The invention relates to a method for manufacturing furnish for a paper product, wherein the manufactured furnish contains fibrillated cellulose material. The method comprises introducing first raw material to a system, which first raw material includes cellulose pulp (2), introducing second raw material to the system, which second raw material comprises cellulose fibers that are oxidized by nitroxyl-mediated oxidation of hydroxyl groups of the cellulose, conveying the first raw material and the second raw material to a refiner (8), and refining and mixing the first raw material and the second raw material in the refiner (8) in order to produce furnish comprising fibrillated cellulose material (4). In addition, this invention relates to a system for manufacturing furnish and a paper product.

Keskintökoeksee menetelmää seosuhteen valmistamiseksi paperituotetta varten, joka valmistettu seosuhde sisältää fibrilliselluloosamateriaalia. Menetelmässä järjestelmään johdetaan ensimmäistä raaka-ainetta, joka ensimmäinen raakaaine sisältää selluloosamassaa (2); järjestelmään johdetaan toista raaka-ainetta, joka toinen raaka-aine käsittää selluloosauskaijua, joka on hapettettu katalyytisesti hapettamalla selluloosan hydroksyylyhyvästä nitroksyylävälttelyssä; johdetaan ensimmäinen raaka-aine ja toinen raaka-aine jauhiimeen (8); ja jauhetaan ja sekoitetaan ensimmäistä raaka-ainetta ja toista raaka-ainetta jauhimessa (8) fibrilliselluloosamateriaalia (4) käsittevän seosuhteen valmistamiseksi. Lisäksi tämä keskintö koskee järjestelmää seosuhteen valmistamiseksi ja paperituotetta.
A PAPER PRODUCT AND A METHOD AND A SYSTEM FOR MANUFACTURING FURNISH

Field of the Invention

This invention relates to a method and a system for manufacturing furnish for a paper product, which furnish comprises fibril cellulose material. In addition, this invention relates to a paper product.

Background of the Invention

Cellulose, which is an abundant natural raw material, is a polysaccharide consisting of a linear chain of several hundreds to ten thousand linked D-glucose units. Cellulose fibers can be refined with a refiner or a grinder to produce fibril cellulose material. Typically, the production of fibril cellulose material requires a significant amount of beating energy. Therefore, there may be an efficiency problem with said material production.

Summary of the Invention

The present invention discloses a method and a system for manufacturing pulp comprising fibril cellulose. In addition, the invention discloses a paper product comprising fibril cellulose.

The present invention is based on a usage of fibril cellulose in paper furnish. The inventors of the present invention have surprisingly found a way to produce cellulose material with increased production efficiency. Fibril cellulose as such may provide a paper product with new functional properties. Moreover, due to the present invention, it may be possible to achieve a simple fibril cellulose process with low energy consumption. The produced pulp comprising fibril cellulose may be used, for example, as a strength additive for a paper product.

According to the present invention, anionized cellulose fibres are fed together with cellulose pulp, such as mechanical pulp or chemical pulp, preferably together with chemical pulp, through beating process in a paper machine approach system.
Aspects of the invention are characterized by what is stated in the independent claims 1, 6 and 8. Various embodiments of the invention are disclosed in the dependent claims.

In the method according to the present invention, wherein the manufactured furnish contains fibril cellulose material, the method advantageously comprises:
- introducing first raw material to a system, which first raw material includes cellulose pulp,
- introducing second raw material to the system, which second raw material comprises anionized cellulose fibers that are oxidized by nitroxyl-mediated oxidation of hydroxyl groups of the cellulose,
- conveying the first raw material and the second raw material to the same refiner,
- refining and mixing the first raw material and the second raw material in the refiner in order to produce pulp comprising fibril cellulose material.

In the system according to the present invention, wherein the manufactured furnish contains fibril cellulose material, the system comprises:
- first means for introducing first raw material to a system, which first raw material comprises cellulose pulp (2),
- second means for introducing second raw material to the system, which second raw material comprises cellulose fibers that are oxidized by nitroxyl-mediated oxidation of hydroxyl groups of the cellulose,
- at least one conveyer to convey the introduced raw materials to at least one refiner (8),
- the at least one refiner (8) to refine and to mix the first raw material and the second raw material in order to produce the furnish comprising fibril cellulose material (4).

