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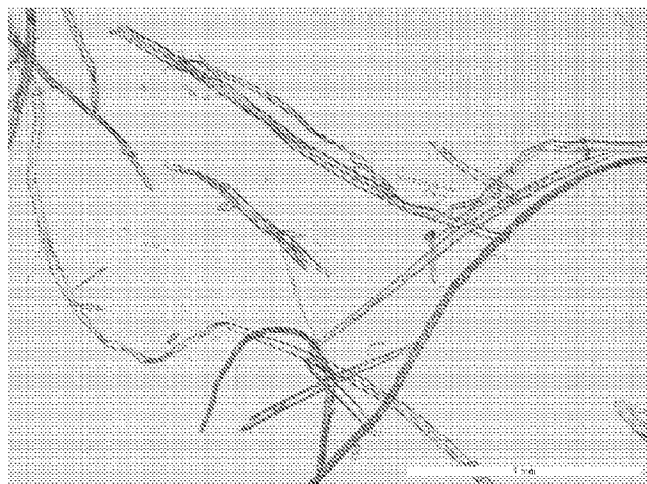
(72) Inventeurs/Inventors:
HILTUNEN, JAAKKO, FI;
HEISKANEN, ISTO, FI;
SAXELL, HEIDI, FI;
KAHELIN, JUKKA, FI;
SAHARINEN, ERKKI, FI

(73) Propriétaire/Owner:
STORA ENSO OYJ, FI

(74) Agent: SMART & BIGGAR LLP

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(54) Title: A METHOD OF PRODUCING OXIDIZED OR MICROFIBRILLATED CELLULOSE



(57) Abrégé/Abstract:

The invention relates to a method of producing oxidized or microfibrillated cellulose (MFC). According to the invention there is provided an aqueous pulp suspension with a consistency of at least 15 %, and at least one oxidant is added to the suspension to oxidize cellulosic hydroxyl groups in the suspension under mechanical mixing or shearing. The oxidized suspension, washed and diluted to a lower consistency, is subjected to homogenization to yield gel-like MFC. Alkali hypochlorite may be used as oxidant, and preferred mediating oxidation catalysts are AZADO and TEMPO. Alkali bromide may be used as a cocatalyst. The MFC product, which as a suspension has an increased viscosity, is suitable as a means of regulating viscosity or for production of films and composites.

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(71) Applicant: STORA ENSO OYJ [FI/FI]; P1 309, FI-00101 Helsinki (FI).

(72) Inventors: HILTUNEN, Jaakko; c/o VTT, PL 1000, FI-02044 Vtt (FI). HEISKANEN, Isto; Kanava-aukio 10 As 13-14, FI-55100 Imatra (FI). SAXELL, Heidi; Koivukylän Puistotie 33 F 30, FI-01360 Vantaa (FI). KAHELIN, Jukka; Kivirannankatu 2 as 8, FI-53950 Lappeenranta (FI). SAHARINEN, Erkki; Tiirismaantie 1-3D 75, FI-00710 Helsinki (FI).

(74) Agent: BERGGREN OY AB; P.O. Box 16, (Antinkatu 3 C), FI-00101 Helsinki (FI).

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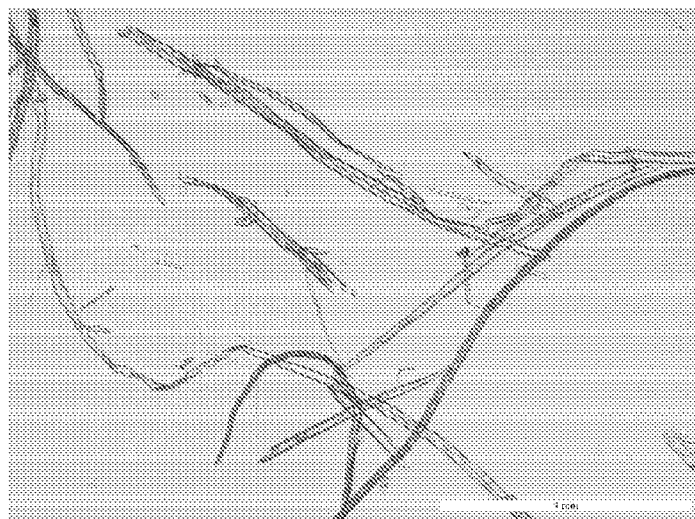


Fig. 1

(57) Abstract: The invention relates to a method of producing oxidized or microfibrillated cellulose (MFC). According to the invention there is provided an aqueous pulp suspension with a consistency of at least 15 %, and at least one oxidant is added to the suspension to oxidize cellulosic hydroxyl groups in the suspension under mechanical mixing or shearing. The oxidized suspension, washed and diluted to a lower consistency, is subjected to homogenization to yield gel-like MFC. Alkali hypochlorite may be used as oxidant, and preferred mediating oxidation catalysts are AZADO and TEMPO. Alkali bromide may be used as a cocatalyst. The MFC product, which as a suspension has an increased viscosity, is suitable as a means of regulating viscosity or for production of films and composites.

