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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 August 2010 (19.08.2010)

PCT

(10) International Publication Number
WO 2010/092239 A1

(51) International Patent Classification:
D21H 11/18 (2006.01) *D21H 17/24* (2006.01)

(21) International Application Number:
PCT/FI2010/050096

(22) International Filing Date:
12 February 2010 (12.02.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20095140 13 February 2009 (13.02.2009) FI

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

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **PALTAKARI, Jouni** [FI/FI]; Tuurinmäentie 14, FI-0220 Espoo (FI). **LAINE, Janne** [FI/FI]; Vanha kirkkotie 22 A, FI-02300 Espoo (FI). **ÖSTERBERG, Monika** [FI/FI]; Kultarinnantie 1, FI-02660 Espoo (FI). **SUBRAMANIAN, Ramjee** [IN/FI]; Lintukorventie 2 C 27, FI-02660 Espoo (FI). **TEIRFOLK, Jan-Erik** [FI/FI]; Rostockinkatu 2 J, FI-20250 Turku (FI).

(74) Agent: **BORENIUS & CO OY AB**; Tallberginkatu 2 A, FI-00180 Helsinki (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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (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, 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))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2010/092239 A1

(54) Title: A METHOD FOR PRODUCING MODIFIED CELLULOSE

(57) Abstract: The present invention provides a method for producing modified nanofibrillated cellulose characterized by bringing cellulosic material into a fiber suspension, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto fibers in said fiber suspension under special conditions and subjecting the obtained fiber suspension derivative to mechanical disintegration. A modified nanofibrillated cellulose obtainable by a method of the present invention is provided. Furthermore, the invention relates to the use of said modified nanofibrillated cellulose.

A METHOD FOR PRODUCING MODIFIED CELLULOSE

FIELD OF THE INVENTION

The present invention relates to a method for producing modified nanofibrillated cellulose characterized by steps of preparing a suspension containing fibers from cellulosic material, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under special conditions and subjecting the fiber suspension comprising said cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration. The invention also relates to modified nanofibrillated cellulose obtainable by a method of the present invention. The invention provides a paper containing the modified nanofibrillated cellulose and method and use thereof. Furthermore, the invention relates to the use of said modified nanofibrillated cellulose in paper, food products, composite materials, concrete, oil drilling products, coatings, cosmetic products and pharmaceutical products. The invention also provides a use of the present method for producing modified nanofibrillated cellulose energy efficiently.

BACKGROUND OF THE INVENTION

Cellulose-based nano-sized fibrils provide new possibilities for producing light and strong materials. For example increasing environmental requirements promote more extensive utilization of new natural fiber based biomaterials in the future. Nanosized materials can provide properties which can not be achieved which larger sized particles. The smaller the particle, the larger the surface area is and more possibilities for desired interactions with other materials exist.

Cellulose fibers (width 30-40 µm, length 2-3 mm) can be dismantled into nanosized structures (width about 5-30 nm, length several µms). Microfibrillated cellulose (MFC) has been produced by combining enzymatic or chemical treatments to mechanical treatments. Microfibrils provide even in minor proportion conventional paper products increased toughness and strength. International patent publication WO 2007/091942 discloses a method for manufacturing microfibrillated cellulose using enzymatic treatment.

Properties of the cellulose fibers used for producing paper can be modified by adding polymers to the fiber suspension. Suitable additive polymers include for example starch-based polymers, such as cationized starch, or synthetic polymers such as polyacryl polymers, polyamineamide-, polyamine- and acrylamino-epichlorohydrine polymers, cellulose derivatives or anionic polymers containing carboxyl groups or carboxylate ions in the form of alkali metals of ammonium salts, for example carboxymethyl polysaccharides, such as carboxymethyl cellulose (CMC). International patent publications WO 01/66600 and WO 00/47628 disclose derivatized microfibrillar polysaccharides, such as cellulose and production methods thereof.

CMC or sodium carboxymethyl cellulose is a water-soluble anionic polymer achieved by introducing carboxymethyl groups along the cellulose chain. The functional properties of CMC depend on the degree of substitution on the cellulose structure (i.e. how many of the hydroxyl groups have taken part in the substitution reaction), and also on the chain length of the cellulose backbone. The degree of substitution (DS) of CMC is usually in the range from 0.6 to 0.95 derivatives per monomer unit.

CMC can be used as an additive during the grinding of paper pulp (B. T. Hofreiter in "Pulp and Paper Chemistry and Chemical Technology", Chapter 14, Volume III, 3rd. edition, New York, 1981; W. F. Reynolds in "Dry strength additives", Atlanta 1980; D. Eklund and T. Lindström in "Paper Chemistry - an introduction", Grankulla, Finland 1991; J. C. Roberts in "Paper Chemistry"; Glasgow and London 1991).

CMC has a low affinity for cellulose fibers, since both are anionically charged. CMC can still be attached irreversibly to pulp fibres and it increases the surface charge density of pulp fibres.

US patents 5,061,346 and 5,316,623 disclose the addition of CMC to pulp in paper making processes. Publications WO 2004/055268 and WO 2004/055267 present fiber suspensions comprising cellulose enzyme-treated microfibrillar sulphate pulp (eMFC) and carboxymethyl cellulose (CMC) as raw material for packages and for surface application in paperboard and paper production, respectively.

CMC is used as thickener to modify the rheology. CMC has also been used as a dispersion agent. Furthermore, CMC has been used as binder. US patent US 5,487,419 discloses CMC as dispersion agent. US patent US 6,224,663 discloses use of CMC as an additive in a cellulose composition. Publication WO 95/02966 discloses the use of

CMC to modify microcrystalline cellulose and in some cases microfibrillated MCC by mixing the two components and the use of this mixture in food compositions.

CMC sorption is known in the art. US Patent 6,958,108 and international patent publication WO 99/57370 disclose a method for producing a fiber product, wherein alkali soluble CMC is added to the pulp under alkali conditions. International patent publication WO 01/021890 discloses a method for modifying cellulose fibers with a cellulose derivative such as CMC. Publication WO 2009/126106 relates to attachment of amphoteric CMC polymers to cellulose fibres before homogenization.

The following articles by Laine et al. disclose modification of cellulosic fibers with CMC: Nord Pulp Pap Res J, 15:520-526 (2000); Nord Pulp Pap Res J, 17:50-56 (2002); Nord Pulp Pap Res J, 17:57-60 (2002); Nord Pulp Pap Res J, 18:316-325 (2003); Nord Pulp Pap Res J, 18:325-332 (2003).

Despite the ongoing research and development in the manufacturing of microfibrillated cellulose there is still a continuing need in the industry to improve the processes. One problem is high energy consumption and thus there is a need for an energy efficient method. There is also a need for a process, wherein the properties of paper are improved. The present invention provides a method for overcoming the problems associated with the prior art.

SUMMARY OF THE INVENTION

The present invention relates to a method for producing modified nanofibrillated cellulose. The method comprises preparing a suspension containing fibers from cellulosic material, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under special conditions and subjecting the fiber suspension comprising said cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration to obtain modified nanofibrillated cellulose modified with said cellulose derivative or polysaccharide or polysaccharide derivative. The present invention also relates to modified nanofibrillated cellulose obtainable by the method of the present invention and characterized by that a diameter of modified nanofibrillated cellulose is less than 1 µm.

A significant advance of the present invention is reduced consumption of refining energy compared to the prior art methods. A novel and efficient method for producing modified nanofibrillated cellulose energy efficiently is thus provided.

Additives such as cellulose derivatives or polysaccharides or polysaccharide derivatives are usually added to already fibrillated material i.e. by addition to suspension after mechanical disintegration.

In the present invention the cellulose derivative or polysaccharide or polysaccharide derivative is added prior and/or during mechanical disintegration. This results in the decreased consumption of energy and better fibrillation. In the present invention a cellulose derivative or polysaccharide or polysaccharide derivative is used in a novel way while adsorbed to cellulosic material under special conditions. Cellulosic material is brought into a fiber suspension and a cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed to said fiber suspension. The fiber suspension containing the adsorbed cellulose derivative or polysaccharide or polysaccharide derivative is then subjected to mechanical disintegration. The cellulose derivative or polysaccharide or polysaccharide derivative is anionic or non-ionic.

