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(54) LYOCELL FIBER WITH NOVEL CROSS SECTION

(57) The present invention provides a lyocell fiber with increased porosity and homogeneous distribution of hemicelluloses over the fiber cross section as well as a method for producing same and products comprising same.

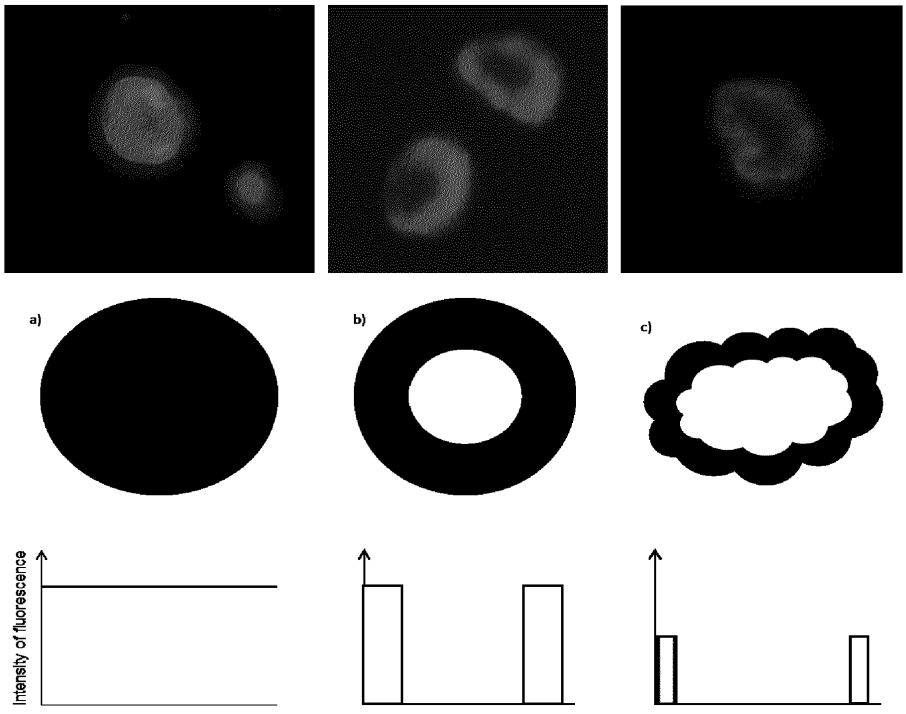

Figure 1: Fibers after fluorescent staining at maximum dye uptake a) fiber in accordance with present invention b) standard lyocell fiber c) standard viscose fiber and a schematic drawing of the intensity of the fluorescence of the tested fiber types

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Description

[0001] The present invention relates to a lyocell fiber with a novel cross sectional structure, a method for producing same as well as to products comprising the lyocell fiber.

State of the art:

[0002] Cellulose based fibers are employed in a wide variety of applications. Due to ever increasing demands even for such fibers based on renewable resources such as wood attempts have been made to increase the variety of raw materials which may be employed for the production of such fibers. At the same time a demand exists towards a further functionalization of such fibers, targeting specific fiber properties. Another aim is to mimic properties and structure of natural fibers. Fibers based on cellulose regeneration differ in their structure from natural fibers in that they typically do not show any internal /lumen. For example viscose fibers show an oval cross section comprising a dense sheath and a sponge like core of the fiber. Lyocell fibers on the other hand show a circular cross section with a three layered structure, comprising an outer compact skin with a thickness of 100 to 150 nm and a small pore size of from 2 to 5 nm, followed by a middle layer with increasing porosity and a dense, non-porous core.

[0003] It is known from the literature that fiber properties correlate with the structure of the fiber cross section. Nevertheless, the process for preparing lyocell fibers offers only limited options to influence fiber properties and structure. However, it would be advantageous if means existed to influence fiber properties to a greater extend even in the lyocell process. One option would be to either add additives to employ by-products of the cellulose production in order to further vary the structure and/or properties of lyocell fibers.

[0004] It is for example known that chemical pre-treatment may influence fiber properties. US 6042769 shows an example of chemical treatments to enhance fibrillation tendency. It discloses chemical treatments to reduce the DP (degree of polymerization) by 200 units, thereby increasing fibrillation tendency. Chemical treatments mentioned in this patent refer to the use of bleaching reagents, such as sodium hypochlorite or mineral acids, such as hydrochloric acid, sulfuric acid or nitric acid. A commercialization of this procedure did not succeed up to now.

[0005] US 6706237 discloses that meltblown fibers obtained from hemicelluloses rich pulps show a decreased or reduced tendency to fibrillate. US 8420004 discloses another example of meltblown fibers for producing non-woven fabrics.

[0006] For viscose fibers it has been shown that the addition of hemicelluloses dissolved in NaOH to the spinning viscose enables the modification of fiber properties (WO2014086883). However, these modifications were always accompanied by a decrease of other important fiber properties, such as tenacity. Such modifications are restricted to the viscose process and cannot at all be applied to lyocell fibers. The use of the direct solvent NMMO excludes the addition of any extra water and NaOH on an industrial scale.

[0007] An attempt has been made to alter the fiber properties by using pulps rich in hemicelluloses. Most publications deal with other ionic liquids than NMMO in a lab scale. Only a few publications are relevant for the lyocell process with NMMO. Zhang et al. (Polymer Engineering and Science 2007, 47, 702-706 and Journal of Applied Polymer Science, 2008, 107, 636-641) describe lyocell fibers with higher hemicellulose contents. The authors postulate that the fibers tend to show an enhanced fiber fibrillation resistance, lower crystallinity and better dyeability. They also postulate that the tensile strength only decreases insignificantly and that the fiber properties could be even increased further by higher hemicelluloses concentrations in the spinning dope.

The fibers described in the papers by Zhang et al. are produced with lab equipment not allowing the production of lyocell fibers in commercial quality These fibers, not being produced with sufficient drawing and an sufficient after-treatment therefore can be expected to show different structure and properties compared to the fibers produced at production scale at titers reflecting market applications. In addition, no information is provided in the paper concerning the distribution of the hemicelluloses over the cross section of the lyocell fibers, nor on the structure of the three layered cross section

[0008] In this regard it is known for viscose fibers that an increase in hemicellulose content leads to an enrichment of the hemicellulose content at the surface of the fiber, with a rapid decrease towards the core of the fiber (Schild and Liftinger Cellulose 2014 21:3031-3039).

No research has been done on standard lyocell fibers up to now, but it is assumed that cellulosic fibers act similar.

