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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 November 2007 (29.11.2007)

PCT

(10) International Publication Number
WO 2007/135245 A1

(51) International Patent Classification:
C08B 3/14 (2006.01) *D21H 11/20* (2006.01)
B27K 3/34 (2006.01) *D06M 101/06* (2006.01)
D06M 13/432 (2006.01)

(21) International Application Number:
PCT/FI2007/050296

(22) International Filing Date: 24 May 2007 (24.05.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20065350 24 May 2006 (24.05.2006) FI

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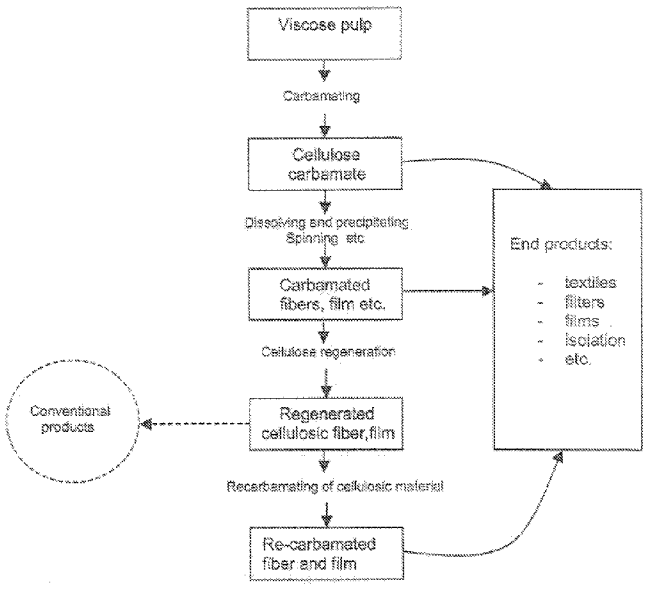
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** ANTIMICROBIAL POLYMER MATERIAL AND ITS USE



(57) **Abstract:** A method is presented for imparting microbiostatic properties to a polysaccharide or to a polysaccharide-containing product by introducing covalently bound carbamate groups in the polysaccharide chain. The polysaccharide may be in isolated form or included in a complex structure. In particular, the invention relates to the use of cellulose carbamate for producing microbiostatic material. Such material may be in the form of fibers or films, or as a wood product treated in order to achieve anti-rot properties.

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ANTIMICROBIAL POLYMER MATERIAL AND ITS USE

Field of the invention

The present invention relates to the field of polysaccharides, especially to providing microbistatic, i.e. bacterio- and fungistatic properties to said polysaccharides so that microbial growth in said polysaccharide and the microbial degradation of the polysaccharide is prevented or blocked. According to the invention, the polysaccharide is blocked from microbial degradation, i.e. splitting of the saccharide chain, by introducing therein a blocking group, namely a carbamate group. Such "blocked" polysaccharides can find a variety of uses in instances where antimicrobial and microbistatic properties are of importance, such as in hygiene and healthcare and medical applications. The invention can also be used for imparting degradation preventing properties to polysaccharides, for example to cellulose based products, such as wood, or wood and paper and viscose fibers, by subjecting said products to a treatment imparting the desired blocking properties to the product by introducing a blocking group in a saccharide unit.

Background of the invention

Cellulose has been converted to cellulose carbamate by means of urea and an alkaline agent in order to render the cellulose soluble. The cellulose is then regenerated from the cellulose carbamate for the formation into various final cellulose products in the form of, for example, fibers, films or membranes. However, cellulose carbamate is a chemically stable cellulose derivative, which also can be used as such, for the formation of various products.

It is known that various products like textile fibers, films etc., can be formulated by spinning or extruding an alkaline water based solution of cellulose carbamate into the desired form in such a manner, that first, the cellulose carbamate is precipitated from the solution by extruding/spinning the alkaline solution into either suitable acid- or suitable salt solution. Regenerated cellulose may be formed by further treatment of the precipitated product in order to remove the carbamate groups.

