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

(11) EP 0 914 503 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
27.12.2000 Bulletin 2000/52

(21) Application number: **97932910.9**

(22) Date of filing: **21.07.1997**

(51) Int Cl.[7]: **D01F 2/00**

(86) International application number:
PCT/GB97/01959

(87) International publication number:
WO 98/03707 (29.01.1998 Gazette 1998/04)

(54) METHOD FOR THE MANUFACTURE OF LYOCELL FIBRE

VERFAHREN ZUR HERSTELLUNG VON LYOCELL-FASER

PROCEDE DE PRODUCTION DE FIBRES DE CELLULOSE FILEES A L'AIDE D'UN SOLVANT ORGANIQUE

(84) Designated Contracting States:
AT BE DE ES FI FR GB IT NL SE

(30) Priority: **23.07.1996 GB 9615431**

(43) Date of publication of application:
12.05.1999 Bulletin 1999/19

(73) Proprietor: **TENCEL LIMITED**
Spondon, Derby DE21 7BP (GB)

(72) Inventor: **PARKER, Dianne**
Coventry CV5 8HA (GB)

(74) Representative: **Hale, Stephen Geoffrey et al**
JY & GW Johnson,
Kingsbourne House,
229-231 High Holborn
London WC1V 7DP (GB)

(56) References cited:
WO-A-92/14871
WO-A-95/24524
WO-A-95/28516
WO-A-97/23668

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 914 503 B1

Description

[0001] This invention relates to processes for the manufacture of lyocell fibre which include the step of contacting the fibre in never-dried state with an aqueous solution of an alkali metal hydroxide.

Background art

[0002] Lyocell fibres are known, and their manufacture is described for example in US-A-4,416,698. Cellulose is dissolved in a solvent containing a tertiary amine N-oxide (which may also be called for brevity an amine oxide), for example N-methylmorpholine N-oxide (NMMO). The solvent generally also contains a proportion of a non-solvent for cellulose, for example water. The resulting solution is extruded through a suitable die to produce fibres, which are coagulated, washed in water to remove the solvent and dried. This process of extrusion and coagulation is referred to as "solvent spinning", and the cellulose fibre produced thereby is referred to as "solvent-spun" cellulose fibre or as lyocell fibre. It is also known that cellulose fibres can be made by extrusion of a solution of a cellulose derivative into a coagulating and regenerating bath. One example of such a process is the viscose process, in which the cellulose derivative is cellulose xanthate. Solvent spinning has a number of advantages over other known processes for the manufacture of elongate cellulose members, such as the viscose process, for example reduced environmental emissions.

[0003] Lyocell fibres are known to be prone to fibrillation. Fibrillation is a phenomenon which in the main occurs when lyocell fibres are subjected to mechanical forces during wet-processing, and it results in the partial detachment of fine longitudinal fibrils from the fibres. Fibrillation is in general considered to be undesirable in textile end-uses, and efforts have been made to reduce or eliminate fibrillation tendency by chemical aftertreatments, such as those described in US-A-5,310,424, or by suitable choice of spinning parameters, as described for example in WO-A-95/02082.

[0004] International Patent Application PCT\GB96\03160 published as WO97/23668 describes a process for the manufacture of an extruded lyocell article such as fibre which includes the characterising step of applying to the reconstituted but never-dried lyocell article an aqueous solution of an alkali metal hydroxide containing from 0.20 to 3.85 percent by weight hydroxide ions. An aqueous solution containing from 0.5 to 9 percent by weight sodium hydroxide may be used. The aqueous solution of alkali metal hydroxide may conveniently be applied to the fibre from a circulating bath, the residence time of the reconstituted article therein conveniently being in the range from 20 to 90 seconds. This process is said to enable the manufacture of lyocell articles having increased dyeability, increased whiteness, reduced yellowness and/or increased absorbency.

[0005] Unpublished International Patent Application PCT\GB97\1459 filed on 29th May 1997 (published as WO 97/45574 on 4th December 1997 after the filing date of the present application) describes a process for the manufacture of lyocell fibre which includes the characterising step of applying to the reconstituted but never-dried fibre for 20 seconds or more an aqueous liquor which comprises from 10 to 18 percent by weight sodium hydroxide. This process is said to enable the manufacture of lyocell fibre with controlled, in particular reduced, fibrillation tendency.

