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(54) **Title**: PROCESS FOR PREPARING MICRO-AND NANOCRYSTALLINE CELLULOSE

(57) **Abstract**: The invention relates to a process for preparing micro-and nanocrystalline cellulose in the presence of an acid. More specifically, the invention relates to a process in which cellulose material is hydrolyzed in the presence of an acid in the gas phase while the moisture content is between 1% and 80%, mono-and oligosaccharides are optionally separated from the hydrolyzed cellulose and the hydrolyzed cellulose is mechanically treated. The invention also relates to a cellulose product prepared by the said process and the use thereof in food and liquid crystal applications as well as in optical, cosmetic and pharmaceutical applications.

Process for preparing micro- and nanocrystalline cellulose

FIELD OF THE INVENTION

The invention relates to a process for preparing micro- and/or nanocrystalline cellulose in the presence of an acid. The invention also relates to a cellulose product prepared by the said process, as well as the use thereof.

BACKGROUND OF THE INVENTION

In plant cell walls, cellulose is organized into microfibrils, in which most of the cellulose in crystalline form. The microfibrils also contain less-organized or amorphous parts. The amorphous parts can be removed by a chemical reaction, *i.e.* selective acid hydrolysis, after which only the crystalline parts of the cellulose remain. The result is either microcrystalline or nanocrystalline cellulose, depending on the conditions. Both are actively used in modern material science applications.

Due to the effect of the acid, the cellulose is hydrolyzed, meaning that it breaks at the glycosidic oxygen bridge, and at the same time one water molecule becomes attached to it. Cellulose hydrolysis therefore requires the presence of a water molecule. Organic or inorganic acids can be used in cellulose hydrolysis. High temperatures (between about 100°C and about 200°C) or large acid concentrations, for instance 65% H_2SO_4 (aq), have been used in the manufacture of nanocrystals.

Dong *et al.* 1998 (Dong *et al.*, Effect of microcrystalline preparation conditions on the formation of colloid crystals of cellulose. Cellulose 5:19-32, 1998) discloses the manufacture of nanocrystalline cellulose by using liquid acid.

Patent publication RU 2281993 discloses a process for preparing microcrystalline cellulose by using gaseous hydrochloric acid (HCl). The HCl gas is prepared separately by a reaction between liquid HCl and calcium chloride, after which the released gaseous hydrochloric acid is mixed with air and the mixture is transferred onto the cellulose substrate that is to be hydrolyzed.

Higgins *et al.* 1982 (Higgins and Ho, Hydrolysis of cellulose using hydrogen chloride: a comparison between liquid phase and gaseous phase processes. Agricultural Wastes 4(2):97-116, 1982) discloses the hydrolyzation of cellulose obtained from newsprint,

paperboard, and wheat straws by using both liquid 41.7% hydrochloric acid and gaseous hydrochloric acid.

Patent publication WO 1996/025553 discloses a method and equipment for hydrolyzing cellulose material in pressurized conditions in a temperature between 160°C and 230°C.

However, the above-presented prior art solutions entail problems. In the known processes, the manufacture of cellulose requires high acid concentrations, heating and large amounts of water for the rinsing performed after the hydrolysis. Efficient and fast cellulose hydrolysis has required high acid concentration. Furthermore, the use of liquid acid and its handling is difficult in high concentrations. In addition, the dialysis used for purification is difficult to perform on industrial scale, and considerable amounts of waste water are formed.

BRIEF DESCRIPTION OF THE INVENTION

The object of the invention is to solve the above-mentioned problems. More specifically, the object of the invention is to provide a process by which micro- and/or nanocrystalline cellulose can be prepared in the presence of an acid in the gas phase.

The object of the invention is reached by a process for preparing micro- and/or nanycrystalline cellulose in the presence of an acid in the gas phase, the process comprising steps in which

- cellulose material is hydrolysed in the presence of at least one acid in the gas phase, the moisture content of the cellulose being between 1% and 80%,
- soluble mono- and/or oligosaccharides are optionally separated from the hydrolyzed cellulose, and
- the hydrolyzed cellulose is mechanically treated in order to obtain micro- and/or nanocrystals.