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A METHOD OF PRODUCING OXIDIZED OR MICROFIBRILLATED CELLULOSE

Background of the invention

The present invention concerns a method of producing oxidized cellulose. The
5 invention even comprises a method of producing microfibrillated cellulose
(MFC) as well as a method of increasing the viscosity of a suspension of a
MFC product. In connection with the invention microfibrillated cellulose also
covers what is known as nanofibrillated cellulose (NFC).

10 Microfibrillated cellulose (MFC) is hereby defined as fibrous material comprised
of cellulosic fibrils and fibril aggregates. Fibrils are very thin, usually of a diam-
eter of about 5 to 100 nm, in average about 20 nm, and have a fibre length of
about 20 nm to 200 μm although usually of 100 nm to 100 μm . Nanofibrillated
cellulose (NFC) is a specific class of MFC with fibre dimensions at the low end
15 of said fibril size range. In the MFC individual microfibrils are partly or totally
detached from each other. Fibres that have been fibrillated and which have
microfibrils on the surface and microfibrils that are separated and located in a
water phase of slurry are included in the definition MFC. MFC has a very large
open active surface area, generally in the range of about 1 to 300 m^2/g , and is
20 useful for a wide range of end uses, notably in the field of papermaking but al-
so in composites like plastic or rubber, food, pharmaceuticals, home care
products, dispersions like paints, etc.

Prior art methods of manufacturing MFC include mechanical disintegration by
refining, milling, beating, homogenizing, and fibrillation by e.g. an extruder.
These mechanical methods may be enhanced by chemical or chemoenzymatic
25 treatments as a preliminary step.

US patent 4,341,807 describes production of MFC by passing a fibrous sus-
pension repeatedly through a small diameter orifice subjecting the liquid sus-
pension to a pressure drop. The starting suspension contains 0.5 to 10 wt-% of
cellulose. The product is a homogenous gel-formed suspension of MFC.

30 WO 2007/091942 A1 describes a process, in which chemical pulp is first re-
fined, then treated with one or more wood degrading enzymes, and finally ho-
mogenized to produce MFC as the final product. The consistency of the pulp is

taught to be preferably from 0.4 to 10 %. The advantage is said to be avoidance of clogging in the high-pressure fluidizer or homogenizer.

There are several studies on preparation of MFC with the aid of oxidants, especially with hypochlorite as a primary oxidant and 2,2,6,6-tetramethyl-
5 piperidine-1-oxyl (TEMPO) radical as a mediating catalyst. An alkali bromide may be used as a cocatalyst. Examples of such solutions are presented in publications by e.g. Saito et al., *Biomacromolecules* 2007, 8, 2485-2491, Fukuzumi et al., *Biomacromolecules* 2009, 10, 162-165, and Okita et al., *Biomacromolecules* 2010, 11, 1696-1700. According to Saito et al., a fibrous slurry
10 of 1 wt-% consistency at pH 10 was oxidized by adding 1.3 to 5.0 mmol NaClO, 0.1 mmol TEMPO, and 1 mmol sodium bromide per 1 g of cellulose, and stirring the mixture at room temperature while adding NaOH. The oxidized cellulose was then agitated to swell the fibres and finally to turn the dispersion highly viscous and transparent. Very similar descriptions are found from Fukuzumi et al. and Okita *et al.* also.
15

Saito et al. *Ind. Eng. Chem.Res.* 2007, 46, 773-780 describe TEMPO-mediated oxidation of cellulose and addition of a cationic polymer such as poly(acrylamide) (C-PAM), poly(vinylamine) (PVAm), and poly(amideamine-epichlorohydrin) (PAE) for obtaining sheets with improved wet tensile strength.

20 Pelton et al, *Biomacromolecules* 2011, 12, 942-948 recognize the environmental and financial drawback of large doses of TEMPO needed for oxidation in dilute pulp suspensions, and approach it by teaching the use of PVAm to adsorb TEMPO onto the cellulose fibres. Oxidation is thus restricted to the exterior surfaces of the fibres, resulting in lower amounts of TEMPO being consumed.

25 The above prior art references relate to what may be defined as reactions and processes taking place in low consistency (LC) refining through use of dilute suspensions of consistencies at most 10 wt-%. WO 2012/097446 A1 instead describes a process of making NFC by multipass high consistency (HC) refining of chemical or mechanical fibres. HC is defined as referring to a discharge
30 consistency of more than 20 wt-%

WO 2012/072874 A1 teaches a multistep process of producing NFC, in which cellulose is refined with a first refiner, the product is divided into an accept fraction and reject fraction, water is removed from the accept fraction, and finally the accept fraction is refined with a second refiner to obtain a gel-like product

with fibre diameter of 2 to 200 nm. At the first refining step the consistency of the material is under 10 wt-% but increased by removal of water to about 15 wt-% or even 20 wt-% to enhance washing of the same. For the second refining the pulp would be diluted back to a consistency under 10 wt-%.

- 5 In WO 2011/114004 there is described a different approach of fibrillating ligno-cellulosic material based on treatment with ionic liquid, i.e. molten salt, which preserves fibres basically intact. Salts comprising an imidazolium type cation are mentioned as an example of such liquids. The process is said to weaken the binding between fibrils or tracheids and separate fibrils or tracheids from fibre walls.

