(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 June 2011 (03.06.2011)

PCT

(10) International Publication Number
WO 2011/064441 A1

(51) International Patent Classification:
D21H 11/18 (2006.01) *D21D 1/20* (2006.01) *D21H 21/30* (2006.01) *D21C 9/00* (2006.01) *D21H 21/32* (2006.01)

(21) International Application Number: PCT/FI2010/050897

(22) International Filing Date: 5 November 2010 (05.11.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20096233 24 November 2009 (24.11.2009) FI

(71) Applicant *(for all designated States except US)*: **UPM-KYMMENE CORPORATION** [FI/FI]; Eteläesplanadi 2, FI-00130 Helsinki (FI).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **NUOPPONEN, Markus** [FI/FI]; Sturenkatu 40 G 83, FI-00550 Helsinki (FI). **PÄIVÄLÄINEN, Taru** [FI/FI]; Lauttasaarentie 37 A 12, FI-00200 Helsinki (FI). **LAUKKANEN, Antti** [FI/FI]; Minna Canthin katu 24 as. 11, FI-00250 Helsinki (FI). **PALTAKARI, Jouni** [FI/FI]; Tuurinmäentie 14, FI-02200 Espoo (FI).

(74) Agent: **TAMPEREEN PATENTTITOIMISTO OY**; Hermiankatu 1 B, FI-33720 Tampere (FI).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2011/064441 A1

(54) Title: METHOD FOR MANUFACTURING NANOFIBRILLATED CELLULOSE PULP AND USE OF THE PULP IN PAPER MANUFACTURING OR IN NANOFIBRILLATED CELLULOSE COMPOSITES

(57) Abstract: The invention relates to a method for manufacturing pulp. The manufactured pulp contains at least 30 w-% nanofibrillated cellulose material measured from the dried pulp. The method comprises the following stages: introducing raw material to a system which raw material includes cellulose, dosing at least one type of an optical brightening agent as a refining additive to the system, and refining the raw material in the presence of the dosed optical brightening agent in at least one pre-refining stage or fibrillation stage in order to form fibrillar cellulose material. The invention further relates to a use of the produced pulp in nanofibrillated cellulose composites or in paper or paperboard manufacturing including base paper production and finishing stages, including, for example, paper and paperboard coatings.

METHOD FOR MANUFACTURING NANOFIBRILLATED CELLULOSE PULP AND USE OF THE PULP IN PAPER MANUFACTURING OR IN NANOFIBRILLATED CELLULOSE COMPOSITES

Field of the Invention

The invention relates to a method of manufacturing nanofibrillated cellulose pulp. The invention further relates to use of the pulp in paper manufacturing or in nanofibrillated cellulose composites.

Background of the Invention

Many stages of pulp production, especially refining stages, consume lots of energy. Specially a production of nanofibrillated cellulose consumes a great deal of energy due to several fibrillarion passages that are needed to achieve nano-sized material. Because the energy consumption of the manufactured pulp increases hugely when the produced pulp includes nanofibrillated cellulose, there may be an efficiency problem when the produced pulp consist at least partly of nanofibrillated cellulose. Sometimes another problem in the nanofibrillated cellulose pulp production is poor water removal due to several strong bonds between cellulose fibers and the water to be removed.

Due to the above mentioned problems, it is beneficial to add at least one compound capable of substantially inhibiting hydrogen bonding of fibrils in cellulose, especially in a process preparing nanofibrillated cellulose. For this purpose some polyhydroxy compounds, such as sucrose, are used in prior art. However, those known compounds have some problems. For example, known additives have generally been used only for refining stages, which will cause extra additive costs. Thus, it would be more beneficial to use those kind of additives which were anyway added to the process for another purpose on later process stages instead of those known additives used only for the above mentioned purpose.

There is, therefore, a need for a new solution for increasing the efficiency of the nanofibrillated cellulose pulp production. There is, thus, a need for an additive that could cause a smaller energy consumption of pre-refining and/or fibrillation stages and a better water removability in the pulp production. The new additive would preferably have features to reduce the inter-fiber bonding and, thus, increase a refining efficiency due to decreased energy consumption of the refining stage. In addition, the additive would preferably have features to reduce fiber-water and fiber-fiber bonding that occurs during drying and concentrating. Moreover, the additive would preferably be some of those additives that are often added for another purpose on later process stages.

Summary of the Invention

The present invention solves at least some of the above mentioned problems by providing a method for pulp manufacturing wherein the produced pulp consist at least partly of nanofibrillated cellulose. The method comprises a step in which at least one type of optical brightening agent (OBA) is dosed before and/or during at least one pre-refining and/or fibrillation stage. The invention further discloses a use of the produced pulp in nanofibrillated cellulose composites or in paper or paperboard manufacturing including base paper manufacturing and finishing stages like, for example, the use in paper or paperboard coatings.

Aspects of the invention are characterized by what is stated in the independent claims 1, 10 and 11. Various embodiments of the invention are disclosed in the dependent claims.

The inventors of the present invention have surprisingly found that optical brightening agents can increase the production efficiency of the nanofibrillated cellulose pulp if the additives are dosed before or during a pre-refining stage and/or a fibrillation stage. Optical brightening agents have been found to be able to create bonding with cellulose in such a way that the optical brightening agents can act as substituents in inter-fiber bonding and, thus, inhibiting hydrogen bonding of fibrils in cellulose. The increased production efficiency is mainly due to decreased energy consumption of the fibrillation stage because of the substituent effect. Optical brightening agents are also able to create bonding with water and, thus, to increase the efficiency of drying and concentrating processes.

