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(54) **Process for treating non-dyed textile**

(57) Exhaust process for treating non-dyed textile,
which comprises treating said non-dyed textile with

(a) at least two different enzymes wherein said mixture
of two enzymes (a) comprises of which

(a1) at least one enzyme is selected from cellulases and

(a2) at least one enzyme is selected from pectinases, and

(b) at least one additional active ingredient, selected from
wetting agents, non-ionic surfactants, and defoamers,
over a period of at least 15 minutes.

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Description

[0001] The present invention relates to an exhaust process for treating non-dyed textile, which comprises treating said non-dyed textile with

(a) at least two different enzymes of which

(a1) at least one enzyme is selected from cellulases and
(a2) at least one enzyme is selected from pectinases, and

(b) at least one additional active ingredient, selected from wetting agents, non-ionic surfactants, and defoamers

over a period of at least 15 minutes.

[0002] The present invention further relates to an aqueous mixture useful for carrying out the process of the present invention and also to treated textile obtainable by the process of the present invention.

[0003] Non-dyed textiles, in particular those from cellulose fibers, are usually treated before dyeing to remove dirt, undesired contaminations and soil. Said process is also known as scouring, alkaline extraction, alkaline boiling off, and kier-boiling. In a particular process non-dyed textiles from cellulose fibers, also termed gray good, can be treated in a way that small fibrils of the fibers are removed. Said process is also known as polishing.

[0004] In traditional scouring processes, strong alkaline solutions such as sodium hydroxide solutions were applied. If combined with a simultaneous or subsequent bleaching step, cellulose would then lose a considerable part of its way due to a damaging impact to the fibers, or huge amount of water are necessary to effect sufficient rinsing.

[0005] Recently, it has been suggested to perform scouring with enzymes, a process also being called bioscouring. For bioscouring, preferably cellulase or pectinase enzymes or combinations of cellulase and pectinase enzymes are used in high-temperature short-time processes, see, e.g., WO 99/32708. The process disclosed in WO 99/32708 yields, however, textiles from cellulose fibers that have an unfavorable grip. Also, the fabric strength can be affected negatively.

[0006] Therefore, it is an objective to provide a process which avoids the disadvantages indicated above. Furthermore, it is an objective to provide a formulation which is useful to treat cellulose fibers with.

[0007] The present invention accordingly provides an exhaust process for treating non-dyed textile, which comprises treating said non-dyed textile with

(a) at least two different enzymes, of which

(a1) at least one enzyme is selected from cellulases and
(a2) at least one enzyme is selected from pectinases, and

(b) at least one additional active ingredient, selected from wetting agents, non-ionic surfactants, and defoamers

over a period of at least 15 minutes.

[0008] Textile for the purposes of the present invention refers to linear or two-dimensional structures such as textile fibers including staple fibers, twine, filaments, rovings, spun yarns, lines, strings, cordage, threads, furthermore to knitted goods and fabrics. Textiles can be of natural origin, examples being flax, linen, ramie, hemp or coir or especially cotton, or synthetic, examples being regenerated cellulose such as for example cuprammonium silk, viscose or cellulose acetates such as acetate and triacetate. Blends are also useful, examples being cotton-polyester blends. A textile for the purpose of the present invention may be present as staple fiber, in the form of filaments or as staple fiber yarn or in particular as knitted good or fabric.

[0009] Textile in a preferred embodiment of the present invention refers to knitted goods or fabrics composed of cellulose fiber like, e.g. cotton, or polyester-cotton blends.

[0010] Textile used as starting material in the context of the present invention is non-dyed and preferably non-bleached.

[0011] The process of the present invention is an exhaust process which includes semi-continuous and in particular batch processes.

[0012] In the inventive process, (a) at least two different enzymes are applied, e.g. three, four or preferably two different enzymes, of which

(a1) at least one enzyme will be selected from cellulases
(a2) and at least one enzyme will be selected from pectinases.

[0013] Cellulase (a1) generally refer to enzymes that are able to hydrolyze cellulose, e.g., endo- β -1,4-D-glucan-4-

glucanohydrolase, (EC 3.2.1.4). Preferably, cellulase (a1) in the context of the present invention refers to enzyme systems, preferably to synergistically active enzyme systems comprising at least one (a1-1) endoglucanase, at least one (a1-2) cellobiohydrolase, and at least one (a1-3) β -glucosidase.

