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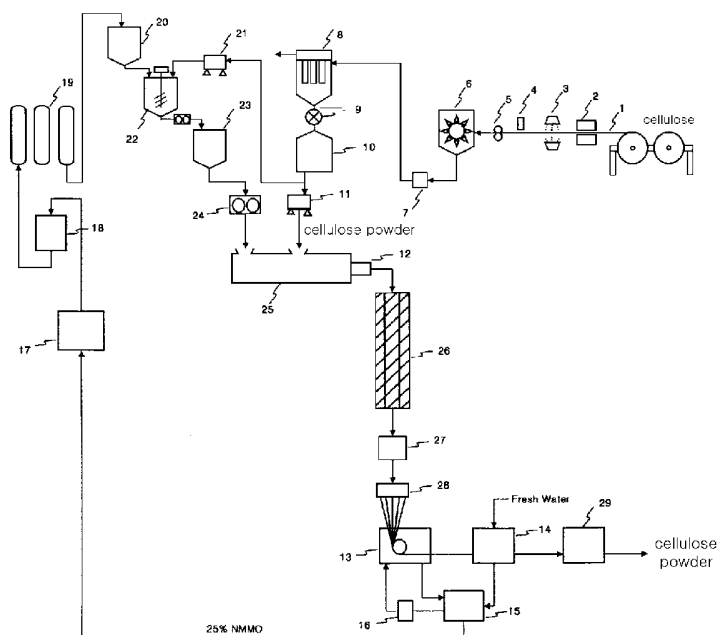
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(54) Title: METHOD FOR PRODUCING CELLULOSE FIBER



(57) Abstract: The present invention relates to a production of a cellulose solution which is homogeneous at low temperatures, by dissolving a small amount of the cellulose powder in concentrated liquid-state to lower the solidification temperature of NMMO, introducing the low-temperature, concentrated liquid-state solution having cellulose dissolved and the cellulose powder into a kneader, mixing and swelling the cellulose in the kneader without a process of reducing pressure to produce a paste, and then supplying the paste into an extruder to dissolve the paste in a homogeneous solution.

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Description

METHOD FOR PRODUCING CELLULOSE FIBER

Technical Field

- [1] The present invention relates to a method for producing a cellulose solution which is homogeneous at low temperatures, and to fiber produced by the method. More particularly, the invention relates to a production of a cellulose solution which is homogeneous at low temperatures, by dissolving a small amount of the cellulose powder in concentrated liquid-state N-methylmorpholine-N-oxide (NMMO) to lower the solidification temperature of NMMO, introducing the low-temperature, concentrated liquid-state NMMO solution having cellulose dissolved and the cellulose powder into a kneader, mixing and swelling the cellulose in the kneader without a process of reducing pressure to produce a paste, and then supplying the paste into an extruder to dissolve the paste in a homogeneous solution.

[2]

Background Art

- [3] The fiber produced from the cellulose solution has excellent tenacity and dimensional stability, and thus can be usefully used for making a single fiber or a filament for clothing, as well as for making an industrial filament fiber or a reinforcing material for rubber products such as a tire and a belt.
- [4] Cellulose has very high affinity for other materials, but cellulose is hardly soluble in general solvents because of the crystalline structure formed from the molecular chain or the strong hydrogen bonding between the chains. Among the solvents that are capable of destroying such the crystalline structure and producing a solution, the most widely used is N-methylmorpholine-N-oxide (NMMO).
- [5] The process for production of cellulose fiber using the NMMO solvent is frequently used in the processes for production of cellulose-based products, from the perspectives that the solvent can be all recovered, recycling of the solvent involves a pollution-free process, and the fiber and film thus produced have high mechanical strength.
- [6] U.S. Patent Nos. 3,447,935 discloses the process for production of cellulose fiber using the NMMO solvent.
- [7] U.S. Patent Nos. 4,142,913, 4,144,080 disclose manufacturing methods for making cellulose solution by obtaining cellulose solution by under reduced pressure distillation of cellulose that is swelled and dispersed in NMMO hydrates, solidifying the cellulose solution to a precursor (solid-state) by cooling the cellulose solution (a kind of 'making chips' and melting in an extruder. These methods simplify the melting process by using an extruder, but require relatively long time and a large amount of energy because of

the preceding 'making chips' And also, the precursor is hard to protect from heat and humidity.

- [8] U.S. Patent No. 5,584,919 discloses a manufacturing method for making cellulose solution by preparing solid-state NMMO comprising 5 to 17% by weight water, feeding the solid-state NMMO with cellulose powder into a horizontal cylinder-type high speed mixer and mixing them to make a granule type precursor, and melting the precursor using an extruder. This method, however, has a disadvantage of a wide distribution of the obtained the precursor and low yield. If the volume of the raw material is larger, the distribution of the obtained precursor is more widened. And a complicated cooling apparatus is required to transfer and store the precursor. And also, the solid-state NMMO is hard to manufacture and store.
- [9] U.S. Patent Nos. 5,094,690, 5,534,113 and 5,603,883 disclose a manufacturing method for making cellulose solution by dispersing cellulose in the NMMO comprising 40% by weight water to make slurry, removing the water from the slurry by using a Force-drive type thin-layer distillation apparatus that can form a thin, solution-layer, and obtaining the cellulose solution. These methods, however, have disadvantages of a low efficiency to the volume of the raw material because the slurry was distilled the water and melted by rotating of the rotor so slurry was downstreamed. It caused a short dwelling time in the above apparatus. And also, these methods require a relatively long time and relatively a large amount of energy to produce cellulose solution, and the obtained fiber using the above cellulose solution gets worse the tenacity by degradation of cellulose and change of color of the NMMO.
- [10] U.S. Patent Nos. 5,421,525, 5,456,748, 5,534,113 and 5,888,288 disclose manufacturing methods cellulose solution by mixing pulp crashed into irregular flat type with NMMO comprising 22% by weight water in a horizontal cylinder-type mixer and swelling them, swelling again by stirring for hours in a storage hopper, removing the water form the high viscid solution by using a Force-drive type thin-layer distillation apparatus so as to obtain the melted cellulose solution. These methods, however, have a disadvantage of extra handling and feeding of dust pulp produced as by-product during when crash the pulp into irregular flat type pulp. And also, it is hard to operate the horizontal cylinder-type mixer to discharge the swelled solution. In U.S. Patent No. 5,921,675 discloses a horizontal cylinder-type mixer comprising a conveyor screw at the outlet of the mixer.
- [11] U.S. Patent No. 5,948,905 discloses a manufacturing method for making cellulose solution by distilling the water from a mixture of cellulose and NMMO hydrates comprising about 23% by weight. In this method, the mixture was distilled under reduced pressure during passing the nozzle having 1.5 to 6.0millimeter diameter. It is composed of multi-stage chambers. The first-stage chamber has a small number of