The present invention further relates to a paper comprising the modified nanofibrillated cellulose prepared according to the method of the present invention.

One of the advantages of the invention is an improvement of the paper properties.

The present invention further relates to the use of said nanofibrillated cellulose in paper, food products, composite materials, concrete, oil drilling products, coatings, cosmetic products or pharmaceutical products.

The present invention further relates to use of a method for producing nanofibrillated cellulose energy efficiently and use of a method for producing paper with improved properties.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the Scott Bond (J/m^2) i.e. the internal strength of a paper sheet, measured on Scott Bond Tester as a function of drainage time, measured using a

dynamic drainage analyzer. From this figure it is evident that by adding the nanofibrillated cellulose (NFC) prepared according to this invention (10 min + CS + CMC modified NFC, filled sphere) to only slightly refined pulp almost fivefold increase in internal strength is achieved without severe loss in dewatering efficiency.

Soft wood (pine) pulp was refined for 10 minutes and the pulp was washed to sodium form. A cationic starch (CS; Raisamyl 50021, DS =0.035, Ciba Specialty Chemicals) was used as an additive in some of the cases (10 min + CS + CMC modified NFC, filled sphere; 10 min + CS + unmodified NFC open sphere). The NFC was dispersed with ultrasound microtip sonication prior to use. All experiments were done in a solution of deionised water containing 1 mM $NaHCO_3$ and 9 mM NaCl.

Pulp was first mixed with cationic starch (CS, 25 mg/g dry pulp) for 15 min, then the dispersed nanofibrillated cellulose (NFC, 30 mg/g dry pulp) was added and the suspension was mixed for another 15 min. In the cases where no CS was used (10 min + unmodified NFC; triangle) only NFC (30 mg/g) was added and the suspension was mixed for 15 min before sheet making. The sheets were prepared in laboratory sheet former (SCAN-C26:76) and dried under restrain. For comparison the effect of refining is shown by the black squares. In this series the pulp has been refined for 10, 15, 20 and 30 minutes, respectively, as shown by black squares. The CMC modified NFC in this example was prepared by sorption of Finnfix WRM CMC and 3 passes through the friction grinder with addition of the same CMC before the second and third pass. Abbreviations: CS, cationic starch; NFC, nanofibrillated cellulose; CMC, Carboxy methyl cellulose.

Figure 2 depicts optical microscopy images of CMC modified nanofibrillated cellulose. CMC (Finnfix WRM, high molecular weight CMC) was added during fibrillation in fluidizer. **Figure 2a** shows modified nanofibrillated cellulose after 1+1 passes through the fluidizer. **Figure 2b** shows modified nanofibrillated cellulose after 1+2 passes through the fluidizer. **Figure 2c** shows modified nanofibrillated cellulose after 1+3 passes through the fluidizer. The decrease in the amount of large particles can be observed.

Figure 3 depicts optical microscopy images of samples after 1+3 passes through the fluidizer. **Figure 3a** shows the image of unmodified nanofibrillated cellulose (NFC). **Figure 3b** shows the image of NFC modified according to this invention by addition of 10 mg/g dry pulp Finnfix, WRM high molecular weight CMC before each pass (a total

of 40 mg/g after 1+3 passes). **Figure 3c** shows the image of NFC modified according to this invention by addition of 10 mg/g dry pulp Finnfix, BW low molecular weight CMC before each pass (a total of 40 mg/g after 1+3 passes).

Figure 4a depicts a schematic diagram of CMC pre-sorption onto the fibre prior to mechanical disintegration. **Figure 4b** depicts a schematic diagram of CMC addition to the pulp suspension prior to and/or during mechanical disintegration. In contrast to the method shown in Figure 4a CMC is allowed to adsorb during the whole disintegration process.

Figure 5 shows the Scott Bond as a function of passes through Masuko or Fluidizer. The corresponding microscopy images are of the Fluidizer samples after 2, 3 and 4 passes through the fluidizer, respectively.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a method for producing modified nanofibrillated cellulose by adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto fibers in a fiber suspension under special conditions and subjecting the fiber suspension comprising a cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration. By combining the adsorption of a cellulose derivative or polysaccharide or polysaccharide derivative onto fibers under special conditions and mechanical disintegration the number of passes through a disintegration device needed to refine the pulp is reduced and the energy demanded is decreased. Special conditions according to the present invention include temperature, presence of monovalent or polyvalent cations, adsorption time and/or mixing. It has surprisingly been found that the amount of refining energy needed in the process is decreased. The present invention provides significant advances compared to the prior art by decreasing the energy consumption during fibrillation. The modification of nanofibrillated cellulose with a cellulose derivative or polysaccharide or polysaccharide derivative prior to and/or during the mechanical disintegration surprisingly increases the processing efficiency.

Furthermore, the modified nanofibrillated cellulose improves the paper properties more than unmodified nanofibrillated cellulose. None of the prior art methods results in the similar strength properties for paper when compared to modified nanofibrillated

cellulose according to the present invention. Nanofibrillated cellulose modified with a cellulose derivative or polysaccharide or polysaccharide derivative contains up to five times more nanofibrils than the unmodified nanocellulose prepared from the same pulp. The strength of paper produced from the modified nanofibrillated cellulose using the special conditions of the present invention is already after the initial pass through the friction grinder considerably increased as compared to unmodified fibrils. Thus, mechanical treatment to obtain modified nanofibrillated cellulose can be reduced to one fifth, while still achieving considerably improved paper qualities. Nanofibrillated cellulose together with a modification by a cellulose derivative or polysaccharide or polysaccharide derivative under special conditions provides a synergistic effect, which can be utilized in paper produced from said modified nanocellulose.

Unless otherwise specified, the terms, which are used in the specification and claims, have the meanings commonly used in the pulp and paper industry. Specifically, the following terms have the meanings indicated below:

The term "nanofibrillated cellulose" or NFC" refers to very refined cellulose where most of the fibrils have been fully liberated from the fibers and occur as individual threads, which are 5 nm – 1 µm thick and several µms long. Conventionally the fibrils having a diameter of less than 1 µm are called nanofibrils and fibrils having a diameter of more than 1 µm and length of several micrometers are called microfibrils.

The term "mechanical disintegration" or "fibrillation" or "grinding" in the present invention relates to producing nanofibrillated cellulose from larger fiber material. Mechanical disintegration includes also for example refining, beating and homogenization. Mechanical disintegration can be carried out with suitable equipment such as a refiner, grinder, homogenizer, colloider, friction grinder, fluidizer such as microfluidizer, macrofluidizer or fluidizer-type homogenizer.

The term "cellulosic material" refers to nonwoody and wood cellulosic materials used. As cellulosic material for the method and process of the present invention almost any kind of cellulosic raw materials is suitable, as described below.

The term "special conditions" in the present invention refers to a specified temperature, presence of monovalent or polyvalent cations, adsorption time and/or mixing which are defined according to the present invention.

The term "chemical pulp" refers to all types of chemical wood-based pulps, such as bleached, half-bleached and unbleached sulphite, sulphate and soda pulps, kraft pulps together with unbleached, half-bleached and bleached chemical pulps and mixtures thereof.

The term "paper", as used herein, includes not only paper and production thereof, but also other web-like products, such as nonwoven, board and paperboard, and the production thereof.

The present invention provides a method for producing modified nanofibrillated cellulose wherein the method comprises steps of preparing a suspension containing fibers from cellulosic material, adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under specified conditions and subjecting the fiber suspension comprising said cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration to obtain modified nanofibrillated cellulose modified with said cellulose derivative or polysaccharide or polysaccharide derivative.

According to an embodiment of the present invention a cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers either prior to mechanical disintegration (sorption) or by adding a cellulose derivative or polysaccharide or polysaccharide derivative during the mechanical disintegration (addition) under special conditions. In still another embodiment of the invention the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers both prior to and during the mechanical disintegration.