The acids that can be used in the invention have such a vapour pressure that they gasify into the gas phase and adsorb onto the cellulose surface in room temperature. For instance, one of the following acids can be used: hydrochloric acid (HCl), nitric acid (HNO_3) and or trifluoroacetic acid. Preferably, the acid is HCl. The concentration of the acid used can be at least 1% by volume.

In the inventive process, the hydrolyzed cellulose can be dispersed in water. Dispersing agent can be added to the hydrolyzed cellulose, and this may for instance comprise carboxymethyl cellulose (CMC). Hydrolyzed cellulose can be mechanically broken down. Mechanical breaking down can comprise for instance mechanical stirring and/or ultrasound treatment.

The inventive process can be carried out in a temperature that is between 0°C and 100°C, preferably the temperature is between 10°C and 40°C, more preferably between 15°C and 35°C, more preferably between 18°C and 22°C, most preferably room temperature. The process is preferably carried out in normal air pressure and room temperature.

In one embodiment of the invention, the process comprises steps in which

- cellulose material is hydrolysed in the presence of at least one acid in the gas phase, the moisture content being between 1% and 80%,
- the hydrolyzed cellulose is dispersed in water in the presence of a dispersing agent, and
- mono- and/or oligosaccharides are separated from the hydrolyzed cellulose, and
- the hydrolyzed cellulose is mechanically treated in order to obtain micro- and/or nanocrystals.

A further object of the invention is a product that contains micro- and/or nanocrystalline cellulose.

The invention also relates to a cellulose product prepared by the said process and the use thereof in food applications and in optical, cosmetic and pharmaceutical applications.

By using an acid in the gas phase, it is possible to avoid several of the environmentally harmful micro- and nanocrystalline cellulose manufacturing steps, which may also be difficult to apply on industrial scale. In the inventive process, large amounts of water are not needed for rinsing the sample, the recycling of the acid is easier and the dialysis used for purification can be omitted. Therefore the recycling of the material and its processability are improved.

A preferred embodiment of the disclosed invention has been discussed in the following detailed description of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following, some preferred embodiments of the invention are presented in more detail by referring to the attached figures in which

Fig. 1 shows an experimental arrangement for hydrolyzing cellulose in the presence of gaseous hydrochloric acid (HCl). Liquid HCl is placed on the bottom of the exsiccator. The cellulose material, here a filter paper made of cotton, is hydrolyzed in the exsiccator in the presence of gaseous hydrochloric acid.

Fig. 2 demonstrates the breakdown rate with different salt concentrations, showing the time in which the LODP (LODP = level-off degree of polymerization) was reached.

Fig. 3 shows the change of cellulose's degree of polymerization (DP) as a function of time with varying hydrochloric acid concentrations.

DETAILED DESCRIPTION OF THE INVENTION

In the following, the invention is described in more detail referring to the exemplary preferred embodiments and the attached drawings.

The terms used in the specification and claims have the meanings generally assigned to them in the field.

The invention relates to a process for preparing micro- and nanocrystalline cellulose in the presence of an acid in the gas phase. The invention also relates to a cellulose product prepared by the said process and the use thereof in food and liquid crystal applications as well as in optical, cosmetic and pharmaceutical applications.

Gaseous hydrochloric acid (HCl) causes the degree of polymerization to decrease in room temperature, which is required for the formation of micro- and nanocrystalline cellulose. The decrease of the degree of polymerization can take place within a few hours, preferably in 30 minutes. Micro- and nanocrystals are obtained by mechanical breaking down following the hydrolysis, for instance by mechanical stirring and/or a following ultrasound treatment.

By using an acid in the gas phase, it is possible to avoid several of the environmentally harmful micro- and nanocrystalline cellulose manufacturing steps, which may also be difficult to apply on industrial scale. Large amounts of water are not needed for rinsing the sample, the recycling of the acid is easier and the dialysis

used for purification can be omitted. Therefore the recycling of the material and its processability are improved.

On the surface of the cellulose fibre, there is a thin aqueous layer, meaning that a high local acid concentration is formed when the gaseous acid adsorbs onto the fibre surface. Preferably the cellulose is dry, but not entirely so. The moisture content of the cellulose is between 1% and 80%. Preferably, the moisture content of the cellulose is between 1% and 10%, more preferably between 2% and 9%, and even more preferably between 3% and 8%, between 4% and 7%, or between 5% and 6%. The absolute amount of water on the fibre surface is so small that the local H_3O^+ concentration is high. This leads to a surprisingly high breakdown rate.