[0014] Cellulase (a1) can refer to natural and/or modified enzymes.

[0015] Endoglucanases (a1-1) (endo- β -1,4-D-glucan-4-glucanohydrolase, (EC 3.2.1.4)) are usually inactive towards crystalline cellulose but they are able to hydrolyze amorphous and water-soluble cellulose derivatives, e.g., carboxymethyl cellulose. Endoglucanases (a1-1) usually cause a random breach of β -glucosidic bonds.

[0016] Cellobiohydrolases (a1-2) (1,4- β -D-glucan cellobiohydrolase (EC 3.2.1.91)) usually hydrolyze amorphous cellulose by breaking β -glucosidic bonds in a regular way, starting from the non-reducing terminus of the respective cellulose and cleaving of cellobiose units.

[0017] β -Glucosidases (a1-3) (EC 3.2.1.21) catalyze the cleavage of cellobiose and celooligosaccharides, starting from the non-reducing terminus of the respective cellobiose or celooligosaccharide.

[0018] A description of (a1-1) endoglucanase, (a1-2) cellobiohydrolase, and (a1-3) β -glucosidase is published in, e.g., M.P. Coughlan, "Biotechnologenetec Engineering Reviews", Interscience, Newcastle-upon-Tyne, 1985, Vol. 3, 37-109.

[0019] Pectinase (a2) can refer to natural and/or modified enzymes.

[0020] Pectinase (a2) can catalyze random hydrolysis of 1,4- α -D-galactosiduronic linkages in galacturonans

[0021] Example for (a2) pectinase are poly(1,4- α -D-galacturonide) glycanohydrolase (EC 3.2.1.15).

[0022] Aforementioned enzymes are commercially available.

[0023] Aforementioned enzymes can be stored advantageously in diluted form, e.g. as aqueous solutions, or further diluted with aqueous NaCl solution or reduced carbohydrates such as, e.g. sorbitol.

[0024] In one embodiment of the present reaction, diluting agent such as NaCl or sorbitol need not be removed before starting the inventive process.

[0025] Enzymes such as cellulase (a1) or pectinase (a2) can be incubated before utilized in the inventive process by, e.g. incubating at a temperature of 35°C. It is preferred, though, to neither incubate cellulase (a1) nor pectinase (a2) before utilization in the inventive process.

[0026] In one embodiment of the present invention, at least one cellulase (a1) has an activity in the range from 5 to 20,000 u/mg, preferably in the range from 100 to 12,000 u/mg. The enzyme activity of cellulase (a1) is usually defined as follows: 1 u/mg releases 1 μ mol of glucose from cellulose at 35°C and a pH value of 5 per hour per mg solid, determined after an incubation period of 2 hours.

[0027] In one embodiment of the present invention, at least one pectinase (a2) has an activity in the range from 5 to 20,000 u/mg, preferably in the range from 500 to 10,000 u/mg. The enzyme activity of pectinase (a2) is usually defined as follows: 1 u catalyzes the liberation of 1 μ mol reducing groups from polygalacturonic acid per minute at a pH value of 4.5 and a temperature of 25°C with D-galacturonic acid as reference.

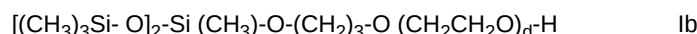
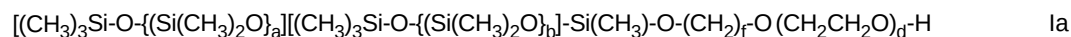
[0028] In one embodiment of the present reaction, the total amount of enzyme applied is in the range of 0.1 to 2% by weight, referring to textile to be treated and independently of the liquor ratio, preferably in the range from 0.5 to 1.5 % by weight and more preferably 0.8 to 1.2 % by weight.

[0029] In the present invention, at least one additional active ingredient (b) is applied, selected from wetting agents, non-ionic surfactants, and defoamers. Preferably, all active ingredients (b) applied in the inventive process are non-ionic.

[0030] Preferred wetting agents include tri-C₁-C₆-alkyl substituted phosphates and phosphonates such as triisobutyl phosphate, triisobutyl phosphonate, particul and mixtures of tri-C₁-C₆-alkyl substituted phosphates and/or phosphonates and their respective mono- and/or disubstituted derivatives.

