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(54) **COLOUR TRANSFER-INHIBITING MATERIAL**

(57) The present invention relates to a colour transfer-inhibiting material consisting of a cellulose substrate functionalised with a quaternary ammonium compound, and is characterised in that the substrate consists of cellulose particles or of cellulose nanofibres obtained by electrospinning. Said material presents high colour trans-

fer-inhibiting capability, thus being of use when employed as an additive in the laundering of clothing. It also relates to a procedure for the preparation of said material and to a compound for the laundering of clothing which incorporates the same as a colour protector.

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Description

Field of the art

- 5 **[0001]** The present invention relates to additives for the laundering of clothing, and in particular to a material which is suitable for colour transfer inhibition during laundering.

State of the prior art

- 10 **[0002]** It is well known that coloured articles of clothing may lose some of the colourant substances contained therein during laundering, which are transferred to the water used for this purpose, and may be transferred therefrom to other articles present, which may be of a lighter colour or white, giving rise to an undesired colouring of these last.

[0003] This represents a serious drawback when laundering clothing, both on a domestic and an industrial level.

- 15 **[0004]** A traditional method to prevent this colour transfer between laundered clothing consists of simply laundering the articles of clothing separately in the washing machine, in accordance with their colour. However, performing this separation is irksome, entails difficulties in the optimisation of the number of washes, and an undesired dyeing cannot always be avoided thus. This separation also entails an increase in laundering time, and a greater water and electricity consumption.

- 20 **[0005]** In response to this issue, products such as additives have been developed, typically in the form of towelling cloths or in liquid form, which are added to the washing machine and which easily absorb the possible colours released during laundering, and thus prevent other articles from becoming dyed. Special detergents for coloured clothing have also been developed.

- 25 **[0006]** Various technical solutions which respond to this pattern have been described in the literature. For example, the North American patent US4380453 describes the use of a substrate intended for the application of or impregnation with a colourant-collecting substance, for example a quaternary ammonium compound of the glycidyl ammonium type, such as glycidyltrimethylammonium chloride, or a derivative of trisubstituted 2-hydroxy-3-halopropyl ammonium. Thus treated, the substrate acts to adsorb the colourants which become dissociated from the dyed materials, and thus to prevent the colouring of other materials present in the washer tub. Regarding the substrates, mention is made of a cellulose textile material which may be woven, non-woven, rope, a ball, knitted or otherwise.

- 30 **[0007]** The French patent application FR-A-2761702 also relates to the same problem of colour transfer during the laundering process. Said application proposes the use of finely-divided lignocellulose substances to gather the colourants which are released from the fabrics during laundering. Among said substances, a description is made of the use of micronised steam-treated wood powder and micronised straw. It is also set forth that said substances are not added to the detergent formula, but are added separately to the washer tub, for example, within a bag whose mesh is adapted to the granulometry of the lignocellulose substances in such a way as to prevent the egress of the same into the tub, as it would be difficult to avoid their redeposition on the clothing.

- 35 **[0008]** The European patent application EP-A-1621604 also puts forward the problem of colour transfer during laundering, and proposes a colourant-collecting material comprising a selected woven or non-woven, synthetic or natural, or paper substrate, and an additive comprised of one of the following polymers: proteins, chitin, chitosan, cationic heterocyclic polymers, polyvinylamine, polyethylenimine, acrylic polymers, vinylic polymers, polyamine N-oxide, and blends of the same. The additive is incorporated in the substrate by means of impregnation or pulverisation.

- 40 **[0009]** In international patent application WO-A-2009/071296 an alternative solution is proposed for the prevention of colouration and greying during the laundering of textiles, comprising using a cationised cellulose substrate prepared from low-quality textile material remnants, such as sections of thread and/or cut fibres. The substrate may also be comprised of cationised cellulose fibres. The substrate is preferably used within a receptacle in order to avoid contact with the clothing.

[0010] International patent application WO-A-02/12424 describes the use of a polyester substrate, cationically modified with a polyepoxyamine, in order to reduce colour transfer during laundering.

- 45 **[0011]** The various solutions proposed in the state of the art have contributed to the reduction of the problem of colour transfer during laundering, although they are not totally satisfactory, as when faced with certain colourants and/or types of textiles, they do not completely prevent the accidental dyeing of the articles of clothing.

[0012] Therefore, in spite of the solutions described in the state of the art, there remains a need to provide new materials with a greater efficacy in the prevention of colour transfer during the laundering of textiles.

- 55 **Object of the invention**

[0013] The object of the present invention is a colour transfer-inhibiting material.

[0014] A procedure for the preparation of said material is also part of the object of the invention.

[0015] The use of said material for the prevention of colour transfer during the laundering process is also part of the object of the invention.

[0016] A laundering procedure including the use of said material is also part of the object of the invention.

[0017] A composition comprising said material is also part of the object of the invention.

Brief description of the drawings

[0018]

Figure 1

Figure 1 depicts graphically the results of the test in Example 9, wherein an assessment was performed of the adsorption capability of the colourant *Direct Red* 83 over time by different materials in accordance with the present invention (Examples 3 to 7), in comparison with three commercial products of reference (Reference Examples A, B and C). A solution of colourant at a concentration of 10 ppm was employed, placed in contact with 10 mg of each material to be tested.

The adsorption capability is represented in ordinates, expressed as mg of colourant adsorbed by each gramme of material tested, and the time of contact between the material tested and the colourant solution is represented in abscissas.

Figure 2

Figure 2 depicts graphically the results of the test in Example 10, wherein an assessment was performed of the maximum adsorption capability of the colourant *Direct Red* 83 subsequent to a contact period of 60 minutes by different materials in accordance with the present invention (Examples 3, 5 and 7), in comparison with three commercial products of reference (Reference Examples A, B and C). A solution of colourant at a concentration of 500 ppm was employed, placed in contact with 10 mg of each material to be tested.

The adsorption capability is represented in ordinates, expressed as mg of colourant adsorbed by each gramme of material tested, and each of the materials is represented in abscissas.

