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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 September 2012 (13.09.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/120071 A1

(51) International Patent Classification:
D01D 1/02 (2006.01)

(21) International Application Number:
PCT/EP2012/053985

(22) International Filing Date:
8 March 2012 (08.03.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11157313.5 8 March 2011 (08.03.2011) EP

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(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, QA, RO, RS, RU, RW, 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, RW, 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))*

— *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 2012/120071 A1

(54) **Title**: METHOD FOR THE MANUFACTURE OF A STABLE HIGH SOLIDS SUSPENSION OF CELLULOSE

(57) **Abstract**: The present invention is directed towards a method for preparing a stable, high solids suspension of neutral or anionically modified cellulose nanofibrils, preferably having a solid content of neutral or anionically modified cellulose nanofibrils of 6 to 80 %, comprising the steps of: (a) isolating neutral or anionic cellulose nanofibrils from cellulose-based material and (b) preparing a stable suspension of the neutral or anionic cellulose nanofibrils in a (viscous) continuous phase that is suitable for use as a basis for fibre spinning.

Method for the manufacture of a stable high solids suspension of cellulose

Field of the Invention

The present invention is directed towards a method for suspending neutral or anionically modified cellulose to obtain a stable, high solids suspension which is suitable for use in the formation of fibres.

Background of the Invention

Cellulose in particular in the form of fibres can be used for many applications and products, so e.g. for the making of paper or board structures, but also for making spun fibres such as viscose fibres or lyocell fibres which show excellent mechanical properties. Due to the chemical nature of cellulose it is a very difficult material to dissolve directly, typically requiring either very polar solvents that are expensive and often toxic and hazardous or else that the cellulose is first derivatised to achieve dissolution in a more convenient solvent. Without a derivatising charge the maximum cellulose that may be suspended in water to obtain a gel composition is in the range of 6 to 9 % (percentage of cellulose nanofibrils in the total gel composition) dependent on particle size. As alternative, prior art systems added a high level to full derivatisation charge to achieve stable suspensions at solids levels of greater than 9%

Applicants have now surprisingly found that suspension can be achieved without the need for full derivatisation and at levels above that normally deemed possible using uncharged cellulose moieties. Thus the present invention allows the preparation of stable suspensions of cellulose nanofibrils to high concentrations which may then be used for further processing to prepare fibres or films directly.

Summary of the Invention

The present invention is directed towards a method for suspending neutral or anionically modified cellulose to obtain a stable, high solids suspension which is suitable for use in the formation of fibres.

More specifically, the invention provides a method for preparing a stable, high solids suspension of neutral or anionically modified cellulose nanofibrils comprising the steps of: (a) isolating neutral or anionic cellulose nanofibrils from cellulose-based material and (b) preparing a stable suspension of the neutral or anionic cellulose nanofibrils in a (viscous) continuous phase that is suitable for use as a basis for fibre spinning.

The term "high solid(s)" as used herein in combination with the suspensions obtained refers to the solid content of neutral or anionic cellulose nanofibrils in the suspension, which solid content refers to the weight ratio of the neutral or anionic cellulose nanofibrils to the continuous phase in the suspension expressed in percentage. Preferably, the solid content of neutral or anionically modified cellulose nanofibrils in the suspension is in the range of 7 to 80 % solids, preferably 9 to 60 %, more preferably 20 to 40 %.

The term "continuous phase" (as used in reference to the high solid suspension) is a viscous continuous state and refers to a liquid in which the anionically charged or neutral cellulose nanofibrils are dispersed, with or without, preferably with, the presence of additives or suspending agents (to obtain said viscous continuous phase).

It is understood that as used herein the term "disperse" may include all states of dissolution, including suspend and dissolve, which are representative for the (lower and upper) limits of dispersing.

A suitable additive (also termed suspending agent) is typically a viscous agent and may be a natural gum (e.g. gum arabic, gum tragacanth, guar gum, locust bean gum, carrageenan) a pectin, an alginate, a cellulose derivative (e.g. hydroxypropylmethylcellulose, methyl cellulose, hydroxyethylcellulose, carboxymethylcellulose), preferably methyl cellulose (such as the methyl cellulose or hydroxyl propyl methyl cellulose supplied by Dow Wolff Cellulosics under the trade name Methocel). Once dispersed into the liquid, the additive or suspending agent will dissolve.