Object of the present invention

[0009] In view of the increasing demands for fibers based on cellulose raw materials it is the object of the present invention to provide cellulose based fibers with improved properties. In particular it would be advantageous to provide fibers with increased WRV and/or reduced crystallinity, preferably while maintaining a substantial degree of the beneficial mechanical properties of lyocell fibers.

Brief description of the invention

[0010] The present inventors accordingly provide the fiber as defined in claim 1, the method for producing same as described in claim 12 as well as products containing same as defined in claim 17 and the use as defined in claim 9. Preferred embodiments are described in the respective subclaims as well as in the specification.

[0011] In particular the present invention provides the following embodiments, which are further explained and illustrated below.

1.) Lyocell fiber with an enhanced porous structure over the fiber cross section and a crystallinity of 40 % or less.
2.) Lyocell fiber according to embodiment 1, with a WRV of 70 % or greater.
3.) Lyocell fiber according to embodiment 1 or 2, with an entire staining over the whole fiber cross section using a fluorescent staining dye.
4.) Lyocell fiber according to any one of the preceding embodiments, wherein the pulp employed for the fiber formation comprises cellulose and hemicelluloses, with a hemicelluloses content of at least 7 wt.-%
5.) Lyocell fiber according to any one of embodiments 1 to 4, having a titer of 6.7 dtex or less, such as 2.2 dtex or less, preferably 1.3 dtex or less.
6.) Lyocell fiber according to any one of embodiments 1 to 5, produced from a pulp having a hemicelluloses content of 7 wt.-% or more and 25 wt.-% or less.
7.) Lyocell fiber according to any one of embodiments 1 to 6, wherein the hemicellulose comprises a ratio of C5/Xylan to C6/Mannan of from 125:1 to 1:3, preferably of from 25:1 to 1:2.
8.) Lyocell fiber according to any one of embodiments 6 or 7, wherein the pulp comprises 6 wt.-% or more xylan, preferably 8 wt.-% or more, more preferably 12 wt.-% or more and/or 3 wt.-% or more mannan, preferably 5 wt.-% or more mannan, and/or 1 wt.-% or less mannan.
9.) Use of a pulp for producing a fiber according to any one of embodiments 1 to 8, wherein the pulp has a hemicelluloses content of 7 wt.-% or more and 25 wt.-% or less.
10.) Use according to embodiment 9, wherein the hemicellulose comprises a ratio of C5/Xylan to C6/Mannan of from 125:1 to 1:3, preferably of from 25:1 to 1:2.
11.) Use according to any one of embodiments 9 or 10, wherein the pulp comprises 5 wt.-% or more xylan, preferably 8 wt.-% or more, more preferably 10 wt.-% or more and/or 3 wt.-% or more mannan, preferably 5 wt.-% or more mannan, and/or 1 wt.-% or less mannan.
12.) Method for producing the lyocell fiber according to any one of embodiments 1 to 8 using a direct dissolution process.
13.) Method for producing the lyocell fiber according to embodiment 12 using a amine oxide process, where an aqueous solution of the amine oxide and the pulp form a cellulose suspension and a shapeable solution which gets shaped and coagulated in a spin bath obtaining the lyocell fiber after washing and pre-treatment steps.
14.) Method for producing the lyocell fiber according to embodiment 13 using an aqueous tertiary amine oxide, preferably aqueous NMMO.
15.) Method according to any one of embodiments 12 to 14, wherein the spinning solution contains a pulp with a hemicelluloses content of greater than 10 wt.-% based on the total weight of cellulose and hemicelluloses contained.
16.) Lyocell fiber, use or method according to any one of the preceding embodiments, wherein the pulp has a scan viscosity of from 300 to 440 ml/g.
17.) Product, comprising the lyocell fiber according to any one of embodiments 1 to 8 or 16, or the fiber produced according to any one of embodiments 12 to 16.
18.) Product according to embodiment 16, wherein the product is a non-woven fabric.
19.) Product according to embodiment 16 and/or 17, selected among tissues and wipes.

Brief description of the Figures

[0012]

Figure 1 shows a comparison of the fiber in accordance with the present invention as compared to a standard lyocell fiber and a standard viscose fiber after fluorescent staining. The fiber in accordance with the present invention shows an even distribution of the stained areas throughout the entire cross section of the fiber, whereas the standard viscose fiber displays only a superficial staining of the outer sheath part of the fiber. The standard lyocell fiber depicts in contrast an unstained core

Figure 2 shows the velocity of enzymatic peeling and Figure 3 the xylan distribution over the fiber cross section in comparison to a standard lyocell fiber and a xylan enriched viscose fiber. The hemicellulose concentration of the

fiber according to the present invention is almost constant over the fiber cross section while the concentration of the standard lyocell fiber decreases rapidly from the shell to the core. The same was observed for a viscose fiber enriched with xylan.

Detailed description of the invention

[0013] As defined in claim 1 the fiber in accordance with the present invention is a lyocell fiber with a novel structure of the cross section, as compared to standard lyocell fibers. While the three layered structure known from standard lyocell fibers is maintained, at least the inner core layer shows an increased porosity, as compared with standard lyocell fibers. The term increased porosity as employed herein refers to the fact that the novel fibers as described herein do show a staining behavior differing from standard Lyocell fibers. While the latter ones only allow for a staining of the outer two layers, the novel fibers in accordance with the present invention can be stained over the entire cross section with fluorescent dyes

A quantitative measure of this novel property can be seen in the possibility to stain the entire cross section of a fiber using the methodology as described in example 5. Fibers in accordance with the present invention show a staining (using the method as described in example 5) over the entire cross section after 24 h or less, preferably 12 h or less, even more preferably 6 h or less, such as 3 h or less.

In embodiments also the surface layer may be less thick and/or the pore size, which is typically for standard lyocell fibers in the range of from 2 to 5 nm, may be larger.

[0014] As defined in claim 1 the fiber in accordance with the present invention is a lyocell fiber.

The lyocell process is well known in the art and relates to a direct dissolution process of cellulose wood pulp or other cellulose-based feedstock in a polar solvent (for example N-methylmorpholine N-oxide [NMMO, NMO] or ionic liquids). Commercially, the technology is used to produce a family of cellulose staple fibers (commercially available from Lenzing AG, Lenzing, Austria under the trademark TENCEL® or TENCEL™) which are widely used in the textile and nonwoven industry. Other cellulose bodies from lyocell technology have also been produced.