Figure 3

Figure 3 depicts graphically the results of a test performed in a Lini-Test in order to measure the inhibition of colour transfer during laundering between a colour donor fabric (*Direct Orange* 39 colourant) and a white cotton cloth, using various products in accordance with the present invention (Examples 3 to 7), in comparison with a detergent without anti-transfer additives and three commercial colour transfer inhibitors (Reference Examples A, B and C), in accordance with the results obtained in Example 11.

The anti-colour transfer efficacy is represented in ordinates, according to a numerical scale from 0 to 5, 5 indicating maximum efficacy. Each of the materials tested is represented in abscissas.

Figure 4

Figure 4 depicts graphically the results of a test performed in a Lini-Test in order to measure the inhibition of colour transfer during laundering between a colour donor fabric (*Direct Red* 83 colourant) and a white cotton cloth, using various products in accordance with the present invention (Examples 3 to 7), in comparison with a detergent without anti-transfer additives and three commercial colour transfer inhibitors (Reference Examples A, B and C), in accordance with the results obtained in Example 11.

The anti-colour transfer efficacy is represented in ordinates, according to a numerical scale from 0 to 5, 5 indicating maximum efficacy. Each of the materials tested is represented in abscissas.

Figure 5

Figure 5 depicts graphically the results of a test performed in a Lini-Test in order to measure the inhibition of colour transfer during laundering between a colour donor fabric (*Direct Black* 22 colourant) and a white cotton cloth, using two products in accordance with the present invention (Examples 3 and 4), in comparison with a detergent without anti-transfer additives and two commercial colour transfer inhibitors (Reference Examples A and C), in accordance with the results obtained in Example 11.

The anti-colour transfer efficacy is represented in ordinates, according to a numerical scale from 0 to 5, 5 indicating maximum efficacy. Each of the materials tested is represented in abscissas.

Figure 6

Figure 6 depicts graphically the results of a test performed in a Lini-Test in order to measure the inhibition of colour transfer during laundering between a colour donor fabric (*Acid Blue* 113 colourant) and a white polyamide cloth, using two products in accordance with the present invention (Examples 3 and 4), in comparison with a detergent without anti-transfer additives and two commercial colour transfer inhibitors (Reference Examples A and C), in accordance with the results obtained in Example 11.

The anti-colour transfer efficacy is represented in ordinates, according to a numerical scale from 0 to 5, 5 indicating maximum efficacy. Each of the materials tested is represented in abscissas.

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known to the expert in the field, such as screening methods, the electric current-sensitive area method (Coulter counter), by laser light dispersion, or by means of the use of electronic microscopy, particularly the Scanning Electron Microscope (SEM) or Transmission Electron Microscope (TEM). In the chapter *Análisis del tamaño de las partículas [Analysis of particle size]* in the book by M.E. Aulton Farmacia. La ciencia del diseño de las formas farmacéuticas [The science of pharmaceutical dosage form design], second edition, Elsevier, Madrid, 2004, Chapter 10, pp 154-167, the most usual parameters and methods used for the definition and measurement of particle sizes are described.

[0028] In accordance with a preferred embodiment of the invention, the particles of cellulose which act as the substrate of the colour transfer-inhibiting material are chosen from the group constituted by microcrystalline cellulose, powdered cellulose, microfibrillated cellulose, nanocrystalline cellulose, and cellulose nanofibres obtained by electrospinning and subsequently pulverised. Preferably, cellulose particles selected from microcrystalline cellulose, microfibrillated cellulose, and cellulose nanofibres obtained by electrospinning and subsequently pulverised. Still more preferably, particles of cellulose chosen from microcrystalline cellulose and microfibrillated cellulose are used.

[0029] In an embodiment of the invention, the particles of cellulose employed as a medium are microcrystalline cellulose.

[0030] Microcrystalline cellulose is a crystalline, powdery substance, obtained by means of the controlled hydrolysis of α -cellulose, whose characteristics are well known and are described, for example, in the book by R.C. Rowe, P.J. Sheskey and P.J. Weller, Handbook of pharmaceutical excipients, fourth edition, Pharmaceutical Press, 2003.

[0031] Microcrystalline cellulose presents an average particle size which usually varies between 20 μm and 300 μm , depending on the different suppliers and procedures used for the obtaining of the same. Preferably, a microcrystalline cellulose with an average particle size of between 40 μm and 150 μm is used, and more preferably, between 50 μm and 120 μm ; still more preferably, between 70 μm and 100 μm .

[0032] Microcrystalline cellulose particles are granular, with an approximately spherical shape, with an aspect ratio usually between approximately 1 and 3.

[0033] Microcrystalline cellulose may be obtained commercially from a number of suppliers, for example from the company FMC Biopolymer, under the generic brand name of AVICEL® or from the company Acros Organics, which distributes microcrystalline cellulose with an average particle size of 50 μm to 90 μm ; the company Sigma-Aldrich also distributes microcrystalline cellulose under the name Cellulose Microcrystalline 310697, with an average particle size of 20 μm ; likewise, the company JRS (J. Rettenmaier & Söhne) markets microcrystalline cellulose under the brand names VIVAPUR® and HEWETEN®, with different particle sizes, for example the so-called HEWETEN® 102, with an average particle size of 90 μm .

[0034] In another embodiment of the invention, the cellulose particles employed as a medium are powdered cellulose.

[0035] Powdered cellulose is a powder obtained by the reduction in size of α -cellulose by mechanical means, and whose characteristics are specified, for example, in the aforementioned book by R.C. Rowe; they present a usual particle size of between 20 μm and 250 μm . Cellulose in powdered form may be obtained commercially, for example, from the company J. Rettenmaier & Söhne, under the generic brand name ARBOCEL®, according to the ARBOCEL® M80 or ARBOCEL® A300 varieties, for example.

[0036] In another embodiment of the invention, the cellulose particles employed as a medium are microfibrillated cellulose.

[0037] Microfibrillated cellulose (MFC) features dimensions which habitually vary between 0.01 μm and 4 μm average thickness, preferably between 0.01 μm and 0.1 μm , and between 1 μm and 100 μm average length. They usually have an aspect ratio of up to 100 (maximum). Alternatively, microfibrillated cellulose may be characterised by the average diameter or equivalent average diameter of the particles, which is usually between 0.05 μm and 15 μm .