[0006] WO-A-92/14871 discloses a process for the manufacture of a solvent-spun elongate member (such as a lyocell fibre) in which the pH of the bath or baths through which the member passes between extrusion and drying is maintained at a figure of 8.5 or less, whereby the fibrillation tendency of such fibre is reduced.

[0007] WO-A-95/28516 discloses a method for reducing the fibrillation tendency of lyocell fibre in which to the never-dried fibre is applied an aqueous solution comprising dissolved therein an inorganic alkali and a chemical reagent bearing a plurality of acrylamido groups, the average number of such groups per molecule of reagent being at least 2.1, and whereafter the fibre is heated to produce reaction between the fibre and the reagent.

[0008] It is known that cellulose exhibits a swelling maximum in aqueous sodium hydroxide at a sodium hydroxide concentration of about 10 percent by weight. It is also known that the degree of swelling of cellulose in aqueous sodium hydroxide generally increases as the temperature is reduced. The present inventors have found that treatment of never-dried lyocell fibres with aqueous solutions containing from 5 to 15 percent by weight sodium hydroxide can damage the fibre, particularly at low temperatures, unless great care is taken. Such damage may manifest itself as loss of tensile properties, loss of lustre, loss of weight by dissolution or by detachment of fibrils, or in severe cases destruction of the fibre. This can render the processes described in the aforementioned International patent applications difficult to control. The present invention seeks to overcome this difficulty.

Disclosure of invention

[0009] Under the present invention lyoceil fibre is manufactured by a method which includes the step of contacting the fibre in never-dried state with an aqueous solution of an alkali metal hydroxide which additionally comprises from 1 to 50, preferably from 5 to 20, grams per litre of an alkali metal silicate (calculated as anhydrous sodium metasilicate, Na_2SiO_3).

[0010] According to the invention there is provided a method for the manufacture of lyocell fibre, including the steps in sequential order of:

(1) extruding a solution of cellulose in an organic solvent through a die, thereby producing an elongate form;
(2) passing the elongate form through at least one water-containing bath to remove the organic solvent from the elongate form, thereby producing a reconstituted cellulosic member;
(3) applying to the reconstituted cellulosic member an aqueous solution of an alkali metal hydroxide;
(4) washing the reconstituted cellulosic member to remove alkali metal hydroxide therefrom; and
(5) drying the reconstituted cellulosic member, thereby forming the lyocell fibre,

characterised in that the aqueous solution of an alkali metal hydroxide additionally comprises an alkali metal silicate at a concentration in the range from 1 to 50, preferably from 5 to 20, grams per litre (calculated as anhydrous sodium metasilicate Na_2SiO_3). The fibre is dried for the first time in step (5), so that the reconstituted cellulosic member may alternatively be referred to as never-dried fibre.

[0011] The method of the invention is applicable to lyocell fibre in the form of continuous filament yarn, tow or staple fibre. The titre of the lyocell fibre may be in the range from 0.5 to 10 decitex. When the method of the invention is carried out such that the reconstituted cellulosic member in the characterising step of the invention is in the form of continuous filament yarn or tow, the reconstituted cellulosic member is preferably maintained in relaxed state during the characterising step of the invention.

[0012] The alkali metal hydroxide is preferably sodium hydroxide, although other compounds such as potassium hydroxide may alternatively be used. The aqueous solution of alkali metal hydroxide may comprise from 5 to 15, preferably from 8 to 13, percent by weight sodium hydroxide.

[0013] The alkali metal in the alkali metal silicate is preferably sodium. The material known as waterglass is a convenient commercial form of sodium silicate for making up an aqueous solution for use in the invention.

[0014] The temperature of the aqueous solution of alkali metal hydroxide is preferably in the range from 0 to 60°C, more preferably from 15 to 30°C.

[0015] The aqueous solution of alkali metal hydroxide may be applied to the fibre by any convenient conventional means, for example using a circulating bath, wicking roller or spray. When a circulating bath is used, the residence time of the fibre therein may conveniently be in the range from 5 to 120 seconds.