[0031] Surfactants are preferably selected from non-ionic surfactants. Non-ionic surfactants include, e.g., alcohol ethoxylates, in particular fatty alcohol ethoxylates and oxoalcohol ethoxylates obtained by reacting a C₈-C₄₀ fatty alcohol with, e.g., in the range from 3 to 80 equivalents of ethylene oxide, and ethoxylated mono-, di- and tri- C₄-C₁₂-alkylphenols obtainable by reacting the respective mono-, di- and tri- C₄-C₁₂-alkylphenol with 3 to 50 equivalents of ethylene oxide. Further suitable non-ionic surfactants are alkylpolyglycosides.

[0032] Defoamers include, e.g., polysiloxanes. Particularly preferred defoamers include polysiloxanes (silicones) that can be ethoxylated such as silicones of general formulae Ia and Ib



a, b being integers, identical or preferably different, in the range from zero to 5,

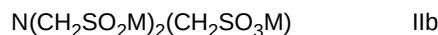
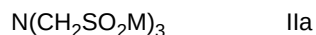
d being an integer in the range from 0 to 50, preferably 0 or 1 to 30 and particularly preferably 3 to 20,

f being an integer in the range from 2 to 10, preferably 3 to 5.

[0033] Other suitable active ingredients (b) can be sequestrants. Examples for sequestrants are being described

below. It is preferred, though, to not apply sequestrants together with enzymes (a1) and (a2).

[0034] Other suitable active ingredients (b) can be reducing agents such as, e.g., Na_2SO_3 , NaHSO_3 , $\text{Na}_2\text{S}_2\text{O}_4$, and $\text{HO-CH}_2\text{-SO}_2\text{Na}$. Further suitable reducing agents are selected from agents of general formula II a, II b and II c



[0035] M being identical or different and selected from hydrogen and alkali metal, in particular sodium.

[0036] In one embodiment of the present invention, in the range from 0.01 to 5% active ingredient (b) or a total of 0.01 to 10% of active ingredients, in each case referring to the amount of textile to be treated, can be applied.

[0037] The process of the present invention is carried out using water that can be but need not be demineralized. It is preferred, though, to use water with a considerable Ca^{2+} and/or Mg^{2+} ion content. It is well possible to use water with a German hardness in the range from 4 to 25° dH.

[0038] In one embodiment of the present invention the inventive process will be performed at a temperature in the range from 45°C to 65°C and preferably in the range from 53 to 58°C.

[0039] In one embodiment of the present invention the inventive process will be performed at a pH value in the range of 5 to 10, preferably in the range from 5.5 to 9, more preferably to 8 and even more preferably in the range from 6.0 to 7.5.

[0040] In one embodiment of the present reaction, the inventive process will be performed over a period of time in the range from 15 minutes to 2 hours, preferably in the range from 20 minutes to 75 minutes.

[0041] In one embodiment of the present invention, the inventive process can be carried out in commonly used textile dyeing machines and apparatuses such as vats, vessels, jet machines, overflows, beam and yarn beam dyeing machines, or jigger machines (jiggers) that repeatedly pull textile through the same bath. Suitable machines are described, e.g., in Ullmann's Encyclopedia of Industrial Chemistry, 6th edition, Wiley VCH, Vol. 36, key word: Textile Dyeing, in particular pages 147 and 149-154.

[0042] In one embodiment of the present invention, the inventive process will be performed as an exhaust process with a long relation bath, e.g. with a liquor ratio in the range from 1:5 to 1:20, preferably from 1:7 to 1:15.

[0043] In a special embodiment of the present reaction, the inventive process is carried out in the presence of

(c) at least one bleaching agent.

[0044] Suitable bleaching agents are, e.g., sodium hypochlorite (chlorine bleach), and peroxides such as hydrogen peroxide.

[0045] In one embodiment of the present reaction, bleaching agent (c) will be added in an amount in the range from 0.01 to 10% by weight, referring to textile to be treated, preferably in an amount in the range from 0.05 to 8 % by weight.

[0046] In one embodiment of the present reaction, bleach stabilizers can be added.