In a preferred embodiment of the invention as cellulosic material for the method of the present invention almost any kind of cellulosic raw materials is suitable. The cellulosic material which is used in the present invention includes pulp such as a chemical pulp, mechanical pulp, thermo mechanical pulp (TMP) or chemi-thermo mechanical pulp (CTMB) produced from wood, non-wood material or recycled fibers. Wood can be from softwood tree such as spruce, pine, fir, larch, douglas-fir or hemlock, or from hardwood tree 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. Non-wood material can also be from algae or fungi or of bacterial origin.

In a preferred embodiment of the invention as a cellulose derivative for the purposes of the present invention almost any kind of cellulose derivative is suitable. A cellulose derivative can be carboxymethyl cellulose, methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, ethylhydroxyethyl cellulose, carboxymethylcellulose, carboxymethylhydroxyethyl cellulose, hydroxypropylhydroxyethyl cellulose, methylhydroxypropyl cellulose, methylhydroxyethyl cellulose, carboxymethylmethyl cellulose, or hydrophobically modified variants thereof, or cellulose acetate, cellulose sulfate, cellulose phosphate, cellulose phosphonate, cellulose vinyl sulfate, or nitrocellulose or other derivatives known by the person skilled in the art can be applied. The present invention is exemplified by using carboxymethyl cellulose (CMC) for producing modified nanofibrillated cellulose. Preferably anionic CMC is used. Even though CMC represents a preferred embodiment, it should be noted, that other cellulose derivatives known by the person skilled in the art can be used.

In a preferred embodiment of the invention a polysaccharide or polysaccharide derivative can be selected from guar gums, chitins, chitosans, galactans, glucans, xantan gums, mannans or dextrins ,which are given here by the way of examples. It should be noted, that other polysaccharides or polysaccharide derivatives known by the person skilled in the art can be used.

The amount of added cellulose derivative or polysaccharide or polysaccharide derivative is at least 5 mg/g of fiber suspension, preferably from 10 to 50 mg/g of fiber suspension, more preferably about 15 mg/g, 20 mg/g, 25mg/g, 30 mg/g, 35 mg/g or 40 mg/g of fiber suspension, the upper limit being 1000 mg/g of fiber suspension, preferably the upper limit is 100 mg/g of fiber suspension.

In an embodiment where CMC is used as the cellulose derivative, different commercially available CMC grades having a suitable degree of substitution and molar mass can be used for carrying out the invention. Typically high molecular weight CMC has suitable characteristics for mechanical disintegration or fibrillation and typically low molecular weight CMC can penetrate the fiber wall, which also increases the amount of adsorbed CMC.

In a preferred embodiment of the invention a cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers at a temperature of at least 5°C, preferably at a temperature of at least 20°C, the upper limit being 180°C. In a more preferred embodiment of the invention temperature is from 75°C to 80°C.

In a preferred embodiment of the invention a cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers for at least 1 minute, preferably for at least 1 hour, preferably for 2 hours. Preferably the adsorption is aided by sufficient mixing.

In a preferred embodiment of the present invention the absorption is made in the presence of monovalent or polyvalent cations such as aluminium, calcium and/or sodium salts containing Al^{3+}, Ca^{2+} and/or Na^{+}, respectively, preferably for example $CaCl_2$. High valencies are advantageous for the adsorption. Generally a higher concentration of electrolyte and a higher valence of the cation increase the affinity of an anionic cellulose derivative, such as CMC, to the pulp. Generally, however, an optimum exists. The preferred concentration interval for salts with divalent cations such as $CaCl_2$ is between 0 and 1 M, preferably about 0.05 M.

In a preferred embodiment of the invention the pH value of the fiber suspension is at least pH 2, preferably from about pH 7.5 to 8, the upper limit being pH 12. A suitable base or acid is used for setting the pH. The pH value is dependent on the origin of the fibers in the mass.

The sorption at specified conditions ensures that a cellulose derivative or polysaccharide or polysaccharide derivative is irreversibly attached to the pulp prior to disintegration. The addition at low temperature during disintegration does not facilitate sorption but indicates the effect of a cellulose derivative or polysaccharide or polysaccharide derivative in solution on fibrillation efficiency.

The present invention comprises a step of mechanical disintegration. In a preferred embodiment of the invention the mechanical disintegration is carried out with a refiner, grinder, homogenizer, colloider such as a supermass colloider, friction grinder, fluidizer such as microfluidizer, macrofluidizer or any fluidizer-type homogenizer known by the person skilled in the art without, however, not limiting to these examples. Typically the fiber suspension is passed through mechanical disintegration at least once, preferably 1, 2, 3, 4 or 5 times.

This enables the reduction of mechanical treatment by up to one fifth, while at the same time considerable improvement for example in paper quality is achieved. It is shown in the Examples that the energy consumption during friction grinding of pulp modified with a cellulose derivative, such as CMC, is lower compared to friction grinding of same pulp without a cellulose derivative, such as CMC adsorbed. The energy consumption of producing the modified nanocellulose of the present invention is lower compared to unmodified pulp. The energy needed to obtain roughly the same amount of nanofibrillated material is halved.

In a preferred embodiment of the invention the fiber suspension containing the cellulose derivative or polysaccharide or polysaccharide derivative is redispersed in water to a concentration of at least 0,1%, preferably at least 1%, more preferably at least 2%, 3%, 4% or 5%, up to 10% prior to mechanical disintegration. In a preferred embodiment using the friction grinder for the mechanical disintegration the fiber suspension containing the cellulose derivative or polysaccharide or polysaccharide derivative is redispersed in water to 3% consistency. Preferably 1-5 passes are run.

The present invention also relates to nanofibrillated cellulose prepared according to the method of any of the claims.

In nanosized structure the surface area of cellulose is maximized and the structure has more chemically functional groups than cellulose in general. This means that nanocellulose fibers attach strongly to surrounding substances. This provides the paper produced from the nanocellulose with good strength properties. Using the modified nanocellulose according to the present invention even higher strength properties than with unmodified nanocellulose are obtained.

The present invention relates to the use of modified nanofibrillated cellulose according to the present invention in paper. The present invention also relates to a paper containing the modified nanofibrillated cellulose of the present invention. In a preferred embodiment the amount of modified nanofibrillated cellulose is at least 0,2%, preferably at least 1%, 2%, 3%, 4% or 5%, up to 20%by weight of the paper. Other ingredients in paper are such that are known to the person skilled in the art. The paper is prepared using the standard methods used in the field and known by the person skilled in the art. The technical paper properties of both fibril sheets of the present invention and paper sheets containing modified nanofibrillated cellulose of the

present invention are tested using standard methods known by the person skilled in the art.

Adsorbed cellulose derivative or polysaccharide or polysaccharide derivative of the present invention is used in a novel way. Combining the adsorption of the cellulose derivative or polysaccharide or polysaccharide derivative and mechanical disintegration provides novel and surprising advantages. It is noted that in the present process, energy savings are achieved. Another advantage of the modification is the new properties of the modified fibrils that can be used for example to improve the properties of paper. The strength of the paper produced from the modified nanofibrillated cellulose of the present invention is already after the initial pass through the refiner considerably increased as compared to unmodified fibrils. Thus, mechanical treatment can be reduced to up to one fifth, while at the same time considerable improvement for example in paper quality is achieved.

The efficiency of the mechanical disintegration or fibrillation is determined by gravimetrically measuring the amount of nano-size particles after each pass through the homogenizing device.

Application areas for the modified nanofibrillated cellulose of the present invention include, but are not restricted to paper, food products, composite materials, concrete, oil drilling products, coatings, cosmetic products and pharmaceutical products. Other possible application areas of the modified nanocellulose of the present invention include for example the use as a thickener, use in composites for vehicles, consumables and furniture, in new materials for electronics and use in moldable light weight and high strength materials.

The following example is given to further illustrate the invention and is not intended to limit the scope thereof. Based on the above description, a person skilled in the art will be able to modify the invention in many ways.

Examples

Example 1

Materials

Pulp

Bleached, never-dried kraft birch pulps provided by UPM-Kymmene Oyj were used.

CMC

Two different CMC grades were used: the high molecular weight Finnfix WRM or low molecular weight Finnfix BW (DS 0.52-0.51) (CP Kelco, Äänekoski, Finland).