[0016] After the alkali treatment step, alkali metal hydroxide is washed from the fibre. In one embodiment of the invention, the fibre is washed with hot water, preferably followed by a sour wash with dilute aqueous acid so that the fibre pH is below 7. In another embodiment of the invention, the fibre is washed with an aqueous acid solution. The acid may be a mineral acid such as hydrochloric acid or sulphuric acid, the concentration thereof in the aqueous acid solution being in the range from 0.1 to 20, preferably from 1 to 15, percent by volume, or it may be an organic acid such as acetic acid, the concentration thereof in the aqueous acid solution being in the range from 25 to 75, preferably from 40 to 60, percent by volume. The washing liquor may be applied to the fibre by any convenient means, for example using a circulating bath, wicking roller or spray. When an aqueous acid solution is used, the residence time of the fibre in such a circulating bath may conveniently be in the range from 5 to 120 seconds.

[0017] The method of the invention has the advantage that it can be carried out on conventional equipment.

[0018] Fibrillation was induced and degree of fibrillation assessed using Test Method 1.

Test Method 1

[0019] Approximately 0.05 g of dry fibre is cut to 10 mm lengths and placed in a laboratory blender. 400 ml of tap water is added and the mixture is blended for 30 seconds - 3 minutes. The actual length of time required depends on the blade being used and is chosen to give a fibrillation index of 6.5 - 8.0 for a sample of standard commercial lyocell fibre (Tencel (Trademark), Courtaulds Fibres (Holdings) Limited, Grimsby, U.K.).

[0020] The blended fibres are collected and a few are placed on a microscope slide. Another few fibres are placed on a second slide. The fibres are compared under a microscope to a set of standard graded photographs of fibrillated lyocell fibre. Three sets of five readings are taken on each slide and averaged to give the Fibrillation Index (F.I.). An F.I. of zero corresponds to zero fibrillation.

[0021] The invention is illustrated by the following Examples, in which parts and proportions are by weight unless otherwise specified.

Example 1

[0022] A solution of cellulose (15%) in NMMO (75%) and water (10%) was extruded through a spinnerette into an aqueous coagulating bath to produce 1.7 dtex filaments. After washing with water to remove NMMO, the filaments

were treated in relaxed state with an aqueous solution comprising 11% w/v sodium hydroxide and varying amounts of sodium silicate for 30 seconds at 25°C, washed in relaxed state with 15% v/v aqueous sulphuric acid solution for 30 seconds, rinsed and dried. Further experimental details and results are given in Table 1:

Table 1

Sodium silicate g/l	Titre dtex	Tenacity cN/tex	Extension %	F.I.
Untreated control	1.84	37.3	15.2	6.2
0	1.87	29.1	13.7	2.1
10	1.79	35.2	15.7	2.3
20	1.73	39.4	15.8	2.6
30	1.75	38.0	16.2	3.1
50	1.80	38.3	15.2	3.7

[0023] The solutions were made up using waterglass nominally containing 244 g/l sodium metasilicate.
[0024] Fibre treated according to the method of the invention exhibited a combination of good tensile properties and a low tendency to fibrillation, as well as good lustre and freedom from damage resulting from alkali treatment.

Claims

1. A method for the manufacture of lyocell fibre, including the steps in sequential order of:

(1) extruding a solution of cellulose in an organic solvent through a die, thereby producing an elongate form;
(2) passing the elongate form through at least one water-containing bath to remove the organic solvent from the elongate form, thereby producing a reconstituted cellulosic member;
(3) applying to the reconstituted cellulosic member an aqueous solution of an alkali metal hydroxide;
(4) washing the reconstituted cellulosic member to remove alkali metal hydroxide therefrom; and
(5) drying the reconstituted cellulosic member, thereby forming the lyocell fibre;

characterised in that the aqueous solution of an alkali metal hydroxide additionally comprises an alkali metal silicate at a concentration in the range from 1 to 50 grams per litre (calculated as anhydrous sodium metasilicate).

2. A method according to claim 1, further characterised in that the concentration of the alkali metal silicate in the aqueous solution of an alkali metal hydroxide is in the range from 5 to 20 grams per litre (calculated as anhydrous sodium metasilicate).

3. A method according to claim 1 or 2, further characterised in that the alkali metal in the alkali metal silicate is sodium.

4. A method according to any one of claims 1 to 3, further characterised in that the alkali metal hydroxide is sodium hydroxide.

5. A method according to claim 4, further characterised in that the concentration of sodium hydroxide in the aqueous solution is in the range from 5 to 15 percent by weight.

6. A method according to claim 5, further characterised in that the sodium hydroxide concentration is in the range from 8 to 13 percent by weight.

7. A method according to any one of the preceding claims, further characterised in that the temperature of the aqueous solution is in the range from 0 to 60°C.