Thanks to the present invention which may solve several issues of fibril cellulose usage on a paper machine, it may be possible to achieve at least some of the below mentioned advantages:
- quite simple (i.e. quite inexpensive) system for fibril cellulose process,
- transportation of low solids content fibril cellulose may be avoided,
- efficient mixing of basic furnish and fibril cellulose may be guaranteed during beating process,
- complicated dosing aggregates may not be needed in a paper machine approach system, and
- paper properties may be improved without significant loss of drainage speed.

Due to the present invention, for example a separate fibrillating process taking place in low solids content is not necessarily needed. Therefore, the invention may significantly simplify the start-up of fibril cellulose usage, because some large investments, such as installation of separate fibrillating aggregates, may be avoided.

**Description of the Drawings**

In the following, the invention will be illustrated by drawings in which

Figs 1a-1d show schematically some example embodiments of the invention, and

Figs 2-7 show results from experimental tests.

**Detailed Description of the Invention**

In the following disclosure, all percentages are by dry weight, if not indicated otherwise.

The following reference numbers are used in this application:

2     cellulose pulp,
30 2a   chemical cellulose pulp,
3     anionized cellulose fibres,
4     fibril cellulose material,
5     chemical pre-treatment,
8     refiner, and
35 10   refined cellulose pulp.
Cellulose is a renewable natural polymer that can be converted to many chemical derivatives. The derivatization takes place mostly by chemical reactions of the hydroxyl groups in the β-D-glucopyranose units of the polymer. By chemical derivatization the properties of the cellulose can be altered in comparison to the original chemical form while retaining the polymeric structure.

The term "cellulose raw material" refers to any cellulose raw material source that can be used in the production of chemically and/or mechanically treated cellulose fibers. The raw material can be based on any plant material that contains cellulose. The plant material may be wood. The wood can be from softwood trees such as spruce, pine, fir, larch, douglas-fir or hemlock, or from hardwood trees such as birch, aspen, poplar, alder, eucalyptus or acasia, or from a mixture of softwood and hardwood. Nonwood material can be from agricultural residues, grasses or other plant substances such as straw, leaves, bark, seeds, hulls, flowers, vegetables or fruits from cotton, corn, wheat, oat, rye, barley, rice, flax, hemp, Manila hemp, sisal hemp, jute, ramie, kenaf, bagasse, bamboo or reed.

The term "chemical (cellulose) pulp" 2a refers to cellulose fibers, which are isolated from any cellulose raw material or any combination of cellulose raw materials by a chemical pulping process. Therefore, lignin is at least for the most part removed from the cellulose raw material. Chemical pulp 2a is preferably sulfate wood pulp. In an example, the chemical pulp is isolated from softwood and/or from hardwood. The used chemical pulp 2a may be unbleached or bleached. Typically, the diameter of the fibers varies from 15 to 25 μm and the length exceeds 500 μm, but the present invention is not intended to be limited to these parameters.

The term "mechanical (cellulose) pulp" refers to cellulose fibers, which are isolated from any cellulose raw material by a mechanical pulping process. The mechanical pulping process could be preceded by a chemical pretreatment, producing chemimechanical pulp. The cellulose fibers used in this invention preferably comprise mechanically and/or chemically and/or chemimechanically treated cellulose fibers. Herein they are also referred as "raw material pulp 2" or "cellulose pulp 2". Therefore, cellulose pulp 2 may
consist of chemical cellulose pulp and/or mechanical pulp and/or chemi-
mechanical pulp.

The term “SEC” refers to specific energy consumption.

The term “SR” refers to so called Schopper-Riegler freeness of pulp.

The term “WRV” refers to water retention value.

It is possible to use fibril cellulose 4 in mechanical pulp containing papers,
such as printing paper. The method according to the present invention may
be used, for example, in Light Weight Coated (LWC) or Super Calendered
(SC) papers. Advantageously the method according to the present invention
is used in paper grades having high chemical pulp share, i.e. in papers
comprising more chemical pulp 2a than mechanical pulp. In an embodiment,
at least 80 % of dry weight, more preferably at least 90 % of dry weight and
most preferably at least 95 % of dry weight of the cellulose fibers used in this
invention is from chemical pulp 2a.