CMC adsorption was carried out with two strategies: either treating the pulp prior to fibrillation with CMC in specific conditions (sorption) or adding the CMC during the fibrillation (addition). The third strategy was to adsorb CMC both prior to fibrillation and during fibrillation.

CMC sorption

The pulp (never dried hardwood) was first washed with deionised water prior to sorption. A slurry with pulp consistency of 30 g/l containing 0.05 M $CaCl_2$ and 0.01 M $NaHCO_3$ was prepared and heated to 75-80°C. 20 mg carboxymethyl cellulose (CMC) was added per gram of pulp (o.d). The pH was adjusted to pH 7.5-8 with 1M NaOH. The slurry was mixed for 2h at 75-80°C. After sorption the pulp was washed with deionised water, excess water was removed by filtration and the moist pulp cakes were stored in cold room until fibrillation. Batches corresponding to about 20-25 l of 3% CMC sorbed pulp were prepared for fibrillation with friction grinder and batches of about 5 l of 3% CMC sorbed pulp were prepared for fluidizer runs. Sorption is presented in Figure 4a.

CMC addition

The CMC was dissolved carefully the day before fibrillation into 2% consistency. After dispersing the pulp the addition was done before each pass by adding the CMC solution calculated as 10 mg per dry gram of fibre for one pass. One to four additions corresponding to total additions of 10-40 mg/g were performed. Between the additions the slurry was mixed 15 minutes without heating. In this case the cellulose derivative adsorption was going on during fibrillation.

Fibrillation

Fibrillation was done with either friction grinder (Masuko Supermass colloider, Masuko Sangyo, Japan) or a laboratory scale fluidizer (Microfluidics M110Y, Microfluidics Corp., USA).

Friction grinding

In friction grinding the CMC sorbed pulp was redispersed in water to 3% consistency using the grinder with 200µm gap. Subsequently 1 to 5 passes were run through the friction grinder with a gap of roughly 100-160 µm and power around 3 kW and samples were taken after each pass. In the cases where CMC was also added during fibrillation, the slurry was heated to 60-80°C for 30 min and mixed for 10 min after CMC addition prior to passing through the colloider.

The following experiments were carried out with friction grinder:

1. Reference, unmodified pulp was passed five times through the friction grinder.
2. High molecular weight CMC (WRM) was sorbed onto pulp, the pulp was washed prior to refining and one to five passes were run through the friction grinder.
3. High molecular weight CMC (WRM) was sorbed onto pulp, the pulp was washed prior to refining. 20 mg/g CMC (WRM) was added to suspension (adsorption) before each pass through the friction grinder. The pulp was run one to three times through the refiner.
4. Low molecular weight CMC (BW) was sorbed to the pulp and the pulp was washed prior to refining, one to five passes were run through the friction grinder.

The concentration of nanofibrils in each of the above listed experiments are presented in the upper part of Table 2, "Masuko Supermass Colloider".

Fluidizer

In the experiments carried out with the fluidizer the well beaten pulp (hardwood pulp) was diluted to 2% consistency and pre-dispersed with a Polytron mixer before first run through the fluidizer. The sample was first passed through the wider chamber pair with diameters of 400 and 200µm at 950 bar and then 1 to 3 times through the smaller chamber pair with diameters of 200 and 100µm at 1350 bar.

The following experiments were carried out with a fluidizer:

1. Reference: unmodified pulp – only fibrillation.
2. Presorption of CMC (high molecular weight, WRM or low molecular weight, BW) prior to fibrillation
3. Presorption of CMC (high molecular weight, WRM or low molecular weight, BW) prior to fibrillation + addition (adsorption) of CMC during fibrillation.
4. Addition (adsorption) of CMC during fibrillation only (WRM or BW).

The concentrations of nanofibrils in each of the above listed experiments are presented in the lower part of Table 2, "Microfluidics fluidizer".

Amount of nanosized material

The proportion of nanosized material in the nanofibrillated cellulose (NFC) was estimated by centrifugation. The more there were unsettled fibrils in the supernatant after centrifugation the more efficient the fibrillation had been. Solids content was determined gravimetrically after drying the samples before and after drying them in oven (105ºC). Based on the value, the samples are diluted into constant (ca. 1.7 g/ml) consistency and dispersed with ultrasound microtip (Branson Digital Sonifier D-450) for 10 min, 25 % amplitude setting. After sonification, samples are centrifuged (Beckman Coulter L-90K) for 45 min at 10 000 G. From clear supernatant, 5 ml is carefully taken with a pipette. Two parallel measurements (10 ml) are combined for gravimetric analysis and results are given as an average value for two measurements.

Optical microscopy imaging

Fibrous material was stained with 1% Congo red (Merck L431640) in order to improve contrast in light microscopy. Staining liquid was centrifuged (13 00 rpm, 2 min) prior to use to remove insoluble material. For microscopical examination a fibre sample (150µl) was mixed with Congo red solution at a ratio of 1:1 in an eppendorf tube and about 100 µl of stained fibre slurry was spread with 50 µl of distilled water on microscope slide and covered with a cover slip. The samples were examined using bright field settings under Olympus BX61 microscope equipped with ColorView 12 camera (Olympus). Images were taken with magnifications of 40 x and 100 x using Analysis Pro 3.1 image processing program (Soft Imaging System GmbH).

Preparation of fibril sheets

To demonstrate the efficiency of the present invention sheets containing 85% NFC and 15 % unrefined soft wood pulp were prepared according to the standard method using a normal laboratory sheet former (SCAN-C26:76).

Preparation of paper sheets with fibrils as additives

Softwood pulp was refined for 10 minutes, and the pulp was washed to sodium form. A cationic starch (Raisamyl 50021, DS =0.035, Ciba Specialty Chemicals) was used as an additive. A 2 g/l starch stock solution was prepared fresh every day. The NFC was dispersed with ultrasound microtip sonication prior to use. All experiments were done in a solution of deionised water containing 1 mM $NaHCO_3$ and 9 mM NaCl.

Pulp was first mixed with cationic starch (CS) for 15 min and then the dispersed nanofibrillated cellulose (NFC) was added and the suspension was mixed for another 15 min. The sheets were prepared in laboratory sheet former (SCAN-C26:76) and dried under restrain.

The paper technical properties of both fibril sheets and paper sheets containing modified NFC were tested using standard methods.

Results

Energy consumption during production

The energy consumption during friction grinding of CMC sorbed pulp is illustrated in Table 1. Furthermore, average solids content after fibrillation and estimated amount of nanosized material are presented.

Table 1. Energy consumption for the fibrillation of pulp after CMC sorption using friction grinder.

Sample	Passes	Cumulative total refining energy (MW*h/t)	Average solids content [%]	Nanomaterial (upper phase) [g/l]
Reference	1	1.84		Too low to determine
Reference	3	6.63		Too low to determine
Reference	5	12.75		0.099
WRM sorption	1	1.59	2.74	0.164
WRM sorption	2	3.16	2.44	0.110
WRM sorption	3	5.30	2.04	0.117
WRM sorption	4	7.95		Not determined
WRM sorption	5	11.06	1.75	0.110

Effect of CMC modification on amount of nanosized material

Table 2. Concentration of nanofibrils in upper phase after centrifugation.

sample ID	Nanomaterial conc (g/l)
Masuko supermass colloider	
unmodified hardwood, 5 pass	0.099
CMC (WRM) sorption only prior to fibrillation, 1 pass	0.16
CMC (WRM) sorption only prior to fibrillation, 3 pass	0.12
CMC (WRM) sorption only prior to fibrillation, 5 pass	0.11
CMC (WRM) sorption + addition during fibrillation, 2 pass	0.18
CMC (WRM) sorption + addition during fibrillation, 3 pass	0.17
CMC (BW) sorption only prior to fibrillation, 1 pass	0.015
CMC (BW) sorption only prior to fibrillation, 3 pass	not determined
CMC (BW) sorption only prior to fibrillation, 5 pass	0.035
Microfluidics Fluidizer	
Unmodified hard wood, 1 + 1 pass	0.339
Unmodified hard wood, 1 + 2 pass	0.348
Unmodified hard wood, 1 + 3 pass	0.452
CMC (BW) sorption only prior to fibrillation, 1 + 1 pass	0.154
CMC (BW) sorption only prior to fibrillation, 1 + 2 pass	0.169
CMC (BW) sorption only prior to fibrillation, 1 + 3 pass	0.218
CMC (BW) addition during fibrillation, 1 + 1 pass	0.322
CMC (BW) addition during fibrillation, 1 + 2 pass	0.343
CMC (BW) addition during fibrillation, 1 + 3 pass	0.415
CMC (BW) sorption + addition during fibrillation, 1 + 1 pass	0.218
CMC (BW) sorption + addition during fibrillation, 1 + 2 pass	0.290
CMC (BW) sorption + addition during fibrillation, 1 + 3 pass	0.196
CMC (WRM) sorption only prior to fibrillation, 1 + 1 pass	0.129