8. A method according to claim 7, further characterised in that the temperature of the aqueous solution is in the range from 15 to 30°C.

9. A method according to any one of the preceding claims, further characterised in that the reconstituted cellulosic member in step (3) is in the form of continuous filament yarn or tow and is maintained in relaxed state.

10. A method according to any one of the preceding claims, further characterised in that the washing step (4) includes washing firstly with hot water and secondly with dilute aqueous acid whereby the pH of the lyocell fibre is below 7.

11. A method according to any one of claims 1 to 9, further characterised in that the washing step (4) includes washing with an aqueous solution containing from 0.1 to 20 percent by volume of an acid selected from the group consisting of hydrochloric acid and sulphuric acid.

12. A method according to claim 11, further characterised in that the aqueous solution used for washing contains from 1 to 15 percent by volume of the acid.

13. A method according to any one of claims 1 to 9, further characterised in that the washing step (4) includes washing with an aqueous solution containing from 25 to 75 percent by volume of acetic acid.

14. A method according to claim 13, further characterised in that the aqueous solution used for washing contains from 40 to 60 percent by volume of acetic acid.

Patentansprüche

1. Verfahren zur Herstellung einer Lyocell-Faser, bei dem man nacheinander:

(1) eine Lösung von Cellulose in einem organischen Lösungsmittel über eine Düse zu einem länglichen Gebilde ausformt,
(2) das längliche Gebilde durch mindestens ein Wasser enthaltendes Bad führt und dabei vom organischen Lösungsmittel befreit, wodurch ein Gebilde aus rekonstituierter Cellulose entsteht,
(3) auf das Gebilde aus rekonstituierter Cellulose eine wäßrige Lösung eines Alkalimetallhydroxids aufbringt,
(4) das Gebilde aus rekonstituierter Cellulose von Alkalimetallhydroxid freiwäscht sowie
(5) das Gebilde aus rekonstituierter Cellulose trocknet, wodurch die Lyocell-Faser entsteht,

dadurch gekennzeichnet, daß die wäßrige Lösung eines Alkalimetallhydroxids zusätzlich ein Alkalimetallsilicat in einer Konzentration im Bereich von 1 bis 50 Gramm pro Liter (gerechnet als wasserfreies Natriummetasilicat) enthält.

2. Verfahren nach Anspruch 1, weiterhin dadurch gekennzeichnet, daß das Alkalimetallsilicat in der wäßrigen Lösung eines Alkalimetallhydroxids in einer Konzentration im Bereich von 5 bis 20 Gramm pro Liter (gerechnet als wasserfreies Natriummetasilicat) enthalten ist.

3. Verfahren nach Anspruch 1 oder 2, weiterhin dadurch gekennzeichnet, daß es sich bei dem Alkalimetall des Alkalimetallsilicats um Natrium handelt.

4. Verfahren nach einem der Ansprüche 1 bis 3, weiterhin dadurch gekennzeichnet, daß man als Alkalimetallhydroxid Natriumhydroxid einsetzt.

5. Verfahren nach Anspruch 4, weiterhin dadurch gekennzeichnet, daß das Natriumhydroxid in der wäßrigen Lösung in einer Konzentration im Bereich von 5 bis 15 Gewichtsprozent vorliegt.

6. Verfahren nach Anspruch 5, weiterhin dadurch gekennzeichnet, daß die Natriumhydroxidkonzentration bei 8 bis 13 Gewichtsprozent liegt.

7. Verfahren nach einem der vorhergehenden Ansprüche, weiterhin dadurch gekennzeichnet, daß die Temperatur der wäßrigen Lösung 0 bis 60°C beträgt.

8. Verfahren nach Anspruch 7, weiterhin dadurch gekennzeichnet, daß die Temperatur der wäßrigen Lösung 15 bis 30°C beträgt.

9. Verfahren nach einem der vorhergehenden Ansprüche, weiterhin dadurch gekennzeichnet, daß das Gebilde aus rekonstituierter Cellulose in Schritt (3) als endloses Filamentgarn oder Kabel vorliegt und im relaxierten Zustand zum Einsatz kommt.

10. Verfahren nach einem der vorhergehenden Ansprüche, weiterhin dadurch gekennzeichnet, daß man beim Waschen (4) zuerst mit heißem Wasser und anschließend mit verdünnter wäßriger Säure wäscht und dadurch der pH-Wert der Lyocell-Faser unter 7 liegt.