It is known to impart microbistatic and antimicrobial properties to cellulose-based materials such as fibers and fabrics, but according to such known methods a *per se* antimicrobial agent or additive is incorporated with the material. Thus for example, US patent 3,594,113 suggests the use of e.g. hexachlorophene as a bacteriostatic agent, which is complexed with a zirconium salt and a finish of the cross-linking wash-wear type. The cross-linking agent can be e.g. dimethylol methyl carbamate.). In US patent application publication no. 2005/0035057, a cellulose carbamate sponge impregnated with silver nitrate and possessing antibacterial properties is disclosed.

There is also a number of publications describing the use of carbamate compounds for providing wrinkle and crease resistant finishes to textiles (US 3,606,994, US 3,450,485.

Summary of the invention

The present invention relates to a method of imparting microbistatic properties to a polysaccharide, or to a polysaccharide containing product, for example a natural or man-made composite structure, like, e.g., wood, wood pulp, non-wood pulp, fiber webs, fabrics, or regenerated cellulose or products made thereof, by introducing covalently bound carbamate groups in the polysaccharide chain. According to the invention, the microbistatic properties are thus a result of modifying the polysaccharide to comprise carbamate groups.

The invention is also directed to the use of a polysaccharide carrying carbamate groups covalently bound to the polysaccharide chain as a microbistatic material, and in the manufacture of a product or material having microbistatic properties due to carbamate groups covalently bound to a polysaccharide chain.

The invention is also related to a method of preparing various microbistatic products from cellulose carbamate by spinning, extruding, casting etc. the dissolved cellulose carbamate, i.e. without regenerating the cellulose component. The carbamate groups in polysaccharide will thus provide the desired antimicrobial property to the product made.

Detailed description

The polysaccharide backbone that can be used according to the invention is derived from at least one natural polysaccharide selected from the group consisting of cellulose, hemicellulose, starch, pectine, amylopectine, and amylose. A preferred polysaccharide is cellulose. The cellulose can be in the form of cellulose fiber pulp, such as paper fiber or viscose (dissolving) fiber. It may appear, for example, as sulfate pulp, sulfite pulp, return fiber, CTMP pulp, TMP pulp, mechanical pulp or refiner pulp. The polysaccharide material can also originate from natural fiber sources like cotton or linen (flax).

The polysaccharide to be treated in order to introduce the carbamate group can be in any form. Possibilities range from the case of a free polymer molecule to a polysaccharide in a piece of wood or timber. In the latter case, the polysaccharide is thus treated when present in the wood fiber, especially at a surface area of said wood or timber. Such wood products or pieces of wood or timber to be treated are typically wood to be used for construction purposes, such as veneer or boards, such as particle board, planks, beams, battens, pillars and posts. Such fiber polysaccharides can be made microbistatic by treating the said fibers in order to incorporate into a monosaccharide unit a carbamate group in order to provide such wood with anti-rot properties and/or to make them decay resistant.

The invention also contemplates carbamation of pure regenerated cellulose, for example in the form of a membrane, fabric, textile fiber or filament, as a way of providing microbial protection to the said regenerated cellulose.

Microcrystalline cellulose, used in various applications e.g. in the pharmaceutical industry, may be carbamated to obtain microbistatic properties, and used according to the present invention.

Carbamates are chemically defined as esters of carbamic acid or its N-substituted derivatives. In the polysaccharides according to the invention, the carbamic acid typically forms an ester with a hydroxyl group in a monosaccharide unit, providing a substituted monosaccharide having the formula

$$MS - O - C(=O) - NH_2$$

wherein MS symbolizes a monosaccharide unit in the polysaccharide, a hydroxyl group of which forms an ester group with the carbamic acid, namely the carbamate group – O – C(=O) - NH_2.

