aqueous solution is less than 84 wt%, solution viscosity may become too high, and if it is greater than 94 wt%, spinning viscosity may become too low, and thus it may be difficult to manufacture uniform fiber in the spinning step.

[0028] The N-methylmorpholine-N-oxide aqueous solution may include N-methylmorpholine-N-oxide and water in a weight ratio of 91:9 to 83:17. If the weight ratio of the N-methylmorpholine-N-oxide and water is greater than 91:9, cellulose may be decomposed when dissolving cellulose, and if the weight ratio is less than 83:17, dissolving performance of the solvent may be lowered and thus it may be difficult to dissolve cellulose.

[0029] The dope for spinning lyocell may be prepared by introducing cotton linter pulp in an aqueous solution of N-methylmorpholine-N-oxide including N-methylmorpholine-N-oxide and water in a weight ratio of 90:10 to 50:50 and swelling it, and then removing water so that the weight ratio of N-methylmorpholine-N-oxide and water may become 93:7 to 85:15, and the final content of the pulp may become 6 to 16 wt%, more preferably 10 to 14 wt%.

[0030] Meanwhile, according to another embodiment, there is provided a method for manufacturing lyocell filament

fiber including: discharging the spinning dope; passing the discharged dope through a coagulation bath to coagulate it into filament; washing the filament that has passed through the coagulation bath; and drying the washed filament.

[0031] The inventors confirmed through experiments that if dope for spinning lyocell including cotton linter pulp is applied to a specific manufacturing method, the biggest problem of lyocell fiber in that it has a high orientation degree and excessive fibrils are formed on the surface of fiber may be solved, and environment-friendly lyocell fiber with excellent quality may be provided, and completed the invention. According to the manufacturing method of lyocell filament fiber, lyocell fiber having a very small amount of fibrils formed on the surface or a low fibrillation degree may be obtained, and thus an additional process need not be conducted to remove fibril, thus simplifying the process and reducing manufacturing cost. According to the manufacturing method, lyocell filament fiber that has excellent surface feel and final product quality, and simultaneously has a low initial modulus may be produced, and thus may be applied for a fabric for high grade clothing such as a lining of a suit, underwear, and the like.

[0032] The details of the dope for spinning lyocell are as explained above.

[0033] The spinner functions for passing fibrous filament through an air gap to discharge as a coagulated solution. The step of discharging the spinning dope from the spinner may be conducted at 80 to 130 °C.

[0034] Further, after discharging the spinning dope, a step of passing it through an air gap may be further conducted. The air gap functions for supplying air to the dope discharged from the spinner and pre-quenching the liquid dope. Since elongation viscosity of the dope is higher than a common dope, the temperature of the air supplied to smoothly progress the spinning process may be 5 to 30 °C, and preferably 5 to 20 °C.

[0035] Also, the air volume provided in the air gap may be 10 to 300 m^3/hr, and preferably 30 to 100 m^3/hr. If the air volume is too small, yarn cutting may be generated due to non-uniform drawing, and if it is too large, yarn cutting may be generated due to cooling of the spinner.

[0036] The dope that is discharged from the spinner and selectively passes through the air gap is coagulated in a coagulation bath and made in the form of filament, wherein the temperature of the coagulation bath is 30 °C or less. The coagulation temperature of 30 °C or less is for appropriately maintaining coagulation speed. The coagulation bath may be manufactured with a composition commonly used in the technological field of the invention without specific limitations.

[0037] Meanwhile, the method for manufacturing lyocell filament fiber may include washing the filament that has passed through the coagulation bath, and drying the washed filament.

[0038] In the step of washing the filament that has passed through the coagulation bath, considering ease of recovery and reuse of the solvent after washing, a washing solution of 0 to 100 °C may be used, water may be used as the washing solution, and if necessary, other additives may be further included.

[0039] The step of drying the washed filament may include applying tension of 0.1 to 2 g/d, preferably 0.2 to 0.5 g/d to the filament at 80 to 200 °C, preferably 100 to 150 °C. The drying step may be progressed as a single-step process, or it may be progressed as a multi-step process wherein drying conditions are varied according to each step. In the multi-step drying process, specific drying conditions of each step may be optionally selected within the above tension and temperature range, and besides the conditions, commonly used conditions in the technological field of the invention may be used.

[0040] Meanwhile, Fig. 1 schematically shows one example of a spinning apparatus that may be used for manufacturing of lyocell filament fiber. Referring to Fig. 1, a common manufacturing apparatus of lyocell multifilament includes a gear pump (11) for supplying a spinning solution at a constant pressure, a spinner (12) for spinning the spinning solution supplied from the extruder in the form of fiber, a first coagulation bath (14) for coagulating non-coagulated fiber (13) discharged from the spinner, and optionally, a second coagulation bath (15). The filament that has passed through the coagulation baths (14, 15) is introduced into a washing apparatus (17) by towing rollers (16), where a solvent and the like included in the spinning dope and the like is removed by water. Subsequently, the filament that has passed through the washing apparatus is dried in a drying apparatus (18), and then wound to obtain final lyocell filament. However, the spinning apparatus is only one example of an apparatus usable for manufacturing of lyocell filament fiber, and the manufacturing method and apparatus that can be applied in the present invention are not limited thereto.

[0041] Meanwhile, according to another embodiment of the invention, there is provided lyocell filament fiber manufactured from the dope for spinning lyocell.