CMC (WRM) sorption only prior to fibrillation, 1 + 2 pass	0.124
CMC (WRM) sorption only prior to fibrillation, 1 + 3 pass	0.123
CMC (WRM) addition during fibrillation, 1 + 1 pass	0.418
CMC (WRM) addition during fibrillation, 1 + 2 pass	0.407
CMC (WRM) addition during fibrillation, 1 + 3 pass	0.492
CMC (WRM) sorption + addition during fibrillation, 1 + 1 pass	0.112
CMC (WRM) sorption + addition during fibrillation, 1 + 2 pass	0.184
CMC (WRM) sorption + addition during fibrillation, 1 + 3 pass	0.179

Abbreviations: CMC, carboxymethyl cellulose;
BW, low molecular weight CMC (Finnfix BW, CP Kelco, Äänekoski, Finland, DS 0.51);
WRM, high molecular weight CMC (Finnfix WRM, CP Kelco, Äänekoski, Finland)

CMC sorption increases the efficiency of the fibrillation (Table 2). Tests using friction grinding indicates that sorption prior to fibrillation in combination with addition during fibrillation gives the highest concentration of fibrils in upper phase after centrifugation. In these cases the total amount of CMC used is also highest, since 20 mg/g was added three times i.e. in total of 60 mg.

However, when fluidizer was used an effective way was to add CMC only during the disintegration.

It was thus observed that the upper phase of the CMC modified nanofibrillated cellulose sample contained five times more nanofibrils than the unmodified nanofibrillated cellulose prepared from the same mass.

Effect of CMC modification on strength of test sheets

The potential of the modified nanofibrillated cellulose (NFC) as a strength additive is illustrated below. In Table 3 the paper properties of test sheets containing 85% NFC and 15% long fibers are compared. A clear increase in paper strength was observed using the modified NFC as compared to unmodified NFC (reference hardwood). Noteworthy is that the density of the paper produced using modified NFC did not increase although the tensile strength was clearly higher than for unmodified NFC. Satisfying results were obtained already after 1 pass through the friction grinder (Masuko colloider).

Table 3. NFC Paper Sheet Characteristics.

	TestPoint	Grammage g/m^2	Apparent density kg/m^3	Tensile strength kNm/kg	Tear Index Jm/kg	Bending stiffness mNm
CMC-treated	WRM sorpt. 1p	66.1	991	93.17	4.51	0.104
	WRM sorpt. 3p	66.2	999	84.40	3.29	0.112
	WRM sorpt. 5p	66.5	987	84.89	2.99	0.126
	BW sorpt. 1p	66.2	991	86.11	3.69	0.115
	BW sorpt. 2p	66.1	1000	88.04	3.20	0.107
	BW sorpt. 3p	67	1030	84.89	2.70	0.125
Ref.	hardwood 5p	67.4	1010	64.84	3.75	0.089

Abbreviations:

WRM sorpt., nanofibril sample modified with high molecular weight CMC (WRM);
BW sorpt., nanofibril sample modified with low molecular weight CMC (BW);
1p, 2p, 3p and 5p, the amount of the passes through the refiner (refining cycles);
Ref., hardwood 5p, the corresponding unmodified fiber suspension from hardwood passed five times through the friction grinder.

It was found that the strength of the paper produced from the modified NFC already after the initial pass through the refiner, was considerably increased as compared to unmodified fibrils. Thus, mechanical treatment can be reduced to one fifth, while still achieving considerably improved paper qualities (Table 3).

The effect of NFC on sheet properties was also studied using NFC as an additive. The results are shown in Table 4 and in Figure 1. In these experiments cationic starch (CS, 25 mg/g) was added to fractionated softwood pulp and adsorbed for 15 minutes, whereupon either unmodified or modified NFC was added (30 mg/g) and adsorbed for 15 minutes and sheets were made. Scott Bond is a measure of the internal strength of the sheet, measured on Scott Bond Tester, expressed in J/m^2. In Table 4 the paper properties achieved using NFC prepared according to the present method using Masuko Mass colloider are shown.

Table 4. Paper Technical paper properties of sheets made from pulp, cationic starch (CS) and nanofibrillated cellulose (NFC) at constant ionic strength, pH and after fines

have been removed. NFC was modified using friction grinder (Masuko super colloider). Reference sample contained pulp only or pulp and cationic starch.

Sample		NFC	CS + NFC	NFC	CS + NFC
	Passes	Tensile index (Nm/g)	Tensile index (Nm/g)	Scott Bond (J/m2)	Scott Bond (J/m2)
Reference	5	64.6	83.37	194	320
CMC sorption (WRM)	1	70.15	90.2	180	405
CMC sorption (WRM)	3	68.97	84.16	193	531
CMC sorption (WRM)	5	68.26	89.49	204	400
CMC sorption + addition (WRM)	1	67.77	85.08	211	446
CMC sorption + addition (WRM)	3	66.42	86.76	190	559

Abbreviations:
CS, cationic starch; NFC, nanofibrillated cellulose; CMC, carboxymethyl cellulose; WRM, high molecular weight CMC; BW, low molecular weight CMC

The efficiency of the fibrillation

The efficiency of the fibrillation made according to this invention is illustrated by optical microscopy images in Figures 2 and 3. The scale bars in the figures are 500 µm. The decrease in the amount of dark thick fibers shows the efficiency of fibrillation. The finest nanosized material is obviously not visible in optical microscopy.

CMC (Finnfix WRM, high molecular weight CMC) was added during fibrillation in fluidizer. In Figure 2 the samples after different amount of passes, 1+1, 1+2 and 1+3 passes, respectively, through the fluidizer are compared, (Figures 2a, 2b and 2c). The decrease in the amount of large particles can be observed.

In Figure 3 CMC-modified samples (Figure 3b and 3c) are compared to a sample of unmodified nanofibrillated cellulose (Figure 3a) after 1 + 3 passes through the fluidizer. NFC was modified according to this invention by addition of 10 mg/g dry pulp Finnfix, WRM high molecular weight CMC before each pass (a total of 40 mg/g after 1+3 passes) (Figure 3b). The image of NFC modified according to this invention by

addition of 10 mg/g dry pulp Finnfix, BW low molecular weight CMC before each pass (a total of 40 mg/g after 1+3 passes) is shown in Figure 3c. Clearly there are much less large particles left in the samples modified according to this invention than in an unmodified sample.

Example 2

Materials

Pulps

Bleached softwood kraft pulp made from Scots Pine (*Pinus sylvestris*) was aquired from UPM-Kymmene Oyj, Kaukas pulp mill in air dry sheets. The dry pulp samples were swollen in deionized water and beaten in a Valley beater according to standard SCAN-C 25:76. Unless otherwise stated the beating time was 10 min. Thereafter any remaining metal ions were removed by acid treatment, and the fibres were washed into their Na-form according to method described by Swerin et al. (1990). Finally the samples were dewatered and stored in a refrigerator at ca. 20 % consistency. Prior to use the samples were diluted to desired consistency and cold disintegrated according to standard SCAN-C 18:65. The salt concentration of the suspensions was adjusted to 9 mM NaCl and 1 mM $NaHCO_3$, and the pH was adjusted to 8.0.

Polyelectrolytes

Two different CMC (carboxymethyl cellulose) grades from CP Kelco Oy (Äänekoski, Finland) were used for preparation of modified NFC. They are hereafter referred to as WRM (high molecular weight) CMC and BW (low molecular weight) CMC.