nozzles having relatively large diameter. As the chamber's stage is increased, the number of nozzle is increased and the diameter of the hole of the nozzle is decreased so as to increase the cross-sectional area in order to upgrade the efficiency of water vaporization. At the stage of eighth, the last stage, an extruder is used. This method, however, has a disadvantage of needing of a highly complicated apparatus that is composed of many chambers different each other and comprised too many screws for shifting the chambers and distilling stages.

[12] PCT WO 1997/47790 discloses a manufacturing method for making cellulose solution by solving cellulose powder in the liquid-state NMMO directly in a twin-screw type extruder. The cellulose solution is produced by feeding the liquid-state NMMO comprising 12% by weight water into the first barrel of the extruder maintaining an inner temperature of 100°C, feeding cellulose powder into the third barrel of the extruder maintaining an inner temperature of 75°C, shifting and mixing them, and obtaining the solution by rising the temperature to 120°C. In this method, however, three barrel of the extruder is used for feeding the cellulose powder and NMMO, and another barrel is required for melting the cellulose. In fact, there is a relatively short swelling zone so as to obtain cellulose solution comprising undissolved cellulose particles. So, this method is effective to proceed relatively small amount of raw material, however, it is not proper to adapt a mass production of cellulose solution because there are too many undissolved moiety. And it is not proper economically because of requiring a lot of filter system. And also, this method has a disadvantage of too short spinning cycle. If the swelling zone of the extruder is increased by increasing the number of blocks and the L/D(length/diameter) of the screw, it is hard to control the swelling condition and the melting condition concurrently because the screws of the extruder are driven by single driving shaft.

[13] Korean patent application laid-open publication No. 2002-24689 discloses a manufacturing method for making highly homogenized cellulose solution by obtaining a mixture of swelled cellulose pulp powder and liquid-state NMMO by using the liquid-state NMMO that is overcooled by cooling air and melting the mixture. This method, however, is hard to control the temperature of the overcooled NMMO by using the cooling air and to control the content of the NMMO because of exposing of the moisture contained in the cooling air.

[14] As described above, the prior arts provided manufacturing methods for making cellulose solution by contacting cellulose with NMMO containing 20 to 40% by weight water firstly, then, distilling the water by using a variety of distillation apparatus, followed by swelling and melting the cellulose. There are, however, some disadvantages of shifting high viscose solution, equipping an apparatus for dwelling the raw materials for the time to distill the water from high viscose solution, an over-

sizing of an apparatus for distilling water under reduced pressure and a large amount of energy consuming, etc. And, there is an idea according to the prior arts to manufacture cellulose solution by solving cellulose powder directly in the liquid-state NMMO comprising about 13% by weight. This method, however, has a disadvantage of remaining undissolved moiety that caused by melting the cellulose immediately without swelling when the cellulose contacts with the NMMO maintaining at the temperature of 80°C(the crystallization temperature of NMMO) or more that has too high reaction activation.

- [15] When observing the cellulose fiber of the pulp for solving morphologically, the holes (hereinafter, referred to as 'pit' that penetrate water and the thickness of the cell walls were distributed not uniformly. So, there are some areas that water can penetrate easily and other areas that water can penetrate hardly. And this made some differences to penetrate NMMO in the cellulose in a pre-determined time. And, these tendencies were showed in case of manufacturing pulp from wood fiber according to the kinds of wood fiber and processes used for making pulp. Consequently, to obtain fully homogenized cellulose solution, it is required that the solvent is fully penetrate to the cellulose wholly and swelled the cellulose. Otherwise, there remains some not- moiety by not fully melted that caused by regional differences of the solubility inter- or intra-fibers of the cellulose fibers. Thus, controlling the packing state of cellulose and the reaction activity of NMMO is a critical technique in the manufacture of cellulose solutions.

[16]

Disclosure of Invention

Technical Problem

- [17] Conventional methods for making cellulose solutions have problems such as complicated processes which are disadvantageous in mass production, undesirable addition of purification processes due to cellulose decomposition and NMMO discoloration occurring as the time for production of solution is lengthened, cellulose decomposition due to high temperature, and low homogeneity of the cellulose solution. In order to solve these problems and thus to produce homogeneous cellulose solutions for lyocell, it is desired that the NMMO solvent sufficiently penetrates into the macrostructure and the microstructure of cellulose over the entire surface area within a short period of time at a low temperature and a low shear force, thereby the NMMO solvent indefinitely swelling cellulose and then dissolving the cellulose.

[18]

Technical Solution

- [19] The present invention solves such conventional problems and, thus provides a ho-

mogeneous cellulose solution even at low temperatures and a method for producing cellulose fiber from the cellulose solution.