[0042] As explained above, it was confirmed through experiments that if dope for spinning lyocell including cotton linter pulp is applied to a specific manufacturing method, lyocell fiber having a low orientation degree and fibrillation degree may be provided.

[0043] Since the lyocell fiber obtained by applying the dope for spinning lyocell to a specific manufacturing method has a very small amount of fibrils formed on the surface or a low fibrillation degree, for example, a fibrillation degree above grade 1, surface feel of the fiber or quality of the final product is excellent, and the fiber has low initial modulus, and thus it may be easily applied for fabric for high grade clothing such as lining of a suit, underwear, and the like.

[0044] Thereby, the lyocell filament fiber may have a fibrillation degree above grade 1. The 'fibrillation degree' means the degree of fibril generation on the surface of the filament, and specifically, it means a value measured from an image obtained by rubbing fiber for a certain time based on a water-immersed fiber to generate fibril, and observing the fibril

with optical microscope. The 'fibrillation degree' may be represented by the following General Formula 1, and as the number of generated fibrils is lower, the fiber has a higher grade of fibrillation degree.

[General Formula 1]

Fibrillation degree (grade) = number of fibril/unit length of filament (0.1 mm)

grade 0 = fibril 0
grade 1 = number of fibril < 10
grade 2 = number of fibril < 20
grade 3 = number of fibril < 50
grade 4 = number of fibril < 100
grade 5 = number of fibril > 100※ In the fibrillation degree (grade), grade 0 is the highest grade.

[0045] As described in the following Experimental Example 1, the lyocell filament fiber may have an initial modulus of 150 to 230 g/d. Further, the lyocell filament fiber may have strength of 4 to 8 g/d. The initial modulus and strength may be measured after drying the lyocell filament fiber manufactured from the dope for spinning lyocell in an oven of 105 °C for 2 hours.

[0046] The lyocell filament fiber has appropriate strength for clothing and the like, and simultaneously exhibits a low initial modulus, and thus it may be easily applied for fabric for high grade clothing such as lining of a suit, underwear, and the like.

[0047] According to yet another embodiment of the invention, there is provided a method for manufacturing lyocell staple fiber including: discharging spinning dope including cotton linter pulp that comprises 99 wt% or more of alpha-cellulose and an aqueous solution of N-methylmorpholine-N-oxide (NMMO) from a spinner; passing the discharged dope through a coagulation bath to coagulate it into filament; washing the filament that has passed through the coagulation bath; drying the washed filament; crimping the dried filament; and cutting the crimped filament.

[0048] As explained above, as result of studies, it was confirmed that according to a specific manufacturing method using dope for spinning lyocell including cotton linter pulp, lyocell fiber having a low orientation degree and fibrillation degree may be manufactured without conducting an additional process. Specifically, if the dope for spinning lyocell including cotton linter pulp is used, the amount of fibrils formed on the surface of the lyocell fiber or fibrillation degree becomes very low, thus improving surface feel of the fiber and quality of the final product, dispensing with an additional post process such as acid cellulose treatment and the like, thereby simplifying the manufacturing process and reducing manufacturing cost. And since the lyocell fiber obtained using the dope for spinning lyocell has high strength and elongation, it may be applied for a fabric for high grade clothing such as lining of a suit, underwear, and the like.

[0049] According to the above-explained manufacturing method, lyocell staple fiber, which is optimized fiber applicable for fabric for high grade clothing among lyocell fiber, may be manufactured by a relatively simplified manufacturing process.

[0050] Therefore, by the above-explained manufacturing method, lyocell staple fiber that has excellent properties due to a low orientation degree and fibrillation degree, and may be appropriately applied for fabric for high grade clothing, may be easily manufactured while simplifying the process.

[0051] The spinning dope used in the manufacturing method of lyocell staple fiber is as explained above.

[0052] In the manufacturing method of lyocell staple fiber, the details of the steps of discharging spinning dope including cotton linter pulp and an aqueous solution of N-methylmorpholine-N-oxide (NMMO) from a spinner, passing the discharged dope through a coagulation bath to coagulate it into filament, washing the filament that has passed through the coagulation bath, and drying the washed filament are as explained in the 'manufacturing method of lyocell filament fiber'.

[0053] After drying the filament, the filament is crimped. The crimping step may be progressed in a common crimper applied for manufacturing of various synthetic staple fibers. In the crimping step, to manufacture lyocell staple fiber having excellent properties, 8~20/inch, preferably 10~16/inch crimps, may be given to the filament. After crimping in this range, lyocell staple fiber is manufactured by a subsequent cutting process, thereby obtaining fiber that exhibits excellent properties such as excellent feel, and may be applied for fabric for high grade clothing.

[0054] After crimping the filament, the filament is cut to manufacture lyocell staple fiber. In the cutting step, the filament may be cut to a length of 20 to 200 mm, preferably 30 to 130 mm, so that it may be preferably used for fabric for high grade clothing. Thereby, lyocell staple fiber having corresponding length may be manufactured. The lyocell staple fiber may have an optimized form for fabric for high grade clothing and the like.

[0055] Meanwhile, Fig. 2 schematically shows one example of a spinning apparatus that may be used for manufacturing lyocell staple fiber. Referring to the construction of Fig. 2, cotton linter pulp is pulverized and stored in the lyocell staple

manufacturing apparatus, and the pulp is dissolved in a concentrated solvent, namely, an aqueous solution of N-methylmorpholine-N-oxide, to form a spinning solution, namely, spinning dope. The preparation method of the spinning dope is as explained above.

