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(71) Applicant *(for all designated States except US)*: **KEMIRA OYJ** [FI/FI]; Porkkalankatu 3, FI-00180 Helsinki (FI).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **KARPPI, Asko** [FI/FI]; Solmukatu 18, FI-20540 Turku (FI). **VUORENPALO, Veli-Matti** [FI/FI]; Nissinmäentie 10 As 11, FI-02780 Espoo (FI). **ROBERTSÉN, Leif** [FI/FI]; Isokaarre 2, FI-21600 Parainen (FI). **PARVIAINEN, Kari** [FI/FI]; Linnustajankuja 1 C 16, FI-02940 Espoo (FI). **DAHL, Olli** [FI/FI]; Mutkaton 2, FI-12400 Tervakoski (FI). **VANHATALO, Kari** [FI/FI]; Abrahaminkatu 8 C 67, FI-00180 Helsinki (FI).

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

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(54) **Title**: PROCESS FOR PRODUCING MICROCELLULOSE

(57) **Abstract**: The present invention relates to a process for producing microcellulose comprising subjecting fibrous cellulosic material to acid hydrolysis at a temperature from 10°C to less than 140°C and at a consistency of at least 8% on dry weight of the cellulose, wherein the amount of added acid is from 0.2 to 2%, preferably from 0.3 to 1.9%, more preferably from 0.5 to 1.5% on dry weight of the cellulose.

PROCESS FOR PRODUCING MICROCELLULOSE

Field of the invention

The present invention relates to a process for preparing microcellulose in high yield by acid hydrolysis of fibrous cellulosic material.

Background of the invention

Microcellulose (also named as e.g. level-off DP cellulose and microcrystalline cellulose) is a versatile product in many industrial applications, e.g. in food, pharmaceutical, cosmetics, paper and board and many other applications. Microcellulose can also be used in the production of derivatives of microcellulose, such as viscose cellulose, CMC, nanocellulose and various composite products.

Several methods have been proposed in the patent literature for producing microcellulose.

US 2 978 446 describes the production of level-off DP (degree of polymerization) cellulose by acid hydrolysis and mechanical treatment. Cellulose is hydrolyzed with boiling in 2.5 normal hydrochloric acid (HCl). Acid concentration is thus 9% and temperature about 105°C. The consistency of the pulp and the amount of added acid are not specified. The method requires subsequent to acid hydrolysis mechanical disintegration in aqueous medium. It is obvious that high dosages of acid and extensive mechanical treatment have prevented the development of any reasonable production economy.

US 3 278 519 describes a similar method for producing level-off DP cellulose by hydrolyzing cellulose either with 2.5 normal HCl at 105°C or with 0.5% HCl at 250°F (121°C). The consistency of the pulp and the amount of added acid are not specified. This patent also describes a harsh energy-consuming mechanical treatment.

US 3 954 727 discloses a method for producing microcrystalline cellulose by hydrolyzing cellulose with dilute sulphuric acid at a temperature of from 120 to 160°C. The dilute sulphuric acid to which the cellulose is added has a concentration of 1% and the cellulose-acid mass has a concentration of 5%. Thus, the consistency of the pulp is low, the heating demand is therefore high and the amount of

acid based on the dry weight of the cellulose becomes high. This makes the process expensive and complicated.

US 7 037 405 describes a method, in which raw pulp material is contacted with acid and heated at elevated temperature and then treated mechanically. A suitable acid concentration is mentioned to be 1 – 5% of the mixture, a suitable pulp consistency 3 – 50%, a suitable temperature range 80 – 120°C and a suitable reaction time 30 min – 4 h. After acid hydrolysis the pulp mixture is treated mechanically for disintegration of the fibres. Preferably the mechanical disintegration process step shears the crystalline cellulose particles into micron size ranging form about 1 to 10 micron size. The process of US 7 037 405 suffers of complicated production process. Mechanical disintegration step is required after acid hydrolysis. This stage requires in production costly refiner unit and high refining energy of 5 – 100 kWh/ton.