Due to the above mentioned things, optical brightening agents are able to enable redispersing of nanofibrillated containing cellulose. Due to the dispersive effect, an optical brightening agent can be used as a dispersing agent in nanofibrillated concentrating and/or redispersing process and, therefore, help the process. In addition, due to the dispersive effect, the quality of the nanofibrillated cellulose pulp can be increased.

According to an embodiment of the present invention, at least one kind of optical brightening agent is added before a pulp pre-refining stage. According to another embodiment, at least one kind of optical brightening agent is added before a pulp fibrillation stage. According to another embodiment, at least one kind of optical brightening agent is dosed into the pulp at the pre-refining stage. According to another embodiment, at least one kind of optical brightening agent is dosed into the pulp at the fibrillation stage.

According to an embodiment, the amount of the nanofibrillated cellulose in the produced pulp is more than 30 w-%, preferably more than 40 w-%, 50 w-%, 60 w-% or 70 w-%, and can be even up to 100 w-% measured from the dried pulp.

The nanofibrillated cellulose pulp that can be produced according to the invention and, thus, contains one or more optical brightening agents, may be used in various end product applications. The cellulose pulp may be used, for example, in nanofibrillated cellulose composites, and/or in paper manufacturing, for example, in a base paper and/or in a finishing stage of produced paper. The finishing stages of produced paper includes, for example, coating stages.

Description of the Drawings

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

Figs. 1a-d	show microscopy pictures of cellulose pulp, refined cellulose pulp and nanofibrillated cellulosepulps;
Fig. 2a-c	show some viscosity results of experimental test together with some optical microscopy pictures taken during experimental test from Masuko grinded samples;
Fig. 3a-b	show optical microscopy images of some fluidisator samples taken during experimental test;
Fig. 4a-b	show SEM (scanning electron microscope) pictures of the samples shown also in figures 3a-3b; and
Fig. 5	shows some turbidity and centrifugation experimental test results of the fluidized samples.

Detailed Description of the Invention

In this application, the term "cellulose raw material" refers to any cellulose raw material source that can be used in a production of cellulose pulp, refined pulp, or microfibrillar cellulose. The cellulose raw material can be based on any plant material that contains cellulose, for example wood material. The wood material 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 acacia, or from a mixture of softwoods and hardwoods. Non-wood 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 "cellulose pulp" refers in this application to cellulose fibers, which are isolated from any cellulose raw material using chemical, mechanical, thermomechanical, or chemithermo - mechanical pulping process(es). Typically the diameter of the fibers varies between 15-25 μm and the length exceeds 500 μm, but the present invention is not intended to be limited to these parameters.

In this application, the term “paper manufacturing” refers to manufacturing process of any paper-like material, for example, paperboards, papers and/or paper composites.

According to an example embodiment of the invention, at least part of the lignin that has been included in cellulose raw material is advantageously removed from the cellulose raw material when it is processed into cellulose pulp to be used in the nanofibrillated cellulose production. Thus, chemical pulp may be used more preferably for nanofibrillated cellulose production than mechanical pulp. According to an example embodiment of the invention, the yield of the process wherein cellulose raw material is processed into cellulose pulp to be used in the nanofibrillated pulp production has been at least 50 %, at least 60 %, at least 70 % or at least 80 %.

According to an example embodiment, the cellulose pulp used in the nanofibrillated cellulose production may be preferably unbleached or bleached chemithermo or chemical pulp, more preferably unbleached or bleached chemical pulp, and the most preferably unbleached chemical pulp, because the method of the invention may be the most advantageous compared to other processes when the used cellulose pulp is chemically produced unbleached pulp.

The term "refined pulp" refers to refined cellulose pulp. The refining of cellulose pulp is carried out with suitable equipment such as a refiner, grinder, homogenizer, colloider, friction grinder, fluidizer such as microfluidizer, macrofluidizer or fluidizer-type homogenizer or ultrasound sonicator. Typically, all cellulose fibers have not been fully fibrillated; a large fraction of cellulose fibers with unchanged dimensions are still present in addition to refined cellulose material. The large fibers in the refined pulp may have fibrillated surface. The finest fraction of cellulose based material in the "refined pulp" consists of nanofibrillated cellulose, i.e. cellulose microfibrils and microfibril bundles with diameter less than 200 nm.

The term “nanofibrillated cellulose, (NFC)” refers to a collection of isolated cellulose microfibrils or microfibril bundles derived from cellulose raw material. Microfibrils have typically high aspect ratio: the length might exceed one micrometer while the number-average diameter is typically below 200 nm. The diameter of microfibril bundles can also be larger but generally less than 1 μm. The smallest microfibrils are similar to the so called elementary fibrils, which are typically 2-12 nm in diameter. The dimensions of the fibrils or fibril bundles are dependent on the raw material and disintegration method. The nanofibrillated cellulose may also contain some hemicelluloses; the amount may be dependent on the plant source.

Mechanical disintegration of nanofibrillated cellulose from cellulose raw material, cellulose pulp, or refined pulp is carried out with suitable equipment such as a refiner, grinder, homogenizer, colloider, friction grinder, ultrasound sonicator, fluidizer such as microfluidizer, macrofluidizer or fluidizer-type homogenizer. Nanofibrillated cellulose can also be any chemically or physically modified derivate of cellulose microfibrils or microfibril bundles. The chemical modification could be based for example on carboxymethylation, oxidation, esterification, or etherification reaction of cellulose molecules. Modification could also be realized by physical adsorption of anionic, cationic, or non-ionic substances or any combination of these on cellulose surface. The described modification can be carried out before, after, or during the production of nanofibrillated cellulose.

There are several widely used synonyms for nanofibrillated cellulose. For example: nanocellulose, microfibrillar cellulose, nanofibrillar cellulose, cellulose nanofiber, nano-scale fibrillated cellulose, microfibrillated cellulose (MFC), or cellulose microfibrils. Nanofibrillated 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 microfibrillar cellulose, which leads to more rigid structure. Cellulose whiskers are also shorter than microfibrillar cellulose; typically the length is less than one micrometer.

