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# (54)METHOD FOR PRODUCING REGENERATED CELLULOSIC FIBERS

(57)The present disclosure relates to a method and processing facility for producing regenerated cellulosic fibers. The method comprises extruding a spinning solution into a coagulation bath which contains a salt and preferably an alkali to produce the fibers. The spinning solution comprising cellulose dissolved in an aqueous solvent comprising NaOH and ZnO. The coagulation bath has a pH-value of at least seven. The method further comprises a continuous process of applying to the fibers in a never-dried state a crosslinking agent with two or more reactive groups and heating the fibers to a curing temperature while maintaining the never-dried condition to produce a reaction between the crosslinking agent and the cellulose of the fiber.



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Processed by Luminess, 75001 PARIS (FR)

## Description

#### Field of the invention

**[0001]** The current disclosure relates to innovations in the field of the production, use and application of manmade cellulosic fibers. Particularly the current disclosure relates to processes for the production of regenerated cellulosic fibers which are produced according to a coldalkali process, the thus produced fibers and their use.

#### **Description of the Related Art**

**[0002]** Man-made cellulosic fibers are manufactured fibers that are based on cellulosic matter as a source material.

**[0003]** In the context of the current disclosure the term "cellulose" denotes an organic compound derived from plant cell walls or synthetically produced. Cellulose is a polysaccharide and is unbranched. Typically, cellulose comprises several hundred to ten thousand  $\beta$ -D-glucose molecules ( $\beta$ -1,4-glycosidic bound) or cellobiose units, respectively. The cellulose molecules that are used by plants to produce cellulose fibers are also used in technical processes to produce regenerated cellulose.

**[0004]** The term "regenerated cellulose" denotes a class of materials manufactured by the conversion of natural or recycled cellulose to a soluble cellulosic derivative or a directly dissolved cellulose solution and subsequent regeneration, forming shaped bodies, such as fibers (e.g., rayon), films or foils (e.g., cellophane) or bulk solids (e.g. beads, powders or pellets).

**[0005]** The term "fibers", as it is used herein, denotes continuous filaments as well as cut staple fibers of any desired length.

**[0006]** Cellulosic fibers can be used to produce woven, knitted or non-woven structures (including fabrics) comprising the cellulosic fibers. Woven fabrics comprise textile planar fabrics made from at least two crossed thread systems, which can be referred to as warp- and weftyarns. By contrast, the yarn in knitted fabrics follows a meandering path (a course), forming symmetric loops (also called bights) symmetrically above and below the mean path of the yarn.

**[0007]** The term "non-woven fabric" denotes fabrics that are neither woven nor knitted. Non-woven fabrics can be in the form of a fabric comprising randomly oriented fibers and/or cut yarns of finite length. Non-woven fabrics can also comprise endless yarns, e.g. produced by a melt-blown-process.

**[0008]** Viscose fibers are regenerated cellulosic fibers, which are manufactured by means of a wet spinning method which is called the viscose-method. The starting raw material of the viscose-method is cellulose which is usually provided on the basis of wood. From this starting raw material a highly pure cellulose in form of chemical pulp is obtained. Additionally or as an alternative other cellulosic materials, such as bamboo, cotton linters, re-

cycled cellulosic materials, reed, etc., or mixtures of such materials can be used as a starting raw material. In subsequent process stages, the pulp is first treated with caustic soda (NaOH), whereby alkali cellulose is formed.

In a subsequent conversion of said alkali cellulose with carbon disulfide, cellulose-xanthogenate is formed. From this, by further supplying NaOH, the viscose-spinning solution is generated which is pumped through holes of shower-like spinning nozzles into a coagulation bath (al-

<sup>10</sup> so referred to as spin bath). There, one viscose-filament per spinning nozzle hole is generated by coagulation. To coagulate the spinning solution, an acidic coagulation bath is used. The thus generated viscose-filaments are subsequently post processed. The post processing usu-

<sup>15</sup> ally comprises several washing- and stretching steps and the filaments are cut to viscose-staple fibers. Several other post-processing steps, such as crimping, bleaching and/or finishing ("soft finish") can be performed on the uncut and/or the cut fibers. In the context of this docu-<sup>20</sup> ment, the term "viscose process" denotes such a xan-

thogenate process. [0009] The term "Lyocell", as used herein, denotes a regenerated fiber type comprising cellulose, which is

manufactured according to a direct solvent method. The cellulose for the lyocell-method is extracted from the raw material containing the cellulose. The thus obtained pulp may subsequently be dissolved in a suitable organic solvent under dehydration without chemical modification. In large-scale industrial implementation N-methylmorpho-

30 line-N-oxide (NMMO) is currently used a solvent, nonetheless it is known that other solvents, such as ionic liquids, can also be used for the process. The solution is then filtered and, for the production of fibers, subsequently extruded through spinning nozzles into an air gap

<sup>35</sup> where they are drawn and coagulated by means of a moist airstream and then are fed into a coagulation bath containing an aqueous NMMO-solution. Subsequently the fibers can be further processed, e.g. washed, bleached, finished, crimped, cut to staple fibers, etc.

40 [0010] It is known that lyocell fibers may exhibit a tendency to fibrillate when subjected to mechanical stress in wet state. Fibrillation means that the fiber structure breaks down in longitudinal direction. Because of mechanical abrasion in the wet state, fine fibrils become

<sup>45</sup> partially detached from the fiber giving a hairy appearance to the fabric containing this fiber. This phenomenon takes place during wet fabric processing steps like dyeing or scouring as well as during laundering of garments. The surface of the fabric may get an aesthetically unde-

50 sirable appearance. The surface of the fabric becomes matted as the fibrils entangle with each other and where fibrillation occurs, the fabric has a lighter color due to spectral reflection from the surface of the fibrils. The fibrillation commonly occurs on the high points of the fabric <sup>55</sup> and lines of whiteness can appear where fibrillation occurs on creases. Fibrillation of a fabric can occur whenever the fabric is subjected to wet abrasion. Longer times and higher temperatures during wet treatment processes

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such as dyeing processes tend to produce greater degrees of fibrillation.

[0011] EP0538977A1 discloses a method for treatment of lyocell fibers with agents having functional groups reactive with cellulose to reduce or inhibit its tendency to fibrillate. A chemical reagent having two to six cellulose reactive functional groups a so called crosslinking agent is applied to the fiber. It is then exposed to conditions that cause the agent to react with the cellulose in the fiber causing the cellulose molecules to be attached together more strongly than can occur with the natural hydrogen bonds which normally bind the molecules in the fiber together. Hydrogen bonds can be broken by wetting with water and hence fibrillation can occur. The bonds formed with the crosslinking agent cannot be broken by exposure to water and hence the fiber does not fibrillate. It has however been found that such methods of treatment may have negative impacts on the mechanical properties of the fiber such as its tenacity and extensibility.

[0012] Another well-known process for the manufacturing of regenerated cellulose fibers is the carbamatemethod, which is similar to the viscose-process but uses urea instead of carbon disulfide. Still another process, which is called modal-process, is a modified viscoseprocess for the production of higher quality fibers. For these processes, also an acidic coagulation bath is used. [0013] Further, processes for manufacturing of cellulosic products are known that can use an alkaline spin bath comprising a salt. To prepare the spinning solution, cellulose is dissolved in an aqueous inorganic alkaline medium comprising zinc oxide (ZnO) under controlled low temperatures. Such processes are herein generally denoted as "cold-alkali process".