According to this method the solution of cellulose is extruded in a so called dry-wet-spinning process by means of a forming tool and the moulded solution is guided for example over an air gap into a precipitation bath, where the moulded body is obtained by precipitation of the cellulose. The molding is washed and optionally dried after further treatment steps.

Such lyocell fibers are well known in the art and the general methodology to produce same is for example disclosed in US 4,246,221 and its analytics in the BISFA (The International Bureau for the Standardization of Man-Made Fibers) publication "Terminology of Man-Made Fibres", 2009 edition. Both references are included herewith in their entirety by reference.

[0015] The term lyocell fiber as employed herein defines a fiber obtained by this process, as it has been found that fibers in accordance with the present invention differ greatly from fibers for example obtained from a meltblown process, even if using a direct dissolution process of cellulose wood pulp or other cellulose-based feedstock in a polar solvent (for example N-methylmorpholine N-oxide [NMMO, NMO] or ionic liquids) in order to produce the starting material.

[0016] The term hemicelluloses as employed herein refers to materials known to the skilled person which are present in wood and other cellulosic raw material such as annual plants, i.e. the raw material from which cellulose typically is obtained. Hemicelluloses are present in wood and other plants in form of branched short chain polysaccharides built up by pentoses and/or hexoses (C5 and / or C6-sugar units). The main building blocks are mannose, xylose, glucose, rhamnose and galactose. The back bone of the polysaccharides can consist of only one unit (f.e. xylan) or of two or more units (e.g. mannan). Side chains consist of arabinose groups, acetyl groups, galactose groups and O-acetyl groups as well as 4-O-methylglucuronic acid groups. The exact hemicellulose structure varies significantly within wood species. Due to the presence of sidechains hemicelluloses show much lower crystallinity compared to cellulose. It is well known that mannan predominantly associates with cellulose and xylan with lignin. In sum, hemicelluloses influence the hydrophilicity, the accessibility and degradation behavior of the cellulose-lignin aggregate. During processing of wood and pulp, side chains are cleaved off and the degree of polymerization is decreased. The term hemicelluloses as known by the skilled person and as employed herein comprises hemicelluloses in its native state, hemicelluloses degraded by ordinary processing and hemicelluloses chemically modified by special process steps (e. g. derivatization) as well as short chain celluloses and other short chain polysaccharides with a degree of polymerization (DP) of up to 500.

[0017] The pulps preferably employed in the present invention do show as outlined herein a high content of hemicelluloses. Compared with the standard low hemicellulose content pulp employed for the preparation of standard lyocell fibers the preferred pulps employed in accordance with the present invention do show also other differences, which are outlined below.

[0018] Compared with standard pulps the pulps as employed herein display a more fluffy appearance, which results after milling (during preparation of starting materials for the formation of spinning solutions for the lyocell process), in the presence of a high proportion of larger particles. As a result the bulk density is much lower, compared with standard pulps having a low hemicellulose content. This low bulk density requires adaptions in the dosage parameters (f.e. dosage

from at least 2 storage devices). In addition the pulps employed in accordance with the present invention are more difficult to impregnate with NMMO. This can be seen by evaluating the impregnating behavior according to the Cobb evaluation. While standard pulps do show a Cobb value of typically more than 2.8 g/g (determined according to DIN EN ISO 535 with the adaptation of employing an aqueous solution of 78% NMMO at 75° C with an impregnation time of 2 minutes), the pulps employed in the present invention do show Cobb values of about 2.3 g/g. This requires an adaptation during spinning solution preparation, such as increased dissolution time (f.e. explained in WO 9428214 and WO 9633934) and/or temperature and/or increased searing during dissolution (f.e. WO9633221, WO9805702 and WO 9428217). This ensures the preparation of a spinning solution enabling the use of the pulps described herein in standard lyocell spinning processes.

[0019] In one preferred embodiment of the present invention the pulp employed for the preparation of the lyocell products, preferably fibers, as described herein, has a scan viscosity in the range of from 300-440 ml/g, especially 320-420 ml/g, more preferably 320 to 400 ml/g. The scan viscosity is determined in accordance with SCAN-CM 15:99 in a cupriethylenediamine solution, a methodology which is known to the skilled person and which can be carried out on commercially available devices, such as the device Auto PulplVA PSLRheotek available from psl-rheotek. The scan viscosity is an important parameter influencing in particular processing of the pulp to prepare spinning solutions. Even if two pulps seem to be of great similarity as raw material for the lyocell-process, different scan viscosities will lead to completely different behaviour different during processing. In a direct solvent spun process like the lyocell-process the pulp is dissolved in NMMO as such. No ripening step exists comparable to the viscose process where the degree of polymerization of the cellulose is adjusted to the needs of the process. Therefore, the specifications for the viscosity of the raw material pulp typically are within a small range. Otherwise, problems during production may arise. In accordance with the present invention it has been found to be advantageous if the pulp viscosity is as defined above. Lower viscosities compromise mechanical properties of the lyocell products. Higher viscosities in particular may lead to the viscosity of the spinning dope being higher and therefore, spinning will be slower. With a slower spinning velocity lower draw ratios will be attained, which significantly alters the fiber structure and its properties (Carbohydrate Polymers 2018, 181, 893-901; Structural analysis of loncell-F fibres from birch wood, Shirin Asaadia; Michael Hummel; Patrik Ahvenainen; Marta Gubitosic; Ulf Olsson, Herbert Sixta). This will require process adaptations and will lead to a decrease in mill capacity. Employing pulps with the viscosities as defined here enables smooth processing and production of high quality products.

[0020] As employed herein the terms lyocell process and lyocell technology relate to a direct dissolution process of cellulose wood pulp or other cellulose-based feedstock in a polar solvent (for example N-methylmorpholine N-oxide [NMMO, NMO] or ionic liquids). Commercially, the technology is used to produce a family of cellulose staple fibers (commercially available from Lenzing AG, Lenzing, Austria under the trademark TENCEL® or TENCEL™) which are widely used in the textile and nonwoven industry. Other cellulose bodies from lyocell technology have also been produced. According to this method the solution of cellulose is usually extruded in a so called dry-wet-spinning process by means of a forming tool and the moulded solution gets for example over an air gap into a precipitation bath, where the moulded body is obtained by precipitation of the cellulose. The moulding is washed and optionally dried after further treatment steps. A process for production of lyocell fibers is described, for instance, in US 4,246,221, WO 93/19230, WO95/02082 or WO97/38153. As far as the present application discusses the drawbacks associated with the prior art and the unique properties for novel products as disclosed and claimed herein in the context of using laboratory equipment (in particular in the prior art) or (semi-commercial) pilot plants and commercial fiber spinning units, the present invention is to be understood to referring to larger scale plants/units, which may be considered as follows concerning their respective production capacity:

semi-commercial pilot plant: about1 kt/a

commercial unit >30 kt/a

[0021] The task and object mentioned above was solved by lyocell fibers with enhanced porosity of the core layer of a lyocell fiber. The fibers in accordance with the present invention show, due to the specific structure, improved properties, such as improved dyeability, increased enzymatic degradability, etc.
Standard lyocell fibers are currently commercially produced from high quality wood pulps with high α-cellulose content and low non-cellulose contents such as hemicelluloses. Commercially available lyocell fibers such as TENCEL™fibers produced from Lenzing AG, show excellent fiber properties for non-wovens and textile applications.