WO2012/050589 describes treating cellulose raw material in a high consistency with at least one chemical at least partly in an extruder, and optionally performing another refining step in the refining part of the extruder in a consistency of at least 5%.

- 15 A problem with conventional low-consistency refining with hammer or ball mills is that large amounts of energy is consumed for continued fibrillation after the initial phase of the process. Partial hydrolysis of semicrystalline lignocellulose by use of chemicals (e.g. TEMPO) or enzymes is helpful, especially when gel-like MFC products are aimed at, but the main drawback then is high material and energy costs. The use of excess chemicals may also require further chemical recovery solutions to be utilized.

- 25 Instead of refining with hammer or ball mills, a microfluidizer or homogenizator may be used. However, the fibrillation process requires pre-treatment of the pulp suspension and a relatively low concentration in order to operate smoothly and energy efficiently.

- A common drawback of low consistency fibrillations is that the resulting suspension is dilute, difficult to handle and requires further process steps especially if transporting to another location for being used. On the other hand, high consistency fibrillation has relatively high energy consumption, initial runnability of the refiner is poor, and the known high consistency methods therefore are not economically viable.

In general the problems with the existing methods are poor productivity and difficulty in scaling up the process. For homogenizator-based fibrillation scal-

ing-up would require a multiple set of fibrillation units as well as a consistency enhancer, which further makes the process difficult to scale up.

5 The known TEMPO-mediated oxidations in particular are uneconomical due to the high chemical cost, and therefore have not won wide practical use so far. Limiting oxidation to the fibre surfaces only, as suggested in the prior art, is not well suited for preparation of gel-like final MFC products.

Summary of the invention

10 The problem solved by the invention is to improve oxidative treatment of cellulosic pulp, in particular in the production of MFC, so as to reduce the material costs and turn this route of manufacture economically viable. The goal is also to reduce overall energy consumption, and to obtain oxidized pulp at an increased consistency, which is suitable for being further dried or then transported wet or dry to another location,
15 where it is turned to MFC for use as the final product. A further goal is to obtain a final MFC product in the form of a suspension with an increased viscosity.

The solution according to the invention is production of oxidized cellulose through the steps of (i) providing an aqueous pulp suspension with a consistency of at least 15
20 wt-%, (ii) adding at least one oxidant to the suspension, and (iii) oxidizing the suspension under mechanical mixing or shearing. According to the invention a gel-like suspension comprising MFC is obtained by the further step of (iv) subjecting the oxidized suspension from step (iii) to fibrillation, preferably homogenization. Oxidation in relatively high consistency, as defined above, under light and gentle mechanical
25 mixing with low shearing forces improves the fibre structure and homogeneity and reduces formation of fines. The amount of chemicals used is typically lower compared to oxidation in lower consistencies. The mild treatment together with the high consistency avoids cutting of the fibres and is thereby conducive to obtaining

MFC with a high aspect ratio. Fibrillation of the oxidized pulp effectively breaks down fibres into individual fibrils and yields a suspension of MFC, which surprisingly was found to have a much increased viscosity as compared to pulp oxidized at a conventional low consistency.

5

In one aspect, the present invention provides a method of producing oxidized cellulose comprising the steps of: (a) providing an aqueous pulp suspension with a consistency in a range of 15 wt-% to 30 wt%, said aqueous pulp suspension having lignin content of less than 5 wt-% from the dry solids of the mass, (b) adding at least
10 one oxidant and at least one mediating catalyst selected from AZADO and TEMPO to the suspension, and (c) oxidizing cellulosic hydroxyl groups under mechanical mixing or shearing of the suspension, to have friction between fibres to open an inner structure of the fibres for catalyzed oxidation.

15 In another aspect, the present invention provides a method of increasing the viscosity of a suspension of a microfibrillated cellulose (MFC) product, wherein the MFC is produced by a process comprising the steps of: (a) providing an aqueous pulp suspension with a consistency in a range of 15 wt-% to 30 wt-%, said aqueous pulp suspension having lignin content of less than 5 wt-% from the dry solids of the mass,
20 (b) adding at least one oxidant and at least one mediating catalyst selected from AZADO and TEMPO to the suspension, (c) oxidizing cellulosic hydroxyl groups under mechanical mixing or shearing of the suspension, to have friction between fibres to open an inner structure of the fibres for catalyzed oxidation and (d) subjecting the suspension obtained at step (c) to fibrillation to yield a gel-like suspension comprising
25 MFC.

According to the invention an increased consistency enhances shearing of fibres and opens their inner structure so as to produce a uniform oxidation

throughout the material. Such disruption brings fibrillation and yields suspensions of increasing transparency, which require very little further fibrillation to obtain MFC as final product. At the same time the amount of mediating oxidation catalyst is reduced to a fraction of the dose needed for oxidation at a conventional low consistency.