In conventional pulp production, it is usually an aim to get long, quite undamaged, fibrillated fibers, while in the nanofibrillated cellulose production an aim is to crush fibers into small pieces. Nanofibrillated cellulose and normal cellulose are usually produced using different kind of refiners, because the refiners that are used conventionally in the pulp refiner production may not, at least efficiently, be used in nanofibrillated cellulose production. However, the refiners used in the conventional pulp production may be used as pre-refiners in nanofibrillated cellulose production. In this application, the term “fibrillation stage” means the stage that causes more fibrillar cellulose, and the term “pre-refiner stage” means the stage that may advantageously be used for pre-refining before a fibrillation stage in nanofibrillated cellulose production.

Properties of nanofibrillated cellulose pulp differs hugely from conventional cellulose pulp due to many nano-sized particles of the nanofibrillated cellulose pulp and, thus, nanofibrillated cellulose cannot be though as a same material as conventional cellulose pulp. Nanofibrillated cellulose is, for example, gel-like material even in low consistency, and its water removal rate is usually slow. Paper sheets that contain a lot of nanofibrillated cellulose have special properties comparing to the sheets made from normal cellulose pulp, for example, they have usually high strength properties, their porosity is very low, and the sheets are usually (at least partly) transparent.

The differences between cellulose pulp, refined cellulose pulp and nanofibrillated cellulose pulp are illustrated in figures 1a-1d in optical microscopy pictures. Magnification is the same in the figures 1a – 1c. Figure 1a shows an optical microscopy picture of typical cellulose pulp. Figure 1b shows an microscopy picture of typical refined cellulose pulp. Figures 1c and 1d show microscopy pictures of typical nanofibrillated cellulose pulp. As can be seen in figure 1c, the large cellulose fibers shown in figures 1a and 1b are not anymore clearly visible. Figure 1d shows the same situation as figure 1c but with higher magnification wherein individual microfibrils and microfibril bundles with diameter less than 100 nm can be detected.

According to an example embodiment the present invention provides a method for manufacturing nanofibrillated cellulose pulp by pre-refining and/or fibrillating the pulp with a presence of at least one kind of optical brightening agent. In addition, according to another example embodiment, the present invention provides the use of the produced pulp in paper manufacturing or in nanofibrillated cellulose composites.

The optical brightening agents (OBAs) are dye-like compounds which absorb short-wave light in the ultraviolet and violet region of the electromagnetic spectrum not visible to the human eye and re-emit the light in the longer-wave blue region. In other words, optical brightening agents make the material, for example paper, to look less yellow to the human eyes and, thus, human eyes interpret the blue light as a higher degree of whiteness. In prior art the optical brightening agents are used to achieve better optical properties of the produced paper, for example, for a whitening effect of the produced paper. Optical brightening agent types that are typically used in the pulp and paper industry are, for example, di-, tetra-, and hexasulphonated stilbene compounds. The amount of sulphonated groups has an effect on the chemical properties of the optical brightening agent and, thus, the type of the used OBA may have an effect on the method according to an example embodiment of the invention. Generally, the more the optical brightening agent has sulphonated groups the bigger may be the effect of the used optical brightening agent on the method accordant with the invention. Some other most commercially available optical brightening agents in pulp and paper industries are based on coumarin and pyrazoline chemistries. Those mentioned optical brightening agent types are only some examples and also other types of optical brightening agents known in prior art can be used in this invention. However, according to an embodiment of the invention, those chemical types mentioned in the application, i.e stilbene, coumarin and pyrazoline, are preferred to use in the practice of this invention. From those chemicals, the anionic stilbene compounds may be the most preferably used in the invention.

Optical brightening agents are quite expensive additives, thus, solutions provided in this invention are intended to be the most efficient if optical brightening agents are used in nanofibrillated pulp production wherein the optical brightening agent is otherwise added in a later stage to the pulp or to the end product. In papermaking, optical brightening agents are typically added at the wet end of the papermaking process, which include, for example, the fan pulp or the machine chest. The use of the optical brightening agent in accordance with some example embodiments of the invention does not necessarily increase additive costs but, quite the contrary, the retention of the optical brightening agent to the nanofibrillated pulp may be improved if the optical brightening agent is added before or during pre-refining stage or before or during a fibrillation step and, therefore, the overall costs of the used optical brightening agent may be decreased. In the other words, it is possible that the total amount of the needed optical brightening agent dosage according to an example embodiment of the invention can be smaller if the optical brightening agent is added accordant with some example embodiments of the invention due to several fiber - optical brightening agent bondings that may be formed during nanofibrillated cellulose pre-refining and/or fibrillation stages.

Therefore, the efficiency of the nanofibrillated cellulose production can further be increased when the optical brightening agent is added to the produced pulp before or during the refining stage, not only because of the decreased energy consumption but also because of less additive costs. Moreover, the optical brightening agent dosage to the nanofibrillated cellulose production according to some example embodiments of this invention may increase an ability of the nanofibrillated cellulose to carry the optical brightening agent and, therefore, a need for other optical brightening agent carriers e.g. Polyvinyl Alcohol (PVOH) may decrease. Thus, the production efficiency can also be increased this way due to the invention.

According to an embodiment of the invention, the method comprises a step wherein at least one type of the optical brightening agent (OBA) is dosed as a refining additive to the pulp which contains cellulose. In the method the dosage is preferably done before a pre-refining and/or fibrillation stage. In addition or alternatively, one type of the optical brightening agent can be added into the pulp at the pre-refining or the fibrillation stage. Thus, it is possible to add the optical brightening agent to a pre-refining stage, and/or the optical brightening agent can be added to some or all of the following fibrillation stages. According to an advantageous embodiment of the invention, the pulp is fibrillated in at least one fibrillation stage after the additive addition, no matter in which stage the additive is added to the process.