By the inventive process, dry hydrolyzed cellulose substrate can be obtained from which mono- and oligosaccharides, such as sugars, can be separated by using water, and the cellulose can be mechanically broken down. If necessary, the obtained micro- and/or nanocrystalline cellulose can be dispersed in water with the help of a dispersing agent, for example carboxymethyl cellulose (CMC).

One embodiment of the invention provides a process for preparing micro- and/or nanycrystalline cellulose in the presence of an acid in the gas phase, the process comprising steps in which

- cellulose material is hydrolysed in the presence of at least one acid in the gas phase, the moisture content of the cellulose being between 1% and 80%,
- soluble mono- and/or oligosaccharides are optionally separated from the hydrolyzed cellulose, and
- the hydrolyzed cellulose is mechanically treated in order to obtain micro- and/or nanocrystals.

Nano- and microcrystalline cellulose differ from each other by their particle size. Nanocrystals are single cellulose crystals: their width corresponds to the width of the native cellulose microfibril (*e.g.*, 7 nm in cotton cellulose) and their length the length of the crystalline area in the microfibril (e.g., between 5 nm and 300 nm in cotton cellulose). The diameter of microcrystalline cellulose particles is several micrometers or tens of micrometres. In principle, cellulose microcrystals consist of nanocrystalline particles, i.e. microcrystals are nanocrystal aggregates. Microcrystals are easier to manufacture than nanocrystals, since with microcrystals there is no need to control or prevent the aggregation that occurs easily. With regard to both micro- and

nanocrystals, it is essential that the acid hydrolysis in the amorphous parts of the microfibril is completed. When all the amorphous parts have been hydrolyzed, the LODP (level off degree of polymerisation) point is reached. After this, the acid hydrolysis decreases the degree of polymerization (DP) only marginally and very slowly.

In scientific literature, cellulose nanocrystals are commonly referred to as cellulose nanocrystals, nanocrystalline cellulose, cellulose whiskers, or cellulose nanowhiskers. In older publications, nanocrystalline cellulose has also been referred to as microcrystalline cellulose.

The cellulose material used in the invention can be obtained from wood-based or non-wood-based material. In the invention, it is possible to use cellulose material that comprises pulp, such as chemical pulp, mechanical pulp, thermomechanical pulp or chemithermomechanical pulp. The wood-based material can be obtained from hardwood or softwood. The non-wood-based material can be obtained from plants, such as cotton, flax or hemp. The cellulose material can be cellophane.

Mechanical treatment refers to mechanical breaking down, for instance by grinding, crushing, dispersing, ultrasound treatment or other breaking down, but not limited to these. The mechanical treatment can be performed by any known method of breaking down.

The process according to the invention is preferably performed in atmospheric conditions, *i.e.* normal atmosphere and normal pressure. The process can be carried out in a temperature that is between 0°C and 100°C, preferably the temperature is between 10°C and 40°C, more preferably between 15°C and 35°C, most preferably between 18°C and 22°C. The temperature is for instance room temperature.

The natural vapour pressure of the acid/water mixture, for instance a HCl/water mixture, which is sufficiently great to gasify the HCl into the vapour phase can be utilized in the invention, meaning that a separate reaction is not needed. As a result, HCl can also be transferred onto a cellulose substrate without a separate mixing with air and without mechanical flow. The inventive process also utilizes adsorption and the following dissociation of HCl on the fibre surface covered by a thin aqueous layer.

Therefore, the vapour pressure of the gas used in the invention is such that it gasifies in room temperature, so that the acid adsorbs onto the cellulose surface. For instance

one of the following can be used as the acid: hydrochloric acid, nitric acid and/or trifluoroacetic acid. The concentration of the acid can be at least 1% by volume. Preferably, the concentration of the acid in the gas phase is between 2% and 99% by volume, for example 15% by volume, 38% by volume, or 68% by volume.

The hydrolyzed cellulose can be dispersed in water. Dispersing agent can be added to the hydrolyzed cellulose, and this may for instance comprise carboxymethyl cellulose (CMC).