US 6 228 213 discloses a process for producing microcrystalline cellulose by adding an acid solution to cellulose and feeding the cellulose and acid solution through an extruder, wherein the cellulose undergoes acid hydrolysis and forms microcrystalline cellulose. The temperature of the extruder barrel during the hydrolysis is from 80 to 200°C. Due to the temperature of the extruder and the pressure created by the die or screw of the extruder, the cellulose melts in the extruder, which allows for more intimate contact between the cellulose and the acid. The compression ratio of the extruder screw is between 1.5:1 and 3:1, preferably about 3:1. Disadvantages with extruders are that they are expensive, the maintenance costs are rather high, and they require a high mechanical energy input, by estimation at least 100 kWh, typically at least 150 kWh per dry ton cellulose (the heating energy input is excluded).

US 5 543 511 describes the production of level-off-DP cellulose using partial hydrolysis with oxygen and/or carbon dioxide at 100 – 200°C.

US 4 427 778 describes the production of level-off-DP cellulose by enzymatic hydrolysis.

Acid hydrolysis is also widely used in dissolving pulp production, e.g. in acidic bisulphite cooking and as a pre-hydrolysis step is used in the kraft process. Acidic bisulphite cooking is described in e.g. Rydholm, S.E., Pulping Processes, pp. 649 to 672. US 5 589 033 describes a pre-hydrolysis kraft process of lignin-containing cellulosic material (i.e. wood chips) at 100 – 160°C for softwoods and at 120 –

180°C for hardwoods for 10 – 200 min. Neutralization and alkaline kraft cooking follows the pre-hydrolysis step. The final product is a pulp with high alpha cellulose purity and can be used as dissolving pulp. Dissolving pulp has a fibrous structure with fiber length of typically 0.5 mm to 2.5 mm dependent on wood raw material. Thus, the physical dimensions are much larger than microcellulose.

In the prior-art microcellulose manufacturing processes high amounts of chemicals such as acids calculated on dry weight of the cellulose are used.

In view of the above described processes for producing microcellulose there is a need for an even more efficient and economical process.

Summary of the invention

According to the present invention it was surprisingly found that microcellulose with rather narrow particle size distribution can be produced in high yields from fibrous cellulosic material by mild acid hydrolysis at a high consistency of at least 8% and a temperature of less than 140°C. The particle size distribution can be easily controlled by varying the conditions of the mild acid hydrolysis.

Brief description of the drawing

Fig. 1 shows the particle size distribution curve of microcellulose produced according to the present invention at 120°C and acid dose of 1.5%.

Detailed description of the invention

According to the present invention there is provided a process for producing microcellulose comprising subjecting fibrous cellulosic material to acid hydrolysis at a temperature from 110°C to less than 140°C and at a consistency of at least 8% on dry weight of the cellulose, wherein the amount of added acid is from 0.2 to 2%, preferably from 0.3 to 1.9%, more preferably from 0.5 to 1.5% on dry weight of the cellulose.

As used in this specification the term “microcellulose” includes microcrystalline cellulose MCC but refers also to similar products which are not totally crystalline but may contain some amorphous regions. The microcellulose of the present invention typically has a hemicellulose content of about 2 to 13%, preferably about

4 to 10% by weight measured by typical carbohydrate analysis methods (Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography, 1996, Nordic pulp and paper research journal nro 4, 1996. s. 216-219).

Suitable acids for the hydrolysis are both organic and inorganic acids. The organic acid may be e.g. formic acid or acetic acid. Preferred acids are mineral acids, such as sulphuric acid, hydrochloric acid, nitric acid, sodium bisulphate or sodium bisulphite. Also mixtures of two or more of these acids may be used. A preferred mineral acid is sulphuric acid.

Preferably the hydrolysis is carried in a reactor without essential compression, the compression ratio of the reactor preferably being below 1.5:1, more preferably below 1.2:1.

The hydrolysis temperature is preferably between 110 and 135°C, more preferably between 115 and 135°C.

The consistency of the cellulosis material during the hydrolysis is preferably from 8 to 50%, more preferably from 15 to 50%, even more preferably from 20 to 50%, and most preferably from 25 to 45% on dry weight of the cellulose.