[0022] The present invention overcomes the shortcomings of the state of the art by providing lyocell fibers as described herein.

[0023] Preferably these are produced from hemicellulose-rich pulps with a hemicellulose content of at least 7 wt.-%. Contrary to the disclosure in the prior art discussed above, such high hemicellulose content surprisingly, for lyocell fibers of the present invention, gives rise to an increased porosity of the core layer of the lyocell fiber structure, while having

only minor effect on the mechanical properties of the fibers. Accordingly the present invention surprisingly achieves the tasks as outlined above while using cellulose based raw material with a higher hemicelluloses content, as compared for standard lyocell fibers.

[0024] As already outlined above, Zhang et al (Polym. Engin. Sci. 2007, 47, 702-706) describe fibers with high hemicellulose contents. The hemicelluloses are described as acting as plasticizers within the fiber. The authors argue that hemicelluloses allow the cellulose chains to align more easily, which would assumably lead to a higher density of the fiber. Contrary thereto however, the present invention provides fibers with completely different properties as with the higher hemicelluloses content the porosity, in particular of the inner core layer of the lyocell fiber increases drastically. One possible explanation for these contrasting findings may be the fact that the fibers in accordance with the present invention are fibers produced using large scale production equipment, while the fibers described in the paper by Zhang et al. are produced with lab equipment not allowing the production of lyocell fibers in commercial quality (as for example drawing ratios, production velocities and after-treatment do not reflect scale-up qualities). The fibers, not being produced with sufficient drawing and a sufficient after-treatment therefore show different structure and properties compared to the fibers produced at production (semi)-commercial scale.

[0025] The content of hemicelluloses in the pulps may be from 7 wt.-% up to 25 wt.-%, such as from 8 to 20, and in embodiments from 10 to 15 wt.-%. The hemicellulose content may be adjusted according to procedures known in the art. The hemicellulose may be the hemicelluloses originating from the woof from which the pulp is obtained, it is however also possible to add individual hemicelluloses depending on the desired fiber properties from other sources to high purity cellulose with a low original hemicellulose content. The addition of individual hemicelluloses may also be employed to adjust the composition of the hemicelluloses content, for example to adjust the ratio of hexoses to pentoses.

[0026] The pulp enabling the preparation of the fibers in accordance with the present invention preferably shows a ratio of C5/xylan to C6/mannan of from 125:1 to 1:3, preferably in the range of 25:1 to 1:2, such as from 10:1 to 1:1. The hemicellulose content may be 7 wt.-% or more, preferable 10 wt.-% or more and in embodiments up to 25 wt.-% or even 30 wt.-%. In embodiments the xylan content is 5 wt.-% or more, such as 8 wt.-% or more, and in embodiments 10 wt.-% or more. In embodiments, either in isolation or in combination with the above mentioned hemicelluloses and/or xylan contents, the mannan content is 3 wt.-% or more, such as 5 wt.-% or more. In other embodiments the mannan content, preferably in combination with a high xylan content as defined above, may be 1 wt.-% or less, such as 0.2 wt.-% or 0.1 wt.-% or less.

[0027] The fibers in accordance with the present invention typically have a titer of 6.7 dtex or less, such as 2.2 dtex or less, such as 1.7 dtex, or even lower, such as 1.3 dtex or even lower, depending on the desired application. If the fiber is intended to be used in non-woven applications a titer of from 1.5 to 1.8 dtex typically is suitable while for textile applications lower tites such as from 1.2 to 1.5 dtex are suitable. However, the present invention also covers fibers with much lower titers, with suitable lower limits for titers being 0.5 dtex or higher, such as 0.8 dtex or higher, and in embodiments 1.3 dtex or higher. These upper and lower values as disclosed here define ranges of from 0.5 to 9 dtex, and including all further ranges formed by combining any one of the upper values with any one of the lower values. Surprisingly the present invention enables the formation of fibers with the desired titers over the whole application range, from non-woven applications to textile applications.

[0028] The fiber in accordance with the present invention preferably shows a reduced crystallinity, preferably of 40% or less. The fiber in accordance with the present invention preferably shows a WRV of 70% or more, more preferably 75% or more. Illustrative ranges of WRV of the fibers of the present invention, in particular in combination with the crystallinity values described herein, are form 72% to 90%, such as from 75% to 85%. The fiber in accordance with the present invention does not show any sulfuric smell so that olfactoric drawbacks of viscose fibers are overcome, while properties such as WRV and working capacity enable the use of the fibers of the present invention as viscose replacement fibers.

[0029] The fiber in accordance with the present invention, in isolation or in any combination with features outlined above as preferred for the claimed fiber, has a crystallinity of 40 % or less, preferably 39 % or less. In particular fibers to be employed for non woven applications do show preferably a low crystallinity of for example from 39 to 30%, such as from 38 to 33 %. The present invention however is not limited to these exemplary crystallinity values. As explained above, in comparison to standard lyocell fibers the fibers in accordance with the present invention do show a reduced crystallinity of 40 % or less.

[0030] The fiber in accordance with the present invention may be prepared using lyocell technology employing a solution of cellulose and a spinning process employing a precipitation bath according to standard lyocell processes, known to the skilled person. It is important that the process employs a solution in equilibrium state in accordance with large scale processing methods, as this enhances the properties and structures associated with the present invention, without sacrificing the mechanical properties to an extend detrimental for the intended end use.