**[0014]** WO2018/169479 discloses an example of a fiber produced by a cold-alkali process. The method comprises: providing a spinning dope comprising a solution of cellulose and an additive in an alkaline solvent, in which solvent cellulose is present at a concentration of from about 5 to 12 percent per weight by weight and the additive is present in the range of from 0.1 - 10 percent per weight calculated on the cellulose; contacting the cellulose spinning dope with an aqueous coagulation bath fluid having a pH value above 7 and comprising a salt; forming a regenerated cellulosic fiber composition; and stretching and washing the fiber composition in one or more washing and stretching baths.

**[0015]** EP3231901A1 discloses a similar process, wherein a spin dope is prepared by dissolving cellulose in an aqueous NaOH solution. The spin bath comprises a coagulation liquid comprising an aqueous sodium salt solution.

**[0016]** EP3231899A1 discloses a method for preparing a spin dope by direct dissolution of cellulose in cold alkali.

**[0017]** WO2020171767A1 discloses a process for forming a fiber tow involving a wet spinning procedure comprising the steps of: dissolving cellulose pulp in an

alkaline aqueous solvent to form a cellulose spin dope composition, spinning the cellulose spin dope composition in a coagulation bath having a pH of more than 7.0, preferably a pH of at least 10, to produce a fiber tow, and passing the produced fiber tow through a sequence of consecutive stretching and washing steps in which the

formed fiber tow is washed with a washing liquid by a counter-current flow washing procedure.[0018] Still, many aspects of the cold-alkali process

<sup>10</sup> are not fully understood and it would be desirable to find further means to improve the fiber quality and increase the efficiency of the production processes.

### Summary

**[0019]** The present disclosure describes methods and apparatus for producing regenerated fibers that are produced according to a cold-alkali process. It has been found that the properties of cold-alkali fibers, although they are being directly spun into a coagulation bath, are very different compared to viscose or modal fibers that use comparable spinnerets. Nonetheless, cold-alkali fibers also differ a lot from lyocell fibers. Further to this, cold-alkali fibers show a strong tendency to fibrillate. This

<sup>25</sup> creates a need for new processing methods that can be used in connection with the cold-alkali process to improve fiber properties.

[0020] In a first aspect the present disclosure relates to a method for producing regenerated cellulosic fibers,
the method comprising extruding a spinning solution into a coagulation bath which contains a salt and preferably an alkali to produce the fibers, the spinning solution comprising cellulose dissolved in an aqueous solvent comprising NaOH and ZnO, the coagulation bath having a pH-value of at least seven, wherein the method further comprises a continuous process of applying to the fibers in a never-dried state a crosslinking agent with two or more reactive groups and heating the fibers to a curing

temperature while maintaining the never-dried condition
 to produce a reaction between the crosslinking agent and
 the cellulose of the fibers. The wet abrasion properties
 and the fibrillation tendency of a cold alkali fiber is re duced by crosslinking. It has been found that according
 to this protocol a crosslinking can be effectuated on the

cold-alkali fibers while mostly maintaining the mechanical properties of the fiber, in particular the tensile strengths and the elongation of the fibers can be retained. Further, an embrittling effect can be avoided. Embrittlement of the cold alkali fiber means that the elongation of
 the fiber becomes so low that processing of the fibers into yarn is difficult or even impossible.

**[0021]** The term "crosslinking agent" as it is used herein, denotes a chemical reagent whose molecules contain a plurality of - i.e. at least 2 and preferably up to 6 - functional groups capable of reacting with the hydroxyl groups in cellulose to form crosslinks.

**[0022]** The molecules of the crosslinking agent may preferably belong to a substance class that can be se-

lected from the group comprising triazines, pyrimidines, acrylamides, methacrylamides / haloacrylamides, vinyl sulfone precursors, vinyl sulfones, epoxides, aldehydes, acetals, resins (e.g. methylol derivatives), carboxylic acids, isocyanates, thioisocyanates, aziridines / sulfonylaziridines, sulfates, thiosulfates, organosilanes, acrylates, vinyl ketones, inorganic acids, acrylate esters, haloacetyls haloheterocycles, 2-step processes or mixed x-linkers (such as (poly)acrylic acids and phosphinates; periodate/amine, e.g. melamine; mixed x-linker substance classes, such as triazine+vinyl sulfone, etc.).

[0023] The functional groups reactive with cellulose may be any of those known in the art. Numerous examples of such groups are, for example, given in the article entitled "Dyes, Reactive" in Kirk-Othmer, Encyclopaedia of Chemical Technology, 3rd edition, Volume 8 (1979, Wiley-Interscience) at pages 374-392. Dyes described therein contain a chromophore system attached directly or indirectly to a unit which carries one or more functional groups reactive with the material to be dyed. The chemical reagents utilised as a crosslinking agent differ from reactive dyes in that they do not contain a chromophore and so are substantially colourless. Treatment with such reagents in the absence of dyes therefore does not substantially alter the colour of the solvent-spun cellulose fiber. Accordingly, the treated fiber is suitable for dyeing in any manner known for cellulose fibers, yarns or fabrics. Nonetheless, crosslinking agents can also comprise a chromophore system, in which case they also act as a dyestuff.

**[0024]** Preferred examples for functional groups are reactive halogen atoms attached to a polyazine ring, for example fluorine, chlorine or bromine atoms attached to a pyridazine, pyrimidine or sym-triazine ring. Other examples of such functional groups include vinyl sulphones and precursors thereof. Each functional group in the reagent may be of the same or a different type.

**[0025]** The crosslinking agent is preferably applied to the fiber in an aqueous system, more preferably in the form of an aqueous solution. The crosslinking agent may contain one or more solubilising groups to enhance its solubility in water. A solubilising group may be an ionic species, for example a sulphonic acid group, or a nonionic species, for example an oligomeric poly(ethylene glycol) or poly(propylene glycol) chain. Nonionic species generally have less effect on the essential dyeing characteristics of the cellulose fiber than ionic species and may be preferred for this reason. The solubilising group may be attached to the chemical reagent by a labile bond, for example a bond which is susceptible to hydrolysis after the chemical reagent has reacted with the cellulose fiber.

**[0026]** The person skilled in the art and having knowledge of the teachings disclosed herein is able to choose a suitable salt for use in the coagulation bath. The salt facilitates a coagulation of the spinning solution and preferably can be present in the coagulation bath in a ratio ranging from 10 percent per weight to 30 percent per weight. Preferably, the salt is a sodium salt, e.g. sodium carbonate or sodium sulfate. Further suitable salts can be chosen by taking into account the Hofmeister series (also known as the lyotropic series), which classifies ions in order of their precipitation capacities. The salt should,

for one thing, allow for a quick coagulation and secondly, it should facilitate recovery and recycling of the compounds. Alternative, but less preferred coagulation sodium salts include sodium salts wherein the counter ion is

<sup>10</sup> a carboxylate (e.g. formate, acetate, propionate, butyrate or benzoate), an aliphatic or aromatic sulfonate (e.g. benzenesulfonate, toluenesulfonate, or methanesulfonate), an aliphatic or aromatic phosphonate ion or mixtures thereof. Preferably, the anionic counter ion has a dense

<sup>15</sup> electric charge, placing it in the beginning of the Hofmeister series. Anionic counter ions having a dense electric charge are characterized as strongly "salting out" proteins, due to their ability to increase surface tension and organize water molecules in solvation shells around

20 them. Further, the coagulation sodium salt is preferably a sodium salt precipitating as a hydrate. Preferably the molar ratio of water to sodium salt in the precipitated hydrate is at least 4:1.