The hydrolysis time is preferably from 5 to 180 minutes, more preferably from 15 to 150 minutes.

Preferably the mechanical energy input during the hydrolysis is provided to ensure even chemical and temperature distribution and without essential mechanical cutting and mechanical defibration of the cellulose matrix, preferably at most 20 kWh per dry ton cellulose, more preferably at most 10 kWh per dry ton cellulose, and most preferably between 1 and 5 kWh per dry ton cellulose.

According to the invention the fibrous cellulosic material and the acid are contacted with each other, preferably by mixing.

After the acid hydrolysis the obtained microcellulose – hydrolysate mixture may be neutralized or the microcellulose may be separated from the hydrolysate. The separated microcellulose may be washed and the separated or washed microcellulose may be neutralized. Also the acid hydrolysate may be neutralized. E.g. sodium carbonate, sodium bicarbonate, potassium hydroxide, magnesium hydroxide or sodium hydroxide may be used for the neutralization.

It has been observed that microcellulose material with an average particle size of about 30 – 100 µm can be produced in high yield from fibrous cellulosic material by mild acid hydrolysis at a consistency of at least 8% and at a temperature of less than 140°C without a subsequent disintegration step. An essential feature of the present invention is the high consistency of the cellulosic material, which is at least 8%, preferably at least 20% on dry weight of the cellulose. The high consistency increases the concentration of the chemicals which has a favourable effect on the reaction speed. In addition, the heating demand will be lower.

The fibrous cellulosic material used as a starting material in the process of the present invention may be any cellulosic material that can be hydrolyzed under the specified conditions. The fibrous cellulosic material does not necessarily have to be a pure cellulosic material but it can also contain other materials such as lignin.

The lignin content of the fibrous cellulosic starting material is preferably at most 5%, more preferably at most 2%, most preferably at most 1%.

The fibrous cellulosic starting material typically has a hemicellulose content of about 3 to 15%, preferably 5 to 10% by weight measured by typical carbohydrate analysis methods (Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography. 1996. Nordic pulp and paper research journal nro 4, 1996. p. 216-219).

The fibre length of the fibrous cellulosic raw material is preferably 5 – 0.2 mm. For non-wood fibrous cellulosic materials, such as cotton the fibre length may be more than 5 mm.

The fibrous cellulosic material may be derived from wood plant material, such as softwoods or hardwoods.

A preferred fibrous cellulosic material is a bleached or unbleached chemical pulp, such as kraft pulp, soda-AQ pulp, sulfite pulp, neutral sulfite pulp, acid sulfite pulp or an organosolv pulp. The pulp may be softwood or hardwood pulp. The pulp may be a pulp obtained immediately after the digestion or a pulp that has been delignified after the digestion or a pulp that has been delignified and bleached. A preferred delignified pulp is an O_2 delignified pulp. A preferred pulp is fully bleached pulp.

According to the present invention it is also possible to use fibrous cellulosic material obtained from non-wood lignocellulosic plant materials such as cotton,

grass, bagasse, straws of grain crops, flax, hemp, sisal, abaca or bamboo. Usually these plant materials are treated with an alkaline substance to break the lignocellulosic material into cellulose, lignin and hemicellulose followed by separating the cellulose from the mixture. Some lignin-poor plant materials, such as cotton linters or cotton textiles do not necessarily require a treatment with an alkaline substance. The latter materials may contain more than 90% cotton fibres of the fibrous material

The fibrous cellulosic material, such as chemical pulp preferably has a lignin content of below 40 kappa number, more preferably below 30 kappa number, and most preferably below 10 kappa number.

According to a preferred embodiment of the invention the produced microcellulose has an average particle size (D50) of 30 – 100 µm, and preferably the particle size distribution (D90) is such that at least 90% by volume of the particles have a size of below 250 µm, preferably below 200 µm and more preferably below 150 µm. The particle size was determined by the procedure described later on in this specification which procedure includes ultrasonic treatment which might cause deagglomerization or disintegration of the sample.