[0031] The fiber in accordance with the present invention shows a novel type of distribution of the hemicelluloses over the cross section of the fiber. While for standard lyocell fibers the hemicelluloses is concentrated within the surface region of the fiber the fibers in accordance with the present invention show an even distribution of the hemicelluloses

over the entire cross section of the fiber. Such a distribution enhances the functionality of the fiber, as hemicelluloses increase for example binding properties towards other additives with a matching chemical reactivity. In addition the even distribution of the hemicelluloses may also contribute towards stabilizing the novel structure of the fibers in accordance with the present invention, comprising larger pores volumes in the surface layer and a porous core layer. This novel structure enhances uptake as well as retention of other molecules, such as dyes or moisture and also contributes towards a faster degradation, in particular biological (enzymatic) degradation.

[0032] The fibers in accordance with the present invention may be employed for a variety of applications, such as the production of non-woven fabrics, but also textiles. The fibers in accordance with the present invention may be employed as the only fiber of a desired product or they maybe mixed with other types of fibers. The mixing ratio can depend from the desired end use. If for example a non-woven or textile product with enhanced coloring and color retention is desired the fibers in accordance with the present invention may be present in a higher amount, relative to other fibers according to the prior art, in order to secure the desired properties, while in other applications a lower relative amount of fibers of the present invention may be sufficient.

[0033] As far as the present application refers to parameters, such as crystallinity, scan viscosity etc., it is to be understood that same are determined as outlined herein, in the general part of the description and/or as outlined in the following examples. In this regard it is to be understood that the parameter values and ranges as defined herein in relation to fibers refer to properties determined with fibers derived from pulp and containing only additives, such as processing aids typically added to the dope as well as other additives, such as matting agents (TiO_2, which often is added in amounts of 0.75 wt.-%), in a total amount of up to 1 wt.-% (based on fiber weight). The unique and particular properties as reported herein are properties of the fibers as such, and not properties obtained by addition of particular additives and/or post spinning treatments (such as fibrillation improving treatments etc.).

[0034] However, it is clear to the average skilled person that the fibers as disclosed and claimed herein may comprise additives, such as inorganic fillers etc. in usual amounts as long as the presence of these additives has no detrimental effect on dope preparation and spinning operation. The type of such additives as well as the respective addition amounts are known to the skilled person.

Examples:

Example 1: Lyocell fiber production and analysis

[0035] 3 different fibers were produced using 3 different types of pulp with different hemicellulose contents (table 1). The lyocell fibers were produced according to WO93/19230 dissolving the pulps in NMMO and spinning them over an air-gap into a precipitation bath to receive fibers with titers from 1.3 dtex to 2.2 dtex, without and with matting agent (0.75% TiO_2).

Table 1: Sugar contents of the different pulps for the lyocell fiber production

sugar [%ATS]	reference pulp	hemi-rich pulp 1	hemi-rich pulp 2
Glucan	95.5	82.2	82.3
Xylan	2.3	8.3	14
Mannan	0.2	5.7	<0.2
Arabinan	<0.1	0.3	<0.1
Rhaman	<0.1	<0.1	<0.1
Galactan	<0.1	0.2	<0.1

[0036] The fiber properties of the lyocell fibers produced were analyzed. The results are summarized in table 2. Fiber 1 is produced from hemi-rich pulp 1 and fiber 2 from hemi-rich pulp 2. The standard lyocell (CLY) fibers are produced from the standard lyocell reference pulp. Bright indicates a textile fiber without matting agent, whereas the dull fibers contain the matting agent identified above.

Table 2: Fiber properties (working capacity determined in accordance with BISFA definitions)

fiber type	Titer [dtex]	working capacity [cN/tex*%]	FFk [cN/tex]	FDk [%]
1.3 dtex / 38 mm fiber 1 bright	1.33	410	31	13.2

(continued)

fiber type	Titer [dtex]	working capacity [cN/tex*%]	FFk [cN/tex]	FDk [%]
1.3 dtex / 38 mm CLY standard bright	1.28	491	35.7	13.8
1.7 dtex / 38 mm fiber 1 bright	1.69	380	30.4	12.5
1.7 dtex / 38 mm CLY standard bright	1.65	571	38.6	14.8
2.2 dtex / 38 mm fiber 1 bright	2.12	339	28.2	12.1
2.2 dtex / 38 mm CLY standard bright	2.14	559	41.7	13.4
1.7 dtex / 38 mm fiber 1 dull	1.67	333	28.7	11.6
1.7 dtex / 38 mm CLY standard dull	1.71	384	32.1	11.9
1.7 dtex /38 mm fiber 2 dull	1.72	315	27.6	11.4
1.7 dtex / 38 mm CLY standard dull (pulp 2)	1.75	386	30.6	12.6

[0037] The displayed results show that the fibers in accordance with the present invention may be prepared over the commercially relevant range of fiber titers, while maintaining sufficient mechanical properties, in particular working capacity, to render these fibers suitable as viscose replacement fibers.

***Example 2*:** Crystallinity measurements

[0038] Crystallinities of the fibers of Example 1 are measured using a FT/IR with a Bruker MultiRAM FT-Raman spectrometer with a Nd-Yag-laser at 1064 nm and 500mW. The fibers are pressed into pellets for a smooth surface. Fourfold determination with a spectral resolution of 4 cm^{-1} with 100 scans respectively. Evaluation of the measurements was done using a chemometric method (calibration with WAXS-data).

[0039] It can be seen that the crystallinities of the fibers of the present invention (fiber 1 and 2) decrease by 16 and 15% respectively compared to the standard CLY fibers.

Table 3: Crystallinities of the different lyocell fibers

fiber type	crystallinity [%]
1.3 dtex / 38 mm CLY standard bright	44
1.3 dtex / 40 mm viscose standard bright	29
1.3 dtex / 38 mm fiber 1 bright	37
1.7 dtex / 38 mm CLY standard dull	47
1.7 dtex / 40 mm viscose standard dull	34
1.7 dtex / 38 mm fiber 1 dull	40
1.7 dtex / 38 mm fiber 2 dull	39

***Example 3*:** WRV determination

[0040] For determining the water retention value, a defined quantity of dry fibers is introduced into special centrifuge tubes (with an outlet for the water). The fibers are allowed to swell in deionized water for 5 minutes. Then they are centrifuged at 3000 rpm for 15 minutes, whereupon the moist cellulose is weighed right away. The moist cellulose is dried for 4 hours at 105 °C, whereupon the dry weight is determined. The WRV is calculated using the following formula:

$$\mathrm{WRV}[\%] = \frac{(\mathrm{mf}-\mathrm{mt})}{\mathrm{mt}*100} \qquad (\mathrm{m_f} = \text{moist mass}, \mathrm{m_t} = \text{dry mass})$$

[0041] The water retention value (WRV) is a measured value that indicates how much water of a moisture penetrated sample is retained after centrifuging. The water retention value is expressed as a percentage relative to the dry weight of the sample.

