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(56) References cited:

EP-A- 1 433 881

EP-A- 1 493 752

US-A1- 2003 155 673

Description**BACKGROUND OF THE INVENTION**

5 **[0001]** The present invention relates to cellulose fiber having homogeneous physical property, in particular cellulose fiber for using as industrial materials, preferably tire-cord produced as following steps: preparing a homogeneous cellulose solution by swelling a cellulose powder with a concentrated liquid N-methyl morpholine N-oxide (NMMO); extruded-spinning the cellulose solution through an air gap using a spinning nozzle with 500 to 2000 of orifices and then obtaining a multi-filaments after solidifying the spun cellulose solution; and winding the multi-filaments after water-washing, drying and treating with a finishing oil.

10 **[0002]** In particular, the present invention relates to cellulose fiber having 500 to 2000 filaments, and is characterized in that the strength of multi-filaments is 35.3 to 79.4 cN/tex (4 to 9 g/d), the breaking elongation is 4 to 15% and the multi-filaments have homogeneous physical properties. More specifically, the present invention relates to the cellulose multi-filaments for use of industrial materials, in which each 100 mono-filaments selected from each three parts divided 15 from the multi-filaments have the properties as following; a) 26.5 to 79.4 cN/tex (3 to 9 g/d) in average, 7 to 15% in average breaking elongation and 0.035 to 0.055 in average birefringence, b) the differences of three parts in average strength, breaking elongation and denier are below 8.8 cN/tex (1.0 g/d), 1.5 % and 0.69 cN (0.7 denier), respectively, c) CV(coefficient of variation)(%) of three parts in average strength, breaking elongation and denier is below 10 %, and d) the differences of the average birefringence of three parts are below 0.004.

20 **[0003]** A cellulose fiber manufactured with cellulose and NMMO is utilized in various fields needing the cellulose fiber in the process of manufacturing, because all the solvent used in the process of manufacture of the cellulose fiber is recycled and therefore the manufacture of the cellulose fiber corresponds to a non-pollution process, and the produced fiber has high mechanical strength, and referring to EPO no. 0356419 a cellulose solution produced using amine oxide together with NMMO is described, and US patent no. 4246221 discloses a method for producing a cellulose solution with a tertiary amine oxide, and according to the above US patent no. 4246221 the cellulose solution is spun using a device for forming such as a spinneret as filaments and then the filaments are precipitated in a bath to pass a coagulating bath and finally the swollen cellulose containing water is produced. But the above method takes a long time from dissolving to spinning, and the degradation of physical properties results from the long time. And also the expense of energy is so much that the cost for manufacturing is non-avoidable.

25 **[0004]** On the other hand, H. Chanzy et al. produced a cellulose fiber with 56.7 cN/tex of strength and 4 % of breaking elongation in a manner that a cellulose solution which a DP 5,000 of cellulose was dissolved by NMMO and ammonium chloride or calcium chloride was added and the resultant was spun through an air gap, but the method for producing the cellulose fiber has difficulty with being available commercially because the number of filament is only 1 strand and the fibril orientated in direction of axis is exfoliated.

30 **[0005]** Referring to other prior invention, US patent no. 5,942,327 describes a cellulose fiber having 50 to 80 cN/tex (5.7 to 9.1 g/d) of strength, 6 to 25 % of elongation and 1.5 dtex of mono strand fineness and produced in a manner that a aqueous NMMO solution into which DP 1,360 of cellulose is dissolved is spun through an air gap, but the number of filaments is only 50 strands. The cellulose fiber produced in the above manner has difficulty with being available commercially, considering that generally the number of filaments for using as industrial materials should be about 1000 strands (1650 dtex (1,500 denier)) because (a) the efficient remove of solvent is necessary in view of process and (b) the capacity of inner skin is enough maximized to resist the repeated fatigue in view of physical property.

35 **[0006]** In general when a spinning process is performed, in view of technology to spin with 500 to 2,000 of orifices per spinning nozzle is more difficult than to spin with 50 orifices per spinning nozzle. The reason is why that the adjustment of spinning pressure is more difficult in proportion to the increase of the number of orifices and thus it is difficult to design 40 a spinning nozzle and a distributing plate, in particular to adjust the condition for cooling evenly in an air gap and for washing and drying homogeneously all the filaments of 500 to 2,000, and as result it is very difficult to make all the filaments posses physical properties above a certain level and the homogeneous physical properties, and therefore the physical properties of 50 strands according to US patent no. 5,942,327 is not sufficient for reference to the application 45 of industrial materials.

50 **[0007]** In particular, because the increase of the number of filaments affects the stability of process relating to adhesion to the filaments spun from the nozzle and the efficiency when a spinning is performed through an air gap, the number of holes in a distributing plate for dispersing evenly the cellulose solution on the nozzle, the space of the holes and the diameter of the holes as well as the outer diameter of the nozzle and the diameter and space of orifices are very important.

55 **[0008]** As described in the above, as the number of filaments increases a new design for spinning is necessary considering the length of air gap, the blowing condition of cooling air, the direction of the coagulating solution and the spinning speed, and the physical properties may be different according to the design.

60 **[0009]** US patent no.5252284 describes a cellulose fiber having 800 to 1,900 of filaments, however, from the spinning condition that air gap below 10mm is too short and spinning speed, 45 m/min is too slow reveals that the 15.4 % of

elongation is sufficiently high, but the 47.8 cN/tex (5.3 g/d) of strength is not sufficient for use of a industrial material, in particular tire-cord and also the cellulose has disadvantage that the physical properties of each filament are not homogeneous.

5 [0010] EP-A-1 433 881 discloses a process for producing a lyocell multifilament from an aqueous NMMO cellulose solution using a special spinning nozzle with orifices having a length of 200 to 2400 μm and a ratio of the length to the diameter (L/D) of 2 to 8 which are spaced from each other at intervals of 2 to 5 mm. Example 1 shows spinning nozzles including 800, 1000 and 1200 orifices. However, this document does neither disclose a distributing plate in the spinning nozzle nor a drying roller operating at 80 °C to 170 °C. So an excellent uniformity in the mechanical properties of the single filaments is not to be expected.