[0027] Surprisingly it was found that the regenerated fibers that are produced according to a cold-alkali process may be crosslinked without the need to fully wash the fibers after the coagulation bath. According to the prior art the fibers first have to be fully washed to remove all residues coming from the coagulation bath.

30 [0028] According to a preferred embodiment, the crosslinking agent is applied to the fibers after the fibers have been partially washed, preferably to a pH of between 10 and 12. Thereby, the inherent alkaline condition of the fibers can be utilized for crosslinking. The functional groups reactive with cellulose in the chemical reagents.

groups reactive with cellulose in the chemical reagents used in the present invention may react most rapidly with cellulose under alkaline conditions and reagents containing such groups may be preferred. Although crosslinking would also be possible with the freshly spun fibers before

40 washing, partial washing of the fibers is preferred to facilitate alkaline recycling. Examples of functional groups that are preferably applied under alkaline conditions are halogenated polyazine rings.

**[0029]** According to another embodiment the crosslinking agent is applied on the fiber after the fiber has been essentially fully washed, preferably to a pH of between 5 and 11, wherein the crosslinking agent is applied in combination with an inorganic alkali.

[0030] According to a further embodiment, the crosslinking agent can be applied to the never dried fibers by directing the never dried fibers through an application bath comprising the crosslinking agent. This is an efficient way to apply the crosslinking agent while the fiber is still uncut and conveyed in form of a fiber tow. In ad<sup>55</sup> dition alkali can be added to the crosslinking agent in the same application system or in later system to increase the pH and effect a better crosslinker fixation to the cellulose.

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**[0031]** The heating of the fibers to a curing temperature while maintaining the never dried condition can preferably comprise one or more steps independently selected from:

- heating a fluid comprising the crosslinking agent to a temperature above the curing temperature before applying the crosslinking agent to the fiber,
- steaming the fiber, preferably with low-pressure steam, after applying the crosslinking agent to the fiber.

**[0032]** In another embodiment the crosslinking agent can be a reactive dyestuff having two or more reactive groups. This allows for a combined crosslinking and dying.

**[0033]** According to another approach, the crosslinking agent and a monolinking dyestuff can be applied to the fibers. The crosslinking of the fibers can improve the dying process.

**[0034]** In another embodiment, a monolinking dyestuff can be added to the crosslinking agent. This allows for crosslinking and dying in a single process step.

**[0035]** According to another embodiment, a water-soluble polymeric alcohol can either be incorporated into the fiber before the application of the crosslinking agent or can be applied as a component in the crosslinking agent. This can increase the dye affinity of the fiber.

[0036] In a second aspect, the present disclosure relates to a processing facility for producing regenerated cellulosic fibers comprising a spinneret for extruding a spinning solution into a coagulation bath which contains a salt and preferably an alkali to produce the fibers, the spinning solution comprising cellulose dissolved in an aqueous solvent comprising NaOH and ZnO, the coagulation bath having a pH-value of at least seven, wherein the processing facility comprises a crosslinking facility in which a crosslinking agent with two or more reactive groups is applied to the fibers in a never-dried state, and wherein the crosslinking facility comprises a curing facility for heating the fibers to a curing temperature while maintaining the never-dried condition to produce a reaction between the crosslinking agent and the cellulose of the fibers. The processing facility allows for the industrial implementation and scale-up of the methods disclosed herein.

[0037] In a preferred embodiment the crosslinking facility comprises an application bath in which the crosslinking agent is provided and applied to the never dried fibers. [0038] According to another embodiment, the processing facility further comprises a washing facility upstream from the crosslinking facility.

**[0039]** In a third aspect, the present disclosure relates to regenerated cellulosic fibers produced in a processing facility as described herein and/or produced by a method as described herein. The fibers can meet enhanced quality standards, both in view of requirements for further

processing steps as well as in terms of properties of intermediate- and end products comprising the fiber. [0040] In a preferred embodiment the fiber comprises

- the crosslinking agent in an amount of 0,5 % per weight
  to 5 % per weight, preferably between 1 % per weight
  and 3% per weight, based on the weight of the dry fiber.
  On the one hand the amount of crosslinking agent bond
  to the cellulose of the fiber should be high enough to
  substantially reduce fibrillation tendencies, on the other
- <sup>10</sup> hand too much of the crosslinking agent could lead to embrittlement of the fibers. The optimal amount also depends on the Molecular weight of the crosslinking molecule.

[0041] In another aspect the present disclosure relates
to a product, particularly a consumer product or an intermediate product, comprising the regenerated cellulosic fibers as disclosed herein. Preferably, the product can be selected from a list comprising yarns, fabrics, textiles, home textiles, garments, nonwovens, hygiene products,
upholstery, technical applications, such as filter material, paper.

#### **Brief Description of the Drawings**

- <sup>25</sup> [0042] Hereinafter, exemplary embodiments of the invention are described with reference to the drawings, wherein
  - Fig. 1 is a schematic and exemplified representation of a fiber production process according to the present disclosure focusing on the spinning dope preparation,
  - Fig. 2 is a schematic and exemplified representation of processing facility according to the present disclosure focusing on the post-processing of the spun fibers and
- Fig. 3 is a schematic representation of a part of the fiber-tow processing facility according to another embodiment.

#### **Detailed Description of the Drawings**

<sup>45</sup> [0043] Fig. 1 shows a flowchart representing an exemplary fiber production process according to the present disclosure. The diagram is a simplified representation and shows the process in a schematized manner.
[0044] The process can be sectioned into the following basic steps, which are denoted in with roman numbers in Fig. 1:

I. Supplying the raw material

<sup>55</sup> **[0045]** For the process according to the present disclosure a broad range of possible cellulosic raw materials can be used. Generally the intrinsic viscosity and the degree of polymerization of the cellulose used as a raw material is lower than it is common for the viscose- or lyocell-process. For example dissolving pulp (kraft or sulphite) with an intrinsic viscosity (measured in Cuen, according to SCAN-CM 15:99) of about 200 mL/g to 700 mL/g (degree of polymerization DP of 500 to 1900), preferably between about 250 and about 400 mL/g (DP or 600 to 950) can be used. Further, recycling pulp or cotton linters (preferably having the same DP as stated above) can be used. The recycling pulp can, for example, be derived from waste paper, recycled viscose textile material, recycled modal textile material, recycled lyocell textile material an/or recycled cotton fiber textile material. Blends of pulps of different origin, such as blends of virgin wood pulp with recycling pulp, are possible and may be even desirable.