[0038] Microfibrillated cellulose is obtained from cellulose, or from microcrystalline cellulose, by a mechanical homogenisation treatment under high pressure, optionally combined with a chemical or enzymatic treatment. Microfibrillated cellulose usually has a thickness of less than 1 μm ; for this reason, it is usually described as nanocellulose, or cellulose nanoparticles.

[0039] Microfibrillated cellulose is well-known to the expert in the field, and may be obtained commercially, in different sizes, from various suppliers, in particular from the company J. Rettenmaier & Söhne, for example, that known under the brand name ARBOCEL® UFC 100, whose fibres have a length of approximately 8 μm .

[0040] In another embodiment of the invention, the cellulose particles employed as a medium are nanocrystalline cellulose.

[0041] Nanocrystalline cellulose is a highly crystalline form of cellulose, presented in the shape of needles, and obtained by means of the hydrolysis of cellulose with a strong acid under controlled conditions, for example, as described in the article by Habibi et al., Cellulose nanocrystals: chemistry, self-assembly, and applications, Chem. Rev., 2010, 110, pp3479-3500. Nanocrystalline cellulose presents usual dimensions of between 3 nm and 5 nm in thickness and up to 200 nm in length.

[0042] In the chapter by Aspler et al., Review of nanocellulosic products and their applications, from the book: Biopolymer nanocomposites. Processing, properties and applications, published by A. Dufresne, S Thomas and L.A. Pothan, 2013, John Wiley & Sons (ISBN 978-1-118-21835-8), chapter 20, pp461-508, the properties of the aforementioned

cellulose microparticles and nanoparticles are described.

[0043] In another embodiment of the invention, the particles of cellulose employed as a medium are prepared by means of the pulverisation of cellulose nanofibres obtained by electrospinning. The particles thus obtained, in the form of fibres or filaments, generally have an average diameter of between 0.1 μm and 1 μm , but preferably between 0.3 μm and 0.8 μm , and an average length of between 2 μm and 100 μm , more preferably between 3 μm and 80 μm , and more preferably still between 4 μm and 50 μm .

[0044] The technique known as "electrospinning" is well-known to the expert in the field, and enables the preparation of nanofibres from a solution of a certain material, usually polymers, by applying an electric current with a sufficiently high voltage, which brings about the expulsion of thin strands from a capillary while the solvent evaporates, thus producing the nanofibres of said material. In order to prepare cellulose nanofibres, for example, a cellulose acetate solution may be used in a solvent or a blend of solvents; for example, a blend of acetone and dimethylacetamide. The cellulose acetate may be obtained commercially; e.g. the Sigma-Aldrich company distributes cellulose acetate with an average molecular weight (M_n) of 30,000.

[0045] Suitable conditions for performing the electrospinning of cellulose acetate are, for example: a voltage of 30 kV, a flowrate of between 3 and 4 mL/h, a distance of 12 cm to the collector and a rotation velocity of 500 rpm.

[0046] Next, the cellulose acetate nanofibres obtained are hydrolysed, usually with a sodium hydroxide solution, in order to deacetylise the product and to obtain cellulose nanofibres. The solid obtained is filtered and dried, preferably at a temperature between 40 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$, and more preferably between 55 $^{\circ}\text{C}$ and 65 $^{\circ}\text{C}$, during a period of usually between 0.5 and 3 hours, and preferably of approximately 1 hour.

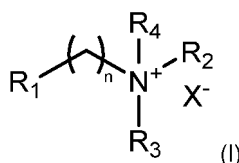
[0047] The nanofibres obtained by means of this electrospinning process are pulverised, for example in an IKA A 11 basic mill, to obtain cellulose particles. The pulverisation stage may be performed on the cellulose acetate nanofibres obtained directly from the electrospinning process and/or subsequent to the hydrolysis stage, once the cellulose has been deacetylated.

[0048] In another embodiment of the invention, the cellulose medium employed in the colour transfer-inhibiting material is cellulose nanofibres, prepared by electrospinning, but unpulverised.

Quaternary ammonium compound

[0049] The colour transfer-inhibiting material consists of a cellulose medium, functionalised by means of a quaternary ammonium compound, characterised in that it has great affinity for colourants or dyes.

[0050] Specifically, the quaternary ammonium compound employed in the material which is the object of the present invention is a product with the formula (I):



where:

n is between 1 and 20;

R_1 is selected between oxiranyl and 2-chloro-1-hydroxyethyl;

R_2 and R_3 are selected independently between C_{1-6} alkyl groups and benzyl;

R_4 is selected between C_{1-20} alkyl groups; and

X is selected from the group formed by Cl, Br, I, tetrafluoroborate, trifluoromethanesulphonate and nitrate.

Definitions

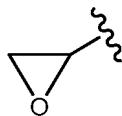
[0051] In the context of the present invention, a C_{1-6} alkyl group refers to a saturated hydrocarbonated group possessing between 1 and 6 carbon atoms, which may be linear or branched, and includes, among others, the methyl, ethyl, n -propyl, isopropyl, sec -butyl, $tert$ -butyl, n -pentyl, 1-methylbutyl or n -hexyl groups.

[0052] Likewise, a C_{1-20} alkyl group refers to a saturated hydrocarbonated group possessing between 1 and 20 carbon atoms, which may be linear or branched, and includes, among others, the methyl, ethyl, n -propyl, isopropyl, sec -butyl, $tert$ -butyl, n -pentyl, 1-methylbutyl, n -hexyl, n -octyl, n -decyl, n -dodecyl, n -tetradecyl, n -hexadecyl or n -octadecyl groups.

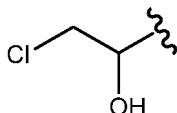
[0053] A $\text{C}_8\text{-C}_{18}$ n -alkyl group refers to a saturated linear hydrocarbonated group possessing between 8 and 18 carbon atoms, and is formed by the n -octyl, n -nonyl, n -decyl, n -undecyl, n -dodecyl, n -tridecyl, n -tetradecyl, n -pentadecyl, n -

hexadecyl, *n*-heptadecyl and *n*-octadecyl groups.