Water-soluble mono- and oligosaccharides can be separated from the hydrolyzed cellulose by extraction. Mono- and oligosaccharides can comprise for instance glucose and its oligomers, arabinose, xylose, mannose and other disintegration products of hemicelluloses. Mono- and oligosaccharides, for instance sugars, can be separated from the hydrolyzed cellulose by extraction. The TOC of the sugars is determined, they are analyzed by HPLC and the amount of eventual residual acid is measured. The separated sugars can be further fermented into ethanol.

The inventive process can be carried out within a few hours, preferably for instance in 30 minutes.

The viscosity of the hydrolyzed and broken-down cellulose is determined. Also the following analysis tools can be used: Cuen viscosity, gel permeation chromatography, and the CCOA method.

In one preferred embodiment of the invention, the process comprises steps in which

- cellulose material is hydrolysed in the presence of at least one acid in the gas phase, the moisture content being between 1% and 80%,
- the hydrolyzed cellulose is dispersed in water in the presence of a dispersing agent,
- mono- and/or oligosaccharides are separated from the hydrolyzed cellulose, and
- the hydrolyzed cellulose is mechanically treated in order to obtain micro- and/or nanocrystals.

A further object of the invention is a product that contains micro- and/or nanocrystalline cellulose.

The invention also relates to a cellulose product prepared by the said process and the use thereof in food and liquid crystal applications as well as in optical, cosmetic and pharmaceutical applications.

EXAMPLE

Acid hydrolysis of cotton cellulose

A filter paper sheet (type Whatman 1, solids content about 95%) was placed in an exsiccator with a small amount of liquid hydrochloric acid (HCl) on the bottom. The test conditions comprised normal air pressure and room temperature. The acid used was 2.1%, 15%, 68%, and 99% HCl in the gas phase, corresponding to 20%, 25%, 30% and 37% liquid acid, respectively. Table 1 shows the concentrations of gaseous hydrochloric acid as compared to the corresponding liquid hydrochloric acid.

Table 1. The concentration of hydrochloric acid in liquid and gas phase in normal air pressure and room temperature.

Hydrochloric acid in liquid [% by weight]	**Hydrochloric acid in gas phase [% by volume]**
20	2.1
25	15
27	38
30	68
37	99

The experimental arrangement is shown in Fig. 1. The natural vapour pressure of liquid HCl was great enough to gasify the HCl into the gas phase in room temperature and transfer the HCl onto the cellulose substrate, which was cotton cellulose.

The results can be analyzed for instance by the following methods:

- Cuen viscosity: DP_v
- gel permeation chromatography (GPC): DPw and DPn,
- CCOA method (carbazole-9-carboxylic acid [2-(2-amino-oxyethoxy)ethoxy]amide): the amount of carbonyl groups.

Fig. 2 shows the results of the acid hydrolysis when using 2.1%, 15%, 68%, and 99% gaseous hydrochloric acid, corresponding to 20%, 25%, 30%, and 37% liquid hydrochloric acid. When the concentration of the hydrochloric acid was increased in room temperature, the LODP point was reached more rapidly. Nanocrystalline cellulose was formed when the LODP value exceeded 100.

Table 2 shows the hydrolysis time, viscosity and DPv with different acid concentrations.

Table 2. Cellulose hydrolysis time, viscosity and DPv with different hydrochloric acid concentrations, 20%, 25%, 30%, and 37%.

Sample	Time (min)	Viscosity	DP_v
20%	0	858	3170
	1	859	3174
	15	779	2848
	30	854	3154
	60	821	3019
	120	673	2420
	240	634	2265
	890	559	1969
	1440	455	1567
	5400	113	333
25%	0	858	3170
	1	781	2856
	15	752	2738
	30	778	2843
	60	712	2577
	120	623	2221
	890	153	467
	1440	141	426
	5400	93	268
30%	0	858	3170
	1	796	2917
	15	681	2452
	30	776	2835
	60	361	1212
	120	290	950
	240	163	501
	895	112	330
	1440	101	294
	5400	105	307
37%	0	858	3170
	1	540	1895
	15	293	961
	30	242	777
	60	175	542
	120	138	416
	240	124	370
	895	101	294
	1440	70	196
	5400	81	230

Table 3. Cellulose hydrolysis time and degree of polymerization (DP) with different hydrochloric acid concentrations, 20%, 25%, 30%, and 37%.