The term “fibril cellulose” 4 refers to a collection of isolated cellulose
microfibrils or microfibril bundles derived from cellulose raw material. There
are several widely used synonyms for fibril cellulose. For example:
nanofibrillated cellulose (NFC), nanocellulose, microfibrillar cellulose,
nanofibrillar cellulose, cellulose nanofiber, nano-scale fibrillated cellulose,
microfibrillated cellulose (MFC), or cellulose microfibrils. Fibril cellulose
described in this application is not the same material as the so called
cellulose whiskers, which are also known as: cellulose nanowhiskers,
cellulose nanocrystals, cellulose nanorods, rod-like cellulose microcrystals or
cellulose nanowires. In some cases, similar terminology is used for both
materials, for example by Kuthcarlapati et al. (Metals Materials and
Processes 20(3):307-314, 2008) where the studied material was called
“cellulose nanofiber” although they clearly referred to cellulose nanowhiskers.
Typically these materials do not have amorphous segments along the fibrillar
structure as fibril cellulose, which leads to a more rigid structure. Cellulose
whiskers are also shorter than fibril cellulose.
The anionization of the cellulose fibers, preferably chemical pulp, is preferably implemented by a reaction wherein the primary hydroxyl groups of cellulose are oxidized catalytically by a heterocyclic nitroxy1 compound. Other heterocyclic nitroxy1 compounds known to have selectivity in the oxidation of the hydroxyl groups of C-6 carbon of the glucose units of the cellulose can also be used. Advantageously, the primary hydroxyl groups of cellulose are oxidized first, after which the material is refined at least partly into fibril cellulose.

The charge (ieq/g) of the anionized cellulose fibers is preferably between -700 and -1200, for example between -900 and -1100.

The term “oxidation of cellulose” refers to the oxidation of the hydroxyl groups (of cellulose) to aldehydes and/or carboxyl groups. It is preferred that the hydroxyl groups are oxidized to carboxyl groups, i.e. the oxidation is complete, before the refining step in a refiner is implemented. “Catalytic oxidation” refers to nitroxy1-mediated (such as "TEMPO"-mediated) oxidation of hydroxyl groups. The term “TEMPO-treated” refers to a material that is treated with so called “TEMPO” chemical, i.e. 2,2,6,6-tetramethylpiperidiny1-1-oxo free radical.

The “catalytic oxidation of fibrous material” in turn refers to a material which contains cellulose that is oxidized by nitroxy1-mediated (such as "TEMPO"-mediated) oxidation of hydroxyl groups of the cellulose. In addition, also the terms “anionized cellulose fibers” and “anionized cellulose material” 3 are used, referring to a material comprising at least 90 w-% (of dry weight) cellulose material, more preferably consisting of cellulose material, in which cellulose is oxidized by nitroxy1-mediated (such as "TEMPO"-mediated) oxidation of hydroxyl groups of the cellulose.

Advantageously the chemical pulp 2a, which may be produced from softwood and/or from hardwood, is extensively oxygenated in the presence of catalytic oxidation, such as TEMPO-mediated oxidation in order to produce anionized cellulose fibres 3. The anionized cellulose fibres 3 have a high anionic charge and, thus, said anionized fibres are relatively easily fibrillated under shear forces.
Advantageously, cellulose pulp 2 and anionized cellulose material 3 are combined with each other before at least one refiner step in at least one refiner 8. The refiner 8 is preferably a grinder or a refiner, such as a conical refiner or a disc refiner or a cylindrical refiner. In an aspect of the invention, at least one refiner 8 is a grinder, a homogenizer, a colloidizer, a friction grinder, a fluidizer or an ultrasound sonicator.

The anionized cellulose material 3 is added to the cellulose pulp 2 which is going to a refiner 8 in a paper machine approach system. The anionized material 3, such as tempo-treated pulp, is fibrillated due to shear forces and energy consumed during the beating process. Most preferably the cellulose pulp 2 to be refined together with the anionized cellulose material 3 comprises unbeaten chemical pulp 2a, but said cellulose pulp 2 may also comprise beaten chemical pulp and/or mechanical pulp.