For improved logistics oxidation may be carried out at the pulp mill where the cellulosic pulp originates, and the resulting oxidized suspension, still at a high consistency, is then transported to another location, e.g. the site of final use of the MFC product, for being washed and fibrillated at a lower consistency to obtain the final product. The oxidized suspension may even be dried for the transport, as it is readily redispersed in water for regenerating the aqueous suspension. The high surface charge density of the fibrils obtained according to this method enhances the re-wettability and dispergation.

Instead of MFC an oxidized suspension at a high consistency may constitute the final product. In other words, the final fibrillation step yielding MFC is not necessary for the invention in its broadest terms. Such suspension of high consistency is useful as a constituent of coating or barrier dispersions for instance.

Instead of homogenization the fibrillation step for producing MFC may be mechanical grinding, fluidization, mechanical fibrillation, extrusion etc., such alternative fibrillation techniques being as such known to a skilled person.

Preferably the consistency of the pulp suspension subjected to oxidation is in the range of 20 to 30 wt- %. Even higher consistencies up to 40 wt-%, 50 wt-% or 60 wt-% or more may be useful. Due to drying the consistency may increase in the course of oxidation, which may take several hours.

Brief description of the figures

Figure 1. Light microscopy image (2,5x magnification) of example 1 (5 w-% consistency oxidation) after oxidation (before fibrillative treatment). Bar length 1 mm.

Figure 2. Light microscopy image of example 2 (2,5x magnification (20 w-% consistency oxidation) after oxidation (before fibrillative treatment). Clearly

more fibrillation of the fibre is seen when compared to example 1. Bar length 1 mm.

Figure 3. Light microscopy images (10xmagnification) of example 1 (low consistency, 5 w-% oxidation) after a) first, b) second and c) third fluidisation cycle. Bar length 100 µm.

Figure 4. Light microscopy images (10xmagnification) of example 2 after a) first b) second and c) third fluidisation cycle. Bar length 100 µm.

Figure 5. Light microscopy image of example 3 (20 wt-% consistency oxidation) after oxidation and Ultra Turrax treatment. Bar length 100 µm.

Figure 6. Light microscopy image of example 4 (20 wt-% consistency oxidation) after oxidation and Ultra Turrax treatment. Bar length 100 µm.

Figure 7. Light microscopy image of example 5 (20 wt-% consistency oxidation) after oxidation and Ultra Turrax.

Detailed description

According to the preferred embodiment of the invention microfibrillated cellulose (MFC) is produced by first providing an aqueous cellulosic pulp suspension with a consistency of at least 15 wt-%, preferably 20 to 30 wt-% without limiting to the upper limit. Preferably the starting cellulosic material has a low lignin content of less than 5 wt-% of lignin of the dry content of the pulp suspension. At least one oxidant and preferably a cocatalyst are added to the suspension and mixed by continued mechanical agitation. Oxidation is then started and carried out by addition of a mediating catalyst while mechanical mixing or shearing is continued. The steps so far may be performed at a pulp mill, which produces the starting material, e.g. an undried kraft pulp, which is centrifuged or pressed to the desired high consistency. The oxidized suspension, still at a high consistency, may then be transported to the site of use of the final MFC product, where the pulp is optionally washed and finally homogenized or fibrillated at a lower consistency to obtain the gel-like product.

From increased consistency follows an increase of the mechanical energy that is needed for agitating the suspension. As a parallel phenomenon, it has been shown in the literature that pressure loss and thus consumption of energy in

pumping of pulp slurries in a tube grows dramatically as the consistency rises stepwise from 8 by 9, 10, 11, 12, 15 and 16 up to 17 wt-%, on a relative scale from 93 by 95, 100, 115, 150, 320 and 400 up to 525. By implication, at a consistency of about 12 wt-% the mechanical forces start rising, and from 15
 5 wt-% upwards they become very effective for shattering bundles of fibres in a pulp suspension, shearing the fibres and thereby making them susceptible to oxidation. At the same time it will be necessary to keep the mechanical energy at a minimum, so as to achieve gentle shearing and avoid cutting the fibrils, which would otherwise spoil the desired high aspect ratio.

10 In general terms the oxidation step as carried out in the invention turns part of the hydroxyl groups of the cellulosic hydrocarbon chain (including polysaccharides) into groups typical of oxidized cellulose, such as carboxylic acid, carboxylate, aldehyde and ketone groups, the last two even in hydrated form. To initiate oxidation a mediating catalyst is usually needed, such catalysts being
 15 known to a person skilled in the art. Without limiting the invention to these two, azaadamantane-N-oxyl (AZADO) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radicals may be mentioned as examples of such oxidation mediating catalysts, which have been tested and found to be useful in the invention.

TEMPO and AZADO catalysts can be used alternatively or together. It is also
 20 possible to select catalyst according to desired properties of the resulting product. AZADO is more powerful but less specific oxidation catalyst when compared to TEMPO. TEMPO catalyst favors oxidation of O6' and thus it is preferred over AZADO when high aspect ratio of fibrils is a wished property.

On the other hand, AZADO oxidation processes can be carried out faster and
 25 with less catalyst. Resulting fibrils have a lower aspect ratio than after using TEMPO catalyst. This is a favored property when lower viscosity of the product is desired. The aspect ratio affects the rheological properties, but potentially also the strength of materials, so that higher aspect ratio gives in general higher viscosity and higher strength enhancement.