In the anhydroglucose units of cellulose, and in the corresponding monosaccharidic unit of other polysaccharides, the position of substitution of the carbamate group is preferably at a primary hydroxyl group.

According to one embodiment of the invention, the polysaccharide is cellulose in which case the carbamate group is preferably substituted to the hydroxyl group in the position 6 of the anhydroglucose unit of cellulose, while a carbamate group also can be formed to hydroxyl groups in carbon atoms number 2 and 3.

The degree of substitution (DS), i.e. the number of carbamate groups per one monosaccharide (or one anhydroglucose) unit can vary, the maximum degree of substitution being the number of hydroxyl groups in the respective monosaccharide unit. Thus for example in the case of the polysaccharide being cellulose, the maximum degree of substitution is 3; however for the purposes of the present invention, a suitable and sufficient degree of substitution varies depending on the type of the polysaccharide substrate and the chemical accessibility of the hydroxyl groups for the substitution reaction. A degree of substitution (DS) of 0.3 thus means that there is on an average 3 carbamate groups for every 10 monosaccharide units.

For the purposes of the present invention, a suitable degree of substitution is in the range 0.05 to 1, preferably 0.25 to 0.4, more preferably 0.2 – 0.3.

For instance, a membrane made of regenerated cellulose can be made microbistatic by adding less that 1 carbamate group on an average of 10 monosaccharidic units. A textile

fiber made of regenerated cellulose requires a somewhat higher degree of substitution, since it has higher amount of specific surface, which is accessible for microbes. Wood pulp or paper made of such wood pulp typically requires a DS of 0.2 to 1.0, depending of the amount specific accessible surface of the wood pulp and the desired level of microbistaticity. Wood has even less polysaccharide molecules which are accessible to microbes, and, accordingly, a lower DS is needed for blocking these polysaccharide molecules against microbial degradation. When bleached wood pulp is used as the starting material, the accessibility of the hydroxyl groups for the carbamation reagent is enhanced by adding alkali to the water based suspension of wood pulp, thus allowing a higher degree of substitution to be achieved. A degree of substitution in the range 0.25 – 0.4 makes the wood pulp alkali soluble. An alkaline solution of cellulose carbamate can then be processed to form fibers, films, membranes, etc. Microbistatic property can be achieved by a lower degree of substitution. When a membrane of regenerated cellulose is carbamated, the DS may typically remain below 0.1, e.g 0.05.

The carbamate group can be introduced in the polysaccharide by known methods. According to one such method the polysaccharide, such as cellulose, is treated with urea in an alkaline solution and then heated, whereby urea is converted to isocyanic acid, which easily reacts with a hydroxyl group in the polysaccharide to form the carbamate group. The product obtained can be further treated for example washed and dried, in a known manner, to yield the desired polysaccharide carbamate.

By dissolving the polysaccharide carbamate, especially cellulose carbamate, in an alkaline solution, the solution obtained can be spun to form a textile fiber, or extruded to a film or membrane, by precipitating the polysaccharide carbamate as a stable product in an acid or salt solution.

Thus, the invention also concerns a method of imparting microbistatic properties to a product or a material comprising manufacturing said product or material from, or incorporating into said product or material a microbistatically effective amount of a polysaccharide carrying covalently bound carbamate groups.

According to the invention, the carbamate substituted polysaccharide or a polysaccharide based structure such as wood, wood fiber, other plant fibers, can be used as a timber, fiber pulp, fiber web or tissue, filament, fiber wool, for example for insulation purposes, as a film, as a non-woven, a textile, a fabric, in paper and paper products, and paper board, having microbistatic properties.

A typical use of a microbistatic polysaccharide according to the invention, or a product or material comprising the same, is in hygiene and healthcare. Such uses include the use in textiles and nonwovens for example for hospital gowns, sterilization bags, sheets and linens, dressings, and other wound care materials, and wipes, including wet wipes, in baby napkins and similar sanitary products in which a microbistatic and antimicrobial effect is desirable. Other uses include the use of the polysaccharide carbamates as degradation resistant insulation materials, such as in sheet form, or as insulation wools, made from the said polysaccharide, such as cellulose carbamate fibers. Another conceivable use is as filters, for example in vehicle and aircraft cabin air filters, and in cleaning and household wipes.