The anionic optical brightening agent is capable of inhibiting hydrogen bonding between the cellulose fibrils in cellulose and can therefore be used to create a dispersive effect, which dispersive effect can increase the quality of the produced nanofibrillated cellulose. Due to the dispersive effect, optical brightening agent can be used as a dispersing agent in the nanofibrillated concentrating/redispersing process and, therefore, may help the process.

Nanofibrillated cellulose that contains optical brightening agent may improve not only the refining efficiency and the quality of the produced pulp but also both the strength and the optical properties of the end product to be produced from the pulp manufactured according to an example embodiment of the invention. The improvements in strength properties are mainly due to the features of nanofibrillated cellulose and the improvements in optical properties are mainly due to the features of the optical brightening agent.

The method according to an example embodiment of the invention comprises at least the following:

- introducing raw material to a system which raw material includes cellulose,
- dosing at least one type of an optical brightening agent as a refining additive to the system, and

  refining the raw material in the presence of the dosed optical brightening agent in at least one pre-refining or fibrillation stage in order to form fibrillar cellulose material.

When compared to the pulp produced according to the invention with pulp produced according to prior art, the novel invention can provide at least some of the following advantages:

- lower energy consumption to reach the targeted pulp fibrillation degree,
- better quality of the produced nanofibrillated cellulose pulp,
- better processing properties, including, for example, better water removability and better dispersing properties,
- better strength properties compared to the same total energy consumption of refining, and

- better optical properties compared to the same amount of the optical brightening agent (due to better retention of the optical brightening agent).

The amount of nanofibrillated cellulose in the pulp manufactured according to the invention may be 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 or 100 w- %, including any and all ranges and subranges therein.

The pulp manufacturing process according to invention has at least one fibrillation stage, possibly at least 2, 3 or 4 fibrillation stages. According to the invention at least one type of the optical brightening agent is added

- before at least one of the mentioned fibrillation stages or before the pre-refining stage, possibly before at least 2, 3, 4 or 5 of the mentioned fibrillation stages or before the pre-fibrillation stage,

  and/or

- to at least one of the mentioned fibrillation stages or to the pre-refining stage, possibly to at least 2, 3, 4 or 5 of the mentioned fibrillation stages or to the pre-refining stage.

In addition, according to the invention, the pulp is fibrillated after at least one additive dosage in at least one fibrillation stage in order to form some nanofibrillated cellulose material.

As it presented above, the addition of the optical brightening agent before or during the refining decreases the cellulose-cellulose bonding through hydroxyl groups by forming hydrogen bonds with the cellulose fibrils. At the same time, the addition of the optical brightening agent creates a dispersive effect to the pulp suspension through the repulsive forces between the anionic groups.

Experimental tests

Experimental tests were carried out in processes wherein some amounts of optical brightening agents were dosed as refining additives. In addition, paper sheets were made from the produced pulps and tested afterwards.

1. Used pulp

A bleached birch pulp made with conventional chemical pulping process was used as raw cellulose pulp.

2. Used optical brightening agents

Two different kinds of optical brightening agents were used as the refining additive: disulphonic type of the optical brightening agent and hexasulphonic type of the optical brightening agent. In addition, reference samples without addition of the optical brightening agent were performed.

3. Pre-refining

The pre-refining stage was performed with Voith refiner. Addition of the used optical brightening agent was always 2 w-%. The whole amount was dosed to the pulp before the pre-refiner stage, after which the samples were refined at energy of 200 kWh/t. The pre-refinings were performed in the consistency of 4%.

The obtained pulps were diluted to 1.6% for fluidizer and to 2% for Masuko. The optical brightening agents were dosed to the pre-refining process in order to improve their bonding to fiber surface.

4. Sample preparation

4a: Fluidizer

The part of the samples was fluidized with the M-700 Microfluidics Processor. Those samples were dispersed with a mixer in 1.6% consistency during 30 minutes. After dispersing, the samples were passed three times through fluidizer so that in the first pass there was only an APM chamber with diameter at 500 µm. In the second pass, the fiber suspension was passed through two sequential chambers with diameters at 500 µm and 200 µm. The third pass was carried out so that the fiber suspension passed through sequential 500 µm and 100 µm diameter chambers. The condenser of the fluidizer was switched off during all these trials, as it was found to improve fibrillation in the first part of experiments.

4b: Masuko ultra-fine friction grinder.

The grinded samples were dispersed in 2% consistency with a mixer during 15 minutes before the treatment with Masuko. The dispersed samples were passed four times through Masuko in such a way that in the first pass the gap between the grinding stones was looser than with the following three passes. The grinder was washed after the first and third pass.

5. Characterization

The gel-like fiber suspensions obtained from Masuko and from fluidizer were characterized by measuring viscosity (Brookfield) and turbidity of the samples and by observing optical microscope and SEM images of the samples. In addition, with centrifugation measurements the dry matter content was measured from both the liquid and the solid phase in order to determine the amount of nano-sized material in the sample.

6. Preparation of paper sheets

Paper sheets were made in a laboratory from the produced pulps.

7. Test results

Refining result can be estimated by measuring the viscosity level of the nanofibrillated cellulose sample, because the viscosity level of the pulp material goes along with the portion of nanofibrillated cellulose in the pulp. In general, more refined, and thus, more fibrillated nanofibrillated cellulose is more gel-like material than less nanofibrillated cellulose. Therefore, more gel-like material means more nanofibrillated cellulose in the sample and this bigger part of nanofibrillate cellulose can be seen in higher viscosity level in the sample. Samples with optical brightening agent - dosage were clearly more viscous than the reference samples. The amount of unfibrillated fibers can be estimated from optical microscopy pictures.