Time (min)	DP			
	20%	**25%**	**30%**	**37%**
0	3170	3170	3170	3170
1	3174	2856	2917	1895
15	2848	2738	2452	961
30	3154	2843	2835	777
60	3019	2577	1212	542
120	2420	2221	950	416
240	2265		501	370
890	1969	467	330	294
1440	1567	426	294	196
5400	333	268	307	230

It is obvious for a person skilled in the art that as the technique advances, the basic principle of the invention may be implemented in several different ways. The invention and its embodiments are therefore not restricted to the above-described example but they may vary within the scope of the claims.

CLAIMS

1. A process for preparing micro- and/or nanocrystalline cellulose, **characterized in that** the process comprises steps in which
   - cellulose material is hydrolysed in the presence of at least one acid in the gas phase, the moisture content of the cellulose being between 1% and 80%,
   - soluble mono- and/or oligosaccharides are optionally separated from the hydrolyzed cellulose, and
   - the hydrolyzed cellulose is mechanically treated in order to obtain micro- and/or nanocrystals.

2. The process according to claim 1, **characterized in that** the vapour pressure of the acid used is such that the acid gasifies into the gas phase in room temperature and adsorbs onto the cellulose surface.

3. The process according to claim 1 and 2, **characterized in that** one of the following is used as the acid: hydrochloric acid, nitric acid and/or trifluoroacetic acid.

4. The process according to any one of claims 1 to 3, **characterized in that** the acid used is HCl.

5. A process according to any one of claims 1 to 4, **characterized in that** the concentration of the acid in the gas phase is at least 1% by volume.

6. The process according to any one of claims 1 to 5, **characterized in that** the hydrolyzed cellulose is dispersed in water.

7. The process according any one of claims 1 to 6, **characterized in that** dispersing agent, preferably carboxymethyl cellulose (CMC), is added to the hydrolyzed cellulose.

8. The process according to any one of claims 1 to 7, **characterized in that** the hydrolyzed cellulose is mechanically broken down.

9. The process according any one of claims 1 to 8, **characterized in that** the mechanical breaking down comprises mechanical stirring and/or ultrasound treatment.

10. The process according to any one of claims 1 to 9, **characterized in that** the process is carried out in normal air pressure.

11. The process according to any of the claims 1 to 10, **characterized in that** the process is carried out in a temperature that is between 0°C and 100°C, preferably between 10°C and 40°C, more preferably between 15°C and 35°C, more preferably between 18°C and 22°C, most preferably in room temperature.

12. The process according to any one of claims 1 to 11, **characterized in that** the process comprises steps in which

- cellulose material is hydrolysed in the presence of at least one acid in the gas phase, the moisture content being between 1% and 80%,
- the hydrolyzed cellulose is dispersed in water in the presence of a dispersing agent,
- soluble mono- and/or oligosaccharides are separated from the hydrolyzed cellulose, and
- the hydrolyzed cellulose is mechanically treated in order to obtain micro- and/or nanocrystals.

13. A product containing micro- and/or nanocrystalline cellulose, **characterized in that** the product has been prepared by a process according to any one of claims 1 to 12.