Examples of a suitable liquid - into which said additive or suspending agent is dispersed (and finally dissolved) to obtain the (viscous) continuous phase - includes aqueous solvents, alcohols, ethers, ketones, preferably aqueous solvents, more preferably water. The term

"aqueous solvent" refers to a solvent comprising at least 50%, preferably at least 80%, more preferably at least 90% and optimally from 95 to 100% water by weight of the solvent. The aqueous solvent may have a pH of from 2 to 10, more preferably from 4 to 8 and optimally from 5.5 to 7.5 at 20° C.

Thus in a specific embodiment, the invention provides a method for preparing a stable, high solids suspension of neutral or anionically modified cellulose nanofibrils (that is suitable for use as a basis for fibre spinning) comprising the steps of: (a) isolating neutral or anionic cellulose nanofibrils from cellulose-based material and (b) preparing a stable suspension of the neutral or anionic cellulose nanofibrils in a (viscous) continuous phase by dispersing the nanofibrils obtained in step (a) in a liquid in the presence of a (dispersed or dissolved) additive.

Thus in preferred embodiments the invention provides a method for preparing a stable, high solids suspension of neutral or anionically modified cellulose nanofibrils, wherein the solid content of neutral or anionically modified cellulose nanofibrils in the suspension is in the range of 6 to 80 %, comprising the steps of: (a) isolating neutral or anionic cellulose nanofibrils from cellulose-based material and (b) preparing a stable suspension of the neutral or anionic cellulose nanofibrils in a (viscous) continuous phase by dispersing the nanofibrils obtained in step (a) in a liquid in the presence of a (dispersed or dissolved) additive .

The term "stable suspension" (or viscous continuous phase) refers to a suspension of the neutral or anionically modified cellulose nanofibrils in a liquid (comprising the dissolved additive or suspending agent) in which (liquid or suspension) said cellulose is substantially insoluble, but wherein upon preparation the cellulose nanofibrils remain overtime, i.e. up to 48 hours, preferably up to 24 hours, evenly dispersed, i.e. not substantially agglomerated within the suspension without any separation (such as floating or sedimentation) is occurring. The term "substantially insoluble" refers to such a small degree of solubility so as not to effect the nanofibrillar structure of the cellulose.

As used herein, the term "nanofibril" or "nanofibrillar" in combination with cellulose refer to cellulose that is substantially completely in the form of nanofibrils, and those which may be substantially nanofibrillated while containing minor but not significant amounts of non-nanofibrillar structure, provided that the cellulose is in sufficient nanobrillar form to confer the benefits necessary for use in the methods of the present invention. Nanofibrils obtained from anionically modified cellulose are referred to as anionic cellulose nanofibrils or

nanofibrillar anionically modified cellulose. Nanofibrils obtained from neutral cellulose are referred to as neutral cellulose nanofibrils or nanofibrillar neutral cellulose.

The cellulose nanofibrils may be extracted from nanofibril containing cellulose-based material, including hydrolyzed or mechanically disintegrated cellulose obtained from cotton linter, hard or soft wood pulp, purified wood pulp or the like, commercially available cellulose excipients, powdered cellulose, regenerated cellulose, microcrystalline and low crystallinity celluloses. Preferred cellulose sources are derived primarily from wood pulp. Suitable wood pulp fibres include ground wood fibres, recycled or secondary wood pulp fibres, and bleached and unbleached wood pulp fibres. Both softwoods and hardwoods can be used. Details of the selection of wood pulp fibres are well known to those skilled in the art.

In case of anionically charged nanofibrils, suitable wood pulp fibres can be obtained from well known chemical processes such as the kraft and sulfite processes, with or without subsequent bleaching. Pulp fibres can also be processed by thermomechanical, chemi-thermomechanical methods, or combinations thereof. Preferably the cellulose is obtained by chemical pulping and extraction. The anionic charge is preferably provided by derivatisation with suitable groups carrying a negative charge, such as sulfur-containing groups (e.g. sulfate, sulfonate, alkylsulfate, alkylsulfonate), carboxyl & carboxymethyl groups, phosphor-containing groups (e.g. phosphate, phosphonate), nitro groups or the like, or combinations thereof.