- [20] It is an object of the invention to provide a cellulose solution by dissolving a small amount of the cellulose powder in concentrated liquid-state N-methylmorpholine-N-oxide (NMMO) to lower the solidification temperature of NMMO; subsequently introducing the low-temperature, concentrated liquid-state NMMO solution and the cellulose powder into a kneader; making a paste by mixing and swelling the cellulose or by partially dissolving the cellulose in the NMMO solution in the kneader without reducing pressure; and then feeding the paste into an extruder to dissolve the cellulose to a homogeneous state; and a fiber produced therefrom.
- [21] The invention is characterized in that when a kneader system is used, complete dissolution does not occur in the kneader, and a paste prepared by mixing and swelling the cellulose or by partially dissolving the cellulose is fed into an extruder, in which only the step of dissolution is carried out. Therefore, according to the invention, a large quantity of solution can be produced in a unit time, compared with the conventional method of using an extruder only, which is constituted of respective compartments for introducing raw materials employing NMMO of high concentration to dissolve cellulose, mixing, swelling, and dissolving. In addition, the method of the present invention is advantageous in that a simple mechanical apparatus is used, compared with the conventional method of using a complicated apparatus in which NMMO of low concentration is used to mix and swell cellulose, and then the cellulose is dissolved while the solvent is concentrated by removing water.
- [22] According to a suitable embodiment of the invention, the method for making a cellulose fiber from a homogeneous cellulose solution comprises the steps of (A) preparing an NMMO solution by dissolving a cellulose powder in concentrated liquid-state N-methylmorpholine-N-oxide (NMMO) to a small amount of 0.01 to 5% by weight; (B) introducing the NMMO solution having a small amount of the cellulose powder dissolved and the cellulose powder into a kneader, subsequently making a paste by mixing and swelling the cellulose in the kneader without reducing pressure, and then feeding the paste into an extruder; (C) spinning the cellulose solution by extrusion through a spinning nozzle, and then solidifying the spun cellulose solution which has passed through an air bed to reach a solidifying bath, to obtain a multi-filament; and (D) washing, drying, oil-treating and winding the obtained multi-filament.
- [23] According to another suitable embodiment of the invention, the liquid-state NMMO having a small amount of cellulose dissolved may be maintained at a temperature of 50°C to 95°C in the step (A).
- [24] According to another suitable embodiment of the invention, the kneader into which

the NMMO solution having the small amount of cellulose dissolved and the cellulose powder are introduced may be maintained at 50°C to 95°C in the step (B).

[25] According to another suitable embodiment of the invention, the NMMO solution at the step (A) may contain moisture in an amount of 10 to 18% by weight of the total weight of the NMMO solution.

[26] According to another suitable embodiment of the invention, after the dissolution in the extruder in the step (B), the final cellulose solution may contain cellulose at a concentration of 5 to 20% by weight of the total weight of the cellulose solution.

[27] According to another suitable embodiment of the invention, the liquid-state NMMO having a small amount of cellulose dissolved at the step (B) may be fed to the kneader while being maintained at a temperature of 50°C to 95°C.

[28] According to another suitable embodiment of the invention, the cellulose powder at the step (A) or the step (B) may be mixed with other polymer materials.

[29]

Advantageous Effects

[30] According to the method of the invention, when an NMMO solution having a small amount of the cellulose powder dissolved in concentrated liquid-state NMMO, the solidification temperature of the NMMO is lowered, and NMMO can be introduced and mixed in definite amounts at a low temperature, thereby rapid generation of film on the surface of the cellulose powder or powder lumps possibly being prevented. Further, a homogeneous cellulose solution can be produced even at a low temperature, and upon spinning, a low temperature homogeneous cellulose solution can be used to inhibit the property of cellulose undergoing decomposition at high temperatures in the extruder, thus allowing production of cellulose molded articles having excellent flexibility and strength.

[31]

Brief Description of the Drawings

[32] Hereinbelow, the present invention will be described in detail with reference to the accompanying drawings in which:

[33] Fig. 1 is a scheme briefly illustrating the process for producing a homogeneous cellulose solution by dissolving a small amount of the cellulose powder in NMMO of the invention;

[34] Fig. 2 is a scheme illustrating the entire production process for according to the invention; and

[35] Fig. 3 is a diagram showing the change behavior of the solidification temperature of NMMO in accordance with the cellulose concentration.

[36]

Best Mode for Carrying Out the Invention

- [37] Fig. 1 is a scheme briefly illustrating the procedure of the process for producing a homogeneous cellulose solution at a low temperature by dissolving a small amount of cellulose in NMMO according to an embodiment of the present invention.
- [38] The cellulose powder used in Fig. 1 is obtained by pulverizing by means of a pulverizer equipped with a knife bar, and has a particle size of 5000 μm or less, and more specifically 500 μm or less. When the size of the cellulose powder exceeds 5000 μm , it is difficult to uniformly disperse the cellulose powder, and thus there is a problem that the swelling process requires a long time.
- [39] In concentrated liquid-state NMMO, a small amount of the cellulose powder having a particle size of 5000 μm or less is first dissolved. The content of the cellulose powder is 0.01 to 5% by weight, and more specifically 0.1 to 3% by weight, with respect to the concentrated liquid-state NMMO. When the content of the cellulose powder is less than 0.01% by weight, the effect of the cellulose powder on the lowering of the solidification temperature of NMMO is negligible, thus not contributing to the swellability. On the other hand, when the content of the cellulose powder exceeds 5% by weight, the viscosity of the NMMO solution increases, thus the process of mixing and swelling in the kneader requiring a long time. Thereafter, the NMMO solution at a concentration of 20 to 30% by weight is concentrated by a conventional method to produce concentrated liquid-state NMMO having a water content of 10 to 18% by weight. When the NMMO solution is concentrated to have a water content of less than 10% by weight, it is economically disadvantageous because of increased costs. When the water content exceeds 18% by weight, the solubility of the cellulose powder may be deteriorated. Subsequently, the NMMO solution having a small amount of the cellulose powder dissolved is introduced into a kneader which has been maintained at 50 to 95°C. Then, the cellulose is mixed and swelled in the kneader without reducing pressure, to form a paste, and then the paste is fed to an extruder, where the paste is dissolved to a homogeneous state to form a homogeneous cellulose solution.
- [40] The NMMO solution having a small amount of the cellulose powder dissolved can be fed to the kneader by means of a gear pump or a screw type feeder, and is preferably introduced into the kneader by means of a screw type feeder.
- [41] The content of the cellulose powder in the cellulose solution mixed and swelled in the kneader is adjusted to 5 to 20% by weight, and more specifically 9 to 14% by weight, with respect to the total weight of the liquid-state NMMO solution in accordance with the degree of polymerization of the cellulose polymer.
- [42] When the content of the cellulose powder in the cellulose solution in the kneader is

less than 5% by weight, the finally obtained fiber may not have the properties required from fiber. On the other hand, when the content of the cellulose powder exceeds 20% by weight, it is difficult to dissolve the cellulose powder in the liquid-state NMMO, and thus a homogeneous solution cannot be obtained.