14. The use of the product according to claim 13 as a reinforcement or a filler.

15. The use of the product according to claim 13 in optical and liquid crystal applications.

16. The use of the product according to claim 13 in food, cosmetic and pharmaceutical applications.

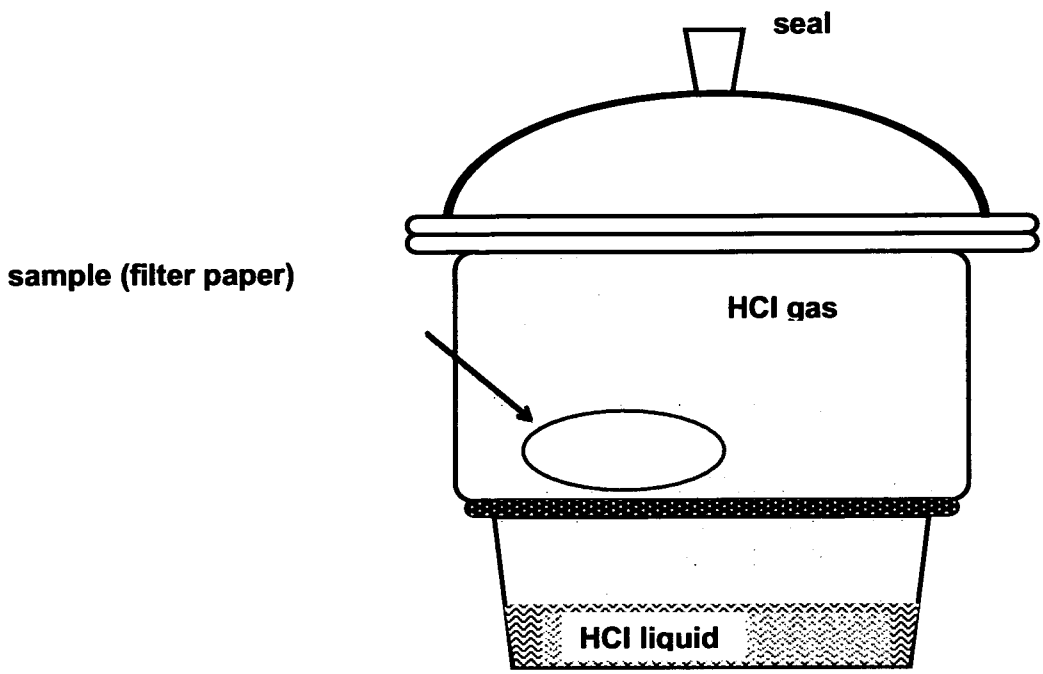


Fig. 1

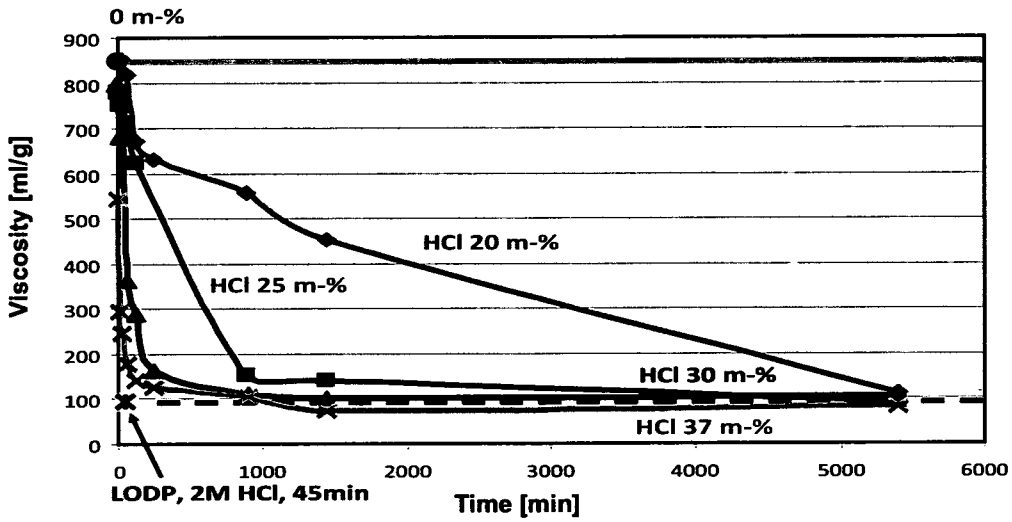

0 m-%
900
800
700
600
500
400
300
200
100
0
Viscosity [ml/g]
HCl 20 m-%
HCl 25 m-%
HCl 30 m-%
HCl 37 m-%
0
1000
2000
3000
4000
5000
6000
LODP, 2M HCl, 45min
Time [min]