[0047] In one embodiment of the present invention, non-dyed textile treated according to the inventive process can be rinsed with, e.g., water after the treatment with (a) at least two enzymes and (b) at least one additional active ingredient.

[0048] In one embodiment of the present reaction, excess bleaching agent will be deactivated. Suitable means of deactivation are, e.g., adding reducing agents such as any of the reducing agents described above.

[0049] After carrying out the inventive process, treated non-dyed textile preferably from cellulose fiber can be further processed such as, e.g., dyed, washed, and - if desired - customized.

[0050] In one embodiment of the inventive process, cellulase (a1) and pectinase (a2) will be deactivated at the end of the inventive process. Suitable means of deactivation are, e.g., heating, adding anionic reagents such as sequestrants, adding NaOH up to of 10, pH value and adding catalase of any activity, and combinations of the aforementioned means of deactivation.

[0051] Heating may include, e.g., raising the temperature to 90 to 105°C over a period of at least 5 minutes, preferably over a period of at least 10 minutes and more preferably over a period in the range from 15 minutes to 30 minutes.

[0052] Sequestrants include complexing agents that can complex metal cations, in particular alkaline earth metal cations such as Ca^{2+} and Mg^{2+} . Sequestrants can be of inorganic or organic nature.

[0053] Examples for sequestrants are polyphosphates, aluminosilicates, silicates, aminopolyphosphonates, polycarboxylates such as polyacrylic acid and copolymers, in particular random of acrylic acid and maleic acid,

fatty acids, and in particular zeolites,

aminopolycarboxylic acids such as nitrilotriacetic acid (NTA), methylglycinediacetic acid (Trilon M), ethylene diamine tetraacetate (EDTA), ethylene diamine tetramethylene phosphonic acid, diethylene triamine pentaacetic acid (DTPA), and the respective salts of the aforementioned aminopolycarboxylic acids such as the potassium salts and sodium salts,

[0054] Polyglyoxylic acids, polyamidocarboxylic acids, polyaspartic acid, gluconic acid, polycondensation products of aspartic acid with one or more further amino acids, C₄-C₂₅-mono- or -dicarboxylic acids and/or C₄-C₂₅-mono- or -diamines.

[0055] In one embodiment of the present invention, enough sequestrant can be added to lower the hardness of the liquor to 0 to 2 °dH (German hardness)

[0056] Another aspect of the present reaction is an aqueous liquor, comprising

(a1) at least one cellulase,

(a2) at least one pectinase

(b) at least one additional active ingredient, selected from wetting agents, non-ionic surfactants, and sequestrants.

[0057] In one embodiment of the present reaction, inventive aqueous liquors comprise in the range from 0.01 to 2%, preferably 0.025 to 1.5, more preferably 0.03 to 1.2 % by weight (a1)

in the range from 0.01 to 2%, preferably 0.025 to 1.5, more preferably 0.03 to 1.2 % by weight (a2)

in the range of from 0.01 to 5%, preferably 0.025 to 2 by weight (b),

percentages being based on the total weight of the respective inventive liquor.

[0058] The above-described treatment process of the present invention may be carried out for example by applying an inventive aqueous liquor.

[0059] Aqueous liquors according to the present invention are preparable for example by mixing components (a1), (a2) and (b) with water. The order of the addition of components (a1), (a2), (b), and water is not critical.

[0060] Aqueous liquors according to the present invention can have a pH value in the range from 5 to 10, preferably in the range from 5.5 to 9, more preferably to 8 and even more preferably in the range from 6.0 to 7.5.

[0061] The present invention further provides for the use of aqueous liquors according to the present invention for treating a non-dyed textile, preferably from cellulose fibers. The present invention further provides a process for treating a non-dyed textile from cellulose fibers by using aqueous mixtures according to the present invention.

[0062] The present invention further provides a non-dyed textile preferably from cellulose fibers obtainable by the process of the present invention. The inventive textile obtainable by the process of the present invention has excellent further-processing properties, an excellent appearance and has very good and soft touch and an excellent pilling-rate.

[0063] Working examples illustrate the invention.