**[0046]** In Fig. 1 an example of a staple of dissolving pulp 1 is depicted as the raw material

#### II. Pretreatment of the raw material

**[0047]** The cellulosic raw material can be subjected to a pretreatment, wherein the degree of polymerization is adjusted to a desired DP to adjust the viscosity of the spinning dope to a value that allows for filtering and spinning. The pretreatment can comprise subjecting the raw material to an acidic pulp treatment, wherein the DP-value is mainly influenced by the duration of the pretreatment and the concentration of the acid. In other cases the pretreatment can be omitted, if the DP-value is already at the desired value. For example, pulp derived from cellulosic regenerated fibers can have a DP that allows for a direct dissolution without a pretreatment.

**[0048]** In a more specific example, an acidic pulp treatment with 1-10 percent per weight sulfuric acid at 50°C to 95°C for a duration from 5min to 2h can be used as a pretreatment. As the profitability of the process is reduced by a long duration of this treatment step, it is generally preferable to minimize the duration of the pretreatment as far as possible. The person skilled in the art, who is aware of the teachings of this disclosure, is able to find suitable parameters and optimize them without undue burden.

**[0049]** The pretreatment further comprises washing the cellulosic material with water and pressing to reduce moisture content, e.g. to about 50 percent per weight of the cellulosic material.

**[0050]** In Fig. 1 a source for a pretreatment chemical 2, e.g. sulfuric acid, and a pretreatment vessel 3 are exemplarily depicted. After the pretreatment in pretreatment vessel 3 the cellulosic material can be squeezed and washed to reduce the amount of acid that is transported to the next step.

III. Preparation of the spinning dope

**[0051]** To prepare the spinning dope (also called spinning solution), the wet and pretreated pulp is first cooled to about 0°C (while freezing of the pulp should be avoid-

ed), and an aqueous solvent comprising NaOH and ZnO is prepared. Preferably the solvent is adjusted to provide a spinning solution comprising 5 to 10 percent per weight NaOH and 0.8 to 3 percent per weight ZnO. The solvent is cooled down to a process temperature, which prefer-

<sup>5</sup> is cooled down to a process temperature, which preferably lies between -5°C and -10°C.
[0052] The pulp and the solvent are blended to dissolve the cellulose in the solvent. To improve the processabil-

ity, the preparation of the spinning dope comprises a mixing step followed by a homogenization step. During the mixing step the blend is mixed with a high shear stress, which can be done in a high-shear mixer. This high shear stress mixing is preferably only performed for a rather short period of time, for example the mixing can be done

<sup>15</sup> for 1 - 2 minutes. In the following homogenization step the blend is agitated with a lower shear intensity. The homogenization step can last longer than the mixing step, for example about 5 minutes.

[0053] During both the mixing and the homogenization step the temperature of the mixture is controlled, especially cooled. Preferably the temperature is kept below 0°C. The process temperature should never exceed 5°C, as the solution could then thicken and be irrecoverably lost.

<sup>25</sup> [0054] The so prepared spinning solution is then filtered and de-aerated. For example, the spinning dope can be filtered at least twice via a KK filter (Kolben-Korb-Filter, Lenzing Technik) with a mesh size of 15 micrometer.

30 [0055] For the de-aeration the spinning solution is exposed to reduced pressure. This step is per-se known from the viscose process. Other techniques for filtering and de-aerating the dope that can be used are known to the person skilled in the art.

<sup>35</sup> **[0056]** The prepared spinning dope should be free of voids, have a homogenous consistency and a proper viscosity that allows for an extrusion in the spinneret used in the following extrusion step.

[0057] In a preferred embodiment the ballfall-viscosity
 of the spinning dope should be in the range of about 30 to 200 s. The ballfall-viscosity can be measured according to DIN 53015-2019. The viscosity of the spinning dope can be adjusted by several different means. For example, the viscosity can be adjusted by altering the DP-value of

the cellulose, by changing the composition of the solvent and/or the concentration of the cellulose in the spin dope. For example, the concentration of the cellulose can be in the range of about 4 percent per weight to about 12 percent per weight, particularly in the range of about 5
percent per weight to about 8 percent per weight preferably about 6 percent to about 7 percent per weight.

**[0058]** The specific parameters of the mixing, homogenization and filtering steps can be found by the person skilled in the art, who is aware of the current disclosure, by routine work and experiments.

**[0059]** In Fig. 1 a chemical repository 4 for the storage of the ingredients of the solvent, a solvent cooling device 5 for the cooling of at least parts of the solvent, a pulp

cooling device 6, a mixing vessel 7 and a de-aerating filter 8 are exemplarily depicted. The mixing vessel 7 is provided with a cooling jacket 9.

IV. Extrusion into the coagulation bath

[0060] The spinning dope can be extruded through a nozzle directly into a coagulation bath. In case additives are added to the spinning dope, the dope can be homogenized via a static mixer to incorporate additives. Before the extrusion step, the dope can preferably be tempered to spinning temperature, for example to a temperature in the range of from 5°C to 30°C. For fiber production, a straightforward approach could be to use as the extrusion nozzle a spinneret comprising, for example, up to 150 cups with a diameter of 12.5 to 16 mm, comprising up to 3000 holes with a diameter of about 40 to 75 micrometer, which corresponds to dimensions as they are known per se and commonly used in connection with the viscose spinning process. Nonetheless, it was surprisingly found that in connection with the cold-alkali process broader diameters can improve process stability and facilitate the coagulation and stretching of the fibers. According to the present disclosure it is therefore suggested to use a spinneret comprising holes with a diameter of about 80-120  $\mu$ m, preferably between 90 and 110  $\mu$ m. For example, in an industrial scale production plant one spinneret could comprise up to 150 cups with a diameter of 12,5 to 16 mm, comprising about 600 to 1400 holes with a diameter of about 80-120  $\mu$ m, preferably between 90 and 110  $\mu$ m. The relatively thick diameter of the spinning holes causes different course of coagulation, i.e. that the freshly extruded fibers first only coagulate at the outer surface, while the middle of the fiber stays in a liquid state for a longer time. This allows for a higher stretching and the stretching conditions can be uphold in a more stable way. [0061] The coagulation bath comprises an alkali, preferably NaOH, and a salt, preferably sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>, or sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>.

**[0062]** As an example, the coagulation bath can comprise from 10 percent per weight to 30 percent per weight Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>SO<sub>4</sub> and from 0 to 3 percent per weight NaOH, preferably from 0.1 to 3 % and still more preferred from 0.2 to 0.7 percent per weight NaOH. In a specific example the coagulation bath can comprise about 22 percent per weight Na<sub>2</sub>CO<sub>3</sub> and about 0.5 percent per weight NaOH. The temperature of the coagulation bath can, for example, be adjusted to between 10°C and 30°C, and preferably be tempered at about 20°C.

**[0063]** The optimal distance, that the freshly extruded fiber travels through the coagulation bath (i.e. the coagulation bath distance) depends, inter alia, on the extrusion speed, the pull-off speed, the composition and consistency of the spinning dope, the composition of the coagulation bath and the temperature. Without being restricted to these values, that under most parameter conditions the optimal coagulation bath distance may be found within a range from about 10 cm to about 100 cm.