[43] According to the invention, after introducing the cellulose solution into the kneader in the step (B), cellulose is mixed and swelled in the kneader without a process of reducing pressure, to form a paste, and then the paste is fed to an extruder, where the paste is dissolved in a homogeneous state to produce a homogeneous solution. The extruder used for this purpose is preferably a twin-screw type extruder, and the twin-screw type extruder may have 3 to 16 barrels or may have the ratio L/D of the screw in the range of 12 to 64. When the number of barrels is less than 3, or when the ratio L/D of the screw is less than 12, the time taken by the cellulose solution to pass over the barrels is short, and thereby undissolved components are likely to be generated. On the other hand, when the number of barrels exceeds 16, or when the ratio L/D of the screw exceeds 64, an excessive stress may be exerted on the screws, and thereby the screws may undergo deformation.

[44] According to the invention, the cellulose powder at the step (A) or step (B) may be mixed with other polymer materials or additives. Especially, in the step (A), a polymer material such as polyvinyl alcohol, polyethylene, polyethylene glycol, polymethyl methacrylate or a cellulose derivative, or an additive such as titanium dioxide, silicon dioxide, carbon or ammonium chloride may be mixed into the cellulose solution, in order to impart stability or spinnability to the cellulose solution, or to impart functionality to the final molded product.

[45] Fig. 2 is a scheme briefly illustrating the process of the invention for producing a highly homogeneous cellulose solution used for the production of lyocell, and the fiber. Referring to Fig. 2, a pulp sheet 1 is conveyed by a nip roller 5 to a pulverizer 6. Here, the pulp sheet 1 is passed through a drying chamber 2 adjusted to a constant temperature and then is cooled by dry air 3 to be maintained at 25°C. Before passing the nip roller 5, the dry temperature of the drying chamber 2 is controlled by a contact-type moisture content measuring device so that the moisture content may not exceed 7%. Commonly supplied pulp has a moisture content of about 8 to 10%. However, the moisture content of the powdered cellulose stored in a storage tank 10 after pulverization may vary depending on the seasonal changes in humidity and temperature. When the moisture content is high, aggregation of the pulp easily occurs, and it is difficult to obtain a homogeneous solution. In addition, there occurs variance in the composition of NMMO/cellulose/water, and there also occurs variance in the thickness of the fiber spun out through a nozzle 28, thus a uniform product not being obtained. The particle size of the powdered cellulose can be adjusted according to the size of the

screen sieve disposed inside the pulverizer 6 equipped with a knife, and a powder having a size of 5000 μm or less, and more specifically, 500 μm or less, can be favorably used. When the particle size of the powder is 5000 μm or greater, aggregation of the pulp may easily occur during the mixing with NMMO in the kneader, and such aggregated pulp may obstruct production of a homogeneous solution. The powdered cellulose passing through the screen sieve of the pulverizer 6 is supplied through a blower system 7 to a backfilter 8, while air is discharged out, with the powdered cellulose being fed to a powdered cellulose storage tank 10 through a rotary valve 9. The powdered cellulose is fed into a kneader 25 through a precise weight metering device 11.

[46] The used NMMO that is generated during the process is controlled at a concentration of 20 to 35% by weight in control bath 15 and fed to a purification column 17, where ionic materials, carbide impurities and the like are removed, and the purified NMMO is stored in the supply tank 18 of a concentration column. The NMMO is supplied in definite amounts from the supply tank of the concentration column sequentially to three falling film concentration columns 19, and is produced into an aqueous solution of NMMO at a final concentration of 86 to 88% by weight. The concentrated NMMO is fed to a jacketed storage tank 20 which is maintained at 95°C, and the liquid-state NMMO 20 and the cellulose powder 21 are metered to a dissolution tank 22 equipped with a combination mixer for high viscosity dissolution, in order to be produced into an NMMO solution having a small amount of 0.01 to 5% by weight of cellulose powder dissolved. The produced solution is transported to a solution base tank 23, and is supplied in definite amounts together with the cellulose powder 11 into the kneader 25 through a gear pump 24.

[47] The kneader 25 which is maintained at a desired temperature by heat medium jacketing can be adjusted to a temperature of about 50 to 95°C, and the suitable temperature may vary depending on the concentration of the cellulose dissolved in the introduced NMMO, the molecular weight of the cellulose powder used, and the final cellulose concentration.

[48] When the low-temperature NMMO in which a small amount of cellulose is dissolved and the cellulose powder are mixed and kneaded in the kneader at 50 to 95°C, NMMO penetrates uniformly to the entire area of the cellulose, thereby forming a paste. As the paste is transported forward, the paste makes cellulose to swell and starts to partially dissolve the cellulose. The paste is supplied to a twin screw extruder 26 through a forced transporting device 12. The internal temperature of the twin-screw type extruder is adjusted in the range of 60°C to 105°C, and the cellulose in the paste is completely dissolved under the effects of the temperature increase and the shear force. The obtained cellulose solution passes through a filter 27 and then is spun through a

nozzle 28, and the spun cellulose is solidified in solidifying bath 13, washed in washing bath 14, and then finally dried to be produced into a cellulose fiber in dryer 29. A concentration of the used NMMO that is generated during the solidifying and washing process is controlled in control bath 15, and then the controlled NMMO is fed to the solidifying bath 13 by pump 16.