30 Instead of TEMPO or AZADO any known derivate thereof with useful catalytic activity may be used, 1-methyl-AZADO being mentioned as an example.

The preferred oxidant for use in the invention is alkali hypochlorite, such as NaClO. Alkali bromide, e.g. NaBr, is suitably added as a cocatalyst. Also chlo-

rine dioxide and chlorite salts can be used either instead or together with hypochlorite.

Additionally, stoichiometric oxidants can also be selected among following chemicals: peroxodisulfate and peroxomonosulfate salts, organic peroxyacids
5 and their salts, perborate salts, percarbonate salts, hydrogen peroxide and organic peroxides, urea peroxide, molecular oxygen and ozone.

Also preferable mixing of different stoichiometric oxidants, e.g. to target specific aldehyde and carboxylate ratios should be noticed.

Beside bromide salts, some other suitable co-catalysts are tungstate salts,
10 vanadate salts, molybdate salts, manganate salts, silver salts, laccase, horseradish peroxidase, copper ligands, manganese ligands, cobalt ligands, tertiary amines and quaternary ammonium salts. It should be noticed that all co-catalyst are not suitable with all stoichiometric oxidants. Tungstate, vanadate, molybdate, manganate salts and horseradish peroxidase are especially suitable
15 with hydrogen peroxide and other peroxide releasing compound, whereas laccase, copper ligands and cobalt ligands are preferable with molecular oxygen.

Optimal temperature and pH are also depending on the practiced oxidation system. Generally, the oxidation is carried out between the ranges of temperature
20 0 to 80 °C and pH 2 to 14. In specific cases it is beneficial to first mix stoichiometric oxidant and possibly co-oxidant with the pulp at temperature between 0 to 20 °C, and after this start the oxidation by increasing the temperature between 20 to 80 °C and preferably adding the mediator.

The oxidant, the cocatalyst and the mediating catalyst can be added to the
25 pulp suspension in any order. According to one embodiment of this invention an oxidant such as alkali hypochlorite and eventual cocatalyst such as alkali bromide are added to the suspension, followed by addition of the mediating catalyst such as AZADO or TEMPO. By mixing and shearing the suspension, friction between fibres opens the fibre structure and the oxidant is dispersed
30 evenly in the suspension, so as to prepare for a simultaneous attack of the oxidant to the entire material as soon as the mediating catalyst has been added. This is to minimize unwanted side reactions with cellulose already dissolved and target the reactants to enhancing fibrillation only.

Especially as TEMPO is used as the mediating catalyst alkali, such as NaOH, is advantageously added at the oxidation step for setting the pH to a range of 9 to 12, preferably to 10 to 11, and most preferably to about 10.

- 5 The oxidized pulp may be washed for removal of the chemicals, in particular AZADO or TEMPO as used, which may bring the pulp suspension to the low consistency range of 10 wt-% or less. The washed and diluted suspension is then subjected to homogenization so as to obtain the final MFC product. Preferably the pulp is homogenized at a consistency of at most 5 wt-%, more preferably in a range of 3 to 4 wt-%. The final MFC production can alternatively be
- 10 carried out by extruded or (twin-screw) kneader at consistencies at least 10 wt-%, preferably at least 15 wt-%, more preferably between 20 to 30 wt-%. The water-content can also be varied during the treatment by simultaneously adding water in the extruder or kneader to facilitate the fibril hydration and separation.
- 15 The pulp used for the invention may be chemical pulp or mechanical, dissolving pulp or recycled pulp, recycled paper or side flows from pulp and paper mills. Even use of cellulosic pulp of non-wood origin, for example bamboo or bagasse is possible. Preferably the pulp is obtained from a chemical kraft pulping process without intermediate drying. Naturally also MFC, nanocellulose or
- 20 microcrystalline cellulose can be used as a starting material. Starting material can also be composed of various pulp sources. Optionally the pulp may be pretreated in order to increase the surface area. The pulp is first disintegrated mechanically, e.g. by milling, and brought to a consistency of at least 15 wt-%. Any known method can be used, e.g. centrifugation or pressing. Preferably the
- 25 starting cellulosic material has a low lignin content of less than 5 wt-% of lignin of the dry content, preferably less than 3 wt-% lignin of the dry content, more preferably less than 2 wt-% lignin of the dry content. Most preferably the starting cellulosic pulp has very low lignin content of 0.01 to 1 wt-% or even 0.01 to 0.5 wt-% of the mass dry content.
- 30 The MFC product obtained by the invention is gel-like and suitably used for regulating viscosity, for production of films, or as an additive for composite materials. At least 50 %, preferably at least 80 % of the fibrils in the product have dimensions in the fibril length and diameter ranges as defined above for MFC.

A particular goal of the invention is to increase the viscosity of a suspension of the final MFC product. A suspension of MFC, preferably aqueous, having a high viscosity is achieved by way of oxidation of pulp at a consistency of at least 12 wt-%, preferably at least 15 wt-%, and most preferably at least 20 wt-% according to the invention, as opposed to lower consistencies as conventionally applied. As a verification, a MFC product obtained in connection with testing the invention was turned to a slurry of a low consistency of about 1 wt-% for measurement of the viscosity. Highly increased viscosities could be measured for the MFC produced according to the invention, as compared to MFC obtained through oxidation at a lower consistency.