[0054] The oxiranyl group refers to the radical:



[0055] The 2-chloro-hydroxyethyl group refers to the radical:



In turn, the tetrafluoroborate anion refers to the BF_4^- group, the trifluoromethanesulphonate (or triflate) is the $\text{SO}_3(\text{CF}_3)^-$ anion, and the nitrate group corresponds to the NO_3^- anion.

[0056] In a preferred embodiment of the invention, the compound with formula (I) is characterised in that *n* is 1, R_2 , R_3 and R_4 are selected from the group formed by methyl, ethyl, *n*-propyl and isopropyl, and X is selected from the group formed by Cl, Br and I. In a still more preferred embodiment, R_2 , R_3 and R_4 are methyl and X is Cl.

[0057] In a preferred embodiment of the invention, R_1 is oxiranyl.

[0058] According to various particular embodiments of the invention, the quaternary ammonium compound with formula (I) is characterised in that:

- *n* is between 1 and 20, preferably between 1 and 10, more preferably between 1 and 5, and still more preferably, *n* is 1;
- R_1 is selected between oxiranyl and 2-chloro-1-hydroxyethyl; more preferably R_1 is oxiranyl;
- R_2 and R_3 are selected independently between C_{1-6} alkyl groups; more preferably they are selected independently from the group formed by methyl, ethyl, *n*-propyl and isopropyl, and still more preferably, R_2 and R_3 are both methyl;
- R_4 is a C_{1-20} alkyl group; more preferably it is selected between methyl, ethyl, *n*-propyl, isopropyl, or a $\text{C}_8\text{-C}_{18}$ *n*-alkyl; still more preferably, R_4 is methyl;
- X is selected from the group formed by Cl, Br, I, tetrafluoroborate, trifluoromethanesulphonate and nitrate; preferably X is selected between Cl, Br and I; and still more preferably, X is Cl.

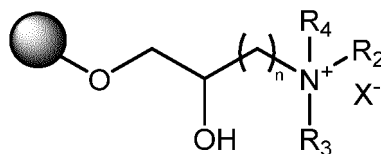
[0059] In a particularly preferred embodiment of the invention, the compound with formula (I) is characterised in that *n* is 1, R_1 is oxiranyl, R_2 , R_3 and R_4 are methyl and X is selected between Cl, Br and I; more preferably, X is Cl. In accordance with this embodiment, the product with formula (I) is glycidyltrimethylammonium chloride (CAS number 3033-77-0), which is commercially available from various suppliers, for example Sigma-Aldrich (Switzerland) or from SKW Quab Chemicals (product Quab® 151).

[0060] In another particularly preferred embodiment of the invention, the compound with formula (I) is characterised in that *n* is 1, R_1 is 2-chloro-1-hydroxyethyl, R_2 , R_3 and R_4 are methyl and X is selected between Cl, Br and I; more preferably, X is Cl. In accordance with this embodiment, the product with formula (I) is 3-Chloro-2-hydroxypropyltrimethyl ammonium chloride (CAS number 3327-22-8), which may be obtained from the Sigma-Aldrich company, or from the company SKW Quab Chemicals (product Quab® 188).

[0061] In another preferred embodiment of the invention, the compound with formula (I) is characterised in that *n* is 1, R_1 is 2-chloro-1-hydroxyethyl, R_2 and R_3 are methyl, R_4 is selected from a $\text{C}_8\text{-C}_{18}$ *n*-alkyl; more preferably, it is selected between *n*-octyl, *n*-dodecyl, *n*-hexadecyl and *n*-octadecyl, and X is selected between Cl, Br and I; more preferably, X is Cl. According to this embodiment, the compound with formula (I) is usually a blend of at least two compounds, with different R_4 , in different proportions. Some of these products are available commercially, via the company SKW Quab Chemicals, for example the commercial product Quab® 342, where R_4 is *n*-dodecyl; the commercial product Quab® 360, a blend of $\text{R}_4 = \text{n-octyl}$ and $\text{R}_4 = \text{n-octadecyl}$; or the commercial product Quab® 426, a blend of $\text{R}_4 = \text{n-dodecyl}$ $\text{R}_4 = \text{n-hexadecyl}$ and $\text{R}_4 = \text{n-octadecyl}$; in all of these R_1 is 2-chloro-1-hydroxyethyl, R_2 and R_3 are methyl, and X is Cl.

Preparation procedure

[0062] In the material of this invention, the cellulose medium is functionalised with the quaternary ammonium product with formula (I). This means that said product binds to the cellulose due to a reaction with the hydroxyl groups present in the same, so as to form functionalised cellulose particles or nanofibres, in accordance with the structure below, where the circle represents the cellulose medium:



[0063] A procedure for the preparation of the material of the present invention also constitutes part of the invention. To prepare said material, that is, to functionalise the cellulose particles, or the cellulose nanofibres obtained by means of electrospinning, a procedure consisting of the following stages, for example, may be employed:

- (a) preparation of an aqueous suspension of the cellulose substrate together with the quaternary ammonium compound with formula (I) at an alkaline pH of between 12 and 14, constantly stirring the combination;
- (b) filtration and subsection of the resulting soaked cellulose material to a temperature of between 60 °C and 110 °C;
- (c) washing of the resulting material with water until neutral pH is reached, and drying at a temperature of between 60 °C and 80 °C.

[0064] In order to obtain the aqueous suspension at an alkaline pH, any alkalisng agent may be used, such as alkaline hydroxides or alkaline carbonates. Preferably, sodium hydroxide should be employed as an alkalisng agent.

[0065] In the suspension prepared initially, in stage (a) the concentration of sodium hydroxide is preferably between 2% and 10%, more preferably between 3% and 5%, and still more preferably between 4% and 4.5%; the concentration of the quaternary ammonium compound with formula (I) is preferably between 2% and 15%, more preferably between 5% and 10%, and still more preferably between 8% and 9%; and the concentration of cellulose is preferably between 1% and 10%, more preferably between 3% and 5%, and still more preferably between 4% and 4.5%; all these percentages are expressed by weight.