10 [0011] EP-A-1 493 752 which has been published after the priority date of this invention shows a process where cooled solid-state NMMO and cellulose powder simultaneously are fed into a twin-screw type extruder to give a cellulose solution. This solution is then spun through a spinning nozzle having 800, 1000 or 1200 orifices. However, neither a distribution plate in the nozzle nor a drying roller operating at 80 °C to 170 °C is disclosed. So again an excellent uniformity in the 15 mechanical properties of the single filaments is not to be expected.

SUMMARY OF THE INVENTION

20 [0012] The present invention provides a solution to the problems that the prior inventions mentioned above has, and according to the present invention, there is provided a method of preparing a cellulose fiber characterized in that it comprises the steps of (A) producing a cellulose solution by swelling and homogenizing a cellulose powder into an aqueous concentrated N-methyl morpholine N-oxide (NMMO) solution; (B) spinning said cellulose solution through a spinning nozzle having 50 to 2000 orifices and a distributing plate with 50 to 300 holes within the nozzle; (C) obtaining multi-filaments by passing said cellulose solution through an air gap supplied with air at 5 to 30 °C in temperature and 10 to 60 % in humidity at 3 to 12 m/sec and coagulating in a bath at 0 to 35 °C; and (D) winding said multi-filaments by 25 water-washing, drying with a drying roller at 80 to 170 °C in temperature and treating with a finishing oil. The fiber produced by this process has the following physical properties: (1) 770 to 3300 dtex (700 to 3000 denier) of original strands, (2) a strength of the multi-filaments of 35.3 to 79.4 cN/tex (4 to 9 g/d), a breaking elongation of 4 to 15% and 30 (3) each 100 mono-filaments selected from each three parts divided from the multi-filaments have the properties as following; a) 26.5 to 79.4 cN/tex (3 to 9 g/d) in average, 7 to 15% in average breaking elongation and 0.035 to 0.055 in average birefringence, b) the differences of three parts in average strength, breaking elongation and denier are below 8.8 cN/tex (1.0 g/d), 1.5 % and 0.77 dtex (0.7 denier), respectively, c) CV (coefficient of variation) (%) of three parts in average strength, breaking elongation and dtex (denier) is below 10 %, and d) the differences of the average birefringence of three parts are below 0.004.

35 DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0013] According to the present invention, the cellulose comprises a distributing plate have 50 to 300 of holes within the nozzle.

40 According to the present invention, the air gap is in 5 to 30°C of temperature and in 10 to 60 % of relative humidity, and the cooling air is supplied with 3 to 12 m/s of velocity.

[0014] According to the present invention, the temperature of the coagulation bath is between 0 and 35 °C.

[0015] According to the present invention, the temperature of the drying roller is between 80 and 170 °C.

[0016] According to a further aspect of the present invention, there may be provided with a tire-cord including the cellulose fiber of the present invention.

45 [0017] In the following the present invention will be described in detail. The following description is illustrative of embodiments of the present invention. The following description is not to be construed as limiting, it being understood that the skilled person may carry out many obvious variants to the invention.

50 [0018] The cellulose used in following examples may be pulverized to particles with a diameter no more than 500 μm , preferably 300 μm . If the diameter is more than 500 μm , then the dispersion and swelling is not performed constantly into a extruder. Meanwhile, according to the present invention, in a known manner a NMMO solution with 50 wt% of concentration is condensed to make a concentrated NMMO solution with 10 to 15 wt% of moisture. In this case, if the contents of moisture are to be made below 10 wt %, then a disadvantage in view of manufacturing expense may be caused owing to the increase of cost, while the solubility may be degraded if above 15 wt%. 0.001 wt% to 0.01 wt % anti-oxidant is added to the concentrated aqueous NMMO solution. And then the concentrated aqueous NMMO solution and the cellulose powder are continuously fed into the extruder at temperature of 65 to 110°C, to produce a homogeneous cellulose solution after mixing, swelling and dissolving. The contents of cellulose powder contained in the cellulose solution which is mixed, swollen and dissolved in the extruder is 3 to 20 wt%, and preferably 9 to 14 wt% compared to the aqueous NMMO depending on the degree of cellulose polymer. If the contents of cellulose powder are below 3 wt%,

then there may not be the properties of fiber, while all the cellulose powder may not be dissolved into the aqueous NMMO solution resulting in non-homogeneous solution if above 20 wt%.

[0019] The extruder which is used for producing the homogeneous cellulose solution in step (A) may be preferably a twin-screw extruder in which the twin-screw extruder preferably may have barrels of 8 to 14 and the length/diameter (L/D) of screws may be preferably 24 to 64. If the number of barrels is less than 8 or L/D of the screws is less than 24, then the time interval for which the cellulose solution passes the barrels is too short to swell and dissolve the cellulose powder and thus a certain cellulose powder may remain not being dissolved, while the expense for manufacturing the extruder may be high and also the pressure exerted on the extruder may be large if the number of barrels is more than 14 or L/D of the screws are more than 64.

[0020] In step (B), the cellulose powder may be used with other high molecular materials or additives mixed. The high molecular materials may include poly vinyl alcohol, poly ethylene, poly ethylene glycol, poly methyl methacrylate and the like, and the additives may comprise viscosity-dropping agents, TiO_2 , SiO_2 carbon, carbon nano tube, inorganic clay and the like.

[0021] The method for producing a cellulose fiber will be described more specifically including the steps of spinning, water-washing, drying and winding in the following.

[0022] Referring to the step (B) corresponding to the process of spinning, a distributing plate having the diameter of 50 to 200 nm and holes of 50 to 300 serves the solution to be dispersed evenly on the nozzle. If the number of holes is less than 50, then the pressure of the cellulose solution may be concentrated on a part of the nozzle and thereby the mono denier of the filaments through the nozzle may be not constant, even to affect the property of spinning. On the other hand, if more than 300, the pressure on the nozzle may be made constant, but the slight difference from the pressure of the solution passing the nozzle may affect the property of spinning.