Advantageously, the furnish comprising cellulose pulp 2 and anionized cellulose material 3 to be conveyed to the refiner 8 comprises between 0.3 and 5 % of dry weight, more preferably between 0.6 and 3 % of dry weight, and most preferably between 1 and 2 % of dry weight cellulose fibers which are oxidized by nitroxy1-mediated oxidation of hydroxyl groups of the cellulose. The cellulose pulp 2 may comprise chemical pulp and/or mechanical pulp. It is also possible to add some additional cellulose pulp(s) after said refiner 8.

The amount of the fibril cellulose in the manufactured paper furnish is preferably between 0.1 and 5.0 % of the pulp (dry weight), more preferably between 0.3 and 4 % (dry weight), and most preferably between 1 and 2 % (dry weight) of the manufactured furnish. The amount is calculated from the whole furnish, including the fibre and the possible filler.

The amount (sum) of the anionized cellulose material 3 and fibril cellulose 10 in a base paper product (before any possible coating step) and/or in the furnish is preferably between 0.01-10.0% or dry weight, more preferably between 0.05 and 5.0% of dry weight and the most preferably between 0.5 and 2.0% of dry weight.
Due to the chemical pre-treatment of the cellulose fibers, charge of cellulose fibrils increases, hence repulsion forces between fibrils increase. In order to achieve efficient fibrillation process, a high oxygenation rate is required. Advantageously, the charge of the anionized cellulose fibers is between -900 and -1100 ieq/g.

According to the present invention, the chemical pre-treatment 5 of the cellulose pulp 2 (in order to produce anionized cellulose material 3) may be a part of the solution for manufacturing paper furnish (as shown in Figures 1a and 1d), or the chemical pre-treatment 5 may be implemented in another process.

Cationic polyelectrolyte, such as starch, is preferably dosed to the cellulose pulp (2) before the dosage of fibril cellulose material (4). Cationic polyelectrolyte can be any retention or strength polymer used in paper manufacturing, e.g. cationic starch, cationic polyacrylamide (CPAM) or polydimethyl diallyl ammonium chloride (PDADMAC). Also, the combinations of the different polyelectrolytes can be used. Preferably, the cationic polyelectrolyte is cationic starch (CS). The cationic polyelectrolyte is added in an amount of 0.01 to 5% of dry weight of fibres in the furnish, preferably approximately 0.10 to 1.00% of dry weight.

Thanks to the present invention, it is possible to mix cellulose pulp 2 with anionized chemical material 3 efficiently while at least some of the anionized cellulose material 3 is fibrillated into fibril cellulose 4 in at least one refiner 8. Therefore, fibril cellulose 4 may be mixed for example with cellulose pulp 2, such as chemical pulp 2a, without any separate mixing and fibrillating aggregates, i.e. an additional mixer may not be required.

According to the present invention, it is possible to avoid transportation of low solids fibril cellulose having the consistency of 5 % at the most. In fibril cellulose production, the concentration of fibril cellulose in dispersions is typically very low, usually around 1-5 %. Therefore the logistic costs are typically too high to transport the material from the production site. The specific surface area of fibril cellulose is very large due to its nanoscopic dimensions, and concentration or drying of fibril cellulose hydrogel is challenging. Respectively, strong water retention is natural for fibril cellulose.
since water is bound on the surfaces of the fibers through numerous hydrogen bonds.

Thanks to the present invention, the fibril cellulose 4 may be produced in the paper mill, i.e. in “on-site fibril cellulose production”, even without need for complicated dosing aggregates in the paper machine approach system. According to an embodiment of the invention, a storage tank, dilution water and dosing pumps are needed to feed said anionized cellulose material 3 to the main pulp line going to beating. Thus, the present invention is advantageously a simplified fibril cellulose dosing process.

The novel solution may be a cost effective way of using fibril cellulose in wet end applications. The invention may cause an effective dispersing of fibril cellulose and a proper mixing with base furnish.