[0066] Thus, the molar ratio between the cellulose material / sodium hydroxide / compound with formula (I) is preferably between the following values: 1 / (3-10) / (1.5-5), more preferably between 1 / (4.0-4.5) / (2.0-2.5), and still more preferably said molar ratio is 1 / 4.1 / 2.1.

[0067] In stage (a) the combination is kept stirred at ambient temperature, for example between 10 minutes and 3 hours, preferably between 15 minutes and 1.5 hours, by means of mechanical stirring at, for example, between 600 and 1500 rpm, or by means of magnetic stirring.

[0068] Next, in accordance with stage (b) of the process, the majority of the solution is eliminated by means of filtration, and the soaked cellulose material is placed in an oven at a temperature between 60 °C and 110 °C, preferably at 100 °C, during a period of preferably between 15 minutes and 24 hours.

[0069] In stage (c), the functionalised cellulose obtained is washed repeatedly with water until the pH of the water used in the washing is approximately neutral. The resulting material is then dried at a temperature between 60 °C and 80 °C, during a period of time of preferably between 12 and 24 hours.

[0070] Two alternative procedures may be followed in stage (a). In accordance with a first alternative, initially an aqueous solution is prepared of the alkalisng agent, preferably sodium hydroxide, with the quaternary ammonium compound with formula (I), and the cellulose particles or cellulose nanofibres obtained by means of electrospinning are added to said solution, subsequently stirring the combination during a period of time preferably between 10 minutes and 3 hours, more preferably between 15 minutes and 1.5 hours.

[0071] Alternatively, a blend may first be prepared by adding the cellulose material to an aqueous solution of the alkalisng agent, preferably sodium hydroxide, stirring during a period of time preferably between 5 minutes and 1.5 hours; the quaternary ammonium compound with formula (I) is then added, stirring once again, preferably during between 5 minutes and 1.5 hours.

[0072] In accordance with this procedure, functionalisation of the cellulose particles and the cellulose nanofibres was achieved. The efficacy of the functionalisation was assessed by performing an elemental analysis of the materials prepared, and calculating the percentage of N assimilated; that is, the grammes of N for each 100 g of functionalised cellulose. Values were obtained which oscillated between 0.3 and 0.9 (see Examples 3 to 8) for the cellulose particles or cellulose nanofibres of the material of the present invention. The same elemental analysis test performed on commercial towelling cloths revealed that said products presented comparable functionalisation values, between 0.4 and 0.6 (see Examples 3 to 8).

Use of the material of the invention

[0073] Various applicative tests were performed in order to compare the anti-colour transfer material according to the present invention with other commercial products based on textile cellulose materials of the towelling type.

[0074] Thus, in Examples 9 and 10 an assessment was made of the capability of the material of the invention, compared

with three anti-colour transfer commercial products of the towelling type, to adsorb colourants; it was observed that the product of the invention has greater adsorption capacity, and also enables decolouration more rapidly than the commercial products with which it was compared.

[0075] The results of the tests described in Examples 9 and 10 are depicted graphically in Figure 1, where the colourant adsorption capacity over time is compared, and in Figure 2, where the maximum adsorption capacity over a 60-minute period is compared.

[0076] On the other hand, in Example 11 the efficacy of the material of the invention in the prevention of inter-fabric colour transfer was assessed, according to a test performed in a Lini-Test apparatus which simulated the washing conditions within a washing machine, and in which coloured fabrics and white fabrics were placed, together with a detergent without anti-colour transfer additives and the material of the invention, or three commercial products, as well as said detergent as a reference. Fabrics dyed with different colourants were tested, and white cotton and polyamide fabrics.

[0077] It was observed that the products in accordance with the present invention were surprisingly more effective than the reference products in the prevention of colour transfer to the white fabrics, especially under the conditions of greatest risk of colour transfer; that is, between direct colourants and cotton fabrics, and between acid-type colourants and polyamide. The results of the test for these particularly relevant cases are depicted graphically in Figures 3, 4, 5 and 6, where it may be seen that the material according to the present invention (dark bars) was more effective in the prevention of colour transfer than the reference products (light bars), obtaining results in the proximity of total prevention (5).

[0078] Therefore, the use of the material of the invention for the prevention of colour transfer during the process of laundering clothing forms part of the object of the present invention.

[0079] Thus, the material of the invention is suited to be incorporated as an additive during the laundering of clothing, typically for the automatic wash provided by any commercially available type of washing machine. Said material may be added, for example, at the start of the main wash program, together with the detergent, or alternatively immediately before or after adding the detergent.

[0080] The quantity of the material of the invention added to the washing machine is usually between 1 g and 50 g per each Kg of clothing, although this quantity may be varied according to needs.

[0081] A procedure for the washing of textiles and comprising the use of said material also forms part of the object of the invention.

[0082] Said procedure consists of following the habitual washing process of each washing machine, according to any of the programs available, at any temperature, and with any duration, and is characterised by the action of adding the colour transfer-inhibiting material which is the object of the present invention during the wash; this is preferably added together with the detergent, or alternatively immediately before or after adding the detergent, so that it may operate during the main washing stage, which is when the risk of colour transfer is greatest.

[0083] The product of the invention, in the form of fine, functionalised cellulose particles, acts in the washer tub, adsorbing the colourant which may be released by coloured articles of clothing, and is eliminated simply during rinsing, leaving no residue and without damaging the clothing. It is therefore unnecessary to eliminate the anti-transfer product on completion of the wash, as is the case with other commercial products of the towelling type.

[0084] The material of this invention may be added to any suitable composition for use in the laundering of clothing; for example, to a laundering additive or a detergent compound.

[0085] For example, the material of this invention may be added to a detergent compound, in such a way that a detergent containing a colour transfer-inhibiting product is obtained.

[0086] Suitable detergent compounds for the addition of the colour transfer-inhibiting product in accordance with the present invention may be, without limit, any type of detergent compound which is suited for the laundering of textile articles, and which are well-known by an expert in the field; for example, as described in the book by J.J. García Domínguez, *Tensioactivos y Detergencia*, Editorial Dossat, Madrid, 1986 (ISBN 84-237-0687-7); or the book by G. Jakobi and A. Löhr, *Detergents and Textile Washing. Principles and Practice*. VCH Verlagsgesellschaft, Weinheim, 1987 (ISBN 3-527-26811-1).