[49] Fig. 3 is a diagram illustrating the change behavior of the solidification temperature of NMMO in accordance with the cellulose concentration. Referring to Fig. 3, it can be seen that even if a small amount (about 0.01 to 6%) of cellulose is dissolved, the solidification temperature of NMMO is remarkably lowered from 75°C to 30°C.

[50] As shown in Fig. 1, according to the invention, a small amount of the cellulose powder is dissolved in concentrated liquid-state NMMO in order to lower the solidification temperature of the NMMO solution. By this, the NMMO solution can be fed to the kneader in the liquid state at a relatively low temperature. Thus, the process can be carried out in a wide range of temperature, and also, the cellulose powder and the NMMO solution can be easily mixed and swelled at a low temperature. This prevents generation of film on the surface of the cellulose powder, and eventually, a cellulose solution which is homogeneous even at low temperatures can be produced.

[51]

[52] The following Examples are provided for the readers' clear understanding of the present invention, but the scope of the invention is not intended to be limited by the Examples. In the Examples described below, the following evaluation methods and measuring methods were employed.

[53]

[54] (a) Homogeneity of cellulose solution

[55] A sample of the cellulose solution produced according to the invention was taken from the solution transport line immediately after passing through a kneader and being discharged from a twin-screw type extruder and was subjected to eye observation with a polarized microscope, and then the solubility of the cellulose solution was evaluated. The extent of the dissolved state was classified into 5 grades. The completely dissolved state was rated as Grade '1', while an unspinnable state where a large quantity of undissolved components were present was rated as Grade '5'. The intermediate grades were classified into Grades 2, 3 and 4 in accordance with the amount of residual undissolved cellulose.

[56]

[57] (b) Degree of polymerization (DPw)

[58] The intrinsic viscosity [IV] of the dissolved cellulose is measured as follows. 0.5M cupriethylenediamine hydroxide solution in the range of 0.1 to 0.6g/dl concentration obtained according to ASTM D539-51T is measured by using an Uberod viscometer at

25±0.01°C. The intrinsic viscosity is calculated from the specific viscosity by using the calculation method of extrapolation and then Mark-Hauwink's equation to obtain the degree of polymerization.

[59]
$$[\text{IV}] = 0.98 \times 10^{-2} \text{DP}_w^{0.9}$$

[60]

[61] (c) The properties of the cellulose fiber produced according to the invention were measured as follows.

[62] Dry strength: strength after drying at 107°C for 2 hours (g/d)

[63] Wet strength: strength measured after standing at 25°C and 65% RH for 24 hours (g/d)

[64]

Mode for the Invention

[65] EXAMPLES 1 THROUGH 12

[66] A cellulose sheet having a weight average degree of polymerization of 1,200 (V-81 available from Buckeye Technologies) was dried in a drying chamber to have a moisture content of 6.5 to 10%. A cellulose powder having a particle size of 500 μm or less and a moisture content of 3.5 to 7% by weight was produced using a pulverizer equipped with a screen sieve having a mesh size of 500 μm, and liquid-state NMMO concentrated to 87.5% by weight in a falling film concentration column and maintained at 90°C was produced. During the process of concentrating the liquid-state NMMO, 0.001% by weight, with respect to the concentrated liquid-state NMMO, of an antioxidant was added and dissolved.

[67] The liquid-state NMMO and the cellulose powder were metered into a dissolution tank equipped with a combination mixer for high viscosity dissolution, and a NMMO solution having cellulose powder dissolved to a small amount of 0.01 to 2.5% by weight was produced. The produced NMMO solution was introduced in definite amounts to a kneader whose internal temperature was maintained at 50 to 95°C, by means of a gear pump. The cellulose powder was metered by a precise weight metering device (K-tron feeder) and was introduced to the kneader, so that the final concentration of the cellulose paste was 11% by weight of the total solution. The kneader used herein had a volume of about 30 L, and the speed of the rotating blade was 20 to 30 rpm. The produced paste was transported by force to be fed into a co-rotating twin-screw type extruder. The twin-screw type extruder used had a screw with a diameter of 47 mmΦ and the barrel temperature at the initial feeding section was maintained at 60 to 70°C, while the barrel temperature at the final discharge section was maintained at 95 to 105°C. The produced paste was swelled and dissolved, and was fed to a nozzle through a gear pump after passing through a filter. For the

evaluation of solution homogeneity, sampling was done from the solution transport line immediately after discharge from the twin-screw type extruder.

[68] The cellulose solution was discharged through a nozzle having 1,000 orifices, in which the orifice diameter was 150 μm , and the orifices's interval was 1.5 mm. The length of the air bed was maintained to be 90 mm, and the temperature and relative humidity of the cooling air blown from the air bed to the filament were 25°C and 45% RH, respectively. The blowing speed was adjusted to 6.5 m/sec. The filament entering a solidifying bath from the air bed was washed, dried, oil-treated and then wound. The fineness of the finally obtained multi-filament was adjusted to 1500 deniers.

[69] The results of Examples 1 through 12 are presented in Table 1.

[70]

[71] Table 1

[72]

Example	1	2	3	4	5	6	7	8	9	10	11	12
Concentration of cellulose dissolved in NMMO solution (%)	0.01	0.1	0.1	0.5	0.5	0.5	1.2	1.2	1.2	1.2	2.0	2.5
Temperature of NMMO solution introduced into kneader (°C)	78	75	75	67	70	65	59	53	60	57	53	87
Temperature of kneader (°C)	75	70	85	70	75	68	67	51	66	66	55	91
Rotating speed of kneader (r.p.m)	30	30	30	30	30	30	30	20	30	25	30	30
Rotating speed of extruder (r.p.m)	200	200	200	180	200	230	200	180	250	200	150	250
Temperature of final barrel in extruder (°C)	105	100	100	95	100	95	105	95	100	95	95	105
Amount of produced solution(k g/h.r)	110	140	130	180	170	180	220	170	230	170	160	235
Moisture content of cellulose powder (%)	4.3	3.9	4.1	3.9	4.0	4.0	4.2	4.8	4.4	4.9	4.0	7.5
Homogeneity of solution (1~5)	2	2	2	1	1	2	1	1	1	3	2	2
Dpw of filament	1010	1030	960	990	1000	970	1040	1020	930	1020	1020	980
Strength of filament (g/d)	7.0	7.3	6.7	7.1	7.0	6.5	7.0	7.5	6.9	6.9	7.3	7.2
Blowratio of filament (%)	5.9	6.1	5.4	6.2	6.7	6.4	5.7	5.9	5.4	5.0	5.5	6.5