As approximated limits, oxidation of pulp at consistencies of 12 wt-% or 15 wt-% yield aqueous MFC suspensions, which at a consistency of 1 wt-% have viscosities of at least 2500 cp or at least 3500 cp, respectively, as measured at rotation speed of 5 rpm with spindle Vane 71.

The high viscosity obtained by means of the invention is very desirable in view of various uses of the MFC suspension, especially as a thickening agent in cosmetics, foods, personal care products as well as oil drilling slurries, emulsion paints, textile printing pastes and paper coating pastes.

The increased viscosity of the MFC suspension is believed to be due not only to improved separation of fibrils but also to an increased aspect ratio, i.e. the ratio of fibril length to fibril diameter, of the final MFC product. Increased aspect ratio is apt to improve the strength properties of MFC.

For the goal of increasing the viscosity TEMPO catalyst may advantageously be used for oxidizing the cellulose. Even the other options and embodiments of the invention as brought forward in the above equally apply for increasing the viscosity.

Examples

Example 1 (comparative). Low-consistency oxidation (cellulose consistency 5 %)

Preparation of reagent solution: Sodium bromide (2 g, purity 99%) was dissolved in ion-exchanged water (3000 ml) and after this 148.9 g of aqueous so-

dium hypochlorite (10 wt-% solution) was added to this solution. The pH of the solution was adjusted to 10.2 with 1 M HCl.

Mixing of reagent solution with pulp: 572.7 g of never-dried kraft pulp (35 wt-% consistency) was mixed with the reaction solution and the pulp suspension
5 was mixed with laboratory stirring device for 90 minutes to evenly disperse sodium hypochlorite and sodium bromide with the pulp. The pH of the suspension was maintained at 10.2 with 1 M NaOH.

TEMPO oxidation: TEMPO (0.312 g) was dissolved in 278 ml of ion-exchanged water. The solution was added into the pulp suspension and the
10 oxidation reaction was maintained for 90 minutes. Finally, 10 ml ethanol was added to eliminate the unreacted hypochlorite.

Example 2. High-consistency oxidation (cellulose consistency 20 %)

Preparation of reagent solution: Sodium bromide (2 g, purity 99%) and Na₂CO₃
15 ·10 H₂O (28.6 g, purity 98 %) were dissolved in ion-exchanged water (200 ml). The pH of the solution was then adjusted to 10.2 with sodium bicarbonate. This solution was mixed with 148.9 g of aqueous sodium hypochlorite (10 wt-% solution, pH adjusted to 10.2 with 1 M HCl). The final pH was confirmed to be 10.2.

20 *Mixing of reagent solution with pulp:* 572.7 g of never-dried softwood kraft pulp (35 wt-% consistency) was placed in a dough mixer and the previously described reagent solution was added into pulp. After this the pulp was mixed for 90 minutes to evenly disperse sodium hypochlorite and sodium bromide.

25 *TEMPO oxidation:* TEMPO (0.312 g) was dissolved in 78 ml of ion-exchanged water. The solution was added into the pulp and the oxidation reaction was maintained for 90 minutes. Finally, 10 ml ethanol was added to eliminate the unreacted hypochlorite.

The resulting fibrous material was washed three times with 2 l of 40 w-% isopropanol solution on a Büchner funnel to remove salts. The cellulose cake was
30 thereafter diluted to 3 wt-% consistency and fibrillated using a fluidizer from Microfluidics Microfluidizer M-110EH-30. The used chambers during the cycles were the following (for cycle 1) first chamber 400 µm and second chamber

200 μm and for (cycles 2 and 3) first chamber 200 μm and second chamber 100 μm .

Brookfield viscosity measurements:

Instrument: Brookfield Rheometer RVDV-III with Vane spindle 71 was used in the measurements. Viscosities were measured at $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ at consistency of 1 wt-% $\pm$ 0.3 wt-%.

Viscosities with five different rotation speeds, 0.5 , 5, 10, 50 and 100 rpm were determined and are shown in Table 1.

10 **Table 1.** Brookfield viscosities.

Spindel (Vane 71) Rotation speed [rpm]	Example 1 Viscosity (average, 5s) cP	Example 2 Viscosity (average, 5s) cP
0.5	7703	41114
5	1163	5705
10	697	3241
50	188	951
100	110	563

Example 1 shows clearly lower viscosities with all rotation speeds compared to Example 2. The light microscopy images show that this is due to much poorer fibrillation of the pulp during fluidisation.

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Example 3. High-consistency oxidation with plain sodium hypochlorite (cellulose consistency 20 %, theoretical DS for oxidation 0.2)

Preparation of reagent solution: 22.8 g aqueous sodium hypochlorite (10 w-% solution) was diluted with ion-exchanged water (17.7 ml) and the pH of the solution was adjusted to 10.2 with 1 M HCl.

