

The present invention relates to cellulosic fibres, and also to a process for the preparation of cellulosic fibres, in which a solution of cellulose in a tertiary amine oxide is extruded through spinning orifices of a spinneret and the extruded filaments are led with a draft across an air gap into a precipitation bath.

As an alternative to the viscose process, a number of processes were described in recent years in which cellulose is dissolved, without the formation of a derivative, in an organic solvent, a combination of an organic solvent with an inorganic salt or in aqueous salt solutions. Cellulosic fibres which are prepared from such solutions were assigned the generic name lyocell by BISFA (The International Bureau for the Standardisation of Man-Made Fibres). BISFA defines lyocell as a cellulosic fibre which is obtained by a spinning process from an organic solvent. "Organic solvent" is understood by BISFA as meaning a mixture of an organic chemical and water. "Solvent spinning" is intended to mean dissolving and spinning without derivatization.

Hitherto, however, only a single process for the preparation of a cellulosic fibre of the lyocell type has got through to industrial implementation. In this process, N-methylmorpholine N-oxide (NMMO) is used as solvent. Such a process is described, for example, in US-A-4,246,221 and yields fibres which are distinguished by a high strength, a high wet modulus and by a high loop strength.

The usability of flat materials, for example woven fabrics, prepared from the fibres mentioned is, however, greatly limited by the marked tendency of the fibres to fibrillate in the wet state. Fibrillation is understood to mean the break-up of the fibres in the longitudinal direction when mechanically stressed in the wet state, as

a result of which the fibre acquires a hairy, furry appearance. A dyed woven fabric prepared from these fibres loses its colour intensity considerably in the course of a few washes. In addition, bright stripes form at abraded and creased edges. As the cause of the fibrillation, it is assumed that the fibre comprises fibrils arranged in the fibre direction, between which a cross connection is present only to a small extent.

WO 92/14871 describes a process for the preparation of a fibre with reduced tendency to fibrillation. This is achieved by all the baths with which the fibre comes into contact before the first drying having a pH of not more than 8.5.

WO 92/07124 also describes a process for the preparation of a fibre with reduced tendency to fibrillation, according to which method the undried fibre is treated with a cationic polymer. A polymer containing imidazole groups and acetidine groups is mentioned as such a polymer. In addition, a treatment with an emulsifiable polymer, such as, for example, polyethylene or polyvinyl acetate, or also a crosslinking with glyoxal can furthermore be carried out.

In a lecture given by S. Mortimer at the CELLUCON Conference, 1993, in Lund, Sweden, it was mentioned that the tendency to fibrillation increases with increasing stretching.

It has been found that the known cellulosic fibres of the lyocell type still leave something to be desired in relation to tendency to fibrillation, and the object of the present invention is consequently to provide a cellulosic fibre of the lyocell type which has a tendency to fibrillation which is reduced further.

This object is achieved in a process of the type mentioned at the outset in that the process is carried out in such a way that the mathematical expression

$$51.4 + 0.033xD + 1937xM^2 - 7.18xT - 0.094xL - 2.50xF + 0.045xF^2,$$

wherein D is the diameter of the spinning orifice in μm , M is the output of spinning material per orifice in g/min, T is the titre of the individual filaments in dtex, L is the width of the air gap in mm, and F is the humidity of the air in the air gap in g of water/kg air, has a maximum value of 10, with the proviso that the width of the air gap provided is greater than 30 mm.

The invention is based on the finding that, by adjusting the spinning parameters, the structure of the cellulosic fibre can be beneficially influenced in such a way that a fibre with little fibrillation is formed.

A preferred embodiment of the process according to the invention is that the process is carried out in such a way that the mathematical expression has a maximum value of 5.

The parameters titre, output of spinning material per nozzle orifice, air-gap width and humidity in the air gap are linked in regard to their effect on the fibrillation behaviour of the fibres by means of the above mathematical expression, that is to say a change in one parameter having an adverse effect on the fibrillation can be compensated for by expedient adjustment of one or more other parameters. Limits naturally exist in this connection as a result of economic or technical factors, for example although a throughput of spinning material of 0.01 g/orifice/min offers excellent conditions for spinning a low-fibrillation fibre, it is unfavourable for

economic considerations. A throughput of spinning material of 0.025 to 0.05 g/orifice/min is therefore preferred.

It has furthermore been found that large air-gap widths have a favourable effect on the fibrillation behaviour, but that this results relatively quickly in the occurrence of spinning faults with the small orifice/orifice spacings used in staple-fibre nozzles. An air-gap width of less than 100 mm is therefore preferred.

With regard to the humidity of the air in the air gap, the humidity of normal room conditions is sufficient in the case of nozzles with a small diameter of the spinning orifices or minimum spinning material throughput, whereas an atmospheric humidity of between 20 and 30 g of water/kg of air is preferred for higher throughputs, or for the more easily spinnable nozzles in the range from 70 to 130 μ m. The temperature in the air gap is chosen so that, on the one hand, it does not drop below the dew point, i.e. that no water condenses in the air gap and, on the other hand, spinning difficulties do not occur as a consequence of excessively high temperature. Values between 10 and 60°C can be set, temperatures between 20 and 40°C being preferred.