[0023] The spinning solution is extruded-spun through orifices being installed on the nozzle and being 100 to 300 μm in diameter and 200 to 2400 μm in length wherein length/diameter (L/D) is 2 to 8 and the space between the orifices is 0.5 to 5.0 mm, and the spun solution is precipitated into a coagulating bath through a air gap to be made a multi-filaments after coagulation.

[0024] The form of the nozzle used for spinning is usually circular, and the diameter of nozzle may be 50 to 200 mm, and preferably 80 to 150 mm. If the diameter of nozzle is less than 50 mm, then the short distance between the orifices may make the cooling efficiency be lowered resulting in adhesion of the spun solution before coagulation, while the device may be so large that it cause disadvantage in view of equipment if the diameter of nozzle is more than 200 mm. And also if the diameter of nozzle is less than 100 μm or more than 300 μm , then the nozzle may affect the spinning property with worse quality, for example, it happens to break strands down frequently. If the length of orifices is less than 20 μm , then the physical properties are poor because of the worse orientation of the solution, while if more than 2400 μm , then the cost and endeavor for manufacturing the orifices may be excessive.

[0025] Considering the cellulose of the present invention to be used for industrial materials, in particular for tire-cord, the number of the orifices is 500 to 2000, and preferably 700 to 1500. Some development of cellulose fiber for use of industrial materials has been reported, but no development of cellulose fiber for use of high strength filaments such as tire-cord, for more is the number of spinning-filaments, more affected the spinning property is by the number of orifices and more excellent spinning technology is required.

[0026] The present invention used a spinning nozzle containing a proper number of orifices for solving the above problem as mentioned above. If the number of orifices is less than 500, then the fineness of each filament is thicker than required and thus the processes of coagulating and water-washing may be performed incompletely because the time interval to remove NMMO from filament is too short. On the other hand, if the number of orifices is more than 2000, then a filament may be easily stucked with adjacent filament during passing the air gap, and the stability of each filament may be degraded after spinning and thus the quality of physical property may be poor, subsequently to cause some problems in the processes of twisting and heat-treatment with RFL solution for application of tire-cord.

[0027] If the diameter of the spun filament is too large when the solution spun from the spinning nozzle is precipitated into the coagulating bath, then it is difficult to obtain a cellulose fiber formed closely and homogeneously owing to the difference of the coagulation speed between skin and core part of filament. Therefore, on spinning a cellulose solution spun through a suitable air gap length, even though the discharging quantity is same, may be precipitated into the coagulating solution keeping the diameter of filament finer. Too short length of the air gap may make it difficult to increase the spinning velocity because fast coagulation of filament-surface and diffusion of solvent increase fine pores, while too long length of the air gap make it difficult to keep process stability because the spinning solution is more subject to the adhesion of filament, ambient temperature and humidity compared to other cases.

[0028] The length of the air gap may be preferably 10 to 200 mm, and more preferably 20 to 100 mm. When the cellulose solution passes through the air gap, a cooling air is provided for avoiding adhesion among adjacent filament and coagulating the filament, and for enhancing the resistance against penetrating into the coagulating solution. And a sensor may be installed between a opening of a cooling air supply and the filament to adjust temperature and humidity by monitoring the temperature and humidity. The temperature of the supplied air is kept between 5 to 30°C. If the

temperature is less than 5 °C, then the expense for cooling is excess as well as high speed spinning is difficult because the coagulation of filament is accelerated, while if more than 30 °C, then broken filaments may occur frequently owing to the degradation of the cooling effect for the discharged solution. On the other hand the contents of the moisture within the air gap may be important factor to affect the process of coagulation, and therefore the relative humidity within the air gap should be properly between RH10% and RH60%.

5 More specifically, for controlling the coagulation speed and preventing the adhesion on the surface of the nozzle, dried air of RH10% to 30% may be supplied in the area adjacent to the nozzle and wet air of RH30% to 50% may be supplied in area adjacent to the coagulating solution. The cooling air may be blown horizontally to the side of the filaments discharged perpendicularly, and the air velocity is 3 to 12 m/sec, preferably 4 to 10 m/s for stability. If the cooling air velocity is too slow, then non-homogeneous filaments may be produced owing to the difference of the solidification speed and the broken strand wherein the difference may be caused by the latest arrival of the cooling air on the spinning nozzle, while if it is too fast, then the spinning stability may be deteriorated by the risk of the adhesion caused from the filaments swing and by the hindrance of the homogeneous flow.

10 [0029] According to the present invention, the concentration of the aqueous solution in the coagulating bath may be 5 to 40%. If the spinning speed is more than 50 m/min when the filaments pass the coagulating bath, then the fluctuation of the coagulating solution may be severely owing to the friction between the filaments and the coagulating solution. For obtaining excellent physical properties and enhancing the productivity with the increase of the spinning speed, the above phenomenon may harm the process stability, and therefore the occurrence of the phenomenon has to be minimized through a coagulating bath design considering the shape and size of the bath, the flow and quantity of the coagulating solution.

15 [0030] In step (C) according to the present invention, the produced multi-filaments are directed toward a water-washing bath to wash. For the remove of solvent and the construction of form that affect the formation of the physical properties are performed concurrently when the filaments pass into coagulation bath, the temperature and concentrate of the solution has to be kept constant. The temperature of the bath is 0 to 35 °C, and preferably 10 to 25 °C. If the temperature is less than 0 °C, then the filament may be washed incompletely, while if more than 35 °C, then the NMMO contained within the filament will be extracted too fast to generate voids within the filament and thereby the degradation of physical properties may be caused. After coagulating, the filament is water-washed in a chamber about at 35 °C until NMMO is removed completely.