Based on both the viscosity results and the optical microscope images, the optical brightening agent dosage had a clear effect on fibrillation. Some of these results can be seen in Figures 2a – 2c wherein viscosity results with some optical microscopy pictures of Masuko grinded samples are shown. The figure 2a presents the viscosity results of the reference sample 21, the sample with disulphonic optical brightening agent dosage 22, and the sample with hexasulphonic optical brightening agent dosage 23. Figure 2b shows an optical microscopy picture of the reference sample 21 and figure 2c shows an optical microscopy picture of the sample 23 with hexasulphonic optical brightening agent dosage.

Also, preliminary redispersion tests on the fluidized samples were performed when the samples were oven dried. Differences in the disintegration of the dried films in water was detected. Reference samples did not broken into smaller pieces almost at all, but the optical brightening agent modified samples disintegrated clearly. Figures 3a and 3b show an optical microscopy images of fluidisator samples, wherein the reference sample (shown in figure 3a) and the sample 32 with hexasulphonic optical brightening agent (shown in figure 3b) are presented. The sample presented in figure 3b with the dosage of the optical brightening agent is clearly better fibrillated than the reference sample shown in figure 3a. Figures 4a and 4b show the same situation with SEM pictures (magnification: 10 000 x) in which the reference sample (in figure 4a) and the sample with hexasulphonated optical brightening agent addition (in figure 4b) are presented. As can be seen, the samples with hexasulphonated optical brightening agent looks clearly better compared to the reference sample, as many smaller fibrils can be seen in the image.

Quality of the nanofibrillated cellulose can be analyzed using centrifugation of nano-sized material and measuring the turbidity of the samples. Centrifugation results are supposed to describe the degree of fibrillation so that the more the nano-sized material has more efficient fibrillation than less nano-sized material. When it comes to turbidity results, the smaller the value for turbidity is, the more there should be nano-sized material in the sample. Figure 5 shows turbidity and centrifugation results of the fluidized samples. In this figure the reference sample 51, the sample 52 with disulphonic type of the optical brightening agent dosage, and the sample 53 with addition of hexasulphonic type of the optical brightening agent are presented. As can be seen, according to the turbidity results, the samples with OBA dosages were the most nano-sized. Also centrifugation results indicated that amount of nano-sized material increases along with OBA addition.

The paper sheets tested afterwards showed that internal strengths of the sheets produced according to the invention were clearly higher than the internal strength properties of the reference sheets produced without optical brightening agent addition.

One skilled in the art understands readily that the different embodiments of the invention may have applications in environments where optimization of a nanofibrillated cellulose pulp fibrillation 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 pulp, wherein the manufactured pulp contains at least 30 w-% nanofibrillated cellulose material measured from the dried pulp, the method comprising:

- introducing raw material to a system which raw material includes cellulose,
- dosing at least one type of an optical brightening agent as a refining additive to the system, and

refining the raw material in the presence of the dosed optical brightening agent in at least one pre-refining stage or fibrillation stage in order to form fibrillar cellulose material.

2. The method according to claim 1, **characterized** in that the refining is made in the presence of the dosed optical brightening agent in at least one fibrillation stage in order to form fibrillar cellulose material.

3. The method according to claim 1 or 2, **characterized** in that manufactured pulp contains at least 40 w-%, at least 50 w-%, at least 60 w-%, or at least 70 w-% nanofibrillated cellulose material measured from the dried pulp.

4. The method according to any preceding claim 1 to 3, **characterized** in that at least part of the raw material is selected from the following group:

- unbleached chemical pulp,
- bleached chemical pulp,
- unbleached chemithermo pulp, and
- bleached chemithermo pulp.

5. The method according to any preceding claim 1 to 4, **characterized** in that at least one type of the optical brightening agent is dosed before the pre-refining stage.

6. The method according to any preceding claim 1 to 5, **characterized** in that at least one type of the optical brightening agent is added to the pre-refining stage.

7. The method according to any preceding claim 1 to 6, **characterized** in that at least one type of the optical brightening agent is dosed before the fibrillation stage.

8. The method according to any preceding claim 1 to 7, **characterized** in that at least one type of the optical brightening agent is dosed to the fibrillation stage.

9. The method according to any preceding claim 1 to 8, **characterized** in that at least one dosed optical brightening agent type is selected from the group of stilbene, coumarin and pyrazoline compounds.

10. A use of a pulp in nanofibrillated cellulose composites, wherein at least part of the pulp is manufactured according to the method of any preceding claim.

11. A use of a pulp in manufacturing of paper or paperboard including
   - base paper production, and
   - finishing stages of paper or paperboard,

wherein at least part of the pulp is manufactured according to the method of any preceding claim 1 to 9.