Preferred values for the coagulation bath distance range from about 15 cm to about 60 cm.

[0064] The fiber tow is drawn out of the coagulation bath to a transporting section, which can comprise several godets and/or guides that transport the fiber tow through a series of post-processing stages. The pull-off force that is exerted on the freshly extruded fibers can be regulated by the extrusion speed and the speed of the first transporting unit (or godet), which preferably can
<sup>10</sup> be positioned outside of the coagulation bath. Due to the pull-off force, which is exerted on the freshly extruded fibers by the first transporting unit, the fibers get stretched already inside the coagulation bath. Further stretching steps can be during the following post processing of the

15 fibers [0065] In Fig. 1 a coagulation bath 10 comprising a coagulation liquid 11, a spinneret 12 and a first godet 13 are exemplarily depicted. The spinneret 12 extrudes a number of fibers 14 (corresponding to the number of 20 holes of the spinneret 12) into the coagulation liquid 11. The freshly extruded fibers 14 are gathered together into a fiber tow 15 by the first godet 13. By adjusting the extrusion speed at the spinneret 12 and the speed of the godet 13 the amount of stretching, that is done directly 25 after extrusion within the coagulation bath 10 can be set. Although an inclined angle of the spinneret 12 (and the freshly extruded fibers 14) is shown in Fig. 1, the skilled practitioner, who is aware of the current teaching, is able to apply other spinning configurations that are per se 30 known in the field, e.g. from viscose production.

V. Post-processing of the fiber tow

[0066] As it is used throughout this disclosure, the term
"post-processing" encompasses all processing steps that are performed on the extruded fibers after they have been withdrawn from the coagulation bath. Post-processing steps can be applied to the fiber tow while it is transported on the transporting unit. Additionally, the
fiber tow can be cut in a cutting apparatus and further post-processing steps can be performed on the cut fibers.
[0067] In Fig. 1 the post-processing is only schematically represented by the respective reference sign V.

[0068] Post-processing of the fibers can comprise, but<sup>45</sup> are not restricted to, any combination of one or more of the following steps:

- washing of the fiber tow and/or the cut fibers,
- pressing the fiber tow and/or the cut fibers to reduce the amount of liquid therein,
- neutralizing the fiber tow and/or the cut fibers with an acidic liquid,
- bleaching the fiber tow and/or the cut fibers,
- crosslinking the fiber tow and/or the cut fibers by ap-

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plying a crosslinking agent on the fibers and curing it,

- applying a finishing agent ("soft finish") to the fibers of the fiber tow and/or the cut fibers,
- drying the fiber tow and/or the cut fibers.

**[0069]** Immediately after the fibers in the fiber tow have been withdrawn from the coagulation bath, they already have been stretched to a certain extent, preferably to about 20-30 % but have not reached their final elongation (and final cellulose specific diameter).

**[0070]** In a different approach, several successive stretching steps during the post-processing can be implemented. For example a counter current flow washing can be implemented in the post processing, wherein the fibers in the fiber tow are being incrementally stretched during and/or in-between the several washing steps until they have reached their final extension.

**[0071]** According to another approach, the fiber tow can be led into a conditioning bath comprising from 10 percent per weight to 30 percent per weight a salt that facilitates a further coagulation of the spinning solution, the conditioning bath preferably being fluidly separated from any downstream washing facilities, and stretched to essentially the final cellulose specific diameter of the fibers and oriented to essentially their final state within the conditioning bath. The conditioning bath can comprise a coagulation liquid that is similar or identical to the coagulation bath liquid. The coagulation speed in the conditioning bath can be adjusted by the temperature of the liquid therein, which preferably can be controlled independently from the coagulation bath.

**[0072]** Following the second bath, the fiber tow can be washed in a downstream washing line, where no additional stretching is applied to the fiber.

**[0073]** The term "fluidly separated", as it is used herein, denotes systems that are either associated to completely separated circulation systems, or that are connected via an installation that significantly changes the properties of the liquid, e.g. by adding substances to and/or removing substances from the liquid or by concentrating or diluting the liquid.

[0074] The salt in the conditioning bath can preferably be identical to the salt that is used in the coagulation bath, or it can be chosen according to the same requirements as the salt in the coagulation bath that are outlined above. [0075] As the case may be (and according to the technical requirements), other post-processing steps can be arranged in the processing line according to any technically useful configuration.

**[0076]** Fig. 2 is a schematic block-diagram showing an exemplary configuration of a post-processing facility for treating a fiber-tow which is produced according to the current disclosure, e.g. by the facility depicted in Fig. 1. **[0077]** Fibers 14 are extruded by a spinneret 12 into a coagulation liquid 11 within a coagulation bath 10 and gathered together into a fiber tow 15 by the first godet 13 (similar to Fig. 1). From the first godet 13 the fiber tow is directed to a second godet 18. Between the first godet 13 an the second godet 18 the fiber tow 15 is diverted via a rotating or static guide 16, e.g. a roller or a bar", and submerged into a conditioning bath 17 containing a coagulation liquid 11'. The coagulation liquid can be identical or similar to the coagulation liquid 11 in the coagulation bath 10. Preferably the coagulation liquid 11 in the coagulation bath 10 and the coagulation liquid 11' in the

conditioning bath 17 are circulated in a common fluid cycle. Preferably the temperature of the coagulation liquid 11' in the conditioning bath 17 can be controlled independently from the temperature of the coagulation liquid 11 in the coagulation bath 10. Generally a higher tem-

perature is preferred for the coagulation liquid 11' in the conditioning bath 17. For example, the temperature of the coagulation liquid 11 in the coagulation bath 10 can be adjusted to a value between about 10 °C and about 20°C and the temperature of the coagulation liquid 11' in
the conditioning bath 17 can be adjusted to a value be-

tween about 20 °C and about 40 °C.

**[0078]** Between the first godet 13 and the second godet 18 and essentially within the conditioning bath 17 the fibers in the fiber tow are stretched to essentially their final cellulose specific diameter and oriented to essen-

<sup>25</sup> final cellulose specific diameter and oriented to essentially their final state .

[0079] The term "stetched to essentially their final cellulose specific diameter", as it is used herein, is to be interpreted to that effect that downstream of this stretch<sup>30</sup> ing step no further stretching steps are preformed on the fiber tow, i.e. the diameter of the fiber is held essentially constant until the fibers are either cut (after which a small amount of relaxation is unavoidable and sometimes even intended) or dried (where the diameter of the fibers as it would be actually measured is reduced due to the loss of liquid, generally without any change of the stretch of the fibers).

[0080] The term "cellulose specific diameter", as it is used herein, denotes a diameter in a virtually washed
<sup>40</sup> and dried state, i.e. only comprising the dry cellulose. One example of a cellulose specific diameter which is used in connection with fibers is the fiber titer, which is defined as the weight of the cellulosic contents of the fiber per unit of length.