[0087] Thus, a combination for the laundering of clothing including the colour transfer-inhibiting material of the present invention also forms part of the object of the invention.

Examples

Preparative example 1: Preparation of cellulose nanofibres by electrospinning

[0088] A solution was prepared, at 22% by weight, of cellulose acetate (Sigma Aldrich 180955, average molecular weight M_n , 30.000) in a blend of the solvents acetone and dimethylacetamide at a proportion of 1:1 by weight.

[0089] The resulting solution was subjected to an electrospinning process in the commercial equipment model NF-

103 of the company MECC Co. Ltd. The conditions employed in said process were as follows: voltage=30kV, flowrate=3-4 mL/h, distance from the collector=12 cm, collector rotation velocity=500 rpm. Cellulose acetate nanofibres were obtained, forming a mesh.

[0090] Next, said nanofibres were deacetylated; to this end they were submerged in 3.5 L of a solution of NaOH 0.3 M for 1 hour, and the deacetylation was monitored by infrared spectroscopy (IR/ATR, *Infrared/Attenuated Total Reflection*); to this end, a commercial apparatus model IRAffinity-1 was used, with a Miracle™ ATR accessory belonging to the company SHIMADZU.

[0091] Next, the nanofibres were filtered, washed with water, and dried overnight at a temperature of 60 °C.

[0092] The cellulose nanofibres thus obtained were characterised using a Scanning Electron Microscope (SEM), specifically using an apparatus model JSM-6010-LV belonging to the company JEOL. The diameter of said fibres was 452 nm ± 130 nm.

Preparative example 2: Preparation of cellulose particles by pulverisation of cellulose nanofibres obtained by means of electrospinning

[0093] Using the cellulose nanofibres prepared in preparative Example 1 as a basis, these were pulverised for 15 minutes in an IKA A 11 basic mill until a fine powder was obtained.

[0094] The size of said particles was characterised using the Scanning Electron Microscope, observing that the particles prepared from the nanofibres had an approximate length of between 4 and 20 µm.

Examples 3 to 8: Functionalised cellulose particles

[0095] The following cellulose particles were functionalised: microcrystalline cellulose (ACROS ORGANICS, Product 38231, particle size 90 µm), microfibrillated cellulose (Arbocel, Product UFC 100, average particle size between 6-12 µm (d₅₀)), and the particles prepared in Preparative Example 2.

[0096] These substrates were functionalised with glycidyltrimethylammonium chloride (Allorachem, product 43831949).

[0097] As starting material, 12 g of the particles obtained in Preparative Example 2 and 100 g of microcrystalline cellulose and microfibrillated cellulose were employed.

[0098] In order to obtain the anti-colour transfer material from said cellulose particles, two alternative procedures, described below, were followed; these being totally analogous, differing only in the order in which the reagents are added. In the case of the cellulose particles from Preparative Example 2, only the first procedure (Procedure 1) was followed, while the microcrystalline cellulose and microfibrillated cellulose were functionalised by means of both methods.

[0099] Procedure 1: An aqueous solution of NaOH and glycidyltrimethylammonium chloride was prepared in a receptacle and the particles of cellulose were added to said solution, in such a way that the proportion by weight of the cellulose particles was 4.2% in all cases, the proportion by weight of NaOH was 4.3%, and the concentration of glycidyltrimethylammonium chloride was 8.3%; this represented a molar cellulose / NaOH / glycidyltrimethylammonium chloride ratio of 1 / 4.1 / 2.1. The combination was mechanically stirred at 1000 rpm for 1 hour at ambient temperature.

[0100] Next, the particles of cellulose were filtered in order to eliminate the majority of the solution, leaving the soaked cellulose material, and immediately said material was arranged in an oven at 100 °C for 30 minutes. Subsequently, the final product was washed repeatedly in water until the water from the washes displayed a neutral pH. The resulting material was dried at 80 °C for 20 hours.

[0101] Procedure 2: An aqueous solution of NaOH was prepared in a receptacle, the particles of cellulose were added and the combination was mechanically stirred at 1000 rpm for 30 minutes at ambient temperature. Next, the glycidyltrimethylammonium chloride was added, and the combination was mechanically stirred at 1000 rpm for another 15 minutes at ambient temperature. As in the previous procedure, the proportion by weight of the cellulose particles in all cases was 4.2%, the proportion by weight of NaOH was 4.3%, and the concentration of glycidyltrimethylammonium chloride was 8.3%; this represented a molar cellulose / NaOH / glycidyltrimethylammonium chloride ratio of 1 / 4.1 / 2.1.

[0102] Next, the particles of cellulose were filtered in order to eliminate the majority of the solution, and from this point onwards, the procedure was continued as in Procedure 1, subsequent to filtration.

[0103] By means of said procedures, particles of cellulose were obtained which were functionalised by the quaternary ammonium compound glycidyltrimethylammonium chloride. In order to verify the degree of functionalisation, an elemental analysis of said products was performed, and the percentage of N contained was calculated; that is, the grammes of N for each 100 g of sample analysed. The results are shown in Table 1.

TABLE 1

Examples	Particles of cellulose employed	Method	Functionalisation (% N)
Example 3	Nanofibres obtained by electrospinning and then pulverised (Preparative example 2)	Proc. 1	0.93
Example 4	Microcrystalline Cellulose	Proc. 1	0.266
Example 5	Microcrystalline Cellulose	Proc. 2	0.460
Example 6	Microfibrillated Cellulose	Proc. 1	0.410
Example 7	Microfibrillated Cellulose	Proc. 2	0.440
Reference Example A	--	--	0.60
Reference Example B	--	--	0.441
Reference Example C	--	--	0.194-2.802*

[0104] The degree of functionalisation was also compared with that of three commercial products (Reference Examples A, B and C), all of these in towelling form, also analysing in this case the percentage of N contained in these products. It was verified that the functionalisation percentage in the case of Reference Examples A and B was comparable to those of the products of the invention. Reference Example C presented widely dispersed results (between 0.194 and 2.802), obtained during 6 repetitions of the test with different samples of the same product; for this reason the average value was not calculated, as the distribution of the quaternary ammonium compound was not consistent in the sample.