A paper produced from the pulp manufactured according to the present invention may have many advantages. For example, the grammage of the paper may be decreased and/or the amount of the filler in use may be increased and/or strength properties of the produced paper may be increased. In addition, the amount of the needed silicone coating on a release paper may be decreased due to the new properties of the produced paper.

The paper comprising (at least mostly, i.e. at least 60% of dry weight, more preferably at least 75% and the most preferably at least 90% of dry weight) or consisting of the pulp manufactured according to the invention is preferably a release paper of a label laminate. The release paper is typically strongly refined, hence, the chemically treated cellulose may be refined into fibril cellulose efficiently. Advantageously, the basis weight range of the manufactured paper is between 30 and 90 g/m², more preferably between 30 and 50 g/m². The produced paper may be coated and/or surface sized and/or calendared.

The label laminate preferably comprises two layers which are laminated together, i.e. a release liner and a face layer, wherein an adhesive layer is provided between the release liner and the face layer. The term “face layer” refers to “the top layer” of the label laminate, also called as the face stock.
The face layer comprises at least one layer that is attached to another surface with an adhesive layer, when the label laminate is used.

The term “release liner” refers to a structure comprising at least one backing material layer as base material and at least one release coating layer on the backing material layer. In other words, the backing material layer is usually coated with a thin layer of release agent, such as silicone. Therefore, the release liner can be easily removed from the face layer when the label is adhered to a substrate. Herein, the term “release paper” refers to said backing material. Advantageously, the produced paper is coated with at least one silicon coating layer in order to produce a release liner for a label laminate.

The pulp from which the handsheet is made is preferably collected from the pulp flow that is going to a headbox of a paper machine. In other words, the pulp preferably comprises every compounds of the base paper to be manufactured, such as fillers, chemicals, pulps etc., but the process parameters of the paper machine cannot have any effect on the results. Typically, fibril cellulose added in small amount in paper has one, two, three or four of the following effects on handsheet, if the handsheet is manufactured from the pulp produced according to the present invention:

- Clearly lower air permeance if compared to a reference handsheets.
- Improved initial wet strength if compared to a reference handsheets.
- Improved Scott Bond if compared to a reference handsheets.
- Higher SR or WRV without adjusting beating if compared to a reference handsheets.

These properties are also presented in Table 2.

**Experimental tests**

In the experimental tests, different kinds of pulps for paper products were manufactured. Paper sheets were made from the produced pulps and tested afterwards.
Raw materials and a trial plan

Chemical pulps made with a conventional chemical pulping process were used as cellulose pulp 2. The chemical pulps used were isolated from pine (so called “Kaukas Pinus” manufactured by UPM) and from birch (so called “Kaukas Betula” manufactured by UPM).

The trial was carried out according to the plan presented in Table 1. SEC, pulp type (Birch, Pine), amount of the anionized cellulose material (“TEMPO pulp”), amount of the readymade fibril cellulose (TEMPO MFC), a place where the fibril cellulose was added and amount of starch were varied as shown in Table 1.

Table 1. Trial plan.

<table>
<thead>
<tr>
<th>TP</th>
<th>Birch</th>
<th>Pine</th>
<th>Birch / Pine</th>
<th>TEMPO pulp</th>
<th>TEMPO MFC</th>
<th>Starch / mg/g</th>
<th>MFC addition to</th>
<th>Birch / pine mixture SEC / kWh/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>70</td>
<td>30</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>1</td>
<td>70</td>
<td>30</td>
<td>100</td>
<td>10</td>
<td></td>
<td></td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>30</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>30</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>10</td>
<td>beating</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>20</td>
<td>beating</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>30</td>
<td>beating</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>10</td>
<td>beating</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>20</td>
<td>beating</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>30</td>
<td>beating</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>20</td>
<td>pulp after starch</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>10</td>
<td>pulp after starch</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>20</td>
<td>pulp after starch</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>30</td>
<td>pulp after starch</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>20</td>
<td>beating</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>70</td>
<td>30</td>
<td>98</td>
<td>2</td>
<td>20</td>
<td>beating</td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

Fibril cellulose material was dispersed with Bamix® - hand mixer for 2 minutes before the dispersed fibril cellulose was added to the chemical pulp. The mixture did not comprise fillers. Starch (Raisamyl 50021) was added to the chemical pulp. If fibril cellulose was added before the beating step, the mixing time of the mixture comprising fibril cellulose, chemical pulp and starch was 20 min. If fibril cellulose was added after the beating step, starch and cellulose pulp were mixed with each other, wherein the mixing time was 15 min, after which fibril cellulose
was added to the mixture. The mixing time of mixture comprising starch, chemical pulp and fibril cellulose was in this case 5 min. A 100 mesh wire was used in the trial.