[73] EXAMPLES 13 THROUGH 22

[74] A cellulose sheet having a weight average degree of polymerization of 850 (V-60 available from Buckeye Technologies) was dried in a drying chamber to have a moisture content of 6.5 to 10%. A cellulose powder having a particle size of 500 μ m or less and a moisture content of 3.5 to 7% by weight was produced using a pulverizer equipped with a screen sieve having a mesh size of 500 μ m, and liquid-state NMMO concentrated to 87.5% by weight in a falling film concentration column and maintained at 85°C was produced. During the process of concentrating the liquid-state NMMO, 0.001% by weight, with respect to the concentrated liquid-state NMMO, of an antioxidant was added and dissolved.

[75] The liquid-state NMMO and the cellulose powder were metered into a dissolution tank equipped with a combination mixer for high viscosity dissolution, and a NMMO

solution having cellulose powder dissolved to a small amount of 0.1 to 5% by weight was produced. The produced NMMO solution was introduced in definite amounts to a kneader whose internal temperature was maintained at 50 to 95°C, by means of a gear pump. The cellulose powder was metered by a precise weight metering device and was introduced to the kneader, so that the final concentration of the cellulose paste was 13% by weight of the total solution. The kneader used herein had a volume of about 30 L, and the speed of the rotating blade was 20 to 30 rpm. The produced paste was transported by force to be fed into a co-rotating twin-screw type extruder. The twin-screw type extruder used had a screw with a diameter of 47 mm Φ and the barrel temperature at the initial feeding section was maintained at 50 to 70°C, while the barrel temperature at the final discharge section was maintained at 95 to 105°C. The produced paste was swelled and dissolved, and was fed to a nozzle through a gear pump after passing through a filter. For the evaluation of solution homogeneity, sampling was done from the solution transport line immediately after discharge from the twin-screw type extruder.

[76] The cellulose solution was discharged through a nozzle having 50 orifices, in which the orifice diameter was 150 mm, and the orifices's interval was 2.5 mm. The length of the air bed was maintained to be 60 mm, and the temperature and relative humidity of the cooling air blown from the air bed to the filament were 23°C and 55% RH, respectively. The blowing speed was adjusted to 7 m/sec. The filament entering a solidifying bath from the air bed was washed, dried, oil-treated and then wound. The fineness of the finally obtained multi-filament was adjusted to 50 to 100 deniers.

[77] In Example 22, a multi-filament was produced by the same method as that used in Examples 13 to 21, except that a cellulose sheet having an average weight degree of polymerization of 700 (Buckeye Technologies) was used.

[78] The results of Examples 13 through 22 are presented in Table 2.

[79] Table 2

[80]

Example	13	14	15	16	17	18	19	20	21	22
Concentration of cellulose dissolved in NMMO solution (%)	0.1	0.1	0.5	0.5	1.2	1.2	1.2	2.0	3.0	5.0
Temperature of NMMO solution introduced into kneader (°C)	75	75	67	70	63	65	65	61	55	52
Temperature of kneader (°C)	70	80	75	75	67	70	75	65	57	54
Rotating speed of kneader (r p m)	30	30	30	30	20	30	25	30	30	30
Rotating speed of extruder (r p m)	180	180	180	230	180	250	200	150	250	250
Temperature of final barrel in extruder (°C)	100	95	95	100	95	100	105	95	105	100
Amount of produced solution(kg/hr)	160	160	210	220	180	220	190	170	180	240
Moisture content of cellulose powder (%)	4.9	4.3	3.7	4.5	4.9	4.2	5.3	4.9	4.5	4.7
Homogeneity of solution (1~5)	1	2	1	1	1	1	2	2	2	1
Dpw of filament	750	730	750	700	720	690	710	760	745	630
Strength of filament (g/d)	5.3	5.7	4.9	5.4	5.5	4.8	5.3	6.1	6.3	4.5
Elongation of filament (%)	7.1	7.4	7.2	6.7	6.9	7.0	6.5	6.3	6.7	8.1

[81] COMPARATIVE EXAMPLES 1 THROUGH 8

[82] Unlike Examples 1 through 22, in Comparative Examples 1 through 5, the high-temperature, pure NMMO containing no dissolved pulp was introduced into a kneader and was mixed with cellulose powder and swelled in the kneader. The resulting product was dissolved in the extruder to produce a cellulose solution.

[83] In Comparative Examples 6 through 8, unlike the Examples, only a twin-screw type extruder was used without using a kneader. Thus, liquid-state NMMO at a concentration 86.5% by weight, which was maintained at 95°C, was introduced into a first barrel, and cellulose powder was introduced to a third barrel through a lateral twin-

screw type feeder. A cellulose solution was produced by mixing, swelling and dissolving the cellulose, while adjusting the temperature of the twin-screw type extruder. The other processing conditions are presented in Table 3, in comparison with those of Examples 1 through 22.