[0042] In table 4 the water retention values of the fibers of the present invention (fiber 1 and 2) compared to the reference fibers are listed and an increase of the WRV by 19% and 26% respectively compared to standard CLY fibers can be observed.

Table 4: WRV of the different lyocell fibers

fiber type	WRV [%]
1.3 dtex / 38 mm CLY standard bright	69.6
1.3 dtex / 40 mm viscose standard bright	89.9
1.3 dtex / 38 mm fiber 1 bright	82.8
1.7 dtex / 38 mm CLY standard dull	65.3
1.7 dtex / 38 mm fiber 1 dull	82.5
1.7 dtex / 38 mm fiber 2 dull	78.0

[0043] These results prove that the fibers in accordance with the present invention display a WRV rendering these fibers suitable as viscose replacement fibers.

***Example 4*:** Orientation and porosity

[0044] The new fibers produced from hemi-rich pulp 1 showed a higher water retention value which indicates an increased pore size and number over the whole fiber cross section. For standard lyocell fibers a low WRV is known combined with a very high orientation of the polymer chains described by high crystallinity. For the new fibers, also the crystallinity decreased significantly underlining a lower orientation of the polymer chains and giving rise to an enhanced pore volume. The results were verified for different fiber types with different titers of 1.3 and 1.7 dtex and the effect is therefore independent of the titer or diameter of the final lyocell fiber.

Table 5: Orientation and porosity of different fiber types.

property	lyocell standard dull	fiber 1 dull	lyocell standard bright	fiber 1 bright
crystallinity [%]	47	40	44	37
polymer orientation	high	decreased	high	decreased
WRV [%]	65.3	82.5	69.6	82.8
core porosity	standard	increased pore volume	standard	increased pore volume

Example 5: Comparison of fluorescent staining

[0045] The fibers of Example 1 fiber 1 bright (1.3 dtex/ 38 mm), CLY standard bright (1.3 dtex / 38 mm) as well as standard viscose standard bright fibers (1.3 dtex / 38 mm) were subjected to staining with Uvitex BHT according to the method of Abu-Rous (J.Appl. Polym.Sci., 2007, 106:2083-2091). The fibers obtained were evaluated after different intervals of immersion in the dye solution, at periods of from 5 min to 24 h. Due to the big size of the dye molecules the penetration is restricted to areas with bigger pore volumes. Conclusions can be drawn from the extent of dye penetration about the porous structure of the fiber cross section. The intensity of the color gives indications about the number of pores and voids, their size and chemical binding of the dye molecules to the inner surface of the fiber pores. Chemical binding is mainly attributed to hemicelluloses and non-crystalline regions. Surprisingly, the fibers in accordance with the present invention showed a fast and complete staining of the entire cross section of the fiber as shown in Figure 1. The fiber is more easily penetrated indicating an increased accessibility due to a bigger pore size and number in the new fibers, a lower crystallinity as shown in Example 2 and a higher hemicellulose content over the whole fiber cross section

as shown in Example 6. The viscose fibers showed an uptake of the dye up to 3 h, thereafter no further uptake of dye was observed. At the same time, the dye uptake was restricted to the outer regions of the viscose fiber. The standard lyocell fibers showed a similar behavior, although the staining was somewhat faster and more intense, compared to the viscose fibers. However, the staining was restricted to the shell and middle layer of the fiber with no staining of the dense and compact core layer of the standard lyocell fibers.

Table 6: Comparison of time and extend of staining

property	standard viscose fiber	standard lyocell fiber	fiber 1 bright
Velocity of staining	Slow	Middle	Fast
Staining extend	Only outer regions	Shell and middle layer	Entire cross section
Intensity of coloring	Slight	Intense	Intense

Example 6: Enzymatic peeling

[0046] The lyocell fibers evaluated in Example 1 were subjected to an enzymatic peeling test according to Sjöberg et al (Biomacromolecules 6:3146-3151, 2005). A viscose fiber with an enhanced xylan content of 7.5% was chosen for comparison from the paper by Schild and Liftinger (2014). This xylan content is close to the xylan content of the new fiber with 6.9%. The test enables the generation of data concerning the hemicellulose distribution over the cross section of fibers, in particular xylan (by HPLC determination) including information relating to different densities and structures of layers (as denser layers show a slower response as well as layers with smaller pore sizes).

[0047] The standard lyocell fibers (1.3 dtex / 38 mm bright) as well as the xylan enriched viscose fibers (1.3 dtex / 38mm bright) showed a slow peeling rate (fig. 2). This effect is even more pronounced for prolonged peeling times due to the denser cores. At the same time, the xylan liberation determined corresponds to fibers with high hemicellulose content at the surface of the fiber and a sharp concentration decrease towards the core (fig. 3). Contrary thereto, the fibers in accordance with the present invention show a peeling behavior corresponding to a fiber structure with an even distribution of the hemicellulose content over the entire cross section. Additionally, the peeling is much faster. This is even more astonishing and completely new as this phenomenon could not be achieved with xylan enriched viscose fibers. Due to the faster peeling rate it can be concluded that the new fibers have more porous core and surface layers with increased pore sizes and numbers and a homogenous distribution of the xylan over the whole fiber cross section.

Claims

1. Lyocell fiber with an enhanced porous structure over the fiber cross section and a crystallinity of 40% or less.

2. Lyocell fiber according to claim 1, with a WRV of 70 % or greater.

3. Lyocell fiber according to claim 1 or 2 with an entire staining over the whole fiber cross section using a fluorescent staining dye.

4. Lyocell fiber according to any one of the preceding claims, wherein the pulp employed for the fiber formation comprises cellulose and hemicelluloses, with a hemicelluloses content of at least 7 wt.-%.

5. Lyocell fiber according to any one of claims 1 to 4, having a titer of 6.7 dtex or less, prefereably 2.2 dtex or less, even more preferably 1.3 dtex or less.

6. Lyocell fiber according to any one of claims 1 to 5, produced from a pulp having a hemicelluloses content of 7 wt.-% or more and 25 wt.-% or less.

7. Lyocell fiber according to any one of claims 1 to 6, wherein the hemicellulose comprises a ratio of C5/xylan to C6/mannan of from 125:1 to 1:3, preferably of from 25:1 to 1:2.