Example 9: Test of colourant adsorption capacity of the material of the invention: kinetic trial

[0105] A test was performed in order to assess the adsorption capacity of *Direct Red* 83 colourant (CAS 15418-16-3) by the material which is the object of the present invention, in comparison with commercial products, according to contact time (or kinetic trial).

[0106] To this end, the quantity of colourant adsorbed was determined, expressed as mg of colourant per gramme of material, after different periods of time (1, 5, 10, 15, 30, 45 and 60 minutes).

[0107] 10 mg of the material to be tested was placed in contact with 10 mL of a solution of *Direct Red* 83 colourant at 10 ppm. In order to determine the quantity of colourant adsorbed by the material after different time periods, the absorbance of the solution was measured by UV-visible spectroscopy, and said values were interpolated in a colourant calibration curve.

[0108] The results obtained are shown in Table 2, and are depicted graphically in Figure 1. It may be seen that all the materials tested in accordance with the present invention displayed a higher adsorption capacity than that of the commercial products, and also displayed a greater speed of action.

[0109] The theoretical maximum adsorption capacity of the *Direct Red* 83.1 colourant solution tested is 10 mg of colourant / g of material. When the adsorption capacity observed was equal to the theoretical maximum, the total decolouration of the solution was observed.

TABLE 2

	Adsorption Capacity (mg colourant / g material)						
Material	1 min	5 min	10 min	15 min	30 min	45 min	60 min
Example 3	10.2958	10.5378	10.4124	10.5009	10.0428	10.4465	10.4278
Example 4	2.8210	6.2198	8.4512	9.33354	9.8157	10.4498	10.4430
Example 5	6.0074	8.8080	10.2615	9.9017	10.3811	10.3166	10.0888
Example 6	4.5296	8.0827	9.9589	10.2894	10.3579	10.3731	10.3396
Example 7	8.9479	10.4402	10.3980	10.5415	10.5930	10.5525	10.4449
Ref.Ex.A	6.6590	4.1113	3.4077	3.0607	2.4993	3.5731	2.2704

(continued)

	<i>Adsorption Capacity (mg colourant / g material)</i>						
<i>Material</i>	1 min	5 min	10 min	15 min	30 min	45 min	60 min
<i>Ref.Ex.B</i>	0.7794	3.0809	3.9133	5.6563	6.7562	6.5282	7.6293
<i>Ref.Ex.C</i>	2.7951	3.2671	3.6412	3.7493	4.2507	4.4080	4.5198

[0110] All the materials in accordance with the present invention were able to adsorb the entirety of the colourant, bringing about the total decolouration of the solution. Complete adsorption occurred at 1, 25, 10, 15 and 5 minutes for examples 3, 4, 5, 6 and 7, respectively. However, none of the Reference Examples reached this theoretical maximum value, but yielded inferior adsorption values.

Example 10: Test of colourant adsorption capacity of the material of the invention: trial at 60 minutes

[0111] This test assessed the adsorption capacity of *Direct Red* 83 colourant (CAS 15418-16-3) by the material which is the object of the present invention, in comparison with commercial products, establishing a contact time of 60 minutes.

[0112] A procedure analogous to that described in Example 9 was followed, placing 10 mg of the material to be tested in contact with 10 mL of a solution of *Direct Red* 83 colourant with a concentration of 500 ppm.

[0113] The materials tested were those corresponding to Example 3 (cellulose nanofibre medium prepared by electrospinning and then pulverised), Example 5 (microcrystalline cellulose medium) and Example 7 (microfibrillated cellulose medium) compared with three commercial products in towelling format (Reference Examples A, B and C).

[0114] The results obtained are shown in Table 3, and are depicted graphically in Figure 2.

TABLE 3

<i>Material</i>	<i>Adsorption capacity at 60 minutes (mg colourant/g material)</i>
Example 3	169.85
Example 5	93.18
Example 7	131.90
Reference Example A	80.30
Reference Example B	15.65
Reference Example C	7.01

[0115] It may be seen that all the materials in accordance with the invention displayed a greater colourant adsorption capacity than that of the reference materials.

Example 11: Test of the efficacy of the materials of the invention as anti-colour transfer agents

[0116] A test was performed to assess the efficacy of the materials in accordance with the present invention as anti-colour transfer agents during the laundering of clothing. Specifically, an assessment was made of the efficacy of several products in the prevention of transfer from a donor fabric to an acceptor fabric. This test is that recommended by the A.I.S.E. (*International Association for Soaps, Detergents and Maintenance Products*) and that defined by the EU in Ecolabel for detergents for coloured clothing.

[0117] The colour acceptor fabrics used in the test were:

- 100% cotton with green stripes, in accordance with ISO standard 2267. Dimensions of each specimen: (5.5 x 16) cm.
- Polyamide in accordance with ISO standard 105 F03. Dimensions of each specimen: (6 x 16) cm.

[0118] The acceptor fabrics were pre-washed three times at 60 °C using a cotton program and a detergent without optical whiteners.

[0119] The colour donor fabrics employed in the test were: *Direct Orange* 39 (CAS 1325-54-8), *Direct Red* 83 (CAS 15418-16-3), *Direct Black* 22 (CAS 6473-13-8) and *Acid Blue* 113 (CAS 3351-05-1), all of these commercially available, for example via EMPA or WFK. 0.3 g of each donor fabric was used for the tests.

[0120] For the performance of the test a Lini-Test Atlas apparatus was employed. Said apparatus consists of a water bath in which a device with 8 hermetically closed receptacles rotates at a speed of (40 ± 2) rpm. Each receptacle contained a donor fabric and an acceptor fabric of each type, together with 100 mL of the solution of the product to be tested.

[0121] When the water bath reached a temperature of $30 \text{ }^{\circ}\text{C} (\pm 5 \text{ }^{\circ}\text{C})$, the pre-prepared receptacles were inserted. At this time, the bath continued to be heated at a rate of $2 \text{ }^{\circ}\text{C}/\text{min}$ until reaching $60 \text{ }^{\circ}\text{C}$, and this temperature was maintained constant for 20 minutes. On completion of the testing time, the acceptor fabrics were removed and were rinsed under running water. The fabrics were air-dried, avoiding direct light.