<sup>45</sup> [0081] The term "oriented to essentially their final state", as it is used herein, is to be interpreted to that effect that the molecular orientation of the cellulose in the fibers is not actively changed in downstream processing steps, i.e. remains constant, apart from minor chang<sup>50</sup> es that may occur naturally or are a (generally unwanted)

side effect of other downstream post-processing steps.
[0082] It was surprisingly found that stretching the fibers to their final cellulose specific diameter and state within the conditioning bath allows for an economic and controllable production of fibers having adequate properties that allow, for example, a spinning of the fibers to yarn.
[0083] In Fig. 2 only one conditioning bath is shown. Nonetheless it would be possible to install more than one

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conditioning bath, for example two successive conditioning bathes or a series of consecutive conditioning bathes. Preferably the conditioning baths share the same fluid circuit with the coagulation bath and have an essentially identical or at least similar content of salt and/or alkali. The temperature of the conditioning baths can either be the same or controlled independently, as the case may be. Depending on the configuration, the fibers can, for example, be stretched in a cascading style, i.e. consecutive conditioning baths have an increasing stretching rate. The fibers could also be stretched to essentially their final state in an upstream conditioning bath (or several upstream conditioning bathes) and than be further coagulated and "fixed" within one (or more) downstream conditioning bath(s) with constant speed and stretch. The person skilled in the art and having knowledge of the teachings disclosed herein is able to optimize the number of conditioning baths, their temperatures and extension rated by routine tests and experiments without deviating from the scope of the current disclosure. The fiber parameters, such as tensile strength, elongation, crystallinity etc., can so be optimized in a methodical manner. From the second godet 18 the fiber tow 15 is directed to a washing line 19 which can comprise several washing steps which are exemplarily depicted in Fig. 2 as washing steps 20 and 20'. As the case may be, the washing line 19 can also comprise only one washing step 20 or any number of washing steps exceeding two. Further, any washing techniques for washing fiber tows, that are known per se in the art, can be used for in the washing line 19.

**[0084]** The transporting means for the fiber tow, such as rollers and godets or the like, in the washing line are operated at a constant speed so that the tension is kept essentially constant and no further stretching of the fibers in the fiber tow occurs. This also keeps the orientation of the fibers essentially at the state they were when leaving the second godet 18 after the stretching within the conditioning bath.

**[0085]** After the washing line 19 the fiber tow 15 is directed to a cutter 21, which cuts the fiber tow into staple fibers 22. During the washing steps 20 the consistency of the fibers has sufficiently settled so that the fibers essentially keep their cellulose specific diameter, elongation and orientation even if they are cut in wet state. Therefore, it is not necessary to dry the fiber tow 15 before cutting, which can reduce costs and allows for the implementation of more efficient post-processing steps.

**[0086]** In the lower part of Fig. 2 an exemplary postprocessing facility for the cut staple fibers is shown. The cut staple fibers are transported (or fall) from the cutter 21 to a fleece-forming device 23 having a basin 24 filled with a liquid, e.g. water, and a conveyer belt 25. The conveyer belt 25 is permeable to liquid and a current is maintained in the basin that transports the fibers that are suspended in the liquid of the basin to the conveyer belt 25, where they are collected and form a non-woven fiber layer 26 on the top surface of the conveyer belt 25. The surface of the conveyor belt is tilted and transports the newly formed non-woven fiber layer 26 out of the liquid and to further transport equipment (which is, for reasons of conciseness, not shown in Fig. 2). The freshly cut staple fibers 22 should be regularly distributed across the width of the fleece-forming device 23 so that the non-

woven fiber layer 26 has a uniform width and consistency.[0087] After leaving the fleece-forming device 23, the non-woven fiber layer 26 is squeezed in a first pressing

<sup>10</sup> device 27a to remove some of the liquid in the non-woven fiber layer 26. Several further pressing devices 27b to 27f can be arranged downstream between several processing steps. Especially the first pressing device 27a, but also the other pressing devices, create a natural

<sup>15</sup> crimp on the fibers in the non-woven fiber layer which is preferable for many fiber applications.[0088] The post-processing that is performed on the

non-woven fiber layer 26, as it is shown in Fig. 2, comprises a first washing facility 31, a crosslinking facility 30, a second washing facility 31', a neutralizer 32, a finishing facility 33, a dryer 34 and a baling press 35. The crosslink-

ing facility 30 comprises a first crosslinker application 28, a second crosslinker application 28' and a curing facility 29. Between the different stages the pressing devices 27a-27f are arranged to squeeze processing liquids out

of the non-woven fiber layer 26.

**[0089]** The crosslinking facility 30 is shown in Fig. 2 with two crosslinker applications 28 and 28'. Before entering the crosslinking facility 30 the fibers in the fiber layer 26 are squeezed by the first pressing device 27a, washed in the first washing facility 31 and squeezed again in the second pressing device 27b. This washing

step reduces the amount of chemicals that are transported into the crosslinking facility 30 and improves recycling
of the process fluids. In the first crosslinker application 28 the non-woven fiber layer 26 is impregnated with an aqueous solution comprising a first crosslinking agent.

The solution is pressed out in the pressing device 27c and in the second crosslinker application 28' another chemical reagent can be applied to the fibers to improve the crosslinking reaction For example, an alkali can be applied in the second crosslinker application 28'. De-

pending on the properties of the fibers after the first washing facility 31 only one crosslinker application 28 could
 be sufficient, depending on the residues of alkali in the fibers.

**[0090]** The fiber layer 26 is again pressed in pressing device 27d and then fed into the curing facility 29, in which the fibers are heated to a curing temperature, which facilitates the reaction between the crosslinking agent and the cellulose of the fibers. The heating can be done by

the cellulose of the fibers. The heating can be done by application of steam at a desired temperature.

**[0091]** After the crosslinking facility 30 the remaining crosslinking agent and alkali is washed out in the second washing facility 31'.

**[0092]** In the neutralizer 32 the fibers that may still contain residues of alkali may be neutralized with an acidic liquid. The acidic liquid may be selected from a list com-

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prising diluted acetic acid, lactic acid, sulphuric acid or the like, without being restricted to this list. It is to be noted that depending on the previous treatment steps and on other parameters of the fibers this neutralization is not always necessary.

**[0093]** If appropriate, a further washing step (not shown in Fig. 2) can be implemented after the neutralizer 32 to remove residues of chemicals that can still be present in the fibers. The used water of this (and any other) washing step can be forwarded to any upstream water-consuming devices, such as the washing steps 20, 20' of the washing line 19 and/or the cutter 21. In this way a a countercurrent washing system can be implemented.

**[0094]** In the finishing facility 33 a finishing agent or soft finish can be applied to the fibers.

**[0095]** After dewatering the non-woven fiber layer 26 in the last pressing device 27g, the non-woven fiber layer 26 is fed into the dryer 34. Before drying, the non-woven fiber layer 26 can be loosend in an opener (not shown), which opens the structure of the fiber layer 26 to improve the drying efficiency in the following dryer 33 and also to improve the further processing of the finished staple fibers.

**[0096]** After the dryer, the staple fibers are pressed to bales in the baling press 35.

**[0097]** The post-processing facilities listed above can be implemented in any technically reasonable and useful order, and the person skilled in the art, being aware of the current teachings, is able to implement numerous configurations without deviating from the current disclosure. The post-processing can also comprise other processing steps known in the art, such as, for example, a bleaching step or a dying step.