20 [0031] After water-washing, the multi-filaments are dried continuously using a drying roller which can adjust the temperature between 80 and 170 °C, and preferably between 100 and 150. If the temperature is less than 80 °C, then the filaments may be dried incompletely, while if more than 170 °C, the filaments may be contracted suddenly and excessively to cause the degradation of the physical property. The dried filaments are wound in a known manner after treating with organic solvent. The multi-filaments according to the present invention are characterized in that the total range of dtex is 770 to 3300 (denier 700 to 3000) and the breaking load is 4.0 to 27.0 kg. The multi-filaments consist of a set of filaments in which each filament is 0.55 to 4.4 dtex (0.5 to 4.0 denier) and the total number of filament is 500 to 2000. And also the multi-filaments are 35.3 to 79.4 cN/tex (4.0 to 9 g/d) in strength and 4 to 15 % in elongation with homogeneous physical property.

25 [0032] The cellulose fiber for use of industrial materials according to the present invention is characterized in that each mono-filament selected 100 strands from every three part divided from multi-filaments have properties as following: (a) 26.5 to 79.4 cN/tex (3 to 9 g/d) in average strength, 7 to 15 % in average breaking elongation and 0.035 to 0.055 in by birefringence, (b) the differences of the above three parts are below 8.8 cN/tex (1.0 g/d) in average strength, 1.5 % in breaking elongation and 0.77 dtex in dtex (0.7 denier in denier), (c) the CV (%) (coefficient of variation) of the above three parts are below 10%, and (d) the birefringence differences of the above three parts are below 0.004.

30 [0033] To produce the cellulose fiber for use of industrial materials to fulfill all the above physical properties, the factors of process mentioned foregoing are important. In particular, the determinant factors to form homogeneous physical properties of the cellulose fiber may be the number of orifices, the distributing plate, the cooling level within the air gap, the temperature of the coagulating bath and the temperature of the drying roller. The proper adjustment of the above factors may lead to the cellulose fiber for use of industrial material according to the present invention.

35 [0034] In the following the cellulose fiber according to the present invention will be described in detail with examples and comparisons, but they are given to clear understand, not to limit the present invention. In examples and comparison, the properties of the cellulose are estimated as following.

50 (a) Degree of polymerization (DP_w):

The intrinsic viscosity [IV] of the dissolved cellulose was measured using 0.5M cupriethylenediamine hydroxide solution obtained according to ASTM D539-51T in the range of 0.1 to 0.6g/dl of concentration at 25±0.01 °C with 55 Ubelohde viscometer. The intrinsic viscosity was calculated from the specific viscosity using extrapolation method according to the concentration and then the value obtained in the above was substituted into Mark-Houwink's equation to obtain the degree of polymerization.

$$[IV] = 0.98 * 10^{-2} DP_w^{0.9}.$$

5 (b) Birefringence
Birefringence was measured with Berek compensator using a polarization microscope for which the light source is Na-D.

10 (c) Strength (cN/tex) and breaking elongation (%) of multi-filaments
The above values were measured immediately after dried with a heat wind dryer for 2 hours at temperature of 107 °C. The measurement was performed with a low-speed elongating tensile strength tester from Instrong LTD., USA and the conditions of measurement are as following: 80 Tpm(80turns twist/m); 250 mm in length of sample; 300 m/mm at speed of elongation.

15 (d) Strength (g/d), breaking elongation (%) and CV (%) of mono-filament
The multi-filaments were divided into three parts after keeping at temperature of 25 °C and at relative humidity of 65 RH% for 24 hour, and then 100 mono-filaments from each of the three parts was selected to measure dtex (denier) and elongation-strength with Vibrozet 200 from Lenzing LTD. Initial load of 200 mg was exerted on the mono-filament of 20 mm in length, and then the denier and elongation-strength was measured with 20 mm/min. The coefficient of variation (CV) was calculated after the average strength and breaking elongation was measured. CV indicates the degree of variation, and is calculated by dividing the standard deviation with the average value.

Example 1

25 [0035] An aqueous concentrated NMMO solution is fed into a twin-screw extruder, which is kept at temperature of 78 °C, at 6900g/hour with a gear pump. And cellulose sheet (V-81 available from Buckeye LTD) with 1200 average degree of polymerization was put into a crusher with 250 µm filter to be made as powder being less than 200 µm in diameter and 5% in contents of moisture, and then the power was fed into the extruder at 1031 g/hour (concentration of 13 wt%) with a screw type supply. The remaining time in swelling area was for 8 to 10 minutes in order to swell sufficiently the cellulose powder, and then the cellulose powder was dissolved completely under condition that each block temperature in the dissolving area of the extruder was 90 to 95 °C and the screws operated at speed of 200 rpm. Subsequently the solution was discharged through a nozzle in which the diameter of orifice was 150 µm, the space between orifices was 1.5 mm and the number of orifices was 800 (example 1-1), 1,100 (example 1-2) and 1,500 (example 1-3), respectively.

30 [0035] The length of an air gap was 100 mm in which cooling air brown to the filaments within the air gap was under temperature of 20 °C, 45 RH% of relative humidity and 6 m/sec of velocity. The filaments precipitated into a coagulating bath (5 °C in temperature) from the air gap were water-washed, dried (140 °C in the temperature of a roller) and treated with organic solvent to be wound finally in which the fineness of the final multi-filaments was adjusted as 1500 denier. Each of the obtained multi-filaments were divided three parts, A, B and C, to select 100 mono filaments from each of the parts, and then the average strength, elongation and dtex (denier) were measured to calculate C V (%), and also the birefringence of each mono filament, was measured.

Comparison 1

45 [0036] The multi-filaments were produced under the same condition as example 1, only except for changing the number of orifices as 450. The result shows that If the number of orifices is 450, the strength was weaker because the time was too short for the NMMO solution to be removed sufficiently owing to thickened fineness of each mono-filament during the processes of coagulation and water-washing and the physical properties was inhomogeneous.

50 [0037] The results are shown in Table 1 in the following.