Figure 1 shows alternative routes to products having properties according to the invention. Viscose pulp (dissolving pulp) prepared according to the state of the art may be treated to yield cellulose carbamate, which may be directly converted into end-use products. The cellulose carbamate may also be dissolved as described above, and fibers, film or other solid forms may be prepared by mild acid treatment. These solids forms may be used to prepare end products. Acid treatment in stronger conditions splits off the carbamate groups to yield regenerated cellulose. Various degrees of incomplete regeneration can be employed to control the degree of substitution. The regenerated cellulose is of high purity and may be used as such, but may also be recarbamated to produce further grades of cellulose carbamate to be converted into end products.

A further aspect of the invention contemplates the treatment of polysaccharides in the form of fibers in a wood product or in timber, in order to introduce into the polysaccha-

ride covalently bound carbamate groups as defined above. In this way it is possible to provide wood and especially wood surfaces, such as veneers and boards, with an antimicrobial finish, and thus improve their decay and degradation resistance and to impart anti-rot properties thereto. In relation to the case of dissolving pulp, the degree of substitution thereby remains lower, and a lower temperature and less severe chemical conditions may be used for treating surface regions that are subject to microbial attack. In plywood or similar laminated products, the treatment may, if desired, be limited to the surface layers or a single surface layer.

The following examples illustrate the invention, without limiting the same.

Example 1

Dissolving pulp was disintegrated in water and treated with a solution containing 37 % w/w of urea and 4,5 % w/w sodium hydroxide in water for twenty minutes. The sample was there after drained and pressed to a consistency of 25-30%. Next stage was fluffing and then drying of the sample in two stages at 70°C and 130°C. The dry sample was then heated to 165°C for 30 minutes. The resulting cellulose carbamate disintegrated in water at 5% suspension washed with water and dried.

Another sample of dissolving cellulose was only washed and dried.

Both samples were examined for microbial activity according to the TAPPI method T 449 om-90. The result of the examination was as follows:

Sample	Heterotrofic number of colonies, mpy/g
Untreated dissolving grade sulfate pulp	13490
Cellulose carbamate	5

From the results it is clear that the cellulose carbamate has a pronounced antibacterial effect in preventing the growth of bacteria in the sample, relative to untreated cellulose.

Example 2

Bleached paper grade sulfate pulp, containing a conventional amount of hemicellulose, was treated with urea and sodium hydroxide in the same way as described in the Example 1. The sample was examined for microbial activity according to the TAPPI method T 449 om-90. The result of the examination was:

Sample	Heterotrofic number of colonies, mpy/g
Bleached paper grade sulfate pulp carbamate	79

From the results, it is clear that the cellulose carbamate has a pronounced antibacterial effect in preventing the growth of bacteria in the sample.

CLAIMS

1. Method of imparting microbistatic properties to a polysaccharide selected from the group consisting of cellulose, hemicellulose, starch, pectine, amylopectine and amylase, by introducing covalently bound carbamate groups into said polysaccharide.

2. The method according to claim 1, wherein the polysaccharide is a regenerated cellulose or microcrystalline cellulose.

3. The method according to any one of the preceding claims, wherein the polysaccharide is cellulose and the carbamate group is formed via the hydroxyl group in the 6-position of the anhydroglucose unit forming the cellulose.

4. The method according to any one of the preceding claims, wherein the degree of substitution is in the range 0.05 to 1, preferably 0.25 to 0.4, more preferably 0.2 – 0.3.

5. The method according to any preceding claim, wherein the polysaccharide is in the form of a fiber, such as in a cellulose, especially paper or viscose pulp, made of wood or other plants, cotton, flax, linters, or in the form of a fibre in wood, such as in veneer or board.