All the known cellulosic spinning materials can be processed by the process according to the invention. Thus, these spinning materials may contain between 5 and 25% cellulose. However, cellulose contents of between 10 and 18% are preferred. Hard or soft wood can be used as raw material for pulp production, and the degree of polymerization of the pulp or pulps may be in the range of the industrially common commercial products. It has been found, however, that if the molecular weight of the pulp is fairly high, the spinning behaviour is better. Depending on the degree of polymerization of the pulp or

solution concentration, the spinning temperature may be between 75 and 140°C and can easily be optimized for any pulp or for any concentration. For a specified titre of the fibres, the draft in the air gap depends on the nozzle orifice diameter and on the cellulose concentration of the solution. In the range of the preferred cellulose concentration, however, it was not possible to observe any influence of said concentration on the fibrillation behaviour provided the spinning temperature is in the optimum range.

The test methods and preferred embodiments of the invention are described in greater detail below.

Assessment of fibrillation

The rubbing of the fibres against one another in the wet state during washing processes or during finishing processes was simulated by the following test: 8 fibres were placed with 4 ml of water in a 20 ml sample bottle and shaken at stage 12 for 3 hours in a laboratory shaker of the type RO-10 supplied by the company Gerhardt, Bonn (FRG). The fibrillation behaviour of the fibres was then assessed under the microscope by counting the number of fibrils per 0.276 mm of fibre length.

Textile data

Strength and elongation were tested in a conditioned state according to the BISFA specification entitled "Internationally agreed methods for testing viscose, modal, cupro, lyocell, acetate and triacetate staple fibres and tows", 1993 edition.

Examples 1-29

Spinning was carried out with a 12%-strength spinning

solution of sulphite and sulphate pulp (12% water, 76% NMMO) at a temperature of 115°C. A standard melt index instrument used in plastic processing and supplied by the Davenport company was used as spinning apparatus. This instrument comprises a heated temperature-regulable cylinder into which the spinning material is loaded. The spinning material is extruded through the spinneret attached to the bottom of the cylinder by means of a piston which is loaded with a weight. This process is referred to as dry/wet spinning process since the extruded filament is immersed in a spinning bath after passing through an air gap.

A total of 29 extrusion experiments were carried out in which the nozzle diameter, the output of spinning material, the titre of the extruded filament, the width of the air gap and the humidity were varied. The results are reported in Table 1. In the column headed "fibrils", the average number of fibrils over a fibre length of 276 μm is reported.

Table 1

Example No.	Orifice diameter	Output	Titre	Gap	Humidity	Fibrils
1	130	0.014	2.16	85	39	4.8
2	130	0.014	2.13	130	16	0.4
3	130	0.015	2.37	40	21	0.8
4 (C)	130	0.041	1.23	85	0	38
5	130	0.043	2.14	85	21	0.4
6	130	0.043	2.13	85	20	1.6
7	130	0.042	2.08	85	20	0.3
8	130	0.041	2.03	85	20	5.4
9	130	0.039	1.94	85	19	5.0
10	130	0.042	2.95	40	19	0.8
11	130	0.039	3.09	85	40	3.5
12 (C)	130	0.102	2.21	130	21	18

13 (C)	130	0.102	2.22	85	0	54
14 (C)	130	0.100	2.23	85	38	22
15	50	0.015	2.37	85	18	3.2
16	50	0.043	2.28	130	18	0.0
17	50	0.045	2.41	40	20	0.6
18	50	0.042	2.25	85	40	0.0
19	50	0.041	2.88	85	18	0.0
20 (C)	250	0.040	1.32	85	20	14
21	250	0.041	2.35	130	18	2.7
22 (C)	250	0.041	2.18	40	22	14
23	250	0.040	2.93	85	19	0.8
24	200	0.017	2.00	85	21	0.0
25 (C)	200	0.041	1.30	85	20	8.0
26	200	0.041	2.17	130	18	0.8
27 (C)	200	0.040	2.14	40	19	10
28	200	0.041	2.90	85	20	0.6
29 (C)	200	0.100	2.16	85	22	19.

In the table, the diameter of the spinning orifice is reported in μm , the output in g of spinning material/orifice/min, the titre in dtex, the air gap in mm and the humidity in g of H_2O /kg of air. The number reported under "fibrils" is an average of several results. The examples 4, 12, 13, 14, 20, 22, 25, 27 and 29 are comparison examples. All the other examples are according to the invention and, when the corresponding parameter is substituted in the empirically found mathematical expression, they yield a number less than 10. From the table it can be seen that the cellulosic fibres according to the invention have conspicuously less fibrils in the test than the comparison fibres.