12. The use according to claim 11, wherein said finishing stages comprise coatings for the paper or paperboard.

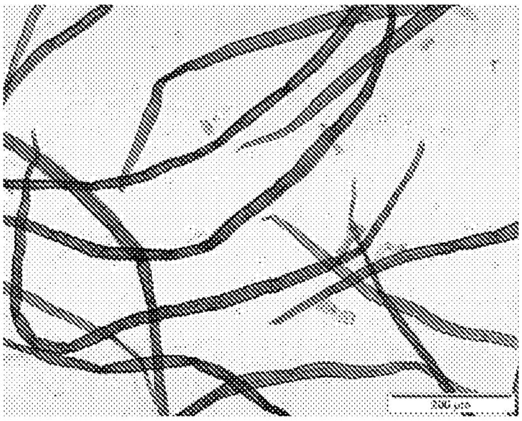

Fig.1a

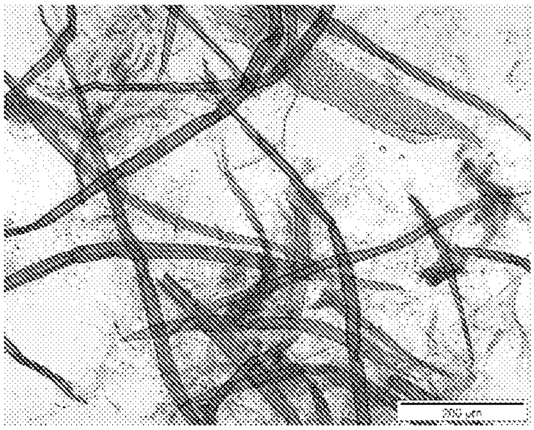

Fig.1b

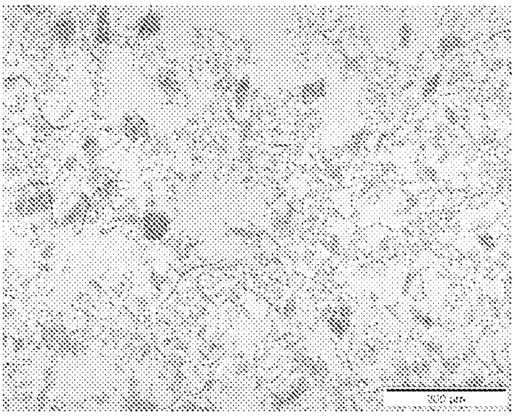

Fig.1c

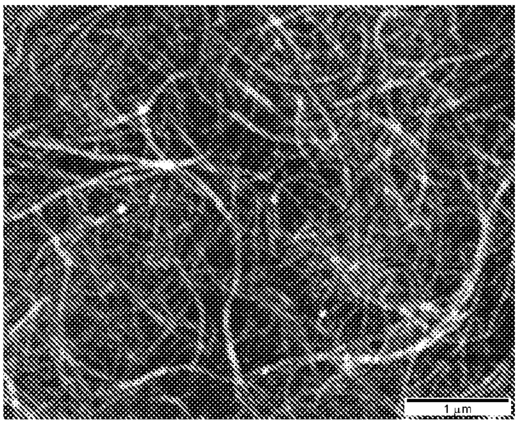

Fig.1d

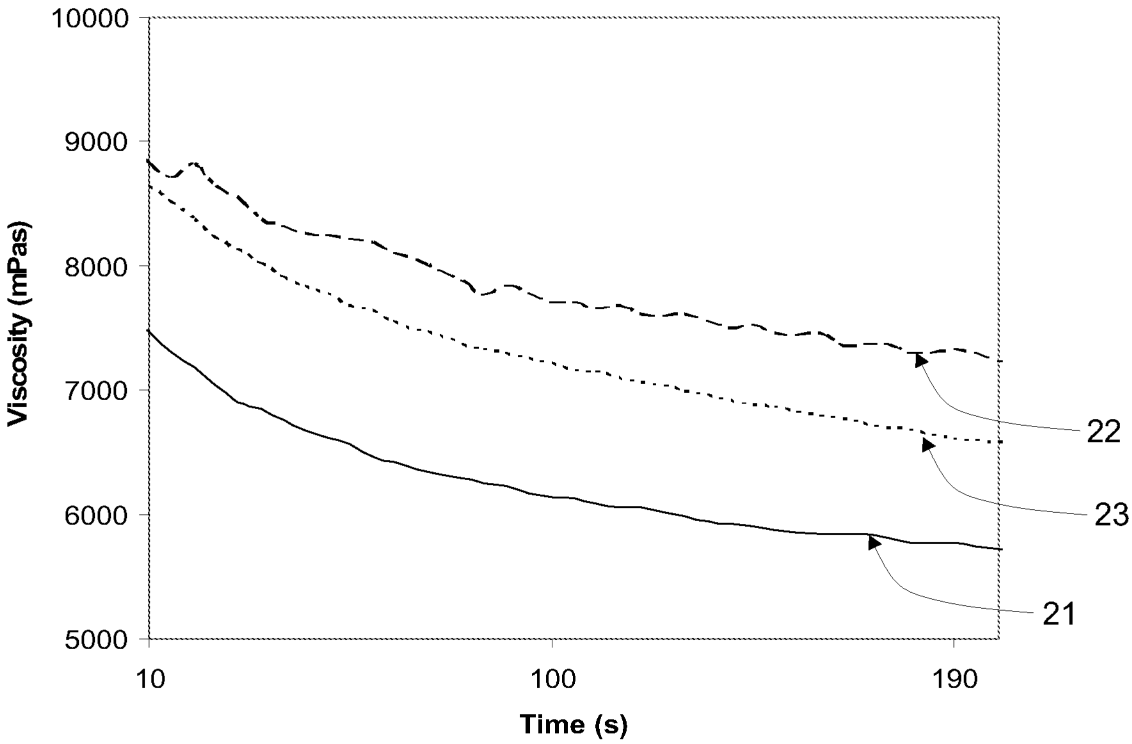

Fig.2a