Table 1

| Kind | | Example 1 | | | | | | | | | Comparison | | |
|-----------------|----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | | 1-1 | | | 1-2 | | | 1-3 | | | | | |
| | | A | B | C | A | B | C | A | B | C | A | B | C |
| Multi-filaments | Strength cN/tex (g/d) | 66.2 (7.5) | | | 70.6 (8.0) | | | 66.2 (7.5) | | | 33.5 (3.8) | | |
| | Breaking elongation (%) | 5.5 | | | 4.5 | | | 5.5 | | | 4.7 | | |
| Mono-filament | Strength (g/d) | 44.1 (5.0) | 46.7 (5.3) | 52.0 (5.9) | 60.0 (6.8) | 52.9 (6.0) | 59.1 (6.7) | 44.1 (5.0) | 45.0 (5.1) | 46.7 (5.3) | 22.1 (2.5) | 23.8 (2.7) | 24.7 (2.8) |
| | Strength CV (%) | 7.3 | 6.6 | 7.0 | 7.7 | 7.4 | 6.4 | 7.0 | 7.0 | 6.5 | 10.3 | 10.8 | 9.3 |
| | Breaking Elongation (%) | 12.0 | 12.9 | 12.1 | 11.3 | 11.1 | 10.9 | 12.3 | 12.4 | 12.8 | 11.2 | 11.7 | 11.5 |
| | Breaking Elongation CV (%) | 5.4 | 5.7 | 6.4 | 6.4 | 6.9 | 7.2 | 5.5 | 4.9 | 5.7 | 9.4 | 9.8 | 10.4 |
| | dtex (Denier) | 2.00 (1.82) | 1.90 (1.73) | 1.88 (1.71) | 1.88 (1.71) | 1.97 (1.79) | 2.09 (1.90) | 1.84 (1.67) | 1.90 (1.73) | 1.99 (1.81) | 2.54 (2.31) | 2.67 (2.43) | 2.50 (2.27) |
| | Denier CV (%) | 9.8 | 8.7 | 8.8 | 8.3 | 8.1 | 9.2 | 7.9 | 8.8 | 7.3 | 11.3 | 12.5 | 13.5 |
| | Birefringence | 0.0449 | 0.0443 | 0.0442 | 0.0443 | 0.0447 | 0.0445 | 0.0442 | 0.0442 | 0.0441 | 0.0390 | 0.0440 | 0.0441 |

Example 2

[0038] Three kind of multi-filaments were produced under the same condition as example 1, but the nozzle for spinning has 1000 orifices with 150 μm in diameter of each orifice, and two distributing plates having 100 holes (example 2-1), 5 200(example 2-2) respectively, were used for producing two kinds of multi-filaments.

Comparison 2

[0039] Example 2 was repeated with a distribution plate having 350 holes (comparison 2-3).

[0040] Further, under the same condition as example 2, spinning was tried on using two kind of distributing plates 10 having 45 holes and 400 holes, but in case of the distributing plate having 45 holes, spinning was impossible because the spinning solution was not discharged owing to the decrease of the solution pressure within the spinning nozzle caused by partially concentrating on some portion of the spinning nozzle. In case of the distributing plate having 400 holes, some filaments was broken within the air gap, but some filaments could be obtained and the physical properties 15 of them were measured.

[0041] The result is shown together with that of example 2 in table 2 in the following.

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Table 2

| Kind | | Example 2 | | | | | | Comparison | | | | | |
|-----------------|----------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| | | 2-1 | | | 2-2 | | | 2-3 | | | 2 | | |
| | | A | B | C | A | B | C | A | B | C | A | B | C |
| Multi-filaments | Strength Cn/tex (g/d) | 68.8 (7.8) | | | 72.3 (8.2) | | | 59.1 (6.7) | | | 47.6 (5.4) | | |
| | Breaking elongation (%) | 5.3 | | | 6.4 | | | 5.7 | | | 4.2 | | |
| Mono-filament | Strength cN/tex (g/d) | 50.3 (5.7) | 46.7 (5.3) | 53.8 (6.1) | 56.4 (6.4) | 54.7 (6.2) | 59.1 (6.7) | 42.3 (4.8) | 37.9 (4.3) | 38.8 (4.4) | 28.2 (3.2) | 27.3 (3.1) | 33.5 (3.8) |
| | Strength CV (%) | 8.4 | 8.3 | 8.9 | 7.5 | 6.4 | 7.1 | 9.3 | 8.4 | 8.8 | 11.0 | 13.7 | 12.1 |
| | Breaking Elongation (%) | 12.3 | 12.8 | 12.9 | 13.4 | 13.0 | 13.1 | 12.2 | 12.9 | 12.4 | 11.3 | 11.8 | 11.4 |
| | Breaking Elongation CV (%) | 8.3 | 8.8 | 8.4 | 6.4 | 6.5 | 7.2 | 7.4 | 8.7 | 8.3 | 12.4 | 11.8 | 11.7 |
| | dtex (Denier) | 2.04 (1.84) | 2.12 (1.91) | 1.99 (1.79) | 1.90 (1.71) | 2.03 (1.83) | 2.08 (1.87) | 2.04 (1.84) | 1.94 (1.75) | 1.96 (1.77) | 1.57 (1.41) | 1.48 (1.33) | 1.43 (1.29) |
| | dtex (Denier) CV (%) | 9.8 | 9.7 | 8.6 | 8.4 | 8.0 | 9.1 | 9.3 | 8.4 | 8.3 | 13.3 | 14.1 | 15.4 |
| | Birefringence | 0.0443 | 0.0441 | 0.0441 | 0.0449 | 0.0447 | 0.0443 | 0.0441 | 0.0442 | 0.0442 | 0.0341 | 0.0331 | 0.0393 |

Example 3

[0042] The filaments were produced under the same condition as example 1, except for the following:

5 150 μm in diameter of orifice; 1.0 mm in space between orifices; 1100 in the number of orifices; and the temperature and relative humidity within air gap were changed as in table 3.

Comparison 3

10 [0043] The filaments were produced under the same condition as example 3, except for the following:

The temperature and relative humidity within the air gap were changed into 35 °C/30RH% and 20 °C/65RH%, respectively. In the condition of 35 °C/30RH% the filament was not cooled to be broken within the air gap.