The microcellulose material obtained by the process of the invention typically has an average particle size between 30 – 100 µm, preferably between 40 – 80 µm – as determined by the procedure described later on in this specification – without any mechanical treatment. It is possible to refine the structure if finer particle size is required. Thus, the microcellulose material obtained from the hydrolysis may, if desired, be refined to a smaller particle size by using suitable devices, such as friction grinders wherein the refining is effected by grinding stones (e.g. Masuko grinder), high shear mixers or jet mills.

A benefit of the process of the invention is that the drainability of the final microcellulose is good and that the product can be easily washed to remove low molecular weight carbohydrates.

As set forth above the microcellulose is obtained in high yields by the process of the present invention. The yield is preferably at least 90%, more preferably at least 95%.

According to the present invention the microcellulose may be produced in any suitable equipment wherein the cellulose-acid mixture is not subjected to any substantial compression, such as a vessel equipped with a mixer or screw conveyor.

The latter one may be a device of the M&D digester type having a screw conveyor. Other devices may be continuous bleaching reactors or down-flow continuous digesters, e.g. of type Kamyr. The compression ratio, if any, is typically below 1.5:1, more preferably below 1.2:1.

Experimental section

The following examples to produce microcellulose describe the procedure according to invention. The cooking experiments were done with an air-bath-digester, manufactured by Haato Oy. The air-bath-digester consists of six separate autoclave units, which all have a volume of 2.5 liter. The units are heated with hot air. Air is heated with an electric resistor and the heated air is circulated with a fan.

All of the cooking experiments were done in the following manner. The cellulose material, pulp or other, was put in an autoclave unit. Pulp in bale sheets was cut in square pieces with edge of about 1 – 2 cm prior to loading to autoclave unit. Fresh cellulose material, e.g. unbleached pulp, was dried to consistency of 45 – 50% and then homogenized with Kenwood household mixer for 5 min, prior to loading into autoclave unit. Acid solution was dosed after cellulose material. Acid was first premixed with de-ionized water and the aqueous acid solution was poured evenly on the pulp. The lid of the autoclave unit was closed and the unit was heated to 80°C. The pre-heating stage took about 20 min in each test. When 80°C start temperature had been reached, the real heating stage started. The autoclave unit was heated in a controlled manner with heating speed of 2°C/min until the cooking temperature target had been reached. Thus heating e.g. to 120 °C took 20 min and to 140°C took 30 min. Cooking time started, when the target cooking temperature had been reached. Temperature was kept at the target temperature value during the whole cooking time. When cooking time was completed, the autoclave unit was immediately removed and cooled with cold water (temperature about 10°C).

Cooled autoclave unit was opened and the cellulose mixture was put into a filter bag (mesh 90). The excess acid solution in the mixture was removed with a spin dryer (Manufacturer UPO. Drying time 2 min, speed about 2800 rpm). Consistency after spin dryer treatment was 45 – 50%. The cellulose material was then washed with 3 liter of de-ionized water, by first mixing the mixture gently for 5 min and drying the mixture with spin dryer to consistency of 45 – 50%. The washing step

with de-ionized water was repeated two times. pH in the last (third) aqueous mixture was about 6 – 7 and washing was considered to be complete.

The washed cellulose material was weighed. Three samples, each about 20 g were taken, combined and weighted. The combined samples were dried in an oven (105°C, 24 h). Using the moisture value of the sample the total amount of dry (absolute) cellulose material was calculated. Process yield was calculated using the amount of dry cellulose material of the washed product and the dry cellulose material in the start.