[84]

[85]

[86]

Table 3

Comparative Example	1	2	3	4	5	6	7	8
DP	1200	1200	1200	1200	850	850	850	850
Concentration of cellulose dissolved in NMMO solution (%)	0	0	0	0	0	0	0	0
Temperature of NMMO solution introduced into kneader (°C)	95	-	-	-	95	-	-	-
Temperature of kneader (°C)	90	-	-	-	90	-	-	-
Rotating speed of kneader (r pm)	30	-	-	-	25	-	-	-
Rotating speed of extruder (r pm)	200	150	200	250	200	150	200	250
Temperature of final Barrel in extruder (°C)	105	95	95	95	105	100	95	105
Amount of produced solution (k g/h r)	105	55	65	80	120	65	70	80
Moisture content of Cellulose Powder (%)	5.1	4.1	4.1	3.9	5.1	4.3	4.5	3.9
Homogeneity of Solution (1~5)	3	3	2	4	3	4	2	2
Dpw of filament	1020	1050	990	900	690	740	700	680
Strength of filament (g/d)	6.3	7.1	6.9	6.5	5.5	5.7	5.4	4.9
Elongation of filament (%)	5.5	5.2	4.8	4.0	6.5	7.0	6.7	6.5

Industrial Applicability

[87]

According to the present invention, cellulose is pulverized by controlling the

moisture content of a pulp sheet, and a small amount of the cellulose powder is dissolved in concentrated liquid-state NMMO to lower the solidification temperature of the NMMO. By this, an NMMO solution can be fed to a kneader at a relatively low temperature, and the cellulose powder and the NMMO solution can be easily mixed and swelled in the kneader at low temperatures. When only a high-temperature NMMO solution is used, rapid swelling and dissolving at the surface of the cellulose powder or powder lumps may occur during the initial mixing and swelling process, and thus aggregation of the cellulose powder may occur. In addition, only the surface of the powder lumps is dissolved or swelled, while the powder at the inner side takes a long time to be dissolved, thus undissolved components possibly being generated. However, according to the method of the invention, when an NMMO solution having a small amount of the cellulose powder dissolved in concentrated liquid-state NMMO, the solidification temperature of the NMMO is lowered, and NMMO can be introduced and mixed in definite amounts at a low temperature, thereby rapid generation of film on the surface of the cellulose powder or powder lumps possibly being prevented. Further, a homogeneous cellulose solution can be produced even at a low temperature, and upon spinning, a low temperature homogeneous cellulose solution can be used to inhibit the property of cellulose undergoing decomposition at high temperatures in the extruder, thus allowing production of cellulose molded articles having excellent flexibility and strength.

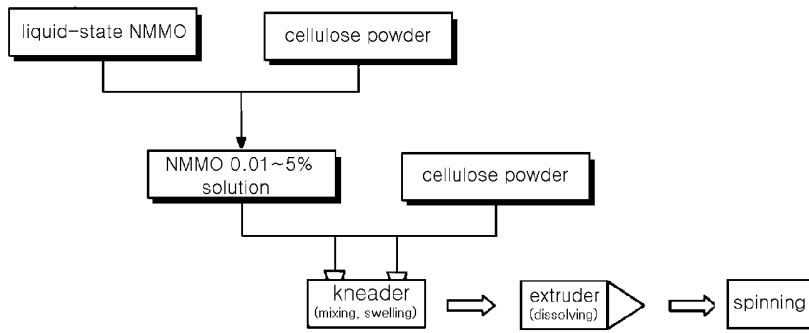
- [88] In particular, pulp having low specific gravity can be easily introduced into a kneader having a high internal space as suggested in the present invention, and thus the output of the solution and the output of the cellulose molded articles can be increased. Also, direct introduction of concentrated NMMO at a concentration of about 86.5% by weight eliminates the need for a separate water evaporating unit utilizing reduced pressure, thus simplifying the structure of the apparatus. In addition, by controlling the particle size and the moisture content of the powdered cellulose, the swelling and dissolution of the surface film of the cellulose due to aggregation of the cellulose powder, and subsequent occurrence of undissolved cellulose particles can be prevented. Accordingly, the filter exchange interval is shortened. Furthermore, a cellulose paste which has been preliminarily swelled is produced in the kneader and fed to a twin-screw type extruder in a state having the minimum volume, and thus screw arrangement inside the twin-screw type extruder is less stressful. That is to say, insertion of reverse screw elements or kneading discs can be minimized, and thus the residence time distribution for the cellulose solution in the extruder may be made narrow, thus decomposition of the cellulose being prevented. The use of a twin-screw type extruder having high shear force efficiency immediately after the kneader, allows reduction of the dissolution time and dissolution temperature, and since reduction of

the original degree of polymerization of pulp is minimized, the high molecular weight can be maintained. Thus, a cellulose fiber having excellent properties can be produced by the method according to the present invention.