[0056] The manufacturing apparatus includes a spinner for spinning the spinning solution in the form of fiber, and a coagulation bath for coagulating non-coagulated fiber discharged from the spinner. The filament that has passed through the coagulation bath is introduced into a washing apparatus by towing rollers, where a solvent included in the spinning dope and the like is removed by water. Subsequently, the filament that has passed through the washing apparatus is supplied with an emulsion and dried in a drying apparatus, and then crimpled in a crimper, cut to a specific length, and finally manufactured into lyocell staple fiber.

[0057] The spinning apparatus of Fig. 2 is only one example used for manufacturing of lyocell staple fiber, and the manufacturing method and apparatus applicable in the present invention are not limited thereto.

[0058] Meanwhile, according to yet another embodiment of the invention, there is provided lyocell staple fiber manufactured by the above method. The staple fiber has a length of 20 to 200 mm, and thus may be appropriately applied for fabric for high grade clothing.

[0059] Since the lyocell staple fiber obtained by the manufacturing method has a very small amount of fibrils formed on the surface or a low fibrillation degree, the fibrillation degree may be above grade 1. Thus, the staple fiber has excellent surface feel and final product quality, high strength, and elongation, and thus it may be preferably applied for fabric for high grade clothing. The 'fibrillation degree' is as defined above.

[0060] As described in the following experimental example, the lyocell staple fiber may have strength of 3 to 8 g/d and elongation at break of 9.5 to 12.0 %. The strength and elongation may be obtained by pre-drying a filament specimen immediately before manufactured into staple fiber at 110 °C for 2 hours below moisture regain, and then standing for 24 hours or more under a KSK 0901 standard state so as to reach a moisture equilibrium state, and measuring with a low speed tension tester (Instron) at a tensile speed of 300 m/min.

[0061] The lyocell staple fiber exhibits appropriate elongation for clothing and excellent strength, and thus may be applied for fabric for high grade clothing such as lining of a suit, underwear, and the like.

ADVANTAGEOUS EFFECT OF THE INVENTION

[0062] According to the present invention, dope for spinning lyocell that may provide lyocell fiber that exhibits a low orientation degree and fibrillation degree, and high elongation, and thus may be applied for fiber for high grade clothing without additional processes, a method for manufacturing lyocell filament fiber using the dope, lyocell filament fiber obtained therefrom, and a method for manufacturing lyocell staple fiber using the dope are provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0063]

Fig. 1 schematically shows one example of a spinning apparatus that may be used for manufacturing lyocell filament fiber.

Fig. 2 schematically shows one example of a spinning apparatus that may be used for manufacturing of lyocell filament fiber.

DETAILS FOR PRACTICING THE INVENTION

[0064] The present invention will be explained in detail with reference to the following examples.

<Example>

Example 1: Manufacture of lyocell filament fiber from cotton linter pulp

[0065] Cotton linter pulp with a polymerization degree (DP) of 1200 (supplied from Korea Minting and Security Printing Corporation) was introduced into a pulverizer equipped with a 100 mesh filter to prepare pulp powder having a diameter of 1700 μm or less.

[0066] The pulp powder was swollen in a 50 wt% NMMO aqueous solution. The NMMO aqueous solution includes 6 wt% of the pulp, and an antioxidant was added in the content of 0.01 wt% to the cotton linter pulp.

[0067] The swollen pulp slurry was injected into a kneader maintaining an internal temperature of 90 °C and absolute pressure of 50 mmHg with a rotary valve pump at a speed of 16 kg/hour, and completely dissolved while removing extra moisture so that a 50 wt% of NMMO aqueous solution may become a 89 wt% NMMO aqueous solution, and then spinning

dope was discharged through a discharge screw.

[0068] The spinning dope was controlled so that total fineness of the final filament may become 1650 denier, and was spun using a nozzle having 1000 nozzles and a cross-sectional area of 0.47 mm^2. At this time, a 30 mm air gap was formed between the nozzle and coagulation bath, and in the air gap, 15 °C cooling air was supplied to the discharged dope at air volume of 30 m^3/hr.

[0069] The multifilament that passed through the air gap and was coagulated in the coagulation bath was washed with water in a 5-stage washing apparatus, and then non-dried multifilament yarn controlled to a moisture content of 170 % was dried in a 3-stage drying roll to obtain lyocell multifilament yarn. The tension between the 1st stage and the 2nd stage of the drying roll was controlled to 0.2 g/d, the tension between the 2nd stage and the 3rd stage was controlled to 0.5 g/d, and the temperature of each roll was sequentially controlled to 100 °C, 130 °C, and 150 °C.

[0070] The number of filaments of the manufactured lyocell filament yarn was 1000, and the mean fineness was 1.5 d.

Example 2: Manufacture of lyocell filament fiber from cotton linter pulp

[0071] Lyocell multifilament yarn was obtained by the same method as Example 1, except using cotton linter pulp of a polymerization degree (DP) of 800.

Example 3: Manufacture of staple fiber from cotton linter pulp

[0072] Cotton linter pulp (supplied from Korea Minting and Security Printing Corporation) of a polymerization degree (DP) of 1200 was introduced into a pulverizer equipped with a 100 mesh filter to prepare pulp powder having a diameter of 1700 μm or less.

[0073] The pulp powder was swollen in a 50 wt% NMMO aqueous solution. The NMMO aqueous solution included 6 wt% of the pulp, and an antioxidant was added in the content of 0.01 wt% to the cotton linter pulp.