6. The method according to claim 1, comprising the additional steps of isolating a carbamate substituted polysaccharide, and forming it into a fiber, filament, fiber wool, film, membrane, non-woven, textile, fabric, paper, paper product, paper board, insulation fibers, sheets or wools having microbistatic properties.

7. The method according to claim 1, wherein the polysaccharide is cellulose, and the method comprises the additional step of dissolving the cellulose carbamate and forming it, e.g. by extrusion, spinning or casting, into a regenerated cellulose carbamate product, such as a fiber, filament, film or membrane.

8. Method of imparting microbistatic properties to a material, comprising incorporating into said material a microbistatically effective amount of a polysaccharide selected from the group consisting of cellulose, hemicellulose, starch, pectin, amylopectin and amylase, carrying carbamate groups covalently bound to the polysaccharide.

9. Use of a polysaccharide selected from the group consisting of cellulose, regenerated cellulose, hemicellulose, starch, pectin, amylopectin and amylose, carrying carbamate groups covalently bound to monosaccharide units of said polysaccharide, as a microbistatic material.

10. Use according to claim 9 wherein the polysaccharide is in the form of fiber, filament, fiber wool, film, non-woven, textile, fabric, paper, paper products, paper board, wood product, insulation fiber, sheet or wool.

11. Use according to claim 10 wherein the polysaccharide is in the form of cotton fiber or flax fiber.

12. Use according to claim 9 in products and materials intended for healthcare and hygiene, including hospital and medical textiles, fabrics and nonwovens, dressings, sanitary towels and napkins, diapers, or wipes.

13. Wood or timber product, wherein polysaccharides in the fibers of the wood or timber material comprise covalently bound carbamate groups.

14. Use of a wood or timber product according to claim 13 as a rot-resistant material, such as a rot-resistant construction material.