11. Verfahren nach einem der Ansprüche 1 bis 9, weiterhin dadurch gekennzeichnet, daß man beim Waschen (4) mit einer wäßrigen Lösung mit einem Gehalt an Salzsäure oder Schwefelsäure von 0,1 bis 20 Volumenprozent wäscht.

12. Verfahren nach Anspruch 11, weiterhin dadurch gekennzeichnet, daß die für das Waschen eingesetzte wäßrige Lösung 1 bis 15 Volumenprozent Säure enthält.

13. Verfahren nach einem der Ansprüche 1 bis 9, weiterhin dadurch gekennzeichnet, daß man beim Waschen (4) mit einer wäßrigen Lösung mit einem Gehalt an Essigsäure von 25 bis 75 Volumenprozent wäscht.

14. Verfahren nach Anspruch 13, weiterhin dadurch gekennzeichnet, daß die für das Waschen eingesetzte wäßrige Lösung 40 bis 60 Volumenprozent Essigsäure enthält.

Revendications

1. Procédé de fabrication d'une fibre de lyocell, comprenant les étapes consistant à, dans cet ordre:

(1) extruder une solution de cellulose dans un solvant organique à travers une filière, pour produire une forme allongée;
(2) faire passer la forme allongée à travers au moins un bain contenant de l'eau pour éliminer le solvant organique de la forme allongée, pour produire un élément cellulosique reconstitué;
(3) appliquer à l'élément cellulosique reconstitué une solution aqueuse d'un hydroxyde de métal alcalin;
(4) laver l'élément cellulosique reconstitué pour en éliminer l'hydroxyde de métal alcalin; et
(5) sécher l'élément cellulosique reconstitué pour former la fibre de lyocell;

caractérisé en ce que la solution aqueuse d'un hydroxyde de métal alcalin comprend en outre un silicate de métal alcalin à une concentration dans la gamme de 1 à 50 grammes par litre (calculée en métasilicate de sodium anhydre).

2. Procédé selon la revendication 1, caractérisé en outre en ce que la concentration du silicate de métal alcalin dans la solution aqueuse d'un hydroxyde de métal alcalin est dans la gamme de 5 à 20 grammes par litre (calculée en métasilicate de sodium anhydre).

3. Procédé selon la revendication 1 ou 2, caractérisé en outre en ce que le métal alcalin dans le silicate de métal alcalin est le sodium.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en outre en ce que l'hydroxyde de métal alcalin est l'hydroxyde de sodium.

5. Procédé selon la revendication 4, caractérisé en outre en ce que la concentration de l'hydroxyde de sodium dans la solution aqueuse est dans la gamme de 5 à 15 pour cent en poids.

6. Procédé selon la revendication 5, caractérisé en outre en ce que la concentration de l'hydroxyde de sodium est dans la gamme de 8 à 13 pour cent en poids.

7. Procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que la température de la solution aqueuse est dans la gamme de 0 à 60°C.

8. Procédé selon la revendication 7, caractérisé en outre en ce que la température de la solution aqueuse est dans la gamme de 15 à 30°C.

9. Procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que l'élément cellulosique reconstitué dans l'étape (3) est sous forme d'un fil ou câble de filaments continu et est maintenu dans l'état relâché.

10. Procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que l'étape de lavage (4) comprend d'abord un lavage à l'eau chaude et ensuite un lavage avec un acide aqueux dilué, de manière à ce que le pH de la fibre de lyocell soit inférieur à 7.

11. Procédé selon l'une quelconque des revendications 1 à 9, caractérisé en outre en ce que l'étape de lavage (4) comprend un lavage avec une solution aqueuse contenant de 0,1 à 20 pour cent en volume d'un acide choisi dans le groupe constitué par l'acide chlorhydrique et l'acide sulfurique.

12. Procédé selon la revendication 11, caractérisé en outre en ce que la solution aqueuse utilisée pour le lavage contient de 1 à 15 pour cent en volume de l'acide.

13. Procédé selon l'une quelconque des revendications 1 à 9, caractérisé en outre en ce que l'étape de lavage (4) comprend un lavage avec une solution aqueuse contenant de 25 à 75 pour cent en volume d'acide acétique.

14. Procédé selon la revendication 13, caractérisé en outre en ce que la solution aqueuse utilisée pour le lavage contient de 40 à 60 pour cent en volume d'acide acétique.