Test results

Summary of the test results is shown in Table 2, wherein

Internal 1: Drainage time was defined by the time until visible water disappears during sheet forming,

and

Internal 2: Wet tensile strength was measured with L&W tensile tester from wet sheets. Two solids content levels were used in which solids content of sheets were between 35 and 50%, and the results were interpolated to 45% solids content

Table 2. Summary of the test results.

<table>
<thead>
<tr>
<th>Paper property</th>
<th>Method</th>
<th>Reference, cationic starch 20 mg/g, 200 kWh/t</th>
<th>Tempo pulp 2%, cationic starch 20 mg/g, 200 kWh/t</th>
<th>Tempo fibrils 2%, cationic starch 20 mg/g, 200 kWh/t</th>
<th>Tempo pulp 2%, cationic starch 20 mg/g, 250 kWh/t</th>
<th>Tempo pulp 2%, cationic starch 20 mg/g, 300 kWh/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drainage time during sheet forming / s</td>
<td>Internal 1</td>
<td>19</td>
<td>21</td>
<td>24</td>
<td>46</td>
<td>150</td>
</tr>
<tr>
<td>Tensile index / Nm/g</td>
<td>ISO 1924-3</td>
<td>115</td>
<td>110</td>
<td>113</td>
<td>109</td>
<td>106</td>
</tr>
<tr>
<td>Bonding strength / J/m²</td>
<td>T 569 pm-07</td>
<td>1496</td>
<td>1613</td>
<td>1930</td>
<td>1717</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>Air permeance / Bendtsen / ml/min</td>
<td>ISO 5636-3</td>
<td>11</td>
<td>8</td>
<td>9</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Wet web tensile index at 45% solids / Nm/g</td>
<td>Internal 2</td>
<td>8,8</td>
<td>10,3</td>
<td>8,9</td>
<td>10,3</td>
<td>10,8</td>
</tr>
</tbody>
</table>
Fibril cellulose addition clearly increased the SR level of the produced pulp. It was noticed that SEC at approximately 225 kWh/t would have brought the SR level of Tempo pulp containing furnish to the level of Tempo fibrils containing furnish beaten at 200 kWh/t SEC. Examples of SR levels are shown in Figure 2.

The results showed generally higher water retention values (WRV) with pulps comprising fibril cellulose material than with reference pulps without fibril cellulose material. It was noticed that SEC approximately at 225 kWh/t would have brought the WRV-level of Tempo pulp containing furnish to the level of Tempo fibrils containing furnish beaten at 200 kWh/t SEC. Some water retention values are shown in Figure 3.

According to the trials, increased beating energy consumption was not necessary when Tempo-treated pulp was fibrillated during beating. The SR and WRV levels of beaten pulp were lower than in case of ready-made Tempo-fibril addition to beaten pulp.

Sheet properties results are based on laboratory sheets. Anionized cellulose fibers added to the beating step seemed to give good paper sheet properties. In Figures 4-7, “T” refers to “Tempo treated”.

Air permeability of the pulp comprising fibril cellulose was clearly lower than air permeability of the reference pulp. In addition, results showed lower porosity, when fibrils were added to beaten pulp instead of unbeaten pulp. Tempo pulp and Tempo fibrils were approximately at the same level when added to beating. Air permeability results are shown in Figure 4.

For Scott Bond, Tempo fibrils seemed to be slightly more effective than Tempo pulp. Tempo addition to unbeaten pulp seemed to be more effective than addition to unbeaten pulp. Scott Bond results are shown in Figure 5.
For Tensile index, a good performance was shown with Tempo pulp added to beaten pulp. Tempo pulp and fibrils added to beating seemed to be slightly better than when fibrils were added to beaten pulp, or at least as good as when fibrils were added to beaten pulp. Tensile indexes are shown in Figure 6.