These are characterized by having an elongated form, having an average length in the range of 15-300 nm, preferably in the range of 50-200 nm. The average thickness is preferably in the range of 3-300 nm, preferably in the range of 3-200 nm, more preferably in the range of 10-100 nm.

In specific embodiments the anionically modified cellulose nanofibril is a cellulose nanofibril derivatized with sulfur containing groups, such as sulfated or sulfonated cellulose nanofibrils.

In a further preferred specific embodiment, the anionically modified cellulose is sulfur-derivatized cellulose, more specifically sulfur-derivatized cellulose nanofibril. Thus, as used herein "sulfur-derivatized cellulose nanofibril" refers to a cellulose nanofibril that has been derivatized with anionically charged sulfur groups by reaction of a cellulose nanofibril with a suitable sulfating agent. It will be appreciated that sulfur-derivatized cellulose nanofibril includes free acid and salt forms where appropriate. A sulfur-derivatized cellulose nanofibril can be produced by reacting a sulfating agent with a hydroxyl group of the cellulose nanofibril

to provide a cellulose sulfate ester according to literature procedures (see e.g. Cellulose (1998) 5, 19-32 by Dong, Revol and Gray).

The degree of substitution of anionically modified groups on the cellulose nanofibril should be sufficiently low such that the derivatized cellulose nanofibril will be substantially insoluble (as indicated above) in the continuous phase (or liquid) that is present in the intended methods of the invention.

In specific embodiments, the anionically modified cellulose nanofibril of the invention can be characterized as having an average degree of substitution by an anionic group of from about 0.001 to about 2. In one embodiment the modified cellulose nanofibil has an average degree of substitution by an anionic group of less than 1.0, preferably less than 0.5, more preferably less than 0.1, and at a level where the anionic cellulose cannot form a stable suspension in water without the use of addition additives or chemicals.

As used herein the "average degree of substitution by an anionic group" refers to the average number of moles of the respective anionic group per mole of glucose unit in the modified nanofibril. Thus, the average degree of e.g. sulfate group substitution refers to the average number of moles of sulfate groups per mole of glucose unit in the modified nanofibril.

The degree of substitution can be determined according to methods known in the art (see for example Zhang K et al, Cellulose 17: 427-435, 2010 and references cited therein).

Preferably the suspension of the anionically modified cellulose (i.e. the anionic cellulose suspension) is prepared in liquid to obtain a (viscous) continuous phase in which the anionically modified cellulose is substantially insoluble. It is understood that the solubility of the anionically modified cellulose depends on the degree of substitution with the anionically charged groups.

In case of neutral cellulose, the neutral cellulose is preferably a (neutral) cellulose nanofibril isolated by use of chemical or mechanical degradation or a combination of both process stages on the starting cellulose-based material as defined hereinabove. In specific embodiments, the neutral cellulose nanofibrils may be obtained by mixing finely shredded cellulose-based starting material as defined hereinabove with a non-derivatising mineral acid, for example hydrochloric acid, boiling said mixture for between 10 minutes and 5 hours. Preferably the concentration of the non-derivatising mineral acid is between 0.1 to 90%, preferably 10 to 60%. The obtained mixture is filtered and the extracted cellulosic material with or without

prior drying is subject to mechanical shear for example using a ball mill or attritor device to obtain the neutral cellulose nanofibrils.

The neutral cellulose nanofibril is characterized by having an elongated form, having an average length in the range of 15-300 nm, preferably in the range of 50-200 nm. The average thickness is preferably in the range of 3-300 nm, preferably in the range of 3-200 nm, more preferably in the range of 10-100 nm.

To obtain the neutral cellulose suspension, the neutral cellulose may then be suspended in a fluid medium or liquid comprising an additive or a suspending agent as defined hereinabove to obtain a (viscous) continuous phase as defined hereinabove. A suitable suspending agent (or additive) may be a natural gum (e.g. gum arabic, gum tragacanth, guar gum, locust bean gum, carrageenan) a pectin, an alginate, a cellulose derivative (e.g. hydroxypropylmethylcellulose, methyl cellulose, hydroxyethylcellulose, carboxymethylcellulose), preferably methyl cellulose (such as the methyl cellulose or hydroxyl propyl methyl cellulose supplied by Dow Wolff Cellulosics under the trade name Methocel). A suitable liquid or continuous phase may be selected from aqueous solvents, e.g. water, or organic solvents, e.g. methylene chloride, methanol, propanol and dimethyl sulfoxide and the like, or as defined hereinabove.