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Mixing of reagent solution with pulp: 59.5 g never-dried kraft pulp (~42 wt-% consistency) was mixed with the reaction solution and the pulp suspension was mixed with laboratory stirring device for 90 minutes to evenly disperse sodium hypochlorite. After this, 25 ml of sodium bicarbonate /sodium carbonate
5 buffer solution (5 wt-% solution, pH 10.2) was added and the pulp was further mixed another 90 minutes.

Finally the pulp was diluted to 2 wt-% consistency with ion-exchanged water and homogenized with Ultra Turrax device. Clear disruption of fiber structure occurred by this treatment. It should be noticed that Ultra Turrax is a device
10 that cannot produce fibrillar material from conventional untreated pulp fibers.

Example 4. High-consistency oxidation with sodium hypochlorite and sodium bromide (cellulose consistency 20 %)

Preparation of reagent solution: 22.8 g aqueous sodium hypochlorite (10 wt-% solution) was mixed with ion-exchanged water (17.7 ml) containing 0.16 g so-
15 dium bromide. The pH of the solution was adjusted to 10.2 with 1 M HCl.

Mixing of reagent solution with pulp: 59.5 g never-dried kraft pulp (~42 wt-% consistency) was mixed with the reaction solution and the pulp suspension was mixed with laboratory stirring device for 90 minutes to evenly disperse so-
20 dium hypochlorite and sodium. After this, 25 ml of sodium bicarbonate /sodium carbonate buffer solution (5 w-% solution, pH 10.2) was added and the pulp was further mixed another 90 minutes.

Finally the pulp was diluted to 2 % consistency with ion-exchanged water and homogenized with Ultra Turrax device. Clear disruption of fiber structure oc-
25 curred by this treatment.

Example 5. High-consistency oxidation with sodium hypochlorite and sodium bromide (cellulose consistency 20 %)

Preparation of reagent solution: 137 g aqueous sodium hypochlorite (10 wt-% solution) was mixed with ion-exchanged water (25 ml) containing 0.16 g sodi-
30 um bromide. The pH of the solution was adjusted to 10.2 with 1 M HCl.

Mixing of reagent solution with pulp: 238 g never-dried kraft pulp (~42 wt-% consistency) was mixed with the reaction solution and the pulp suspension was mixed with Hobart pulper for 90 minutes to evenly disperse sodium hypochlorite and sodium. After this, 95 ml of sodium bicarbonate /sodium carbonate
 5 buffer solution (5 wt-% solution, pH 10.2) was added and the pulp was further mixed another 90 minutes.

Finally the pulp was diluted to 2 wt-% consistency with ion-exchanged water and homogenized with Ultra Turrax device. A complete disruption of fiber structure occurred by this treatment.

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Example 6. Brookfield viscosity

Brookfield viscosity measurements for samples of Examples 3, 4 and 5 were as follows:

Instrument: Brookfield Rheometer RVDV-III with Vane spindle 71 was used in
 15 the measurements. Viscosities were measured at $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ at consistency of $1.5 \text{ wt-\%} \pm 0.3 \text{ wt-\%}$.

Viscosities with two different rotation speeds 10 and 100 rpm were determined and are shown in Table 2.

20 **Table 2.** Brookfield viscosities of examples 3, 4 and 5 at 1.5 % consistency.

Spindel (Vane 71) Rotation speed [rpm]	Example 3 Viscosity (average, 5s) cP	Example 4 Viscosity (average, 5s) cP	Example 5 Viscosity (average, 5s) cP
10	2760	3780	2407
100	590	750	521

CLAIMS:

1. A method of producing oxidized cellulose comprising the steps of:
 - (a) providing an aqueous pulp suspension with a consistency in a range of 15 wt-% to 30 wt%, said aqueous pulp suspension having lignin content of less than 5 wt-% from the dry solids of the mass,
 - (b) adding at least one oxidant and at least one mediating catalyst selected from AZADO and TEMPO to the suspension, and
 - (c) oxidizing cellulosic hydroxyl groups under mechanical mixing or shearing of the suspension, to have friction between fibres to open an inner structure of the fibres for catalyzed oxidation.
2. The method of claim 1, wherein the aqueous pulp suspension has lignin content in a range of 0.01 to 1 wt-%, from the dry solids of the mass.
3. The method of claim 1 or 2, wherein the oxidized suspension from step (c) is subjected to fibrillation to yield a gel-like suspension comprising microfibrillated cellulose (MFC).
4. The method of claim 3, wherein said fibrillation is homogenization.
5. The method of any one of claims 1 to 4, wherein the consistency of the suspension at step (a) is 20 to 30 wt-%.
6. The method of any one of claims 1 to 5, wherein the oxidant is alkali hypochlorite.
7. The method of any one of claims 1 to 6, wherein alkali bromide is added as a cocatalyst.
8. The method of any one of claims 1 to 7, wherein alkali hypochlorite and alkali bromide are first added to the suspension, followed by addition of AZADO or TEMPO or a combination thereof.