For wet tensile strength at 45% solids content, a good performance was shown with Tempo pulp added to beating and Tempo fibrils added to beaten pulp. This is shown in Figure 7.

Drainage was comparable to reference samples but with higher strength properties. Tempo-treated fibrils and Tempo-treated pulp with higher SEC gave most dense sheet but also slowest drainage.

It can be easily seen from the refining results of the experimental tests that SR and WRV are increased with the refining step of the chemical pulp and Tempo pulp clearly more than refining step of the chemical pulp without Tempo pulp, thus, Tempo pulp is clearly fibrillated into fibril cellulose material during the refining step.

Thanks to the present invention, a production of fibril cellulose for paper applications may be possible with low energy consumption. One skilled in the art understands readily that the different embodiments of the invention may have applications in environments where optimization of a paper product comprising fibril cellulose is desired. Therefore, it is obvious that the present invention is not limited solely to the above-presented embodiments, but it can be modified within the scope of the appended claims.
Claims:

1. A method for manufacturing furnish for a paper product, wherein the manufactured furnish contains nanofibrillar cellulose material, the method comprising:
   - introducing first raw material to a system, which first raw material includes cellulose pulp (2),
   - introducing second raw material to the system, which second raw material comprises anionized cellulose fibers that are oxidized catalytically by nitroxyl-mediated oxidation of hydroxyl groups of the cellulose,
   - conveying the first raw material and the second raw material to a refiner (8),
   - refining and mixing the first raw material and the second raw material in the refiner (8) in order to produce furnish comprising nanofibrillar cellulose material (4).

2. The method according to claim 1, characterized in that the sum of the nanofibrillar cellulose (4) and the anionized cellulose fibers (3) in the manufactured furnish is between 0.01-10.0% of dry weight.

3. The method according to claim 1 or 2, characterized in that the amount of the nanofibrillar cellulose (4) in the manufactured furnish is between 0.1 and 5.0 dry weight percent.

4. The method according to any of the preceding claims, characterized in that the first raw material comprises chemical pulp (2a).

5. The method according to any of the preceding claims, characterized in that the refiner (8) is placed in a paper machine approach system.

6. A paper comprising cellulose pulp and nanofibrillar cellulose material, characterized in that the nanofibrillar cellulose material is produced by refining from anionized cellulose fibers comprising cellulose that is oxidized catalytically by nitroxyl-mediated oxidation of hydroxyl groups of the cellulose, the paper comprising an amount of the anionized cellulose fibers (3) and the nanofibrillar cellulose (4), the nanofibrillar cellulose being dispersed and mixed with the base furnish of the paper.

7. The paper according to the claim 6, characterized in that the basis weight of the paper is between 30 and 90 g/m², preferably between 30 and 50 g/m².
8. The paper according to the claim 6 or 7, characterized in that the paper has at least one of the following:
- improved bonding strength properties,
- improved wet web tensile index, and
- lowered air permeability properties
compared with paper made of pulp without nanofibrillar cellulose.

9. The paper according to the claim 6, 7 or 8, characterized in that the paper is a release paper for a label laminate.

10. The paper according to the claim 6,7 or 8, characterized in that the paper is sandpaper base.

11. The paper according to the claim 6, 7 or 8, characterized in that the paper is a printing paper.

12. The paper according to the claim 6, 7 or 8, characterized in that the paper is a packing material and/or a paperboard.

13. The paper according to any of the preceding claims 6 to 12, characterized in that the amount of the fibril cellulose (4) in the paper is between 0.5 and 2.5 w-%.