15 [0044] The results are shown in Table 3 in the following.

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Table 3

| Kind | Air gap Tem. °C/ Hum.RH% | Example 3 | | | | | | | | | Comparison 320 °C/65RH% | | | | | |
|-----------------|-----------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-------------------------|----------------|----------------|--|--|--|
| | | 3-1 | | | 3-2 | | | 3-3 | | | | | | | | |
| | | 10°C/40RH% | | | 20°C/55RH% | | | 25°C/20RH% | | | | | | | | |
| | | A | B | C | A | B | C | A | B | C | A | B | C | | | |
| Multi-filaments | Strength cN/tex (g/d) | 73.2 (8.3) | | | 45.0 (5.1) | | | 76.7 (8.7) | | | 34.4 (3.9) | | | | | |
| | Breaking elongation (%) | 4.7 | | | 6.9 | | | 5.0 | | | 7.1 | | | | | |
| Mono-filament | Strength cN/tex (g/d) | 60.9 (6.9) | 60.0 (6.8) | 59.1 (6.7) | 30.9 (3.5) | 27.3 (3.1) | 32.6 (3.7) | 60.9 (6.9) | 62.6 (7.1) | 61.7 (7.0) | 18.5 (2.1) | 24.7 (2.8) | 23.8 (2.7) | | | |
| | Strength CV (%) | 7.4 | 7.1 | 6.3 | 7.3 | 6.9 | 6.9 | 6.3 | 6.4 | 7.0 | 10.3 | 11.1 | 10.8 | | | |
| | Breaking Elongation (%) | 11.3 | 11.4 | 11.7 | 13.4 | 13.1 | 13.4 | 12.0 | 12.4 | 12.8 | 14.2 | 14.3 | 13.8 | | | |
| | Breaking Elongation CV (%) | 7.4 | 7.2 | 7.0 | 6.8 | 7.3 | 7.1 | 7.2 | 7.1 | 6.4 | 10.7 | 9.7 | 11.0 | | | |
| | dtex (Denier) | 1.86 (1.69) | 1.87 (1.70) | 1.98 (1.80) | 1.87 (1.70) | 2.01 (1.83) | 1.99 (1.81) | 1.83 (1.66) | 1.86 (1.69) | 1.89 (1.72) | 1.86 (1.69) | 2.24 (2.04) | 2.10 (1.91) | | | |
| | dtex (Denier) CV (%) | 8.4 | 8.4 | 9.0 | 7.3 | 7.2 | 7.5 | 6.9 | 7.0 | 6.8 | 14.3 | 10.2 | 12.3 | | | |
| | Birefringence | 0.0442 | 0.0452 | 0.0453 | 0.0413 | 0.0421 | 0.0423 | 0.0443 | 0.0443 | 0.042 | 0.0350 | 0.0348 | 0.0410 | | | |

Example 4

[0045] The cellulose fiber was produced under the same condition as example 1, except for changing the degree of cellulose sheet polymerization and concentration of cellulose solution into DP1500 (Buckeye V5S) and 10%, respectively.

5 The solution was spun using a spinning nozzle with 1000 orifice in which the diameter of each orifice was 250 μm and the space between orifices was 2.0 mm, and the final denier of the cellulose multi-filaments were adjusted as 2000. The temperature of the coagulating bath was adjusted as 5 °C, 15 °C and 25 °C to produce the filaments.

Comparison 4

10 [0046] The multi-filaments were produced under the same condition as example 4, except for the temperature of the coagulation bath of 40 °C. In case of the bath of 40 °C, the NMMO was escaped rapidly from the coagulated filaments to generate voids, resulting in the degradation of the physical properties.

[0047] The results are shown in Table 5 in the following.

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Table 4

| Kind | Temperature of the coagulating bath | Example 3 | | | | | | | | | Comparison 3 40 °C | | | | | |
|-----------------|-------------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|--------------------|----------------|----------------|--|--|--|
| | | 4-1 | | | 4-2 | | | 4-3 | | | | | | | | |
| | | 5°C | | | 15 °C | | | 25 °C | | | | | | | | |
| Multi-filaments | Strength cN/tex (g/d) | A | B | C | A | B | C | A | B | C | A | B | C | | | |
| | Strength cN/tex (g/d) | 68.8 (7.8) | | | 64.4 (7.3) | | | 57.3 (6.5) | | | 29.1 (3.3) | | | | | |
| Mono-filament | Breaking elongation (%) | 4.1 | | | 4.7 | | | 6.2 | | | 7.1 | | | | | |
| | Strength cN/tex (g/d) | 50.3 (5.7) | 51.2 (5.8) | 49.4 (5.6) | 46.7 (5.3) | 50.3 (5.7) | 51.2 (5.8) | 36.2 (4.1) | 39.7 (4.5) | 43.2 (4.9) | 18.5 (2.1) | 26.5 (3.0) | 23.8 (2.7) | | | |
| | Strength CV (%) | 7.0 | 7.0 | 7.3 | 7.1 | 6.9 | 6.9 | 7.4 | 7.8 | 7.9 | 9.3 | 9.1 | 9.8 | | | |
| | Breaking Elongation (%) | 11.3 | 11.4 | 10.7 | 10.4 | 11.1 | 11.2 | 13.1 | 13.0 | 13.0 | 14.2 | 14.3 | 11.8 | | | |
| | Breaking Elongation CV (%) | 7.0 | 7.1 | 6.3 | 6.5 | 7.1 | 7.3 | 7.1 | 7.0 | 6.9 | 9.1 | 9.4 | 10.0 | | | |
| | dtex (Denier) | 2.61 (2.35) | 2.68 (2.41) | 2.54 (2.29) | 2.59 (2.33) | 2.79 (2.51) | 2.68 (2.41) | 2.46 (2.22) | 2.56 (2.31) | 2.55 (2.30) | 2.62 (2.36) | 2.49 (2.24) | 2.41 (2.17) | | | |
| | dtex (Denier) CV (%) | 8.0 | 8.1 | 7.8 | 8.4 | 7.8 | 7.9 | 8.0 | 7.9 | 7.4 | 6.3 | 8.2 | 10.3 | | | |
| | Birefringence | 0.0443 | 0.0441 | 0.0433 | 0.0442 | 0.0442 | 0.0431 | 0.0431 | 0.0433 | 0.0431 | 0.0317 | 0.0341 | 0.0381 | | | |