9. The method of any one of claims 1 to 8, wherein the oxidized suspension is washed and then subjected to fibrillation at a consistency below that of the consistency of the aqueous pulp suspension provided in step (a).
10. The method of claim 9, wherein the suspension is fibrillated at a consistency of at most 5 %.
11. The method of claim 9, wherein the suspension is fibrillated at a consistency in a range of 3 to 4 %.
12. The method of any one of claims 1 to 11, wherein the cellulosic pulp for step (a) is obtained from a kraft pulping process without intermediate drying.
13. The method of claim 12, wherein the kraft pulp is disintegrated mechanically and brought to a consistency of at least 15 %, by centrifugation or pressing.
14. The method of any one of claims 1 to 8, wherein the oxidized suspension is subjected to fibrillation at a consistency of at least 10 wt-%.
15. The method of claim 14, wherein the oxidized suspension is washed and then subjected to fibrillation at a consistency of at least 10 wt-%.
16. A method of increasing the viscosity of a suspension of a microfibrillated cellulose (MFC) product, wherein the MFC is produced by a process comprising the steps of:
- (a) providing an aqueous pulp suspension with a consistency in a range of 15 wt-% to 30 wt-%, said aqueous pulp suspension having lignin content of less than 5 wt-% from the dry solids of the mass,
- (b) adding at least one oxidant and at least one mediating catalyst selected from AZADO and TEMPO to the suspension,

(c) oxidizing cellulosic hydroxyl groups under mechanical mixing or shearing of the suspension, to have friction between fibres to open an inner structure of the fibres for catalyzed oxidation and

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(d) subjecting the suspension obtained at step (c) to fibrillation to yield a gel-like suspension comprising MFC.

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Fig. 1

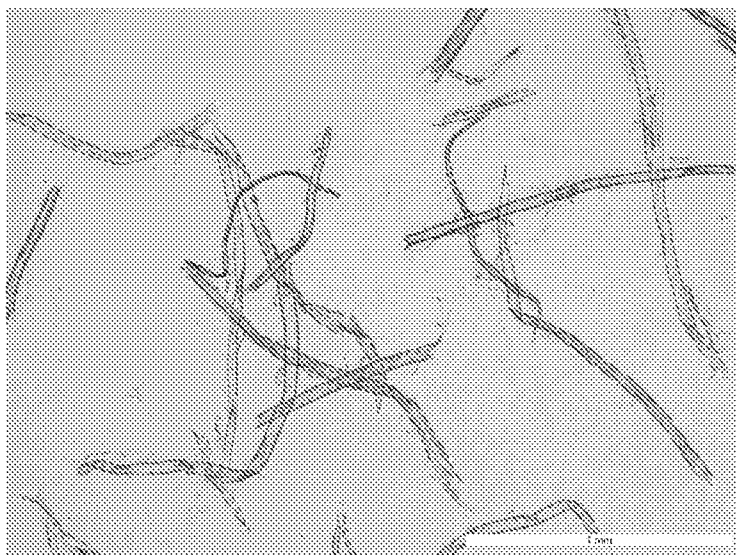


Fig. 2

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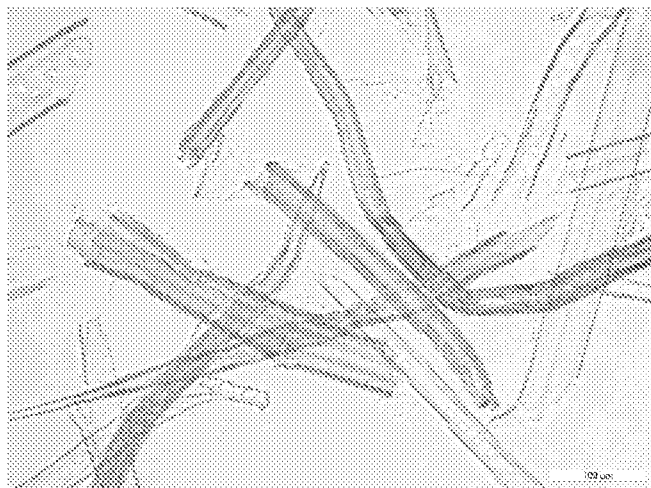
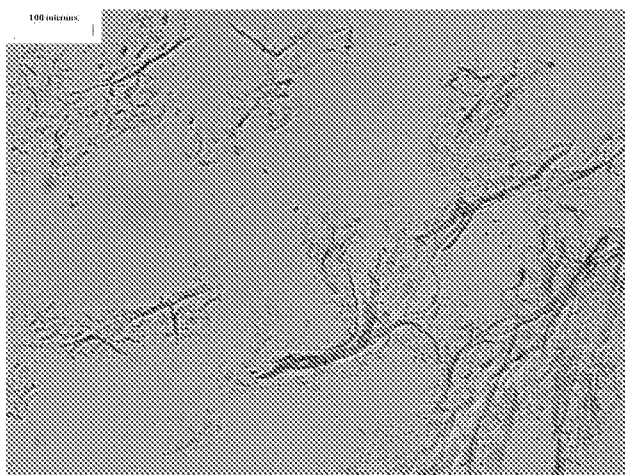


Fig. 3

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**Fig. 4**

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Fig. 5**Fig. 6****Fig. 7**