I. Preparation of textile auxiliaries

I.1 Preparation of a bleach

In a beaker, the following ingredients were mixed:

0.7 g Aminotris(methylenephosphonic acid),

0.3 g 40% aqueous solution of random copolymer of acrylic acid (70%) and maleic acid (30%), fully neutralized with NaOH, pH value 7.9, M_w 70,000 g/mol

5 ml aqueous 30% by weight H₂O₂ solution

1 g (38 Bé) aqueous solution of Na₂CO₃

The mixture so obtained was stirred. Bleach BI-1 was obtained.

II. Treating non-dyed textile with inventive mixture

II.1 Inventive treatment of textile with enzymatic deactivation

In a beaker, the following ingredients were mixed:

0.7 g ethoxylated C₉-oxo alcohol, degree of ethoxylation: 5, as active ingredient (b.1)

0.3 g ethoxylated C₁₆-fatty alcohol, degree of ethoxylation: 10, as active ingredient (b.2), and

1 liter of water (4 ° dH), and the liquor so obtained was stirred at room temperature for 5 minutes. Then a patch (100 g) of non-bleached, non-dyed grey cotton (knitted good), grammage 160 g/m², was added to the liquor and stirring was continued for 10 minutes.

Then, in a beaker, the following enzymes were mixed: 0.5 g pectinase, activity 200 u/mg, and 0.5 g cellulase, activity 3,000 u/mg, and added to the above liquor. An inventive liquor with cotton was obtained. The liquor was heated to 57°C and kept at 57°C for 60 minutes.

Then, BI-1 was added, and the liquor was heated to 90°C within 10 minutes. The liquor was kept at 90° and for 10 minutes and was allowed to cool down to 60°C within 10 minutes. The so-treated cotton was rinsed with water at

60°C for about 15 minutes and then added to 1 l of a fresh liquor, temperature 30°C. The pH value was adjusted to 6 with citric acid. The fresh liquor was then heated to 50°C within 5 minutes. 1 g of catalase, activity 100 u/mg, were added and the treatment continued over a period of 20 minutes.

Inventive cotton C-1 so obtained was then rinsed with water and dried. It had a pilling note of 4 - 5 and a domestic washing note (5 cycles) of 4. It had a wonderful touch even after repeated washing. The loss of fabric strength was negligible, and the loss of weight only about 3%.

II.2 Treatment with non-enzymatic deactivation

In a beaker, the following ingredients were mixed:

0.7 g ethoxylated C₉-oxo alcohol, degree of ethoxylation: 5, as active ingredient (b.1)

0.3 g ethoxylated C₁₆-fatty alcohol, degree of ethoxylation: 10, as active ingredient (b.2), and

1 liter of water (4 ° dH), and the liquor so obtained was stirred at room temperature for 5 minutes. Then a patch (100 g) of non-bleached, non-dyed grey cotton (knitted good), grammage 160 g/m², was added to the liquor and stirring was continued for 10 minutes.

Then, in a beaker, the following enzymes were mixed: 0.5 g pectinase, activity 200 u/mg, and 0.5 g cellulase, activity 3,000 u/mg, and added to the above liquor. An inventive liquor with cotton was obtained. The liquor was heated to 56°C and kept at 56°C for 60 minutes.

Bleach BI-1 were added, and the liquor was heated to 110°C within 10 minutes. The liquor was kept at 110° for 10 minutes and was allowed to cool down to 60°C within 10 minutes. The so-treated cotton was rinsed with water at 60°C for about 15 minutes and then added to 1 l of a fresh liquor, temperature 30°C. The pH value was adjusted to 6 with citric acid. The fresh liquor was kept at 30°C for 10 minutes and then allowed to cool to room temperature.

Inventive cotton C-2 so obtained was then rinsed with water and dried. It had a pilling note of 4 - 5 and a domestic washing note (5 cycles) of 4. It had a wonderful touch even after repeated washing. The loss of fabric strength was negligible, and the loss of weight only about 3%.

Claims

1. Exhaust process for treating non-dyed textile, which comprises treating said non-dyed textile with

(a) at least two different enzymes of which

(a1) at least one enzyme is selected from cellulase and

(a2) at least one enzyme is selected from pectinase, and

(b) at least one additional active ingredient, selected from wetting agents, non-ionic surfactants, and defoamers

over a period of at least 15 minutes.