[0074] The swollen pulp slurry was injected into a kneader maintaining an internal temperature of 90 °C and absolute pressure of 50 mmHg with a rotary valve pump at a speed of 16 kg/hour, and completely dissolved while removing extra moisture so that a 50 wt% NMMO aqueous solution may become an 89 wt% NMMO aqueous solution, and then spinning dope was discharged through a discharge screw.

[0075] The spinning dope was controlled so that total fineness of the final filament may become 45,000 denier, and was spun using a nozzle having 30,000 nozzles and a diameter of 0.2 mm. At this time, a 50 mm air gap was formed between the nozzle and the coagulation bath, and in the air gap, 15 °C cooling air was supplied to discharged dope at an air volume of 1500 m^3/hr.

[0076] The multifilament that passed through the air gap and was coagulated in the coagulation bath was washed with water in an 8-stage washing apparatus, and then non-dried multifilament yarn controlled to a moisture content of 250 % was dried in a 3-stage drying roll to obtain lyocell multifilament yarn. The tension between the 1st stage and the 2nd stage of the drying roll was controlled to 0.2 g/d, the tension between the 2nd stage and the 3rd stage was controlled to 0.5 g/d, and the temperature of each roll was sequentially controlled to 130 °C, 150 °C, and 170 °C.

[0077] The number of filaments of the manufactured lyocell filament yarn was 30,000, and the mean fineness was 1.5 d. 13/inch crimps were given to the dried filament tow in a crimper, and the crimped tow was completely dried at 120 °C in a non-tension drier (lattice drier), and then cut to 38 mm for cotton spinning, to manufacture staple fiber.

Example 4 : Manufacture of staple fiber from cotton linter pulp

[0078] Lyocell staple fiber was obtained by the same method as Example 3, except using cotton linter pulp of a polymerization degree (DP) of 800.

<Comparative Example>

Comparative Example 1: Manufacture of lyocell filament fiber from softwood pulp sheet

[0079] Softwood pulp sheet (Buckeye company, V81, DP 1200) was introduced into a pulverizer equipped with a 100 mesh filter to prepare pulp powder having a diameter of 1700 μm or less.

[0080] The pulp powder was swollen in a 50 wt% NMMO aqueous solution. The NMMO aqueous solution included 6 wt% of the pulp, and an antioxidant was added in the content of 0.01 wt% to the cotton linter pulp.

[0081] The swollen pulp slurry was injected into a kneader maintaining an internal temperature of 90 °C and absolute pressure of 50 mmHg with a rotary valve pump at a speed of 16 kg/hour, and completely dissolved while removing extra moisture so that a 50 wt% NMMO aqueous solution may become an 89 wt% of NMMO aqueous solution, and then spinning dope was discharged through a discharge screw.

[0082] The spinning dope was controlled so that total fineness of the final filament may become 45,000 denier, and was spun using a nozzle having 30,000 nozzles and a diameter of 0.2 mm. At this time, a 50 mm air gap was formed between the nozzle and the coagulation bath, and in the air gap, 15 °C cooling air was supplied to discharged dope at an air volume of 1500 m^3/hr.

[0083] The multifilament that passed through the air gap and was coagulated in the coagulation bath was washed with water in an 8-stage washing apparatus, and then non-dried multifilament yarn controlled to a moisture content of 250 % was dried in a 3-stage drying roll to obtain lyocell multifilament yarn. The tension between the 1st stage and the 2nd stage of the drying roll was controlled to 0.2 g/d, the tension between the 2nd stage and the 3rd stage was controlled to 0.5 g/d, and the temperature of each roll was sequentially controlled to 130 °C, 150 °C, and 170 °C.

[0084] The number of filaments of the manufactured lyocell filament yarn was 30,000, and the mean fineness was 1.5 d. 13/inch crimps were given to the dried filament tow in a crimper, and the crimped tow was completely dried at 120 °C in a non-tension drier (lattice drier) and then cut to 38 mm for cotton spinning, to manufacture staple fiber.

Comparative Example 2: Manufacture of lyocell filament fiber from softwood pulp sheet

[0085] Lyocell filament fiber was manufactured by the same method as Comparative Example 1, except that softwood pulp sheet (Buckeye company, V-60, DP 800) was introduced into a pulverizer equipped with a 100 mesh filter to prepare pulp powder having a diameter of 1700 μm or less.

Comparative Example 3: Manufacture of staple fiber from softwood pulp sheet

[0086] Softwood pulp sheet (Buckeye company, V81, DP 1200) was introduced into a pulverizer equipped with a 100 mesh filter to prepare pulp powder having a diameter of 1700 μm or less.

[0087] The pulp powder was swollen in a 50 wt% NMMO aqueous solution. The NMMO aqueous solution included 6 wt% of the pulp, and an antioxidant was added in the content of 0.01 wt% to the cotton linter pulp.

[0088] The swollen pulp slurry was injected into a kneader maintaining an interior temperature of 90 °C and absolute pressure of 50 mmHg with a rotary valve pump at a speed of 16 kg/hour, and completely dissolved while removing extra moisture so that a 50 wt% NMMO aqueous solution may become an 89 wt% of NMMO aqueous solution, and then spinning dope was discharged through a discharge screw.