In sheet preparation and dewatering experiments cationic starch (CS, Raisamyl 50021 from Ciba Specialty Chemicals Ltd), of which degree of substitution (D.S.) ca 0.035, and charge density of ca. 0.2 meq/g was used to enhance the retention of the NFC on the fibres.

Nanofibrillar cellulose

Different grades of modified NFC were used. The NFC was prepared from never dried birch pulp, obtained from UPM-Pietarsaari and grinded to SR 90. NFC samples were prepared either using the Masuko Mass Colloider (Masuko Sangyo Co., Kawaguchi,

Japan) or the laboratory scale fluidizer (M-110Y, Microfluidics Corp.). As a reference a sample prepared by passing the pulp 5 times trough the Masuko colloider was used.

Electrolytes (NaCl and $NaHCO_3$) were of analytical grade and dissolved in deionized water. Analytical grade HCl and NaOH solutions were used for pH adjustments. The used water was deionized.

Methods

Sheet forming

The pH and electrolyte concentration of the fibre suspension was kept constant using 1 mM $NaHCO_3$ and 9 mM NaCl. Polyelectrolyte (cationic starch or PDADMAC) was first added to the fibre suspension and the suspension was vigorously mixed for 15 min. The NFC was dispersed using ultrasound, added to polyelectrolyte treated pulp and the suspension was mixed for another 15 min. Sheets were formed in a laboratory sheet former, Lorentzen & Wettre AB, Sweden (ISO 5269-1) with a 100 mesh wire. The grammage of sheets was adjusted to about 60 g/m^2 by dilution of the suspension when necessary. The sheets were wet pressed under 4.2 bars for 4 minutes and dried in a frame to avoid shrinkage during drying (105°C for 3 minutes). The samples were conditioned over nigh in 50% humidity and 20°C according to the standard SCAN_P 2:75 before testing.

Sheet testing

All the sheet properties were measured according to SCAN or ISO standards. Grammage (ISO 536:1995(E)), thickness and bulk were determined with Lorentzen & Wettre micrometer (ISO 534:2005(E)). The Scott Bond was determined using Huygen Internal bond tester) and Tensile strength, fracture toughness index and TEA were measured with Lorentzen & Wettre tearing tester (SE009 Elmendorf, SCAN-P 11:73).

Results

Strength of sheets

In Tables 5 and 6 the sheet properties of sheets made using NFC prepared with Masuko supermass colloider (Table 5) or microfluidics fluidizer (Table 6) are summarized. Cationic starch, CS, Raisamyl 50021 was used in the experiments presented in table 5 and 6.

Table 5. Sheet properties of sheets made from pulp, cationic starch (CS, 25 mg/g)) and nanofibrillated cellulose (NFC, 30 mg/g). NFC was prepared with Masuko supermass colloider. Reference sample contains only pulp.

NFC grade	Passes	Grammage (g/m^2)	Density (kg/m^3)	Tensile index (Nm/g)	Scott Bond (J/m^2)
Reference	No NFC	60,8	558	58,35	132
WRM sorption	1	58	579	90,2	405
WRM sorption	3	58,3	599	84,16	531
WRM sorption	5	56,4	573	89,49	400
WRM sorption + addition	1	59	584	85,08	446
WRM sorption + addition	3	61,4	608	86,76	559
BW sorption	1	59	564	76,26	347
BW sorption	3	59,5	582	84,62	426
BW sorption	5	59,8	603	85,77	470

Abbreviations: WRM, high molecular weight CMC; BW, low molecular weight CMC

Table 6. Sheet properties of sheets made from pulp, cationic starch (CS, 25 mg/g)) and nanofibrillated cellulose (NFC, 30 mg/g). NFC was prepared with microfluidics fluidizer. Reference sample contains pulp, cationic starch (CS) and unmodified NFC.

NFC grade	Passes	Grammage (g/m^2)	Density (kg/m^3)	Tensile index (Nm/g)	Scott Bond (J/m^2)
BW sorption	4	62,4	575	79,26	383
BW addition	4	62,8	597	85,16	520
WRM addition	4	62,6	589	82,68	427
WRM sorption	4	62,8	592	79,91	520
REF no CMC	4	62,3	572	82,97	411
BW sorption + addition	2	65,1	589	74,21	480
BW sorption + addition	3	63,5	583	78,1	446
BW sorption + addition	4	66	608	84,59	517
WRM sorption + addition	2	62,9	574	84,63	380
WRM sorption + addition	3	62,6	593	82,65	434
WRM sorption + addition	4	63,3	608	83,1	561

Abbreviations: WRM, high molecular weight CMC; BW, low molecular weight CMC

In Figure 5 both the way of preparing NFC and the effect of passes through the Fluidizer are compared. The corresponding microscopy images show that the fibril size is decreasing with the passes through the Fluidizer. No clear difference between Masuko and Fluidizer samples are found in this case. Compared to the reference at 132 J/m^2, the Scott Bond increases clearly and also compared to unmodified NFC (411 J/m^2 after 4 passes) CMC modified NFC gives higher Scott Bond.

The present invention has been described herein with reference to specific embodiments. It is, however clear to a person skilled in the art that the process(es) may be varied within the bounds of the claims.

CLAIMS

1. A method for producing modified nanofibrillated cellulose, **characterized** by the steps of
- preparing a suspension containing fibers from cellulosic material;
- adsorbing a cellulose derivative or polysaccharide or polysaccharide derivative onto the fibers in said suspension under special conditions; and
- subjecting the fiber suspension comprising said cellulose derivative or polysaccharide or polysaccharide derivative to mechanical disintegration;
to obtain modified nanofibrillated cellulose modified with said cellulose derivative or polysaccharide or polysaccharide derivative.

2. The method according to claim 1, **characterized** in that the cellulosic material is a pulp such as a chemical pulp, mechanical pulp, thermo mechanical pulp or chemi-thermo mechanical pulp produced from wood, non-wood material or recycled fibers.

3. The method according to claim 2, **characterized** in that wood is from softwood tree, hardwood tree, or a mixture of softwoods and hardwoods.

4. The method according to any of the preceding claims, **characterized** in that the cellulose derivative is carboxymethyl cellulose.

5. The method according to claims 1 to 4, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers prior to or during mechanical disintegration.

6. The method according to claims 1 to 5, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers both prior to and during mechanical disintegration.

7. The method according to any of the preceding claims, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers at a temperature of at least 5°C, preferably at a temperature of at least 20°C, the upper limit being 180°C.

8. The method according to any of the preceding claims, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers at a temperature of 75°C - 80°C.

9. The method according to any of the preceding claims, **characterized** in that the cellulose derivative or polysaccharide or polysaccharide derivative is adsorbed onto the fibers for at least 1 minute, preferably for at least 1 hour, preferably for 2 hours.

10. The method according to any of the preceding claims, **characterized** in that the method takes place in the presence of monovalent or polyvalent cations such as aluminium, calcium and/or sodium salts, preferably $CaCl_2$.

11. The method according to any of the preceding claims, **characterized** in that the pH value of the fiber suspension is at least pH 2, preferably from pH 7.5 to 8, the upper limit being pH 12.

12. The method according to any of the preceding claims, **characterized** in that the amount of added cellulose derivative or polysaccharide or polysaccharide derivative is at least 5 mg/g of fiber suspension, preferably from 10 to 50 mg/g, preferably 20 mg/g, the upper limit being 1000 mg/g of fiber suspension.

13. The method according to any of the preceding claims, **characterized** in that mechanical disintegration is carried out with a refiner, grinder, homogenizer, colloider, friction grinder, fluidizer such as microfluidizer, macrofluidizer or fluidizer-type homogenizer.

14. The method according to any of the preceding claims, **characterized** in that the fiber suspension is passed through mechanical disintegration at least once, preferably 2, 3, 4 or 5 times.

15. The method according to any of the preceding claims, **characterized** in that the fiber suspension containing the cellulose derivative or polysaccharide or polysaccharide derivative is redispersed in water to a concentration of at least 0,1%, preferably at least 1%, more preferably at least 2%, 3%, 4% or 5%, up to 10% prior to mechanical disintegration.