**[0098]** A dying step can for example be combined with the crosslinking step, either by using dyestuffs that also act as crosslinking agents or by using dyestuffs that show improved staining properties after the application of a crosslinking agent.

**[0099]** In Fig. 2 the post-processing steps of crosslinking, neutralizing, finishing and drying are done on the never-dried fibers in the non-woven fiber layer 26, i.e. after cutting of the never-dried fibers. Nonetheless, some or even all of these steps can also be applied on the fibers before cutting, i.e. on the still uncut fiber-tow. Such embodiments are well within the scope of the present disclosure and the skilled practitioner, who is aware of the teachings herein, is able to implement such configurations.

**[0100]** In another embodiment, the treatment of the fibers, i.e. all the washing, crosslinking, curing, neutralizing, finishing, etc. steps can be done on the uncut fiber tow and also the fibers can be dried while still in the fiber tow. In this case a crimp can be applied on the fibers, for example by stuffer-box-crimping, and the fibers can then be supplied as tow for stretch breaking applications or cut to staple fibers and pressed into bales. Fig. 3 shows the washing line 19, 19' of an alternative processing fa-

cility, wherein the crosslinking step is done on the still uncut fiber tow 15. The crosslinking facility 30 of Fig. 3 comprises a crosslinker application 28, which has the form of an application bath into which the fiber tow is

<sup>5</sup> submerged, and a curing facility 29, which heats the fibertow 25 after application of the crosslinking agent to improve the reaction between the crosslinking agent and the cellulose of the fibers in the fiber tow. The fiber tow 15 is led to the crosslinking facility 30 after having been

<sup>10</sup> directed through a first washing line 19, which performs at least one washing step 20 on the fiber tow. After the first washing line 19 the fibers in the fiber tow 15 have only been partially washed, for example to a pH of between 10 and 12, i.e. the fibers still contain an amount

<sup>15</sup> of alkali that is adjusted to improve the effect of the crosslinking agent.

**[0101]** After applying and curing the crosslinking agent, the fiber tow is led to a second washing line 19', wherein the remaining chemicals, for example the excess

20 crosslinking agent and the remaining alkali, are further washed out of the fiber tow 15. Any further processing steps can be arranged in a technically feasible way upstream or downstream of the washing and crosslinking line shown in Fig. 3.

#### **Execution examples**

**[0102]** In the following paragraphs several examples for putting the teachings of the current disclosure into practice are disclosed.

#### EXAMPLE 1

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**[0103]** The fibers can be produced according to the cold-alkali process disclosed herein, for example with a titer of 1.3 dtex. After extrusion and stretching of the fibers the fibers are partially washed to a pH of about 11 and then passed through an aqueous bath containing 1,3,5-triacryloyl -hexahydro-1,3,5-hexahydrotriazine (TAHT).

40 This bath is maintained at steady state (TAHT ca. 15g/l) and at a temperature of ca. 50°C by addition of solid TAHT to the circulating liquor using an in-line high shear mixer/pump. The fibers are squeezed in a nip before being exposed to saturated steam for a treatment time that

<sup>45</sup> allows for curing the crosslinking agent. The fibers are then washed and dried.

## EXAMPLE 2

<sup>50</sup> [0104] The fibers can be produced according to the cold-alkali process disclosed herein, for example with a titer of 1.3 dtex. After extrusion and stretching of the fibers the fibers are essentially fully washed within the fiber tow. The never dried and uncut fibers are passed through an aqueous bath containing 1,3,5-triacryloyl-hexahydro-1,3,5-hexahydrotriazine (TAHT) and trisodium phosphate (TSP). This bath is maintained at steady state (TAHT ca. 15g/l and TSP ca. 15g/l) at a temperature of

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ca. 50°C by addition of solid TAHT and TSP to the circulating liquor using an in-line high shear mixer/pump. The fibers are squeezed in a nip before being exposed to saturated steam for a treatment time that allows for curing the crosslinking agents. The fibers are then washed and dried.

## EXAMPLE 3

**[0105]** Fibers can be produced according to the coldalkali process disclosed herein, for example with a titer of 1.3 dtex. After extrusion and stretching of the fibers the fibers are essentially fully washed within the fiber tow. The washed fiber tow is passed into a first impregnation bath into which 8.3 weight% of p-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]benzenesulfonic acid, sodium salt (SDTB) on cellulose was dosed into an aqueous circulation system at a temperature of 35°C to give a concentration of 10-40g/l of an aqueous paste-like suspension. The fiber tow is then pressed to a moisture content of ca. 200%, and then passed through a second impregnation bath at 10°C into which 1.3% of NaOH and 1.1% of Na<sub>2</sub>CO<sub>3</sub> on weight cellulose are dosed into an aqueous circulation system.

**[0106]** The fibers are then pressed to a moisture content of ca. 200%, heated to 100°C in a steaming chamber for 8.5 minutes and then washed thoroughly by adding acidic water (pH 3.5) and then by water until they are free of excess chemicals and then dried.

#### **Reference signs:**

#### [0107]

dissolving pulp 1 source for a pretreatment chemical 2 pretreatment vessel 3 chemical repository 4 solvent cooling device 5 pulp cooling device 6 mixing vessel 7 de-aerating filter 8 cooling jacket 9 coagulation bath 10 coagulation liquid 11 spinneret 12 first godet 13 fibers 14 fiber tow 15 guide 16 conditioning bath 17 second godet 18 washing line 19 washing step 20 cutter 21 staple fibers 22 fleece-forming device 23 basin 24

conveyer belt 25 non-woven fiber layer 26 pressing device 27 crosslinker application 28 curing facility 29 crosslinking facility 30 washing facility 31 neutralizer 32 finishing facility 33 dryer 34 baling press 35

# Claims

- 1. Method for producing regenerated cellulosic fibers, the method comprising extruding a spinning solution into a coagulation bath which contains a salt and preferably an alkali to produce the fibers, the spinning solution comprising cellulose dissolved in an aqueous solvent comprising NaOH and ZnO, the coagulation bath having a pH-value of at least seven, wherein the method further comprises a continuous process of applying to the fibers in a never-dried state a crosslinking agent with two or more reactive groups and heating the fibers to a curing temperature while maintaining the never-dried condition to produce a reaction between the crosslinking agent and the cellulose of the fibers.
- 2. Method according to Claim 1, wherein the crosslinking agent is applied on the fibers after the fibers have been partially washed, preferably to a pH of between 10 and 12.
- 3. Method according to Claim 1, wherein the crosslinking agent is applied on the fiber after the fiber has been essentially fully washed, preferably to a pH of between 5 and 11, wherein the crosslinking agent is applied in combination with an inorganic alkali.
- Method according to any of the Claims 1 to 3, wherein the crosslinking agent is applied to the never dried fibers by directing the never dried fibers through an application bath comprising the crosslinking agent.
- 5. Method according to any of the Claims 1 to 4, wherein the heating of the fibers to a curing temperature while maintaining the never dried condition comprises one or more steps independently selected from:

- heating a fluid comprising the crosslinking agent to a temperature above the curing temperature before applying the crosslinking agent to the fiber,

- steaming the fiber, preferably with low-pressure steam, after applying the crosslinking agent to the fiber.