[0089] The spinning dope was controlled so that total fineness of the final filament may become 45,000 denier, and was spun using a nozzle having 30,000 nozzles and a diameter of 0.2 mm. At this time, a 50 mm air gap was formed between the nozzle and the coagulation bath, and in the air gap, 15 °C cooling air was supplied to discharged dope at an air volume of 1500 m^3/hr.

[0090] The multifilament that passed through the air gap and was coagulated in the coagulation bath was washed with water in an 8-stage washing apparatus, and then the non-dried multifilament yarn controlled to a moisture content of 250 % was dried in a 3-stage drying roll to obtain lyocell multifilament yarn. The tension between the 1st stage and the 2nd stage of the drying roll was controlled to 0.2 g/d, the tension between the 2nd stage and the 3rd stage was controlled to 0.5 g/d, and the temperature of each roll was sequentially controlled to 130 °C, 150 °C, and 170 °C.

[0091] The number of filaments of the manufactured lyocell filament yarn was 30,000, and the mean fineness was 1.5 d. 13/inch crimps were given to the dried filament tow in a crimper, and the crimped tow was completely dried at 120 °C in a non-tension drier (lattice drier) and then cut to 38 mm for cotton spinning, to manufacture staple fiber.

Comparative Example 4: Manufacture of staple fiber from softwood pulp sheet

[0092] Staple fiber was manufactured by the same method as Comparative Example 3, except that softwood pulp sheet (Buckeye company, V-60, DP 800) was introduced into a pulverizer equipped with a 100 mesh filter to prepare pulp powder having a diameter of 1700 μm or less.

<Experimental Example>

Experimental Example 1: Measurement of tensile strength and initial modulus of lyocell filament fiber

[0093] Strength and elongation of the lyocell filament fiber obtained in the examples and comparative examples were measured using a universal testing machine (Model 5566, Instron) according to ASTM D-885. For this, the lyocell filament fiber obtained in Examples 1 to 2 and Comparative Examples 1 to 2 was dried in an oven at 105 °C for 2 hours.

[0094] Specific measurement conditions are as follows, and the measurement results are shown as mean values of 10 repeated experiments.

(1) tensile strength

1) crosshead speed: 300 mm/min
2) experimental error: ±1 MPa

(2) Initial modulus

1) Head Speed: 300 mm/min
2) Grip Distance: 250 mm
3) 25 °C and 60 RH% atmosphere

Experimental Example 2: Measurement of tensile strength and elongation at break of lyocell staple fiber

[0095] To measure tensile strength and elongation at break, the filament tow immediately before being finally cut in Examples 3 and 4 and Comparative Examples 3 and 4 was extracted as a specimen. The length of the specimen was controlled to 250 mm.

[0096] After pre-drying each specimen at 110 °C for 2 hours below moisture regain, it was allowed to stand under a KSK 0901 standard state for 24 hours or more so as to reach a moisture equilibrium state, and tensile strength and elongation at break were measured at a tensile speed of 300 mm/min using a low speed elongation tensile tester (Instron).

Experimental Example 3: Measurement of alpha-cellulose content of raw pulp

[0097] The pulp powder of the examples and comparative examples were immersed in a 17.5 % NaOH solution at 20 °C for 20 minutes, and then non-dissolved material was dried and the weight was measured. The non-dissolved material is alpha cellulose, and the content was calculated according to the following General Formula 2.

[General Formula 2]

$$\text{Content of alpha cellulose of raw pulp (\%)} = W/S \times 100$$

[W = dried weight of remaining fiber (g), S = dried weight of pulp sample (g)]

Experimental Example 4: Measurement of Fibrillation degree

[0098] 0.1g of a filament cut to 5 mm and 1 ml of pure water were introduced into a cylindrical cylinder with a diameter of 10 mm and a length of 30 mm, and the cylinder was sealed and then fibrillation degree of the lyocell filament fiber obtained in the examples and comparative examples was measured using an apparatus for reciprocating 10 times per second. the specific measurement method and conditions are as follows.

[0099] The image of generated fibril was analyzed with an optical microscope to measure the number of generated fibrils per unit length. The 'fibrillation degree' may be represented by the following General Formula 1.

[General Formula 1]

$$\text{Fibrillation degree (Grade)} = \text{number of fibrils/unit length of filament (0.1 mm)}$$

Grade 0 = fibril 0

Grade 1 = number of fibril < 10

Grade 2 = number of fibril < 20

Grade 3 = number of fibril < 50

Grade 4 = number of fibril < 100

Grade 5 = number of fibril > 100

[0100] The results of the Experimental Examples 1 to 4 are described in the following Table 1.

[Table 1]

	Spinning dope raw material	Pulp polymerization degree (DP)	Tensile strength (g/d)	Initial modulus (g/d)	Elongation at break of Staple fiber (%)	Alpha cellulose content of raw pulp (wt%)	Fibrillation degree
Example1	Cotton linter	1200	7.5	220		99.5	1
Example2	Cotton linter	800	5.3	190		99.5	1
Example3	Cotton linter	1200	5.5		10.5	99.5	1
Example4	Cotton linter	800	4.4		10.4	99.5	1
Comparative Example1	Softwood pulp	1200	6.8	260		97.1	4
Comparative Example 2	Softwood pulp	800	4.7	240		95.5	5
Comparative Example 3	Softwood pulp	1200	5.2		10.7	97.1	4
Comparative Example 4	Softwood pulp	800	4.1		10.3	95.5	5

[0101] Referring to the Table 1, it was confirmed that the lyocell staple fiber manufactured in the examples exhibits elongation equal to or better than the conventional fiber of the comparative examples, and simultaneously exhibits better strength and remarkably superior fibrillation degree.