Particle sizes of the cellulose products were determined by laser diffraction with Mastersizer 2000 (made by Malvern Instruments Ltd) equipped with a wet dispersion unit Hydro 2000MU. The determinations were done according to the following procedure:

A sample of the cellulosic material was dispersed in 500 ml of distilled water. The sample concentration was adjusted in a manner that the obscuration was 10%. Pump/stir rate of the dispersion unit was adjusted to 1500 rpm. The sample was treated with ultrasonic for 60 sec prior to the particle size measurement. Particle sizes were measured in 3 sequential measurements in 60 sec intervals. The average value of three measurements was calculated. Background was measured each time prior to the sample. The measuring time for each background and each sample measurements was 5 sec. The measurements were done using Fraunhofer parameters. More data for laser diffraction measurement principles are presented in Master sizer 2000 application note MRK 561 (Wet method development for laser diffraction measurements) by Malvern Instruments and ISO-13320-1 (1:1999), Particle size analysis – Laser diffraction General Principles.

Example 1 Acid hydrolysis of fully bleached pulp, acid dosage 1.5 or 2.0% (of dry pulp), cooking temperature 120°C

A series of hydrolysis experiments was done with fully bleached softwood pulp (moisture 10%). The parameters and the results of this example are presented in table 1. Particle size distribution curve of experiment 8-5 is presented in Fig. 1.

Table 1

Exp.	Sulphuric acid dosage	Cooking time	Temperature	Consistency	Yield	Average particle size	Particle size, 90 %
	(%)	(min)	(°C)	(%)	(%)	(µm)	(µm)
8-1	1,5	150	120	20	97	56	164
8-2	2,0	150	120	20	97	49	134
8-3	1,5	90	120	30	97	55	154
8-4	2,0	90	120	30	97	44	112
8-5	1,5	150	120	30	96	45	115
8-6	2,0	150	120	30	91	41	102

The results show that when pulp is cooked with low acid concentration at 120°C even for long times, the yield of the microcellulose is very good, over 90%. For certain microcellulose applications the obtained product can be used without refining. Over 10% of the particles have particle size over 100 µm and thus for certain microcellulose applications refining might be necessary.

Claims

1. A process for producing microcellulose comprising subjecting fibrous cellulosic material to acid hydrolysis at a temperature from 110°C to less than 140°C and at a consistency of at least 8% on dry weight of the cellulose, wherein the amount of added acid is from 0.2 to 2%, preferably from 0.3 to 1.9%, more preferably from 0.5 to 1.5% on dry weight of the cellulose.

2. The process according to claim 1, wherein the added acid is a mineral acid, preferably sulphuric acid, hydrochloric acid or nitric acid.

3. The process according to claim 1 or 2, wherein the hydrolysis is carried in a reactor without essential compression, the compression ratio of the reactor preferably being below 1.5:1, more preferably below 1.2:1.

4. The process according to any of claims 1 to 3, wherein the temperature is between 110 and 135°C, preferably between 115 and 135°C.

5. The process according to any of claims 1 to 4, wherein the consistency of the cellulose is from 8 to 50%, preferably from 15 to 50%, more preferably from 20 to 50%, and most preferably from 25 to 45% on dry weight of the cellulose.

6. The process according to any of claims 1 to 5, wherein the hydrolysis time is from 5 to 180 minutes, preferably from 15 to 150 minutes.

7. The process according to any of claims 1 to 6, wherein the fibrous cellulosic material and the acid are mixed with each other.

8. The process according to any of claims 1 to 7 wherein the obtained microcellulose – hydrolysate mixture is neutralized or the microcellulose is separated from the hydrolysate, the separated microcellulose is optionally washed and the separated or washed microcellulose is neutralized, or the separated hydrolysate is neutralized

9. The process according to any of claims 1 to 8, wherein the fibrous cellulosic material is derived from wood plant material, such as softwoods or hardwoods.