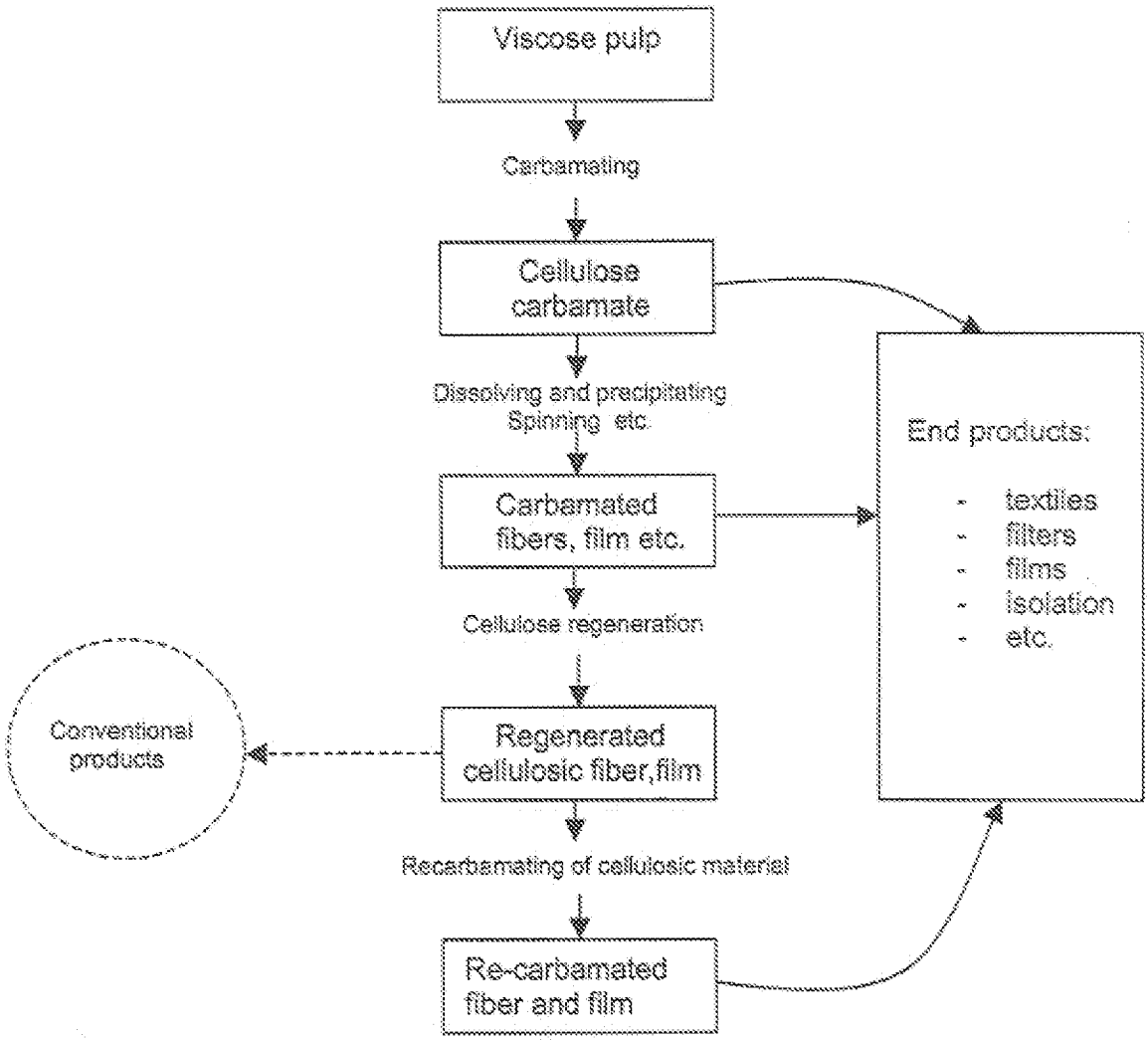
Viscose pulp
Carbamating
Cellulose carbamate
Dissolving and precipitating
Spinning etc.
Carbamated fibers, film etc.
Cellulose regeneration
Regenerated cellulosic fiber,film
Recarbamating of cellulosic material
Re-carbamated fiber and film
Conventional products
End products:
- textiles
- filters
- films
- isolation
- etc.

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2007/050296

A. CLASSIFICATION OF SUBJECT MATTER

IPC: 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: B27K, C08B, D06M, D21H

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

SE,DK,FI,NO classes as above

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

EPO-INTERNAL, WPI DATA, PAJ, COMPENDEX, CHEM.ABS DATA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 0224420 A1 (ATELIER REGIONAL DE CONSERVATION ARC-NU-CLEART), 28 March 2002 (28.03.2002), page 15; page 17; page 26, abstract --	1-14
X	WO 03099873 A1 (ZIMMER AKTIENGESELLSCHAFT), 4 December 2003 (04.12.2003), page 8, claim 1, abstract --	1-12
X	US 20040091977 A1 (TEERI ET AL), 13 May 2004 (13.05.2004), paragraph [0137] --	1-12

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
10 Sept 2007	13 -09- 2007
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Barbro Nilsson/ELY Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2007/050296

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	RATAJSKA MARIA ET AL, "Physical and chemical aspects of biodegradation of natural polymers", Reactive & Functional Polymers 1998, Vol. 38, p. 35-49	1-14
A	WO 2004022846 A2 (LONZA INC.), 18 March 2004 (18.03.2004), page 7, line 5 - line 8	1-14

International patent classification (IPC)

C08B 3/14 (2006.01)
B27K 3/34 (2006.01)
D06M 13/432 (2006.01)
D21H 11/20 (2006.01)
D06M 101/06 (2006.01)

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Paper copies can be ordered at a cost of 50 SEK per copy from PRV InterPat (telephone number 08-782 28 85).

Cited literature, if any, will be enclosed in paper form.

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