[0102] Accordingly, the staple fiber of the examples maintains excellent strength and elongation, and simultaneously exhibits excellent feel due to the excellent fibrillation degree and thus it may be preferably applied for a fabric for high grade clothing and the like.

Symbols

[0103]

11: gear pump
12: spinner
13: non-coagulated fiber
14: first coagulation bath
15: second coagulation bath
16: towing roller
17: washing apparatus
18: drying apparatus

Claims

1. Dope for spinning lyocell, comprising:

   cotton linter pulp that comprises 99 wt% or more of alpha-cellulose; and
   an aqueous solution of N-methylmorpholine-N-oxide (NMMO).

2. The dope for spinning lyocell according to claim 1, comprising:

   6 to 16 wt% of the cotton linter pulp; and
   84 to 94 wt% of the aqueous solution of N-methylmorpholine-N-oxide.

3. The dope for spinning lyocell according to claim 1, wherein the aqueous solution of N-methylmorpholine-N-oxide comprises N-methylmorpholine-N-oxide and water in a weight ratio of 91:9 to 83:17.

4. A method for manufacturing lyocell filament fiber, comprising:

   discharging the spinning dope according to any one of claims 1 to 3 from a spinner;
   passing the discharged dope through a coagulation bath to coagulate it into a filament;
   washing the filament that has passed through the coagulation bath; and
   drying the washed filament.

5. The method for manufacturing lyocell filament fiber according to claim 4, wherein the discharging of the spinning dope from a spinner is conducted at 80 to 130 °C.

6. The method for manufacturing lyocell filament fiber according to claim 4, wherein the drying of the washed filament comprises applying tension of 0.1 to 1 g/d to the filament at 80 to 200 °C.

7. Lyocell filament fiber manufactured according to any one of claims 4 to 6.

8. The lyocell filament fiber according to claim 7, wherein the lyocell filament fiber has strength of 4 to 8 g/d and an initial modulus of 150 to 230 g/d.

9. A method for manufacturing lyocell staple fiber, comprising:

   discharging spinning dope comprising cotton linter pulp that comprises 99 wt% or more of alpha-cellulose and an aqueous solution of N-methylmorpholine-N-oxide (NMMO) from a spinner;
   passing the discharged dope through a coagulation bath to coagulate it into a filament;
   washing the filament that has passed through the coagulation bath;
   drying the washed filament;
   crimping the dried filament; and
   cutting the crimped filament.

10. The method for manufacturing lyocell staple fiber according to claim 9, wherein the step of crimping includes giving 8~20/inch of crimps to the filament.

11. The method for manufacturing lyocell staple fiber according to claim 9, wherein the step of cutting includes cutting the filament into a length of 20 to 200mm.

Patentansprüche

1. Spinnlösung zum Spinnen von Lyocell, umfassend:

   Baumwolllinterzellstoff, der 99 Gew.-% oder mehr alpha-Cellulose enthält; und
   eine wässrige Lösung von N-Methylmorpholin-N-oxid (NMMO).

2. Spinnlösung zum Spinnen von Lyocell nach Anspruch 1, umfassend:

6 bis 16 Gew.-% des Baumwolllinterzellstoffs; und
84 bis 94 Gew.-% der wässrigen Lösung von N-Methylmorpholin-N-oxid.

3. Spinnlösung zum Spinnen von Lyocell nach Anspruch 1, wobei die wässrigen Lösung von N-Methylmorpholin-N-oxid N-Methylmorpholin-N-oxid und Wasser in einem Gewichtsverhältnis von 91:9 bis 83:17 umfasst.

4. Verfahren zur Herstellung von Lyocell-Filamentfaser, umfassend:

Abziehen der Spinnlösung nach irgendeinem der Ansprüche 1 bis 3 von einem Spinner;
Passieren der abgezogenen Spinnlösung durch ein Koagulationsbad, um diese zu einem Filament zu koagulieren;
Waschen des Filaments, welches das Koagulationsbad passiert hat; und
Trocknen des gewaschenen Filaments.

5. Verfahren zur Herstellung von Lyocell-Filamentfaser nach Anspruch 4, wobei das Abziehen der Spinnlösung von einem Spinner bei 80 bis 130°C durchgeführt wird.

6. Verfahren zur Herstellung von Lyocell-Filamentfaser nach Anspruch 4, wobei das Trocknen des gewaschenen Filaments das Anlegen einer Spannung von 0,1 bis 1 g/d an das Filament bei 80 bis 200°C umfasst.

7. Lyocell-Filamentfaser, hergestellt nach irgendeinem der Ansprüche 4 bis 6.

8. Lyocell-Filamentfaser nach Anspruch 7, wobei die Lyocell-Filamentfaser eine Festigkeit von 4 bis 8 g/d und einen Anfangsmodul von 150 bis 230 g/d aufweist.

9. Verfahren zur Herstellung von Lyocell-Stapelfaser, umfassend:

Abziehen einer Spinnlösung, umfassend Baumwolllinterzellstoff, welcher 99 Gew.-% oder mehr alpha-Cellulose und eine wässrige Lösung von N-Methylmorpholin-N-oxid (NMMO) enthält, von einem Spinner;
Passieren der abgezogenen Spinnlösung durch ein Koagulationsbad, um diese zu einem Filament zu koagulieren;
Waschen des Filaments, welches das Koagulationsbad passiert hat;
Trocknen des gewaschenen Filaments;
Kräuseln des getrockneten Filaments; und
Schneiden des gekräuselten Filaments.