16. A modified nanofibrillated cellulose obtainable by a method according to any of claims 1 to 15 and characterized by that a diameter of nanofibrillated cellulose is less than 1 µm.

17. Use of modified nanofibrillated cellulose according to claim 16 in food products, composite materials, concrete, oil drilling products, coatings, cosmetic products, pharmaceutical products or paper.

18. A paper containing the modified nanofibrillated cellulose of claim 16.

19. A paper according to claim 18, **characterized** in that the amount of modified nanofibrillated cellulose is at least 0,2%, preferably at least 1%, 2%, 3%, 4% or 5%, up to 20% by weight of the paper.

20. Use of a method according to claims 1 to 15 for producing modified nanofibrillated cellulose energy efficiently.

21. Use of a method according to claims 1 to 15 for producing paper with improved properties.

22. A method for manufacturing paper with improved properties **characterized** by the steps of

- preparing a fiber suspension from cellulosic material; and
- adding modified nanofibrillated cellulose according to claim 16 to the fiber suspension.

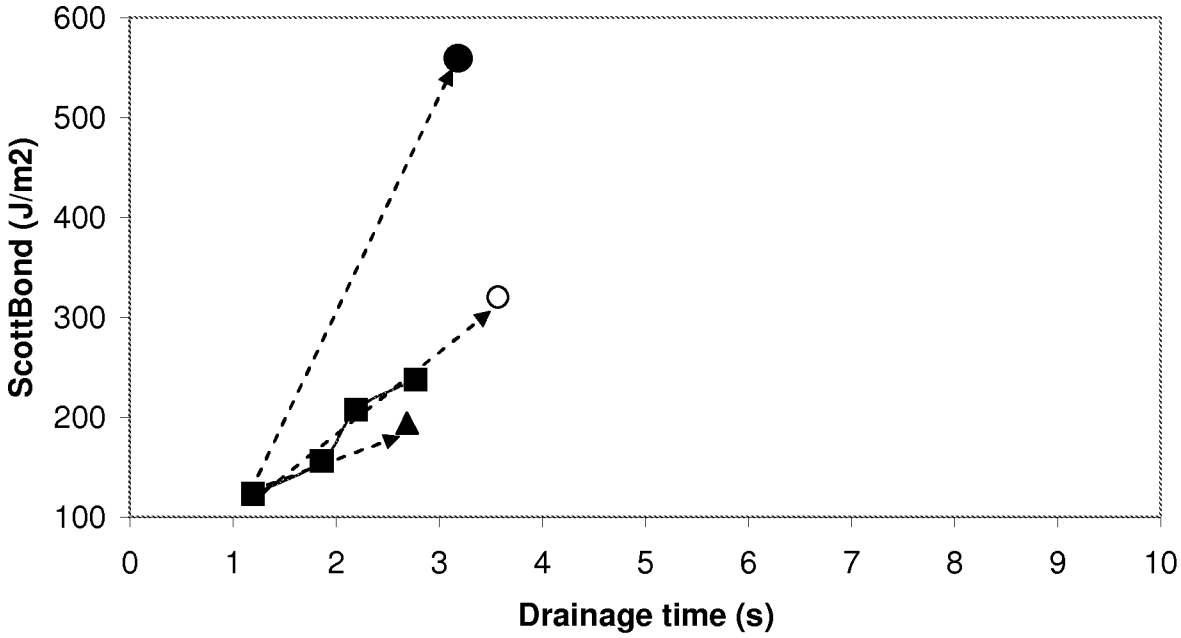
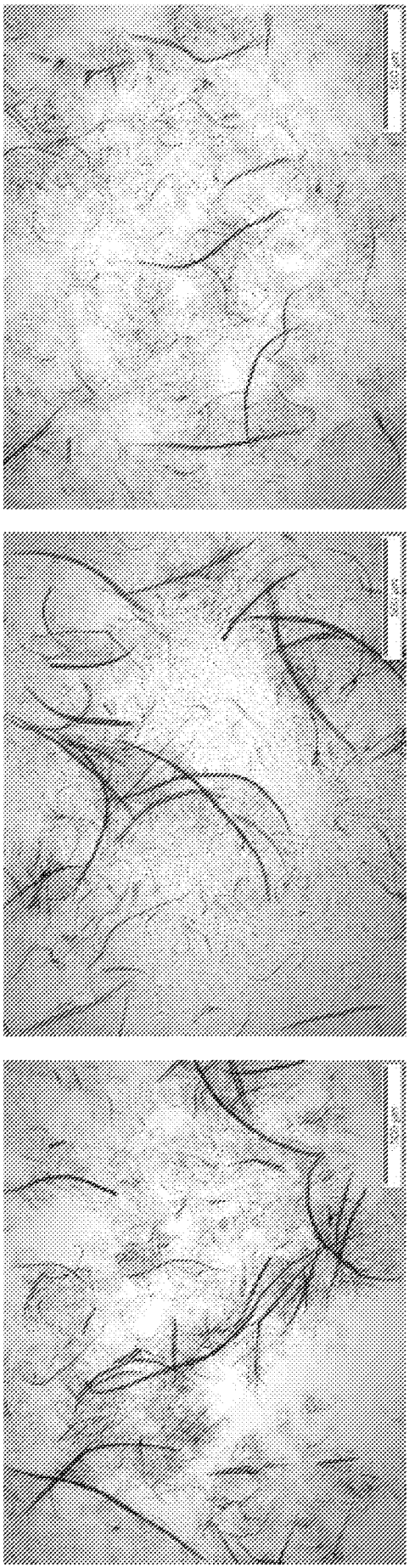

600
500
400
300
200
100
ScottBond (J/m2)
0
1
2
3
4
5
6
7
8
9
10
Drainage time (s)