Example 5

5 [0048] The cellulose solution was produced under the condition the same as example 1, except for changing the degree of cellulose sheet polymerization and the concentration of the solution into DP 850 (Buckeye V60) and 14 %, respectively. The solution was spun through the spinning nozzle with 1000 orifices in which the diameter of each orifice was 250 μm and the space between the orifices was 2.0 mm, and the final denier of the cellulose multi-filaments was adjusted 2000. The temperature of the drying rollers were adjusted as 100 $^{\circ}\text{C}$, 130 $^{\circ}\text{C}$ and 160 $^{\circ}\text{C}$ to produce the filaments.

10 **Comparison 5**

[0049] The filaments were produced under the same condition as example 1, except for the 75 $^{\circ}\text{C}$ in temperature of the drying roller. In case of 75 $^{\circ}\text{C}$, drying was performed incompletely to result in the degradation of the physical properties.

[0050] The results are shown in Table 5 in the following.

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Table 5

| Kind | The temperature of the drying roller | Example 3 | | | | | | | | | Comparison 75 °C | | | | | |
|-----------------|--------------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|------------------|----------------|----------------|--|--|--|
| | | 5-1 | | | 5-2 | | | 5-3 | | | | | | | | |
| | | 100 °C | | | 130 °C | | | 160 °C | | | | | | | | |
| Multi-filaments | Strength cN/tex (g/d) | A | B | C | A | B | C | A | B | C | A | B | C | | | |
| | Strength cN/tex (g/d) | 51.2 (5.8) | | | 60.9 (6.9) | | | 73.2 (8.3) | | | 29.1 (3.3) | | | | | |
| Mono-filament | Breaking elongation (%) | 10.9 | | | 6.4 | | | 4.1 | | | 7.1 | | | | | |
| | Strength cN/tex (g/d) | 32.6 (3.7) | 33.5 (3.8) | 31.7 (3.6) | 41.5 (4.7) | 41.5 (4.7) | 42.3 (4.8) | 53.8 (6.1) | 59.1 (6.7) | 60.0 (6.8) | 36.2 (4.1) | 26.5 (3.0) | 41.5 (4.7) | | | |
| | Strength CV (%) | 9.1 | 9.4 | 9.7 | 7.7 | 7.8 | 7.3 | 6.3 | 6.4 | 5.9 | 10.3 | 14.1 | 13.8 | | | |
| | Breaking Elongation (%) | 15.3 | 15.4 | 15.7 | 13.4 | 13.1 | 12.8 | 11.1 | 11.0 | 10.7 | 14.0 | 15.3 | 14.8 | | | |
| | Breaking Elongation CV (%) | 7.4 | 7.7 | 7.4 | 6.8 | 7.2 | 7.7 | 6.3 | 5.3 | 6.4 | 8.1 | 13.4 | 11.9 | | | |
| | dtex (Denier) | 2.53 (2.30) | 2.54 (2.31) | 2.50 (2.27) | 2.40 (2.18) | 2.65 (2.41) | 2.63 (2.39) | 2.55 (2.32) | 2.46 (2.24) | 2.43 (2.21) | 2.54 (2.31) | 2.35 (2.14) | 2.52 (2.29) | | | |
| | dtex (Denier) CV (%) | 7.8 | 7.3 | 7.4 | 7.4 | 7.1 | 7.3 | 7.8 | 6.7 | 7.4 | 8.3 | 9.2 | 9.3 | | | |
| | Birefringence | 0.0432 | 0.0398 | 0.0410 | 0.0420 | 0.0420 | 0.0412 | 0.0431 | 0.0423 | 0.0412 | 0.0360 | 0.0347 | 0.0400 | | | |

[0051] The cellulose filaments according to the present invention consists of 500 to 2000 filaments, and is characterized in that the strength and breaking elongation of the filaments are 35.3 to 79.4 cN/tex (4 to 9 g/d) and 4 to 15 %, respectively and the physical properties are homogeneous. Therefore, the cellulose filaments can be used as industrial materials, in particular tire-cord requiring the high strength and homogeneous properties. More specifically, that each mono-filament selected 100 strands from every three part divided from multi-filaments have properties as following: (a) 26.5 to 79.4 cN/tex (3 to 9 g/d) in average strength, 7 to 15 % in average breaking elongation and 0.035 to 0.055 in birefringence, (b) the differences of the above three parts are below 8.8 cN/tex (1.0 g/d) in average strength, 1.5 % in breaking elongation and 0.77 dtex (0.7 denier) in denier, (c) the CV (%) (coefficient of variation) of the above three parts are below 10%, and (d) the birefringence differences of the above three parts are below 0.004.

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Claims

1. A method for preparing a cellulose fiber for using industrial materials which comprises the steps of:

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- (A) producing a cellulose solution by swelling and homogenizing a cellulose powder into an aqueous concentrated N-methyl morpholine N-oxide solution;
- (B) spinning said cellulose solution through a spinning nozzle having 50 to 2000 orifices and a distributing plate with 50 to 300 holes within the nozzle;
- (C) obtaining multi-filaments by passing said cellulose solution through an air gap supplied with air at 5 to 30 °C in temperature and 10 to 60 % in humidity at 3 to 12 m/sec and coagulating in a bath at 0 to 35 °C; and
- (D) winding said multi-filaments by water-washing, drying with a drying roller at 80 to 170 °C in temperature and treating with a finishing oil.