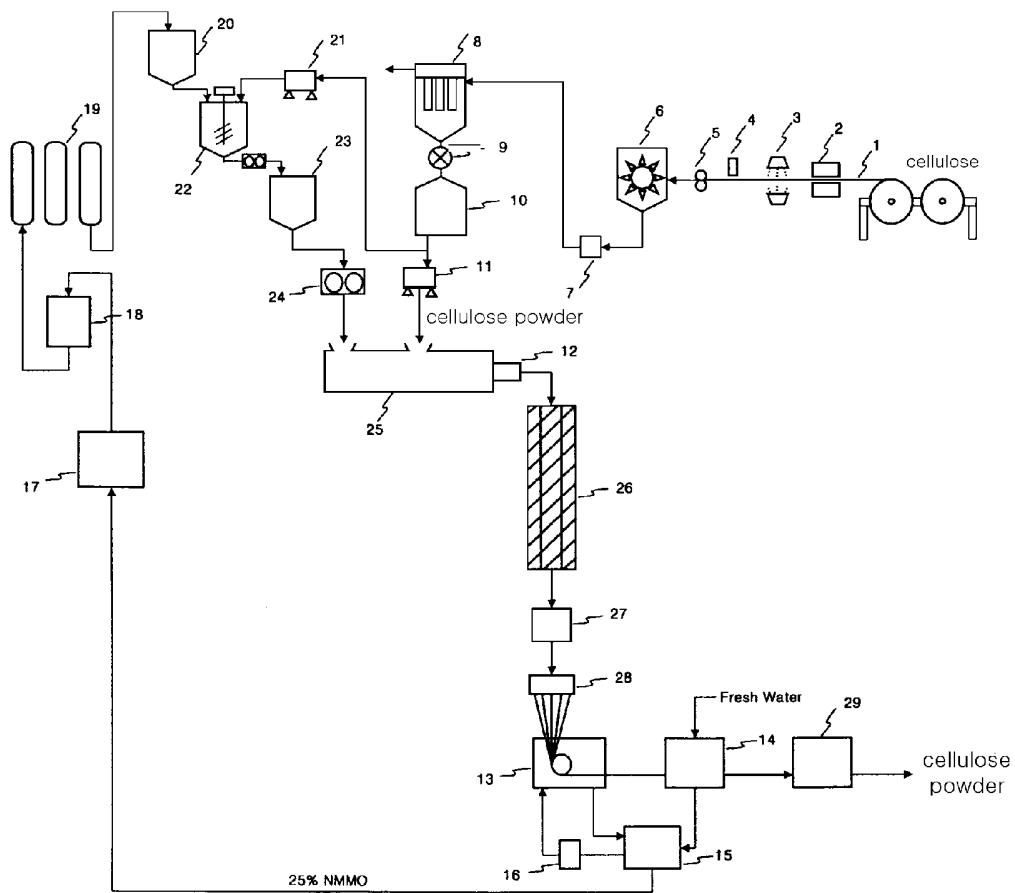
Claims

- [1] A method for producing a cellulose fiber comprising the steps of:
(A) preparing an N-methylmorpholine-N-oxide solution by dissolving a cellulose powder in concentrated liquid-state N-methylmorpholine-N-oxide (NMMO) to a small amount of 0.01 to 5% by weight;
(B) introducing the N-methylmorpholine-N-oxide solution having a small amount of the cellulose powder dissolved and cellulose powder into a kneader, mixing, swelling and partially dissolving the cellulose in the kneader without reducing the pressure to produce a paste, and then feeding the paste to an extruder to obtain a homogenized cellulose solution;
(C) spinning the cellulose solution by extrusion through a spinning nozzle, and then solidifying the spun cellulose solution which has reached a solidifying bath through an air bed to obtain a multi-filament; and
(D) washing, drying, oil-treating and winding the obtained multi-filament.
- [2] The method for producing a cellulose fiber according to claim 1, wherein the liquid-state N-methylmorpholine-N-oxide having a small amount of cellulose dissolved is maintained at a temperature of 50°C to 95°C in the step (A).
- [3] The method for producing a cellulose fiber according to claim 1, wherein the kneader into which the N-methylmorpholine-N-oxide solution having a small amount of cellulose dissolved are introduced is maintained at 50°C to 95°C in the step (B).
- [4] The method for producing a cellulose fiber according to claim 1, wherein the final cellulose solution prepared by dissolution in the extruder in the step (B) contains cellulose at a concentration of 5 to 20% by weight with respect to the total weight of the solution.
- [5] The method for producing a cellulose fiber according to claim 1, wherein the N-methylmorpholine-N-oxide solution at the step (A) contains moisture in an amount of 10 to 18% by weight with respect to the total weight of the solution.
- [6] The method for producing a cellulose fiber according to claim 1, wherein the liquid-state N-methylmorpholine-N-oxide having a small amount of cellulose dissolved is supplied to the kneader while being maintained at a temperature of 50°C to 95°C in the step (B).
- [7] The method for producing a cellulose fiber according to claim 1, wherein the cellulose powder at the step (A) or step (B) is mixed with other polymer materials.

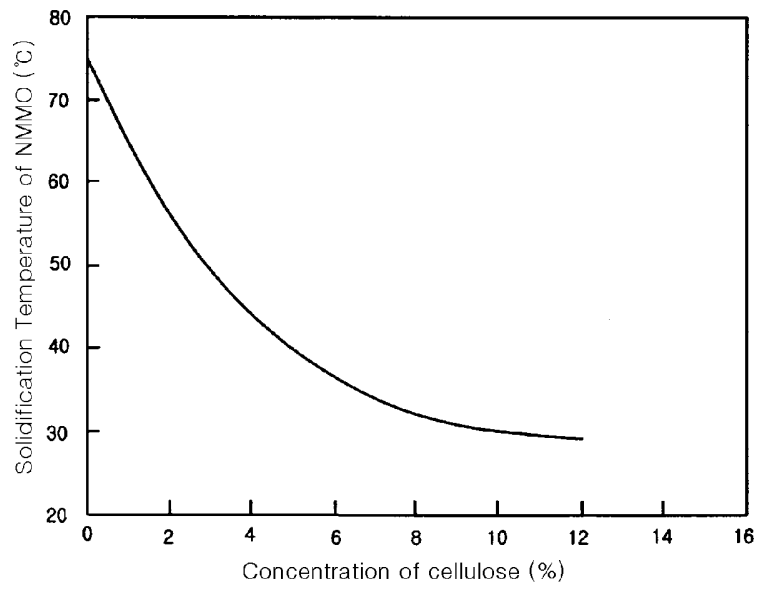
[Fig. 1]



[Fig. 2]



[Fig. 3]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2005/004677**A. CLASSIFICATION OF SUBJECT MATTER***D01F 2/00(2006.01)i*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC8 D01F

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

KR, JP : IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CA 2400709 A (HYOSUNG CORP.) 30 November 2003 (30.11.2003) see the whole documents	1-7
A	US 5891375 A (ALFACEL S.A.) 06 April 1999 (06.04.1999) see the whole documents	1-7
A	US 5951933 A (ALFACEL S.A.) 14 September 1999 (14.09.1999) see the whole documents	1-7
A	KR 2003-79053 A (HYOSUNG CORP.) 10 October 2003 (10.10.2003) see the whole documents	1-7

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

* Special categories of cited documents:

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2005/004677

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CA 2400709 A	30.11.2003	CA 2400709 A KR 2003-92895 A JP 16-2623 A	30.11.2003 06.12.2003 08.01.2004
US 5891375 A	06.04.1999	US 5891375 A	06.04.1999
US 5951933 A	14.09.1999	US 5951933 A	14.09.1999
KR 2003-79053 A	10.10.2003	KR 2003-79053 A	10.10.2003