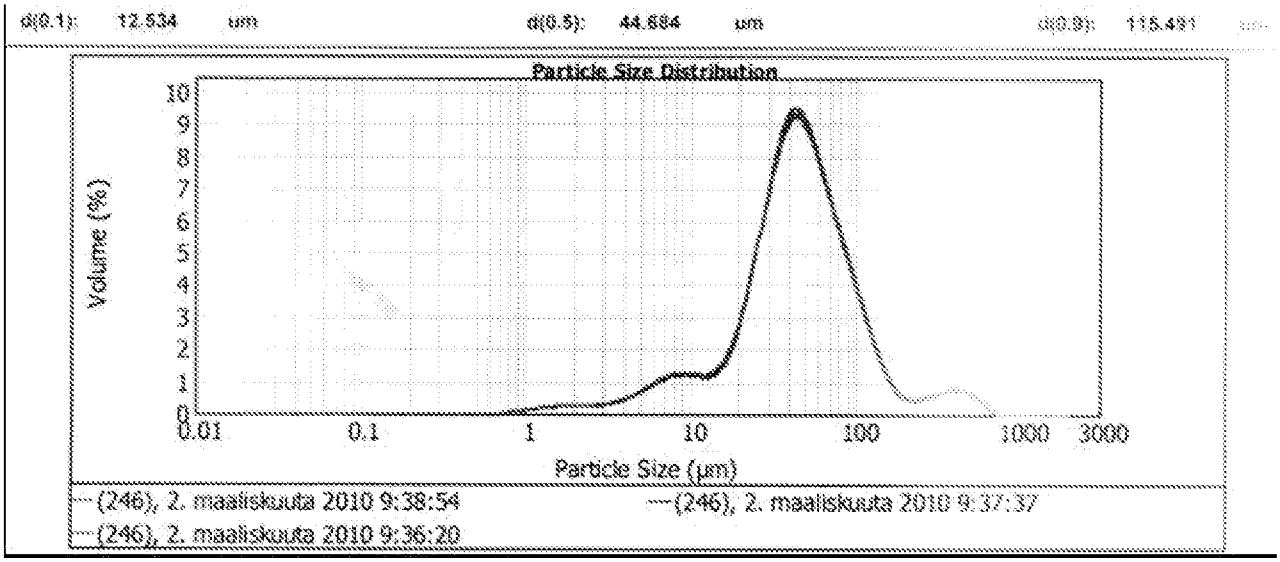
10. The process according to any of claims 1 to 9, wherein the fibrous cellulosic material comprises bleached or unbleached chemical pulp, such as kraft pulp, soda-AQ pulp, sulfite pulp, neutral sulfite pulp, acid sulfite pulp or organosolv pulp.

11. The process according to any of claims 1 to 8, wherein the fibrous cellulosic material is derived from non-wood plant material, such as cotton, grass, bagasse, straws of grain crops, flax, hemp, sisal, abaca or bamboo.

12. The process according to any of claims 1 to 11, wherein the fibrous cellulosic material, such as chemical pulp has a lignin content of below 40 kappa number, preferably below 30 kappa number, more preferably below 10 kappa number.

13. The process according to any of claims 1 to 12, wherein the produced micro-cellulose has an average particle size of 30 – 100 µm, and preferably the particle size distribution is such that at least 90% by volume of the particles have a size of below 250 µm.

14. The process according to any of claims 1 to 13, wherein the yield of the microcellulose is at least 90%, preferably at least 95%.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d(0.5): 44.684 um
d(0.9): 115.491
Particle Size Distribution
Volume (%)
10
9
8
7
6
5
4
3
2
1
0
0.01
0.1
1
10
100
1000
3000
Particle Size (µm)
(246), 2. maaliskuuta 2010 9:38:54
(246), 2. maaliskuuta 2010 9:37:37
(246), 2. maaliskuuta 2010 9:36:20

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. C08B15/02
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)
C08B

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 practical, search terms used)
EPO-Internal, BIOSIS, COMPENDEX, INSPEC, 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	US 6 228 213 B1 (HANNA MILFORD [US] ET AL) 8 May 2001 (2001-05-08) cited in the application column 6, line 54 - line 62 claims	1-14
X	US 3 954 727 A (TOSHKOV TOSHKO SOKOLOV ET AL) 4 May 1976 (1976-05-04) cited in the application claims; example 2	1-14
X,P	WO 2010/131088 A1 (BLANVER FARMOQUIMICA LTDA [BR]; FRANGIONI GIUSEPPE [BR]; FRANGIONI ALE) 18 November 2010 (2010-11-18) examples	1-14

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

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Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Vaccaro, Eleonora

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