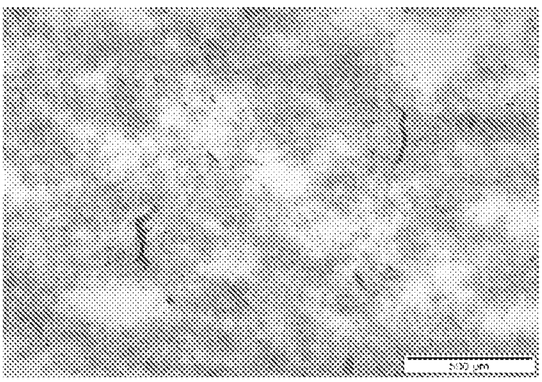

Fig.2b

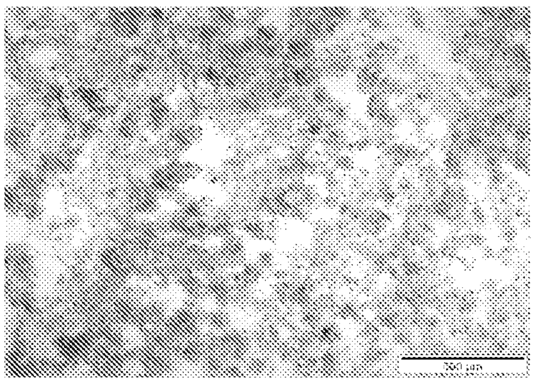

Fig.2c

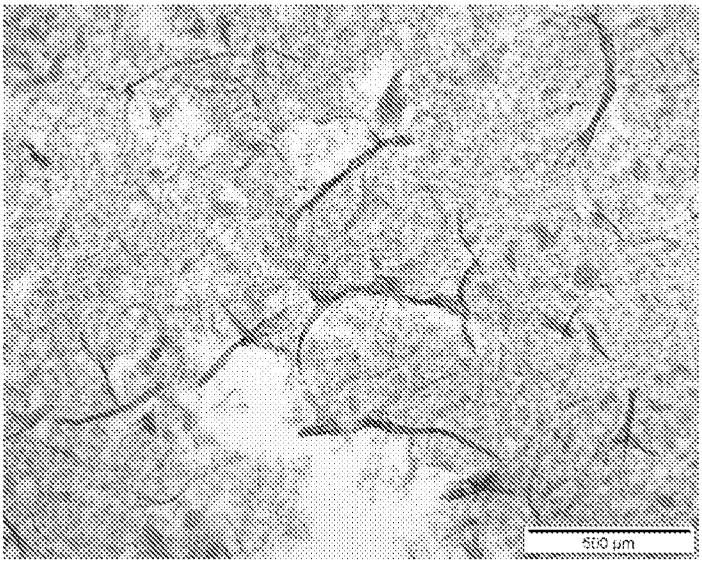

Fig.3a

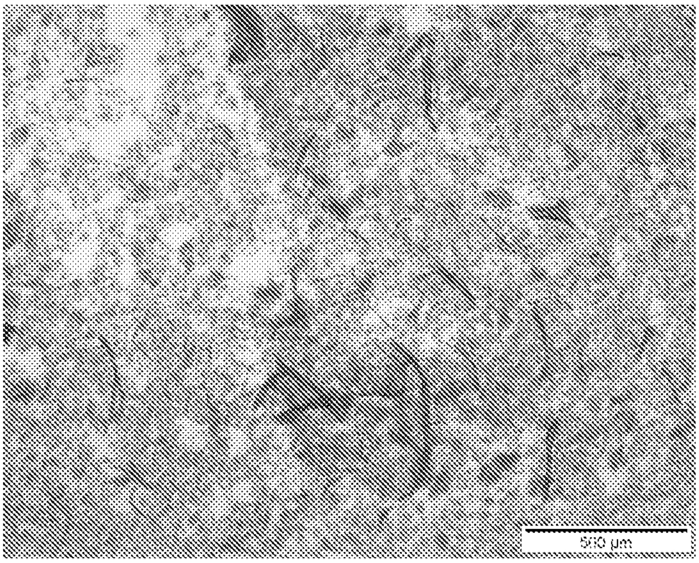

Fig.3b

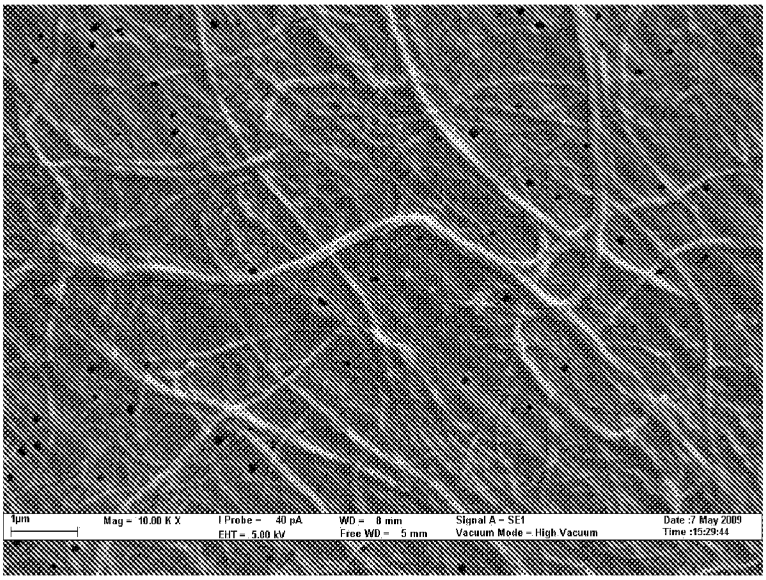
1µm
Mag = 10.00 K X
I Probe = 40 pA
EHT = 5.00 kV
WD = 8 mm
Free WD = 5 mm
Signal A = SE1
Vacuum Mode = High Vacuum
Date :7 May 2009
Time :15:29:44