10. Verfahren zur Herstellung von Lyocell-Stapelfaser nach Anspruch 9, wobei der Schritt des Kräuselns das Vorsehen von 8-20/Inch Kräuselungen an dem Filament beinhaltet.

11. Verfahren zur Herstellung von Lyocell-Stapelfaser nach Anspruch 9, wobei der Schritt des Schneidens das Schneiden des Filaments zu einer Länge von 20 bis 200 mm beinhaltet.

Revendications

1. Pâte pour le filage de lyocell, comprenant:

de la pulpe de linter de coton comprenant 99% en poids ou plus d'alpha-cellulose, et
une solution aqueuse de N-méthylmorpholine-N-oxyde (NMMO).

2. La pâte pour le filage de lyocell selon la revendication 1, comprenant:

de 6 à 16% en poids de la pulpe de linter de coton; et
de 84 à 94% en poids de la solution aqueuse de N-méthylmorpholine-N-oxyde.

3. La pâte pour le filage de lyocell selon la revendication 1, dans laquelle la solution aqueuse de N-méthylmorpholine-N-oxyde comprend du N-méthylmorpholine-N-oxyde et de l'eau dans un rapport pondéral de 91:9 à 83:17.

4. Un procédé de fabrication d'une fibre de filament de lyocell, comprenant:

le déchargement de la pâte pour le filage selon l'une quelconque des revendications 1 à 3 à partir d'une centrifugeuse;
le faire passer de la pâte déchargée dans un bain de coagulation pour la coaguler en un filament;
le lavage du filament qui a traversé le bain de coagulation; et
le séchage du filament lavé.

5. Un procédé de fabrication d'une fibre de filament de lyocell selon la revendication 4, dans lequel la décharge de la pâte à filer à partir d'une centrifugeuse est conduite à une température de 80 à 130 ° C.

6. Le procédé de fabrication d'une fibre de filament de lyocell selon la revendication 4, dans lequel le séchage du filament lavé comprend l'application d'une tension de 0,1 à 1 g / d sur le filament de 80 à 200 ° C.

7. Une fibre de filament de lyocell fabriquée selon l'une quelconque des revendications 4 à 6.

8. La fibre de filament de lyocell selon la revendication 7, dans laquelle la fibre de filament de lyocell a une résistance de 4 à 8 g / d et un module initial de 150 à 230 g / d.

9. Un procédé de fabrication d'une fibre discontinue de lyocell, comprenant:

le déchargement d'une pâte pour le filage comprenant une pulpe de linter de coton comprenant 99% en poids ou plus d'alpha-cellulose et une solution aqueuse de N-méthylmorpholine-N-oxyde (NMMO) à partir d'une centrifugeuse;
le faire passer de la pâte déchargée dans un bain de coagulation pour la coaguler en un filament;
le lavage du filament qui a traversé le bain de coagulation;
le séchage du filament lavé;
le sertissage du filament séché; et
la coupe du filament sertissé.

10. Le procédé de fabrication d'une fibre discontinue de lyocell selon la revendication 9, dans lequel l'étape de sertissage comprend la fourniture de 8 à 20 / pouce de sertissages au filament.

11. Le procédé de fabrication d'une fibre discontinue de lyocell selon la revendication 9, dans lequel l'étape de coupe comprend la coupe du filament sur une longueur de 20 à 200 mm.