14. A use of a furnish for manufacturing of paper or paperboard, wherein at least part of the furnish is manufactured according to the method of any of the preceding claims 1 to 5.
Patenttivaatimukset:

1. Menetelmä paperituotteen seossuhteen valmistamiseksi, jossa valmistettu seossuhde sisältää nanofibrilliseellulosamateriaalia, jossa menetelmässä:
   - johdetaan järjestelmään ensimmäistä raaka-ainetta, joka ensimmäinen raaka-aine sisältää seelluloosamassa (2),
   - johdetaan järjestelmään toista raaka-ainetta, joka toinen raaka-aine käsittää anionoituja selluloosakuituja, jotka on hapetettu katalyytisesti hapettamalla seelluloosan hydroksyyliryhmiä nitroksyylivälitteisesti,
   - siirretään ensimmäinen raaka-aine ja toinen raaka-aine jauhimeen (8),
   - jauhetaan ja sekoitetaan ensimmäistä raaka-ainetta ja toista raaka-ainetta jauhimessa (8) nanofibrilliseelluloosaa (4) käsittävän seossuhteen valmistamiseksi.

2. Patenttivaatimuksen 1 mukainen menetelmä, tunnettu siitä, että nanofibrilliseelluloosan (4) ja anionoitujen selluloosakuitujen (3) yhteenlaskettu määrä valmistetussa seossuhtessa on 0,01–10,0 % kuivapainosta.

3. Patenttivaatimuksen 1 tai 2 mukainen menetelmä, tunnettu siitä, että nanofibrilliseelluloosan (4) määrä valmistetussa seossuhtessa on 0,1–5,0 % kuivapainosta.


5. Jonkin edellisen patenttivaatimuksen mukainen menetelmä, tunnettu siitä, että jauhin (8) on sijoitettu paperikoneen lähestymisjärjestelmään.

6. Paperi, joka käsittää seelluloosamassa ja nanofibrilliseellulosamateriaalia, tunnettu siitä, että nanofibrilliseellulosamateriaali on valmistettu jauhamalla anionoiduista selluloosakuiduista, jotka käsittävät selluloosaa, joka on hapetettu katalyytisesti hapettamalla seelluloosan hydroksyyliryhmiä nitroksyylivälitteisesti, ja paperi käsittää määrän anionoituja selluloosakuituja (3) ja nanofibrilliseelluloosaa (4), joka nanofibrilliseelluloosa on dispergoitunut ja sekoittunut paperin perusseossuhteeseen.
7. Patenttivaatimuksen 6 mukainen paperi, **tunnettu** siitä, että paperin neliömässä on 30–90 g/m², sopivimmin 30–50 g/m².

8. Patenttivaatimuksen 6 tai 7 mukainen paperi, **tunnettu** siitä, että paperilla on ainakin jokin seuraavista:
   - parantuneet sidoslujuusominaisuudet,
   - parantunut rainan märkävetonäkymi, ja
   - pienentyneet ilmanlämpäisevyydentäytymisyysominaisuudet verrattuna paperiin, joka on valmistettu massasta ilman nanofibrilliselluloolaa.

9. Patenttivaatimuksen 6, 7 tai 8 mukainen paperi, **tunnettu** siitä, että paperi on irrokepaperi tarralaminaattia varten.

10. Patenttivaatimuksen 6, 7 tai 8 mukainen paperi, **tunnettu** siitä, että paperi on hiekkapaperin pohjapaperi.

11. Patenttivaatimuksen 6, 7 tai 8 mukainen paperi, **tunnettu** siitä, että paperi on painopaperi.

12. Patenttivaatimuksen 6, 7 tai 8 mukainen paperi, **tunnettu** siitä, että paperi on pakkausmateriaali ja/tai kartonki.

13. Jonkin edellisen patenttivaatimuksen 6–12 mukainen paperi, **tunnettu** siitä, että fibrilliselluloolosan (4) määrä paperissa on 0,5–2,5 p%.

Air permeance Bendtsen / ml/min

Tempo (T) pulp or fibrils added to beating / pulp before starch
CS [mg/g]
SEC [kWh/t], ref level 200 kWh/t
95% confidence level given if available

Air permeance Bendtsen / ml/min

Fig. 4
Fig. 7

Wet web tensile index @45% solids / Nm/g

Tempo (T) pulp or fibrils added to beating / pulp before starch
CS [mg/g]
SEC [kWh/t], ref level 200 kWh/t
95% confidence level given if available

* Wet web tensile index @45% solids / Nm/g