8. Lyocell fiber according to any one of claims 6 or 7, wherein the pulp comprises 6 wt.-% or more xylan, preferably 8 wt.-% or more, more preferably 12 wt.-% or more and/or 3 wt.-% or more mannan, preferably 5 wt.-% or more mannan, and/or 1 wt.-% or less mannan.

9. Use of a pulp for producing a fiber according to any one of claims 1 to 8, wherein the pulp has a hemicelluloses content of 7 wt.-% or more and 25 wt.-% or less.

10. Use according to claim 8, wherein the hemicellulose comprises a ratio of C5/xylan to C6/mannan of from 125:1 to 1:3, preferably of from 25:1 to 1:2.

11. Use according to any one of claims 9 or 10, wherein the pulp comprises 5 wt.-% or more xylan, preferably 8 wt.-% or more, more preferably 10 wt.-% or more and/or 3 wt.-% or more mannan, preferably 5 wt.-% or more mannan, and/or 1 wt.-% or less mannan.

12. Method for producing the lyocell fiber according to any one of claims 1 to 8 using a direct dissolution process.

13. Method for producing the lyocell fiber according to claim 12 using a amine oxide process, where an aqueous solution of the amine oxide and the pulp form a cellulose suspension and a shapeable solution which gets shaped and coagulated in a spin bath obtaining the lyocell fiber after washing and pre-treatment steps.

14. Method for producing the lyocell fiber according to claim 13 using an aqueous tertiary amine oxide, preferably aqueous NMMO.

15. Method according to any one of claims 12 to 14, wherein the spinning solution contains a pulp with a hemicelluloses content of greater than 10 wt.-% based on the total weight of cellulose and hemicelluloses contained.

16. Lyocell fiber, use or method according to any of the preceding claims, wherein the pulp has a scan viscosity of from 300 to 440ml/g.

17. Product, comprising the lyocell fiber according to any one of claims 1 to 8 or 16, or the fiber produced according to any one of claims 12 to 16.

18. Product according to claim 17, wherein the product is a non-woven fabric.

19. Product according to claim 17 and/or 18, selected among tissues and wipes.

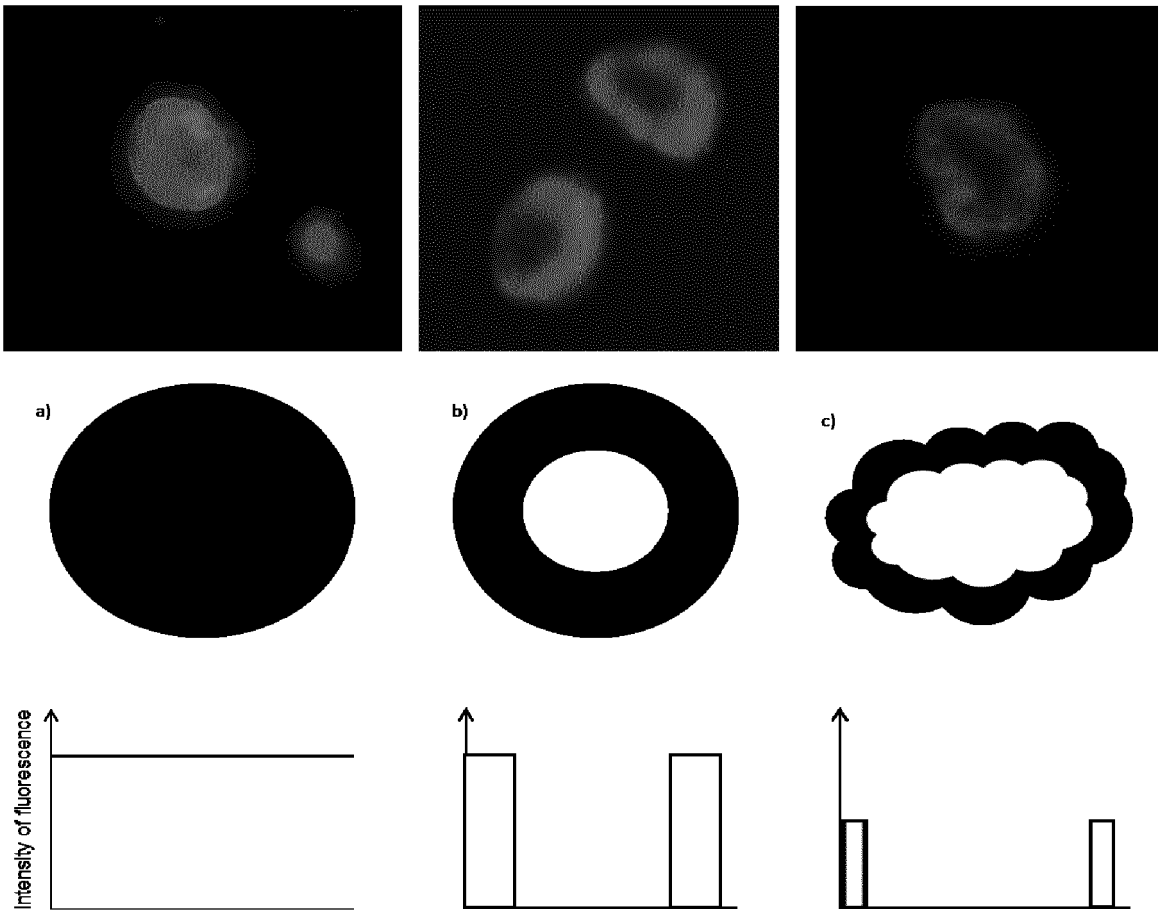

Figure 1: Fibers after fluorescent staining at maximum dye uptake a) fiber in accordance with present invention b) standard lyocell fiber c) standard viscose fiber and a schematic drawing of the intensity of the fluorescence of the tested fiber types