Figure 1

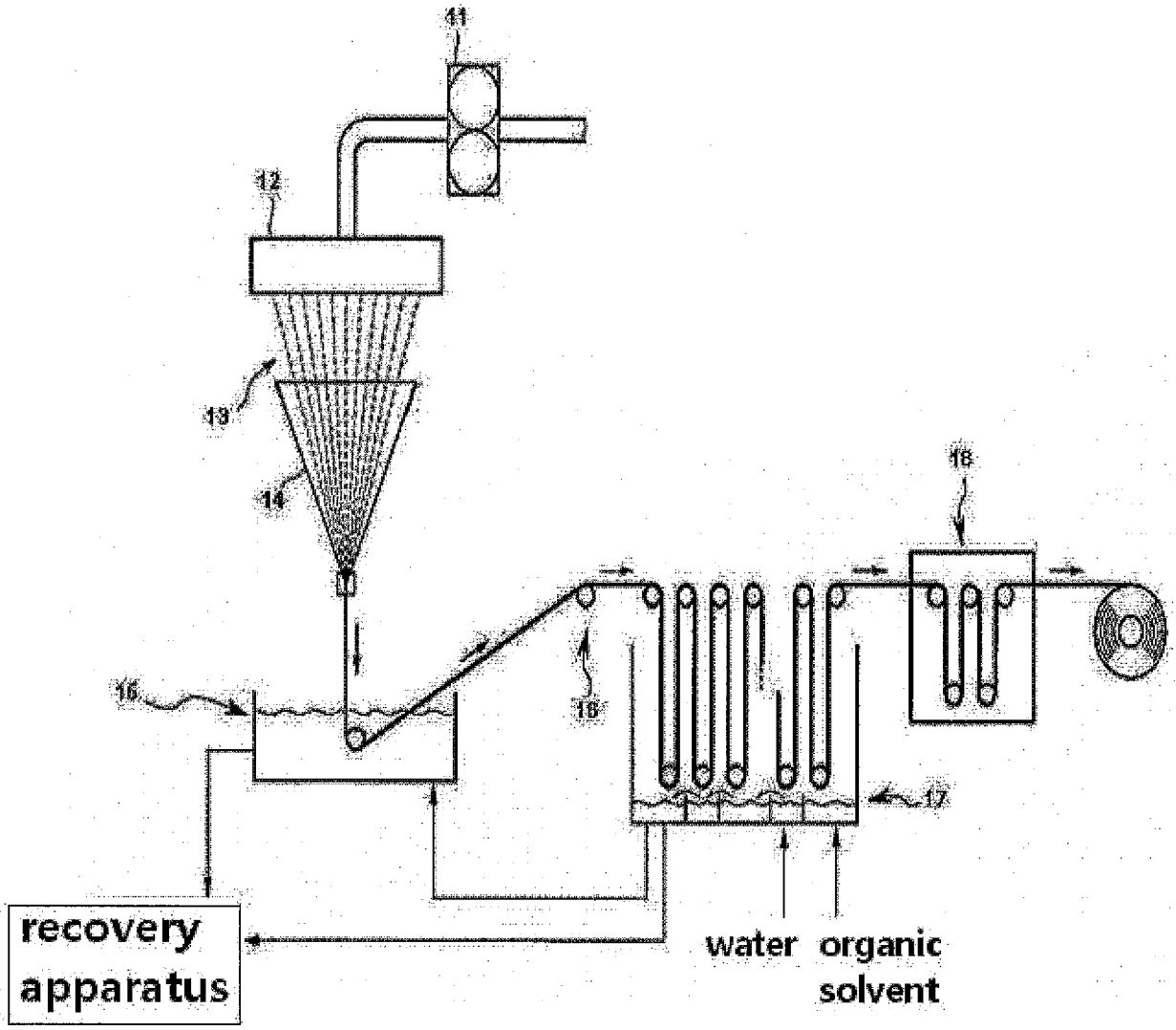
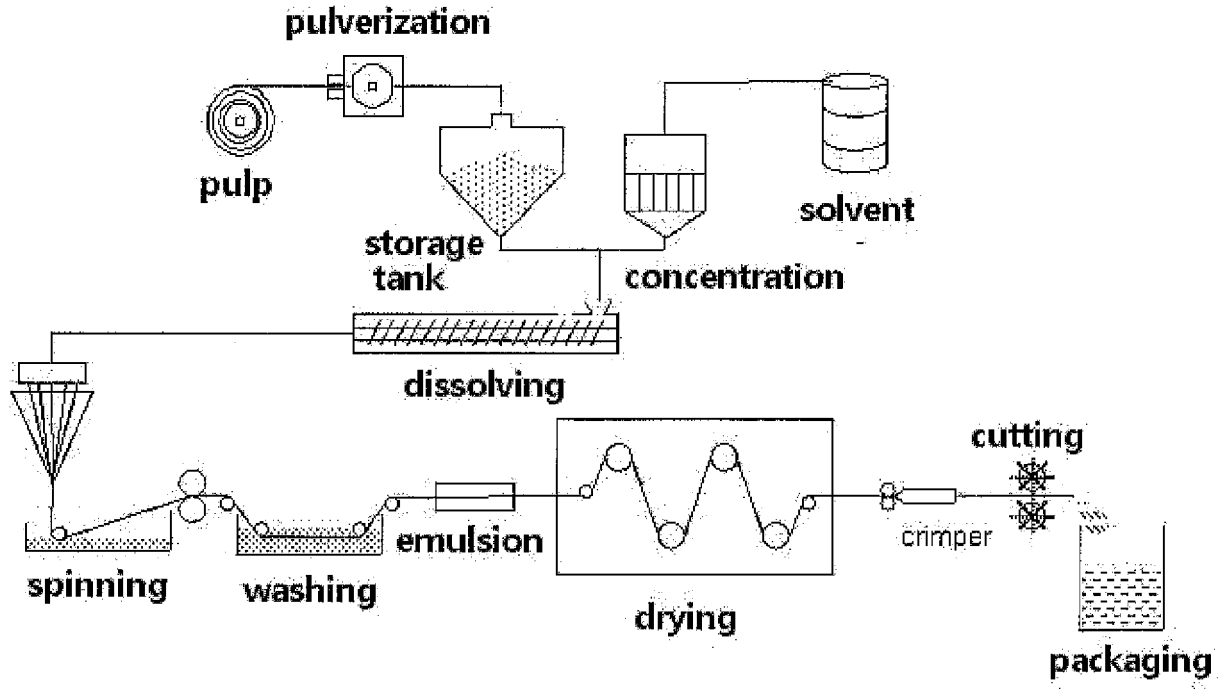

11
12
13
14
15
16
17
18
recovery apparatus
water
organic solvent

Figure 2


pulverization
pulp
storage tank
concentration
solvent
dissolving
spinning
washing
emulsion
drying
cutting
crimper
packaging

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

- WO 2009118262 A1 **[0008]**
- KR 20090025977 **[0009]**
- EP 1433881 A2 **[0010]**
- US 20080173419 A1 **[0012]**

Non-patent literature cited in the description

- **AXEL SCZOSTAK.** Cotton Liners: An Alternative Cellulosic Raw Material. *Macromolecular Symposia,* June 2009, vol. 280 (1), 45-53 **[0011]**