Fig. 4a

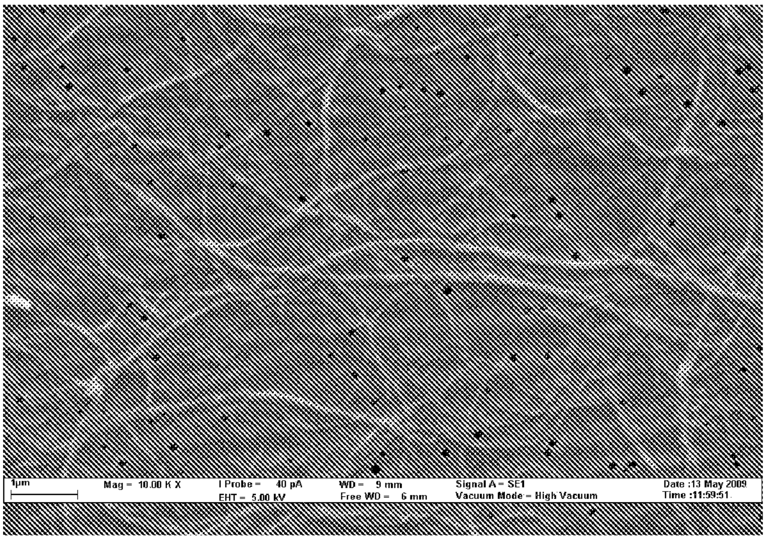
1µm
Mag = 10.00 K X
I Probe = 40 pA
EHT = 5.00 kV
WD = 9 mm
Free WD = 6 mm
Signal A = SE1
Vacuum Mode = High Vacuum
Date :13 May 2009
Time :11:59:51

Fig. 4b

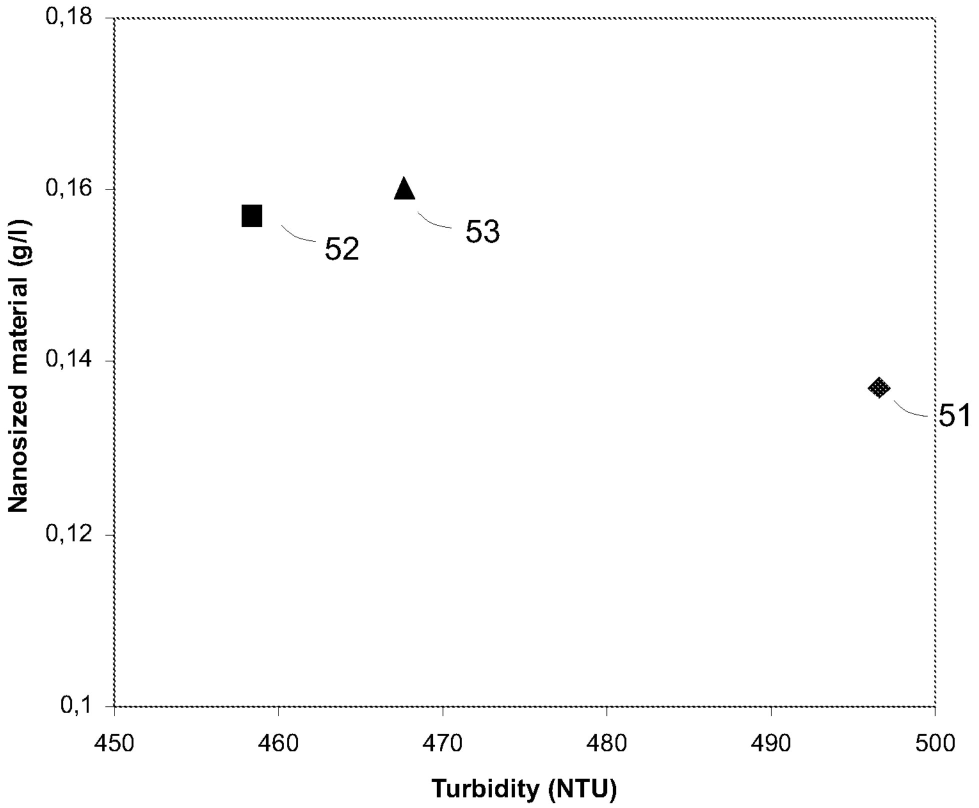
0,18
0,16
0,14
0,12
0,1
Nanosized material (g/l)
450
460
470
480
490
500
Turbidity (NTU)
52
53
51

Fig.5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2010/050897

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: D21H, D21D, D21C, D21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI, XPESP

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2006185808 A1 (NGUYEN XUAN T) 24 August 2006 (24.08.2006) claims 1, 9 ; paragraph [0045]; Examples 5-7	1-12
A	US 2009205795 A1 (NI YONGHAO et al.) 20 August 2009 (20.08.2009) paragraphs [0062]-[0066]	1-12

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 February 2011 (25.02.2011)	01 March 2011 (01.03.2011)

Name and mailing address of the ISA/FI
National Board of Patents and Registration of Finland
P.O. Box 1160, FI-00101 HELSINKI, Finland
Facsimile No. +358 9 6939 5328

Authorized officer
Heimo Koskinen
Telephone No. +358 9 6939 500

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2010/050897

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
US 2006185808 A1	24/08/2006	NZ 561652 A	29/10/2010
		US 2010252213 A1	07/10/2010
		US 2007193707 A1	23/08/2007
		WO 2006089274 A1	24/08/2006
		RU 2007134269 A	20/03/2009
		EP 1848856 A1	31/10/2007
		CN 101128630 A	20/02/2008
		CA 2601926 A1	24/08/2006
		BR PI0607171 A2	11/08/2009
		AU 2006213983 A1	24/08/2006
US 2009205795 A1	20/08/2009	None	

CLASSIFICATION OF SUBJECT MATTER

Int.Cl.
D21H 11/18 (2006.01)
D21H 21/30 (2006.01)
D21H 21/32 (2006.01)
D21D 1/20 (2006.01)
D21C 9/00 (2006.01)