Preferably, for the spinning step, the suspension of the anionically modified cellulose is provided in a concentration range of between about 0.01 % and about 100 % (i.e. < 100%), more specifically between about 0.01 % and about 80 %, preferably between about 1.0 % and 75 %, more preferably between about 1.0% up to about 60 %, more preferably between about 5.0% up to about 60 %, most preferably between about 7.0% up to about 60 %.

Detailed Description of the Invention

The invention shall now be illustrated and supported by specific examples, however these examples shall no be used or construed to limit the scope of the invention as detailed above and as defined in the appended claims.

Example 1:

Cellulose nanofibrils extracted using hydrochloric acid followed by mechanical grinding are suspended with mixing in a 3 % solution of a Dow Wolff Methocel A grade (methyl cellulose) having a number average molecular weight of 180,000 and a solution viscosity of

40,000 mP.s (measured as a 2 % solution at 20 °C using an Ubbelohde viscometer). The concentration of the neutral nanofibrils in the suspension is 30 %w/w.

Example 2:

Cellulose nanofibrils extracted using hydrochloric acid followed by mechanical grinding are suspended with mixing in a 1.2 % solution of a Dow Wolff Methocel J grade (hydroxyl propyl methyl cellulose) having a number average molecular weight of 220,000 and a solution viscosity of 75,000 mP.s (measured as a 1% solution at 20 °C using a Brookfield viscometer). The concentration of the neutral nanofibrils in the suspension is 27%w/w.

Example 3

Cellulose nanofibrils extracted using sulfuric acid and having a degree of substitution of < 0.5 is mechanically processed to break-up the cellulose structure in order to release the nanofibrils. The nanofibrils are dried and fractionated to recover the fraction 100-200 nm in length. These nanofibrils are dispersed, with mixing in a 2.5 % solution of hydroxyl propyl methyl cellulose having a solution viscosity of 40,000 mP.s. The cellulose concentration is 28% w/w

Example 4

Anionic cellulose nanofibrils derived from the sulfuric acid hydrolysis of microcrystalline cellulose are purified via dialysis against reverse osmosis purified/deionized water for three days. To the resultant suspension of nanofibrils (1000g, 8% solids by weight) is added an aqueous solution of Methocel A (methyl cellulose, supplier Dow Wolff, Mw ca. 180 kDa) (400g, 2% solids by weight and system rendered visually homogeneous via gentle mechanical agitation. The resultant viscous, composite gel is then dehydrated by freeze drying to yield a finally divided powder (theoretical yield = 88 g). The composite cellulose-cellulose ether powder (88g) is then reconstituted into a highly concentrated, viscous, aqueous gel by mixing with aqueous sodium chloride solution (0.001M, 163g) in a 0.25 litre screw topped jar and subjecting to resonant acoustic mixing (LabRam mixer, ResoDyn Inc) for 5 minutes.

Example 5

Neutral cellulose nanofibrils derived from the hydrochloric acid hydrolysis of microcrystalline cellulose are purified via dialysis against reverse osmosis purified/deionized water for three days. To the resultant suspension of nanofibrils (1000g, 8% solids by weight) is added an aqueous solution of Methocel A (methyl cellulose, supplier Dow Wolff, Mw ~ 180 kDa) (400g, 2% solids by weight and system rendered visually homogeneous via gentle mechanical

agitation. The resultant viscous, composite gel is then dehydrated by freeze drying to yield a finally divided powder (theoretical yield = 88 g). The composite cellulose-cellulose ether powder (88g) is then reconstituted into a highly concentrated, viscous, aqueous gel by mixing with water (88g) in a 0.25 litre screw topped jar and subjecting to resonant acoustic mixing (LabRam mixer, ResoDyn Inc) for 6 minutes.