Fig. 2

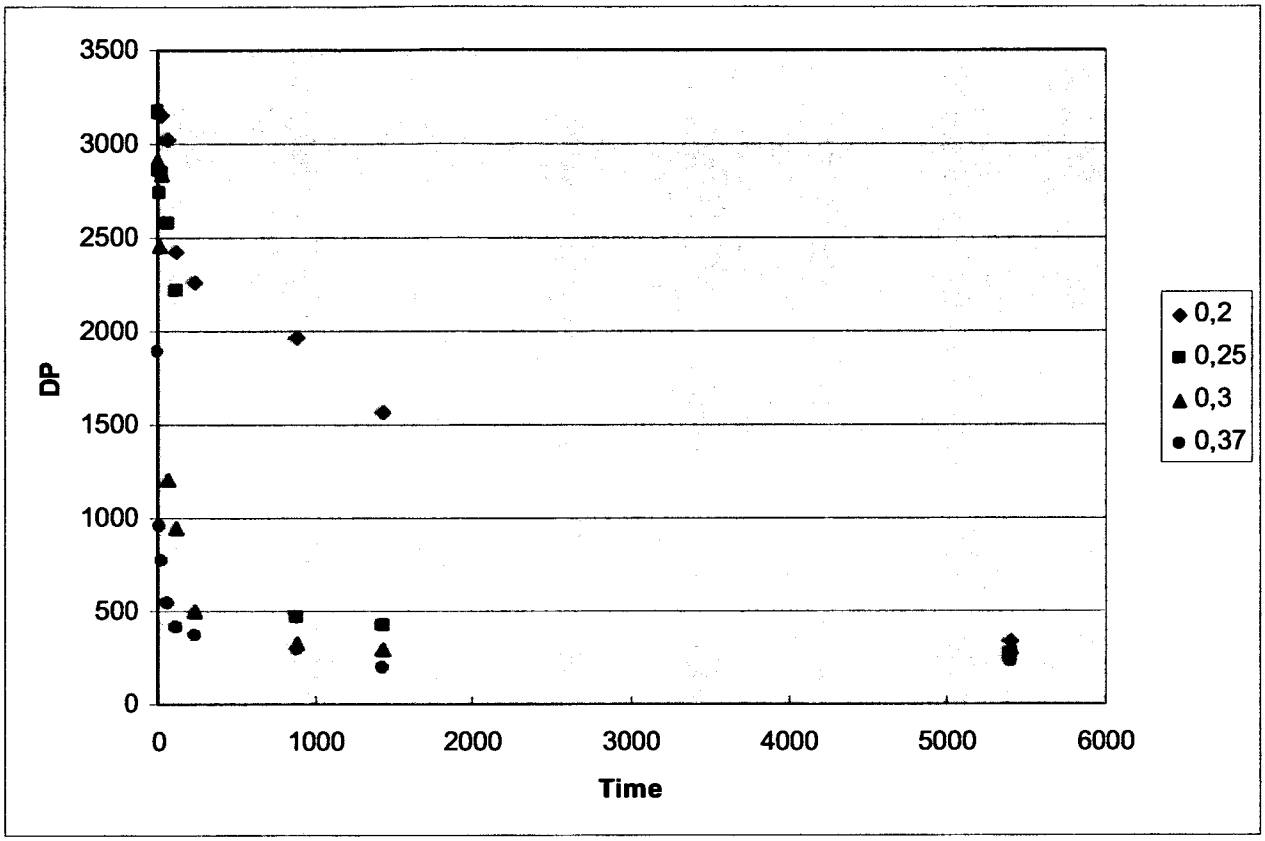

3500
3000
2500
2000
1500
1000
500
0
DP
0
1000
2000
3000
4000
5000
6000
Time
0,2
0,25
0,3
0,37

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2011/050235

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: C08B

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RU 2281993 C1 (VASIL EV VLADIMIR ALEKSANDROVI) 20 August 2006 (20.08.2006) cited in the application	1-14, 16
X	EP 0248252 A2 (WOLFF WALSRODE AG) 09 December 1987 (09.12.1987)	1-14, 16
X	Holbery & al., A technique for production of nanocrystalline cellulose with a narrow size distritbution. Cellulose (2009) 16:455-465	13-16

☐ 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
13 June 2011 (13.06.2011)	16 June 2011 (16.06.2011)

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2011/050235

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
RU 2281993 C1	20/08/2006	None	
EP 0248252 A2	09/12/1987	FI 872378 A	01/12/1987
		JP 62285901 A	11/12/1987
		DE 3618377 A1	03/12/1987

INTERNATIONAL SEARCH REPORT

International application No.
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CLASSIFICATION OF SUBJECT MATTER

Int.Cl.
C08B 15/08 (2006.01)