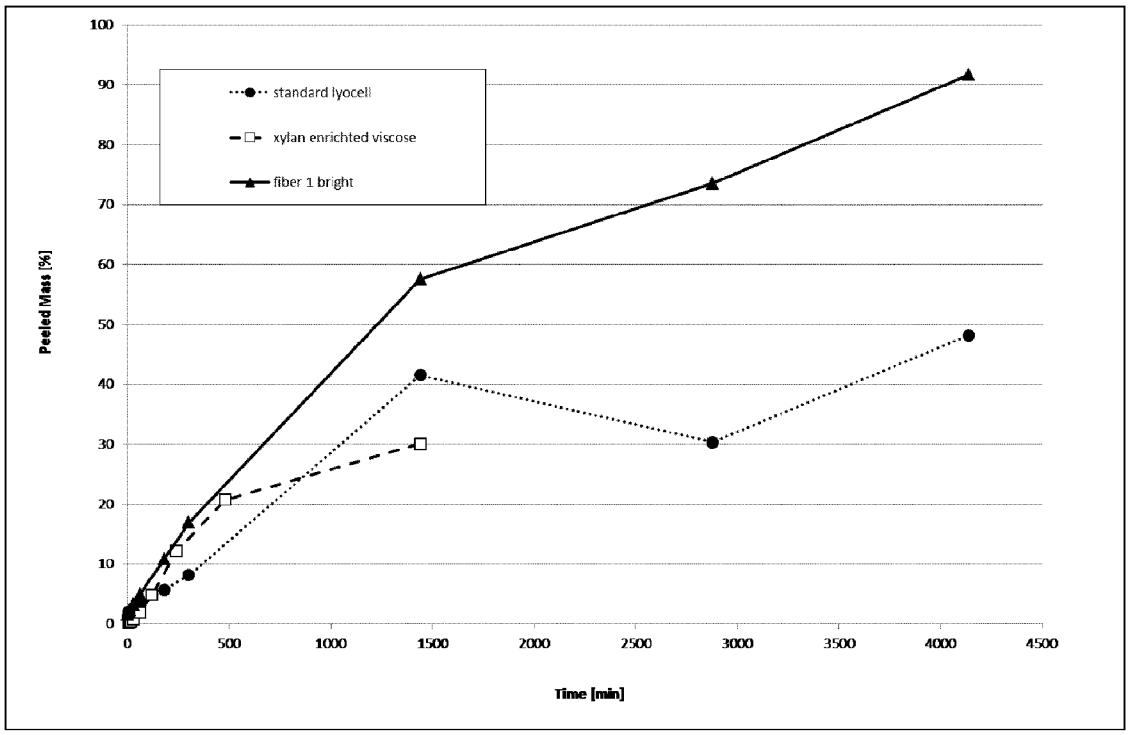

Figure 2: Velocity of enzymatic peeling for the new lyocell fiber with increased porosity compared to a standard lyocell fiber and a xylan enriched viscose fiber

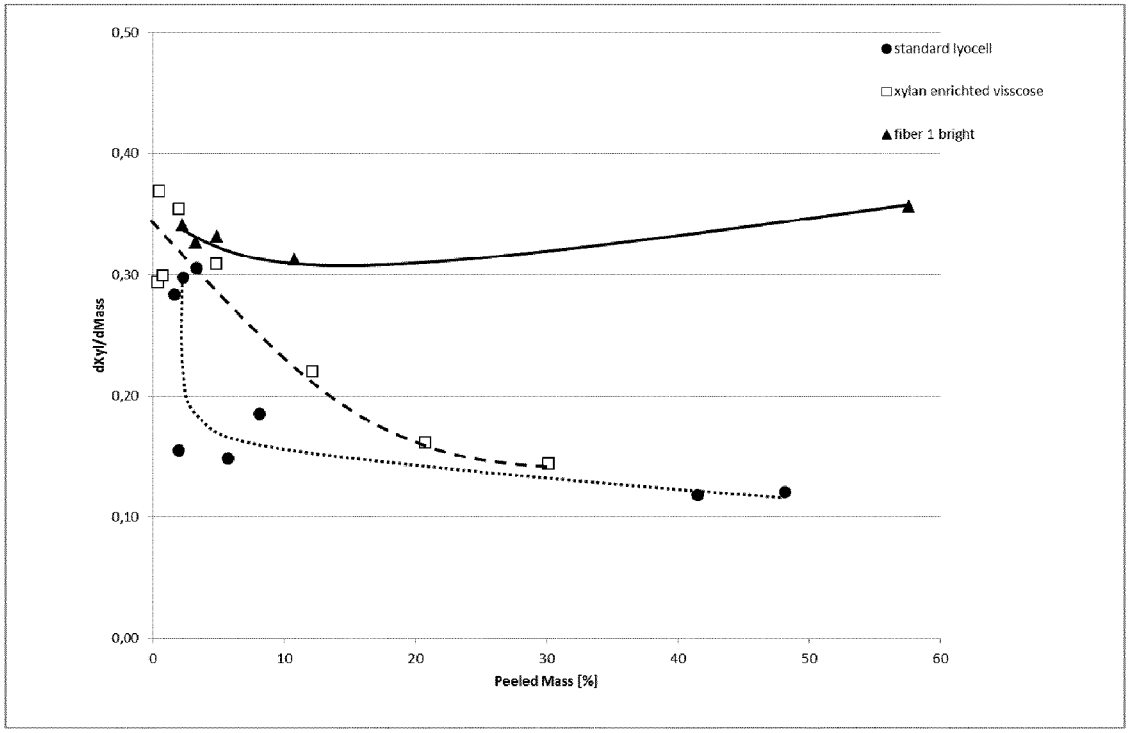

Figure 3: Xylan concentration over the fiber cross section of the new lyocell fiber with increased porosity compared to a standard lyocell fiber and a xylan enriched viscose fiber

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EUROPEAN SEARCH REPORT

Application Number
EP 18 16 0130

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X A	WO 01/62845 A1 (ZIMMER AG [DE]; ZIKELI STEFAN [AT]; ENDL THOMAS [AT]; MARTL MICHAEL GE) 30 August 2001 (2001-08-30) * examples 3,4 * * tables 7,9 * * claims 5,15,18,21 * * page 4, lines 5-9 *	1-3,5, 12-14, 16-19 4,6-11, 15	INV. D01F2/00
X	US 2009/004473 A1 (LUO MENGKUI [US]) 1 January 2009 (2009-01-01) * tables 1,2 * * paragraphs [0009], [0010], [0015], [0016], [0025], [0035] *	1-19	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	16 August 2018	Verschuren, Jo

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A	FRANK WENDLER ET AL: "Morphology of polysaccharide blend fibers shaped from NaOH,-methylmorpholine--oxide and 1-ethyl-3-methylimidazolium acetate", CELLULOSE, KLUWER ACADEMIC PUBLISHERS (DORDRECHT), NL, vol. 18, no. 5, 5 July 2011 (2011-07-05), pages 1165-1178, XP019936834, ISSN: 1572-882X, DOI: 10.1007/S10570-011-9559-2 * the whole document *	1-19	TECHNICAL FIELDS SEARCHED (IPC)

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