2. A process of claim 1, wherein said non-dyed textile is made from natural cellulose fibers.

3. A process of any of claims 1 or 2, wherein said process is carried out at a pH value in the range from 5 to 10.

4. A process of any of claims 1 to 3, wherein said process is carried out in the presence of

(c) at least one bleaching agent.

5. A process of any of claims 1 to 4, wherein no further enzymes from types other than pectinase and cellulase are used.

6. A process of any of claims 1 to 5, wherein said process is carried out at temperature in the range from 45 to 65°C.

7. Aqueous liquor, comprising

(a1) at least one cellulase,

(a2) at least one pectinase

(b) at least one additional active ingredient, selected from wetting agents, non-ionic surfactants, and defoamers.

8. An aqueous liquor of claim 7, comprising
in the range from 0.01 to 2% by weight (a1)

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in the range from 0.01 to 2% by weight (a2)
in the range from 0.01 to 5% by weight (b),
percentages being based on the total weight of said aqueous liquor.

5 **9.** A process of any of claims 1 to 6, wherein an aqueous mixture according to any of claims 7 or 8 is applied.

10. Non-dyed textile obtainable by a process according to any of claims 1 to 6 or 9.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 05 00 7261

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 03/069050 A (COGNIS DEUTSCHLAND GMBH & CO. KG; LILLOTTE, WOLFGANG; REICHERT, GERO) 21 August 2003 (2003-08-21)	1-3,5-10	INV. D06M16/00 D06L1/12 D06L3/02 D06L3/11
Y	* page 7; example *	4	
Y	----- WO 03/002810 A (NOVOZYMES NORTH AMERICA, INC) 9 January 2003 (2003-01-09) * page 2, line 21 - page 3, line 17 *	4	
X	----- WO 98/24965 A (NOVO NORDISK BIOCHEM NORTH AMERICA, INC) 11 June 1998 (1998-06-11) * example 8 *	1,2,6,7,9,10	
X,D	----- WO 99/32708 A (NOVO NORDISK BIOCHEM NORTH AMERICA, INC) 1 July 1999 (1999-07-01) * example 3 * * tables 2,3 *	1-4,7,9,10	
A	----- LI Y ET AL: "ENZYMATIC SCOURING OF COTTON: EFFECTS ON STRUCTURE AND PROPERTIES" TEXTILE CHEMIST AND COLORIST, AM. ASSOC. OF TEXTILE CHEMISTS AND COLORISTS. NORT CAROLINA, US, vol. 29, no. 8, August 1997 (1997-08), pages 71-76, XP000722185 ISSN: 0040-490X * tables II,III *	1-10	TECHNICAL FIELDS SEARCHED (IPC) D06M D06L C11D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 6 July 2006	Examiner Fiocco, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 05 00 7261

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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06-07-2006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03069050 A	21-08-2003	BR 0307530 A	21-12-2004
		CN 1630754 A	22-06-2005
		DE 10205929 A1	21-08-2003
		EP 1474562 A1	10-11-2004
		MX PA04007707 A	07-12-2004
		US 2005155634 A1	21-07-2005
WO 03002810 A	09-01-2003	BR 0210718 A	20-07-2004
		CA 2450755 A1	09-01-2003
		CN 1522323 A	18-08-2004
		EP 1425462 A1	09-06-2004
WO 9824965 A	11-06-1998	AU 7626098 A	29-06-1998
		BR 9712489 A	19-10-1999
		CN 1236409 A	24-11-1999
		EP 0943028 A1	22-09-1999
		JP 2001506708 T	22-05-2001
		PL 332634 A1	27-09-1999
		TR 9900715 T2	21-06-1999
WO 9932708 A	01-07-1999	AU 1922199 A	12-07-1999
		BR 9813800 A	03-10-2000
		CA 2315528 A1	01-07-1999
		CN 1282389 A	31-01-2001
		EP 1047827 A1	02-11-2000
		JP 2001527167 T	25-12-2001
		PL 341512 A1	23-04-2001
		TR 200001925 T2	21-11-2000

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 9932708 A [0005] [0005]

Non-patent literature cited in the description

- **M.P. COUGHLAN.** Biotechnologenic Engineering Reviews. Interscience, Newcastle-upon-Tyne, 1985, vol. 3, 37-109 [0018]
- Ullmann's Encyclopedia of Industrial Chemistry. Wiley VCH, vol. 36 [0041]