Example 6

Neutral cellulose nanofibrils derived from the hydrochloric acid hydrolysis of microcrystalline cellulose are purified via dialysis against reverse osmosis purified/deionized water for three days. To the resultant suspension of nanofibrils (1000g, 8% solids by weight) is added an aqueous solution of hydroxypropylmethyl cellulose, supplier Dow Wolff) (400g, 2% solids by weight and system rendered visually homogeneous via gentle mechanical agitation. The resultant viscous, composite gel is then dehydrated by freeze drying to yield a finally divided powder. The composite cellulose-cellulose ether powder is then reconstituted into a highly concentrated, viscous, aqueous gel by mixing with water in a screw topped jar and subjecting to resonant acoustic mixing (LabRam mixer, ResoDyn Inc) for 6 minutes.

Claims

1. Method for preparing a stable, high solids suspension of neutral or anionically modified cellulose nanofibrils comprising the steps of: (a) isolating neutral or anionic cellulose nanofibrils from cellulose-based material and (b) preparing a stable suspension of the neutral or anionic cellulose nanofibrils in a (viscous) continuous phase by dispersing the nanofibrils obtained in step (a) in a liquid in the presence of a suspending agent.

2. Method according to claim 1 wherein the neutral or anionically modified cellulose nanofibrils is present in the suspension in a solids content of 7 to 80 % solids, preferably 9 to 60 %, more preferably 20 to 40 %.

3. Method of any of the preceding claims, wherein the neutral or anionically modified cellulose is substantially in form of neutral or anionic cellulose nanofibrils.

4. Method of any of the preceding claims, wherein the anionic cellulose nanofibrils are obtained from nanofibril containing cellulose-based material using chemical, thermomechanical, chemi-thermomechanical processes, or combinations thereof, preferably by chemical pulping and extraction.

5. Method according to any of the preceding claims, wherein the neutral cellulose nanofibrils are obtained by (i) mixing finely shredded nanofibril containing cellulose-based material, with a non derivatising mineral acid to obtain a mixture, (ii) filtering said mixture to obtain an intermediate cellulosic material, and (iii) subjecting said cellulosic to mechanical shear to obtain the neutral cellulose nanofibrils.

6. Method of any of the preceding claims, wherein the anionically modified cellulose is substituted with groups carrying a negative charge, such as sulfur-containing groups (e.g. sulfate, sulfonate, alkylsulfate, alkylsulfonate), carboxyl groups, phosphor-containing groups (e.g. phosphate, phosphonate), nitro groups or the like, or combinations thereof.

7. Method of any of the preceding claims, wherein the anionically modified cellulose has a degree of substitution of less than 0.5.

8. Method according to any of the preceding claims, wherein the high solids suspension is obtained by dispersing the neutral or anionically modified cellulose

in a liquid comprising a dissolved suspending agent in which the neutral or anionically modified cellulose is substantially insoluble.

9. Method according to any of the preceding claims, wherein the suspending agent is natural gum (e.g. gum arabic, gum tragacanth, guar gum, locust bean gum, carrageenan) a pectin, an alginate, a cellulose derivative (e.g. hydroxypropylmethylcellulose, methyl cellulose, hydroxyethylcellulose, carboxymethylcellulose).

10. Stable, high solids suspension of neutral or anionically modified cellulose nanofibrils obtained through a method according to any of the preceding claims.

11. Use of a stable, high solids suspension of neutral or anionically modified cellulose nanofibrils according to any of the preceding claims for use in fibre spinning.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/053985

A. CLASSIFICATION OF SUBJECT MATTER
INV. D01D1/02
ADD.

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)
D01F D01D D21H

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2010 242063 A (KURARAY CO) 28 October 2010 (2010-10-28) abstract examples 4,7 paragraphs [0011], [0021], [0026], [0033], [0040] - [0043] ----- -/--	1-11

[X] Further documents are listed in the continuation of Box C.

[X] 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)

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

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"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
27 June 2012	05/07/2012

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ELITON S. MEDEIROS ET AL: "Electrospun Nanofibers of Poly(vinyl alcohol) Reinforced with Cellulose Nanofibrils", JOURNAL OF BIOBASED MATERIALS AND BIOENERGY, vol. 2, no. 3, 1 September 2008 (2008-09-01), pages 231-242, XP55031138, ISSN: 1556-6560, DOI: 10.1166/jbmb.2008.411 paragraphs [02.1] - [02.3] figures 2-8,12	1-11
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/053985

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