Fig. 1

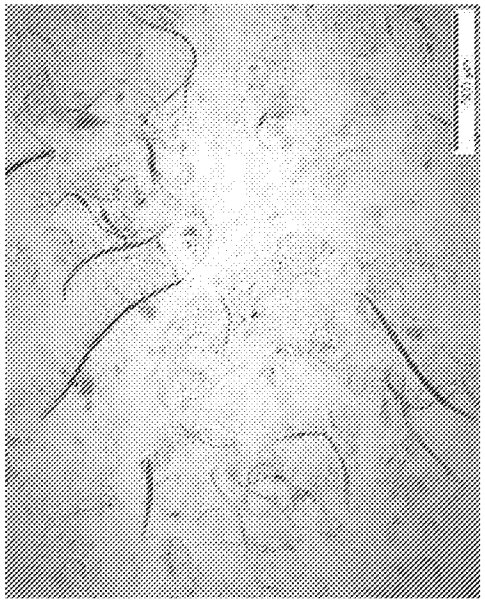


2c

2b

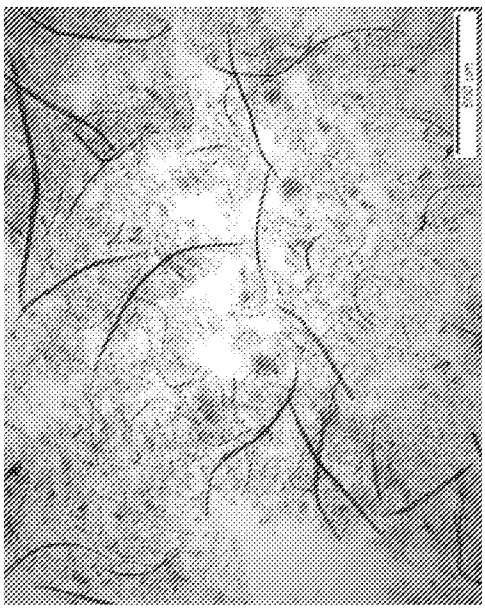
2a

Fig. 2



3c

3b



3a

Fig. 3

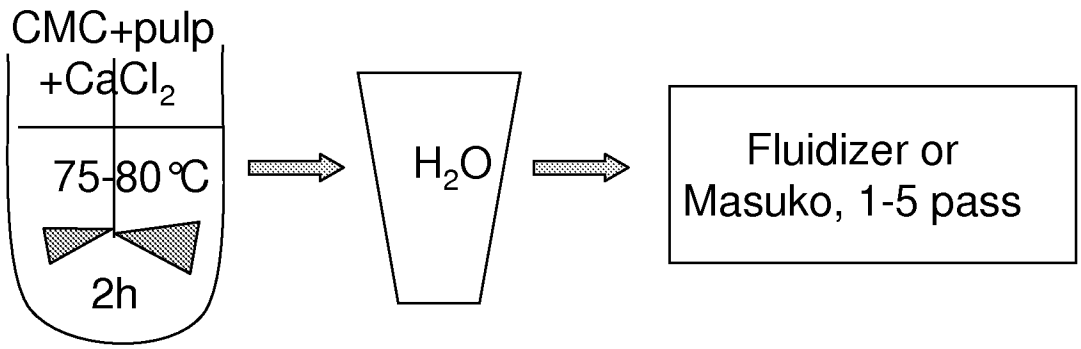

CMC+pulp
+CaCl2
75-80 °C
2h
H2O
Fluidizer or
Masuko, 1-5 pass

Fig. 4A

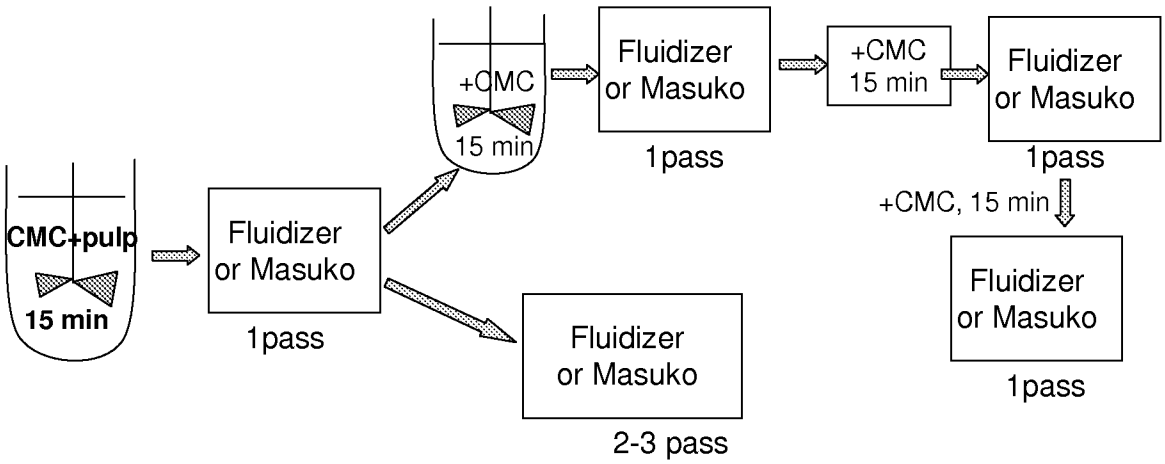

CMC+pulp
15 min
Fluidizer
or Masuko
1pass
+CMC
15 min
Fluidizer
or Masuko
1pass
Fluidizer
or Masuko
2-3 pass
+CMC
15 min
Fluidizer
or Masuko
1pass
+CMC, 15 min
Fluidizer
or Masuko
1pass

Fig. 4B

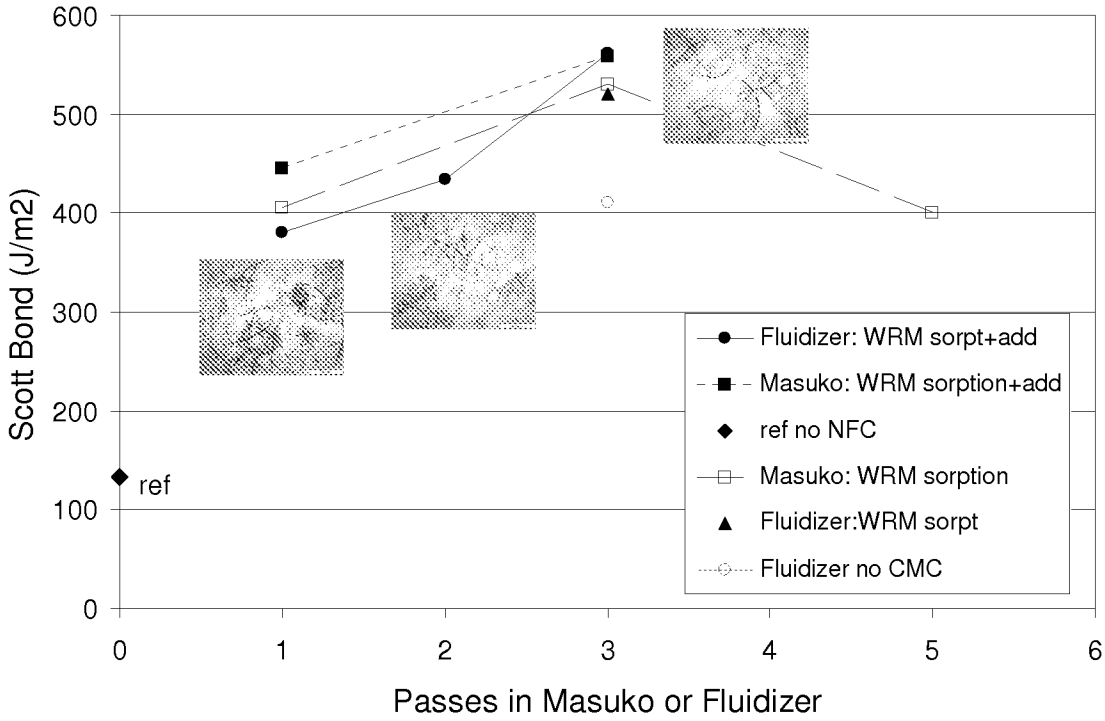

600
500
400
300
200
100
0
Scott Bond (J/m2)
0
1
2
3
4
5
6
Passes in Masuko or Fluidizer
ref
Fluidizer: WRM sorpt+add
Masuko: WRM sorption+add
ref no NFC
Masuko: WRM sorption
Fluidizer:WRM sorpt
Fluidizer no CMC

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2010/050096

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, C08L

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.
X	US 2005272836 A1 (YAGINUMA YOSHIHITO et al.) 08 December 2005 (08.12.2005) claims 10-13, paragraphs [0012]-[0034], [0049], [0047], [0070], [0078], [0083]	1-17
A	WO 2007001229 A1 (AKZO NOBEL NV et al.) 04 January 2007 (04.01.2007) page 1, line 28 - page 2, line 29; page 3, line 33 - page 4, line 34; example 3	
E	WO 2009126106 A1 (STFI PACKFORSK AB et al.) 15 October 2009 (15.10.2009) the whole document	1-5, 7-18, 20, 21

☐ 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
17 June 2010 (17.06.2010)	22 June 2010 (22.06.2010)

Name and mailing address of the ISA/FI	Authorized officer
National Board of Patents and Registration of Finland P.O. Box 1160, FI-00101 HELSINKI, Finland	Heimo Koskinen
Facsimile No. +358 9 6939 5328	Telephone No. +358 9 6939 500

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2010/050096

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
US 2005272836 A1	08/12/2005	TW 231819B B	01/05/2005
		WO 2004007558 A1	22/01/2004
		EP 1553103 A1	13/07/2005
		CN 1668646 A	14/09/2005
		AU 2003281045 A1	02/02/2004
		JP 2004041119 A	12/02/2004
WO 2007001229 A1	04/01/2007	NZ 564484 A	30/04/2010
		NO 20080479 A	28/03/2008
		KR 20080023739 A	14/03/2008
		MX 2007015340 A	11/02/2008
		AR 055978 A1	12/09/2007
		ZA 200711043 A	24/06/2009
		RU 2008102975 A	10/08/2009
		JP 2008544112T T	04/12/2008
		EP 1896508 A1	12/03/2008
		CN 101208358 A	25/06/2008
		CA 2612065 A1	04/01/2007
		AU 2006262963 A1	04/01/2007
WO 2009126106 A1	15/10/2009	SE 0800807 A	11/10/2009

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2010/050096

CLASSIFICATION OF SUBJECT MATTER

Int.Cl.
D21H 11/18 (2006.01)
D21H 17/24 (2006.01)