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2. A cellulose fiber produced by the method of claim 1, **characterized in** having following physical properties:

- (1) 770 to 3300 dtex (700 to 3000 in denier) of original strands;
- (2) 35.3 to 79.4 cN/tex (4 to 9 g/d) and 4 to 15 % in strength and breaking elongation of the multi-filaments, respectively;
- (3) each 100 mono-filaments selected from each three parts divided from the multi-filaments have the properties as following;

 - a) 26.5 to 79.4 cN/tex (3 to 9 g/d) in strength, 7 to 15 % in breaking elongation and 0.035 and 0.055 birefringence, respectively;
 - b) the differences of the three parts in average strength, average breaking elongation and average denier are less than 8.8 cN/tex (1.0 g/d), 1.5 % and 0.77 dtex (0.7 denier), respectively;
 - c) CV (coefficient of variation) of average strength, average breaking elongation and denier of said three parts less than 10 %; and
 - d) the differences of average birefringence of said three parts are less than 0.004.

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3. A tire cord comprising the cellulose fiber according to claim 2.

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Patentansprüche

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1. Verfahren zum Herstellen einer Cellulosefaser zur Verwendung in industriellen Materialien mit den Schritten:

- (A) Herstellen einer Celluloselösung durch Aufquellen und Homogenisieren eines Cellulosepulvers in einer wässerigen konzentrierten N-Methyl-Morpholin-N-Oxid-Lösung;
- (B) Spinnen der Celluloselösung durch eine Spindüse mit 50 bis 2000 Öffnungen und einer in der Düse angeordneten Verteilerplatte mit 50 bis 300 Löchern;
- (C) Erzeugen von Multifilamenten durch Durchleiten der Celluloselösung durch einen Luftspalt, dem Luft mit einer Temperatur von 5 bis 30°C und einer Feuchtigkeit von 10 bis 60% mit einer Geschwindigkeit von 3 bis 12 m/s zugeführt wird, und Koagulieren in einem Bad bei einer Temperatur von 0 bis 35°C; und
- (D) Wickeln der Multifilamente nach einem Waschprozess mit Wasser, einem Trocknungsprozess durch eine Trocknungswalze bei einer Temperatur von 80 bis 170°C und einer Behandlung mit einem Finishing-Öl.

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2. Cellulosefaser, hergestellt durch das Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Cellulose-

faser folgende physikalischen Eigenschaften besitzt:

5 (1) eine Fadenstärke der Originalfäden von 770 bis 3300 dtex (700 bis 3000 Denier);
 (2) eine Festigkeit der Multifilamente von 35,3 bis 79,4 cN/tex (4 bis 9 g/d) und eine Reißdehnung der Multifilamente von 4 bis 15%;
 (3) wobei jeweils 100 Monofilamente, die von jeweils drei Teilen ausgewählt werden, in die die Multifilamente geteilt werden, die folgenden Eigenschaften haben:

10 a) eine Festigkeit von 26,5 bis 79,4 cN/tex (3 bis 9 g/d), eine Reißdehnung von 7 bis 15% und eine Doppelbrechung von 0,035 bis 0,055;
 b) die Differenzen der drei Teile hinsichtlich der mittleren Festigkeit, der mittleren Reißdehnung und des mittleren Denier-Wertes sind kleiner als 8,8 cN/tex (1,0 g/d), 1,5% bzw. 0,77 dtex (0,7 Denier);
 c) der CV-Koeffizient (Änderungskoeffizient) der mittleren Festigkeit, der mittleren Reißdehnung und des Denier-Wertes der drei Teile ist kleiner als 10%; und
 15 d) die Differenzen der mittleren Doppelbrechung der drei Teile sind kleiner als 0,004.

3. Reifencord mit einer Zellulosefaser nach Anspruch 2.

20 **Revendications**

1. Procédé de préparation d'une fibre de cellulose destinée à une utilisation en tant que matériau industriel, lequel procédé comportant les étapes consistant à :

25 (A) produire une solution de cellulose en faisant gonfler et en homogénéisant une poudre de cellulose dans une solution aqueuse concentrée de N-méthyl morpholine N-oxyde,
 (B) filer ladite solution de cellulose à travers une buse de filage ayant 50 à 2 000 orifices et une plaque de distribution avec 50 à 300 trous à l'intérieur de la buse,
 (C) obtenir des multifilaments en faisant passer ladite solution de cellulose à travers un espace d'air alimenté en air à une température de 5 à 30 °C et une humidité de 10 à 60 % à 3 à 12 m/s et faire coaguler dans un bain à 0 à 35 °C, et
 30 (D) enrouler lesdits multifilaments par un lavage à l'eau, sécher à l'aide d'un rouleau de séchage à une température de 80 à 170 °C et traiter en utilisant une huile de finition.

35 2. Fibre de cellulose produite par le procédé de la revendication 1, **caractérisée en ce qu'elle possède les propriétés physiques suivantes :**

40 (1) 770 à 3 300 dtex (700 à 3 000 en deniers) de brins d'origine,
 (2) 35,3 à 79,4 cN/tex (4 à 9 g/d) et 4 à 15 % de résistance et d'allongement de rupture des multifilaments, respectivement,
 (3) chaque 100 monofilaments sélectionnés dans chacune des trois parties divisées à partir des multifilaments ont les propriétés suivantes :

45 a) 26,5 à 79,4 cN/tex (3 à 9 g/d) de résistance, 7 à 15 % d'allongement de rupture et 0,035 et 0,055 de biréfringence, respectivement,
 b) les différences des trois parties en termes de résistance moyenne, d'allongement de rupture moyen et de denier moyen sont inférieures à 8,8 cN/tex (1,0 g/d), 1,5 % et 0,77 dtex (0,7 denier), respectivement,
 c) CV (coefficient de variation) de résistance moyenne, d'allongement de rupture moyen et de denier desdites trois parties inférieur à 10 %, et
 50 d) les différences de biréfringence moyenne desdites trois parties sont inférieures à 0,004.

3. Câble pour pneumatique comportant la fibre de cellulose selon la revendication 2.

REFERENCES CITED IN THE DESCRIPTION

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