Examples 30-41

The conditions of Examples 1-29 were employed, but the parameters were modified as stated. In the column headed "fibrils", the average number of fibrils over a fibre

length of 276 μm is reported.

Table 2

Example No.	Orifice diameter	Output	Titre	Gap	Humidity	Fibrils
30(C)	130	0.045	1.8	12	5.3	27
31(C)	130	0.045	1.8	12	4.0	43
32	100	0.026	1.7	60	23.5	2.8
33(C)	100	0.025	1.7	45	13.4	16
34	100	0.025	1.7	60	25.4	3.2
35(C)	100	0.025	1.7	30	13.3	15.1
36(C)	100	0.025	1.7	30	12.7	19
37	100	0.025	1.7	60	24.4	1.9
38(C)	100	0.049	1.7	90	0.5	84
39	100	0.049	3.2	90	19.0	0
40	100	0.041	1.8	90	29.0	0.9
41	130	0.025	1.3	90	30.0	3.2

The spinning parameters are quoted in the units stated in Table 1.

Examples 30, 31, 33, 35, 36 and 38 do not fulfil the mathematical expression used according to the invention and are comparison examples. From the table, it can be seen that these fibres have an increased number of fibrils (more than 10 fibrils per 276 μm of fibre length).

Characteristic fibre data are summarized in Table 3 for the fibres stated in Table 2.

Table 3

Ex. No.	Cond. fibre strength cN/tex	Cond. fibre elongation %	Wet fibre strength cN/tex	Wet fibre elongation %
30 (C)	46.1	10.5	33.8	14.2
31 (C)	50	11.3	41.4	14
32	31.9	17.7	27.5	24.5
33 (C)	34.3	15.2	29.1	23.5
34	28.8	16.5	24.5	21.8
35 (C)	34.1	14.8	29.3	19.8
36 (C)	33.3	16.3	30.5	18.8
37	29.4	17.2	23.9	21.3
38 (C)	30.4	11.8	22.5	14.3
39	25.6	15.6	19.5	22.5
40	24.6	14.8	18.2	21.4
41	28.5	15.8	24.2	20.9

Examples 42 to 54

Work was carried out analogously to the conditions of Examples 1-29, but the parameters were modified as stated. In the column headed "Fibrils" of Table 4 below, the average number of fibrils over a fibre length of 276 μm is reported.

Table 4

Example No.	Orifice diameter	Output	Titre	Gap	Humidity	Fibrils
42 (C)	100	0.025	1.7	10	13	18.0
43 (C)	100	0.025	1.7	20	13	14.0
44 (C)	100	0.025	1.7	25	13	9.0
45 (C)	100	0.025	1.7	30	13	6.0
46 (C)	100	0.025	1.7	60	13	5.5
47 (C)	100	0.025	1.7	10	13	19.0

48 (C)	100	0.025	1.7	20	13	9.5
49 (C)	100	0.025	1.7	25	13	3.5
50 (C)	100	0.025	1.7	30	13	1.0
51 (C)	100	0.025	1.7	60	13	1.0
52 (C)	100	0.025	1.7	10	20	14
53 (C)	100	0.025	1.7	10	20	11.0
54	100	0.025	1.7	60	20	4.0

The spinning parameters are quoted in the units stated in Table 1.

Table 4 shows a marked drop in the number of fibrils as soon as an air gap of about 25-30 μm is exceeded.



CLAIMS

1. Process for the preparation of cellulosic fibres by extruding a solution of cellulose in a tertiary amine oxide through spinning orifices in a spinneret and leading the extruded filaments under tension across an air gap into a precipitation bath, with the proviso that the width of the air gap provided is greater than 30 mm, characterized in that the process is carried out in such a way that the mathematical expression

$$51.4 + 0.033xD + 1937xM^2 - 7.18xT - 0.094xL - 2.50xF + 0.045xF^2,$$

wherein D is the diameter of the spinning orifice in μm , M is the output of spinning material per orifice in g/min, T is the titre of the individual filaments in dtex, L is the width of the air gap in mm, and F is the humidity of the air in the air gap in g of water/kg air, has a maximum value of 10.

2. Process in accordance with Claim 1, characterized in that the process is carried out in such a way that the mathematical expression has a maximum value of 5.

3. Process in accordance with one of Claims 1 or 2, characterized in that the output of spinning material per orifice is between 0.025 and 0.05 g/min.

4. Process in accordance with one or more of Claims 1 to 3, characterized in that the width of the air-gap is less than 100 mm.

5. Process in accordance with Claims 1 or 2, characterized in that in the case of a spinneret having spinning orifices whose diameter is between 70 and 130 μm , the humidity of the air in the air gap is adjusted to between



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20 and 30 g of water/kg air.

6. Cellulosic fibres of the lyocell type with reduced tendency to fibrillation obtainable in accordance with a process as claimed in Claims 1 to 5.