- 6. Method according to any of the Claims 1 to 5, wherein the crosslinking agent is a reactive dyestuff having two or more reactive groups.
- 7. Method according to any of the Claims 1 to 6, wherein the crosslinking agent and a monolinking dyestuff is applied to the fibers.
- Method according to Claim 7, wherein a monolinking dyestuff is applied to the fiber in combination with <sup>10</sup> the crosslinking agent.
- Method according to any of the Claims 1 to 8, wherein a water-soluble polymeric alcohol is either incorporated into the fiber before the application of the <sup>15</sup> crosslinking agent or is applied in combination with the crosslinking agent.
- 10. Processing facility for producing regenerated cellulosic fibers comprising a spinneret for extruding a 20 spinning solution into a coagulation bath which contains a salt and preferably an alkali to produce the fibers, the spinning solution comprising cellulose dissolved in an aqueous solvent comprising NaOH and ZnO, the coagulation bath having a pH-value of at 25 least seven, wherein the processing facility comprises a crosslinking facility in which a crosslinking agent with two or more reactive groups is applied to the fibers in a never-dried state, and wherein the crosslinking facility comprises a curing facility for 30 heating the fibers to a curing temperature while maintaining the never-dried condition to produce a reaction between the crosslinking agent and the cellulose of the fibers.
- **11.** Processing facility according to Claim 10, wherein the crosslinking facility comprises an application bath in which the crosslinking agent is provided and applied to the never dried fibers.
- **12.** Processing facility according to Claim 10 or 11, further comprising a washing facility upstream from the crosslinking facility.
- A regenerated cellulosic fiber produced in a processing facility according to any of the Claims 10 to 12 and/or by a method according to any of the Claims 1 to 9.
- 14. Regenerated cellulosic fiber according to Claim 13, 50 the fiber comprising the crosslinking agent in an amount of 0,5 % per weight to 5 % per weight, preferably between 1 % per weight and 3% per weight, based on the weight of the dry fiber.
- **15.** A product, particularly a consumer product or an intermediate product, comprising the regenerated cellulosic fiber according to Claim 13, wherein the prod-

uct preferably is selected from a list comprising yarns, fabrics, textiles, home textiles, garments, nonwovens, hygiene products, upholstery, technical applications, such as filter material, paper.

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Fig. 3





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# **EUROPEAN SEARCH REPORT**

Application Number

EP 21 18 7686

		DOCUMENTS CONSID			
	Category	Citation of document with ir of relevant pass	ndication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
10	X,D	WO 2020/171767 A1 ( 27 August 2020 (202	TREETOTEXTILE AB [SE]) 0-08-27) -29: claims 1-33:	10-12	INV. D01D1/02 D01D5/06
	1	figure 2 *		13-15	D01D10/02 D01D13/00
15	Y	CN 110 172 754 A (U 27 August 2019 (201 * abstract; claims	NIV NATIONAL DONG HWA) 9-08-27) 1-10; example 6 *	1-9, 13-15	D01F2/02 D01F11/02
20	x	US 2021/062369 A1 ( CHRISTOPH [AT] ET A 4 March 2021 (2021- * paragraphs [0081]	KLAUS-NIETROST L) 03-04) , [0082]; figure 2 * 	10-12	
25	A	WO 95/28516 A1 (COU LTD [GB] ET AL.) 26 October 1995 (19 * abstract; claims	RTAULDS FIBRES HOLDINGS 95-10-26) 1-12 * 	1–15	
	A	WO 2020/126931 A1 (CHEMIEFASER LENZING AG [AT]) 25 June 2020 (2020-06-25) * abstract: claims 1-20 *		1–15	TECHNICAL FIELDS SEARCHED (IPC)
30					D01D D01F
35					
40					
45					
:	L	The present search report has		E and an	
50	P04C01)	The Hague	5 January 2022	Malik, Jan	
55	X:par           X:par           Y:par           doc           Y:par           doc           A:tecl	ATEGORY OF CITED DOCUMENTS ticularly relevant if taken alone ticularly relevant if combined with anot ument of the same category nnological background	T : theory or principle E : earlier patent doc after the filing dat her D : document cited in L : document cited fo	a underlying the i ument, but publi a the application or other reasons	nvention shed on, or
55	O:nor P:inte	n-written disclosure rmediate document	& : member of the sa document	me patent family	/, corresponding

# EP 4 124 680 A1

## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 21 18 7686

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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10	ci	Patent document cited in search report		Publication date		Patent family member(s)		Publication date
	WC	2020171767	A1	27-08-2020	AU	2020226195	<b>A1</b>	12-08-2021
					CA	3130944	A1	27-08-2020
					CN	113631766	А	09-11-2021
15					EP	3927873	<b>A1</b>	29-12-2021
					SE	1950223	<b>A1</b>	22-08-2020
					WO	2020171767	<b>A1</b>	27-08-2020
	CN	110172754	A	27-08-2019	NON	ле Ле		
20	ບຮ	5 2021062369	A1	04-03-2021	CN	111868314	A	30-10-2020
					EP	3511449	<b>A1</b>	17-07-2019
					JP	2021511446	A	06-05-2021
					KR	20200106047	A	10-09-2020
					TW	201940765	A	16-10-2019
25					US	2021062369	<b>A1</b>	04-03-2021
						2019138097	A1	18-07-2019
	WC	9528516	A1	26-10-1995	AT	183262	т	15-08-1999
					AU	2219295	A	10-11-1995
30					BR	9507346	A	23-09-1997
					CN	1146223	A	26-03-1997
					CZ	291981	в6	18-06-2003
					DE	69511394	т2	13-01-2000
					EP	0755467	<b>A1</b>	29-01-1997
25					ES	2136286	тЗ	16-11-1999
35					FI	964127	A	14-10-1996
					IN	190376	в	26-07-2003
					$\mathbf{JP}$	3479079	в2	15-12-2003
					JP	H09512062	A	02-12-1997
					KR	100347380	в1	29-11-2002
40					RU	2143017	C1	20-12-1999
					SK	117196	A3	05-03-1997
					TR	28782	A	06-03-1997
					TW	347420	в	11-12-1998
					US	577 <del>9</del> 737	A	14-07-1998
45						9528516	A1	26-10-1995
	WC	2020126931	A1	25-06-2020	BR	112021007090	<b>A</b> 2	20-07-2021
					CA	3117595	<b>A1</b>	25-06-2020
					CN	113195805	A	30-07-2021
					EP	3899113	<b>A1</b>	27-10-2021
50					KR	20210096602	A	05-08-2021
					TW	202035812	A	01-10-2020
	_				WO	2020126931	A1	25-06-2020
55	ORN							
	й [ О							

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

## **REFERENCES CITED IN THE DESCRIPTION**

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

## Patent documents cited in the description

- EP 0538977 A1 [0011]
- WO 2018169479 A [0014]
- EP 3231901 A1 [0015]

- EP 3231899 A1 [0016]
- WO 2020171767 A1 [0017]
- Non-patent literature cited in the description
- Dyes, Reactive. Kirk-Othmer, Encyclopaedia of Chemical Technology. Wiley-Interscience, 1979, vol. 8, 374-392 [0023]