[0122] The fabrics were assessed spectrophotometrically at the commencement and on completion of the test, in order to calculate the quantity of colour accepted (dyeing) by each specimen.

[0123] For this assessment, a Datacolor Spectraflash SF 600 PLUS-CT spectrophotometer was used, with the following reading conditions:

Measuring geometry: d/80

D65/10° observer

420 nm cut-off

[0124] The cotton and polyamide fabrics were assessed independently, as their behaviour is completely different, as were each of the colourants.

[0125] The materials of the invention prepared in Examples 3, 4, 5, 6 and 7 were tested, each at a dose of 0.5 g, to compare them with three types of anti-colour transfer towelling (Reference Examples A, B and C), dosed in accordance with the manufacturer's recommendations by surface area and not by weight.

[0126] The products from Examples 3-7 and the Reference Examples A-C were tested with a simple commercial detergent, without anti-colour transfer additives, which was also tested alone as a reference (Product *Det*).

[0127] The assessment of anti-transfer efficacy was based on a numerical assessment assigned on the basis of a scale of greys according to the UNE EN ISO 105-A04 standard. The values range from 0 (black) to 5 (white). The higher the value, the better the prevention of colour transfer.

[0128] Table 4 summarises the results obtained in the test on the materials in accordance with the present invention (Examples 3 to 7) compared with the commercial products (Reference Examples A, B and C) and with the commercial detergent without any anti-colour transfer additive (*Det*). The transfer of colour from each donor fabric was tested independently for each type of acceptor fabric (cotton and polyamide).

TABLE 4

Donor fabric (acceptor fabric)	Comparisons				Material of the invention				
	Det	A	B	C	3	4	5	6	7
Direct Orange (cotton)	2.3	2.5	2.3	2.5	4.0	4.0	3.5	4.0	3.8
Direct Orange (polyamide)	4.8	5.0	4.8	5.0	4.0	5.0	5.0	5.0	5.0
Direct Red (cotton)	2.5	3.0	2.8	3.0	4.0	4.3	4.3	4.5	4.3
Direct Red (polyamide)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Direct Black (cotton)	3.0	3.0	--	3.0	4.5	4.5	--	--	--
Direct Black (polyamide)	4.5	4.5	--	4.5	5.0	5.0	--	--	--
Acid Blue (cotton)	4.0	4.5	--	4.5	5.0	4.5	--	--	--
Acid Blue (polyamide)	3.5	3.5	--	3.5	5.0	5.0	--	--	--

[0129] It may be observed that for the three direct colourants tested (*Direct Orange*, *Direct Red* and *Direct Black*), the anti-colour transfer results with the product of the invention are considerably superior to those of the compared commercial products in the tests performed with cotton as acceptor fabric. In the case of polyamide, the inhibition of colour transfer is easier for all the products, as direct colourants present greater affinity for cotton than for polyamide; therefore, the results obtained do not permit differentiation of the efficacy of the different products analysed.

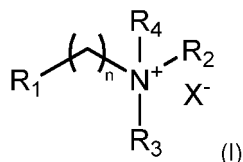
[0130] It may also be observed that for the acid colourant tested (*Acid Blue*) the anti-colour transfer results obtained with the material of the invention on polyamide are clearly superior to those obtained with the reference commercial products. Acid colourants present greater affinity for polyamide; therefore, in the test on cotton, the colour transfer inhibition results were good for all the products, and it was not possible to differentiate their relative efficacy.

[0131] Figures 3, 4, 5 and 6 depict graphically the results from Table 4 for the three direct colourants on cotton, and

for the acid colourant on polyamide. In all of these it is possible to observe the superiority of the material of the invention in comparison with the commercial products assessed.

Claims

1. A colour transfer-inhibiting material consisting of a cellulose substrate functionalised with a quaternary ammonium compound with the formula (I):



where:

n is between 1 and 20:

R₁ is selected between oxiranyl and 2-chloro-1-hydroxyethyl;

R₂ and R₃ are selected independently from C₁₋₆ alkyl groups and benzyl;

R₄ is selected from C₁₋₂₀ alkyl groups; and

X is selected from the group formed by Cl, Br, I, tetrafluoroborate, trifluoromethanesulphonate and nitrate;

and where the cellulose substrate is selected from the group consisting of:

- (a) particles of cellulose and
(b) cellulose nanofibres obtained by means of electrospinning.

2. Material as claimed in claim 1, **characterised in that** the cellulose substrate consists of cellulose particles.
3. Material as claimed in claim 2, **characterised in that** the cellulose particles have an average size of between 0.01 μm and 400 μm .
4. Material as claimed in either of claims 2 or 3, **characterised in that** the cellulose particles are selected from the group formed by microcrystalline cellulose, powdered cellulose, microfibrillated cellulose, nanocrystalline cellulose, and cellulose nanofibres obtained by electrospinning and subsequently pulverised.
5. Material as claimed in claim 4, **characterised in that** the cellulose particles are selected from the group formed by microcrystalline cellulose, microfibrillated cellulose, and cellulose nanofibres obtained by electrospinning and subsequently pulverised.
6. Material as claimed in claim 5, **characterised in that** microcrystalline cellulose with an average particle diameter of between 40 μm and 150 μm is employed.
7. Material as claimed in claim 5, **characterised in that** microfibrillated cellulose with an average particle diameter of between 0.05 μm and 15 μm is employed.
8. Material as claimed in any of claims 1 to 7, **characterised in that** in the compound with formula (I), n is 1, R₂, R₃ and R₄ are selected from the group formed by methyl, ethyl, n-propyl and isopropyl, and X is selected from the group formed by Cl, Br and I.
9. Material as claimed in claim 8, **characterised in that** R₂, R₃ and R₄ are methyl and X is Cl.
10. Material as claimed in claim 9, **characterised in that** the product with formula (I) is glycidyltrimethylammonium chloride.
11. A procedure for the preparation of the colour transfer-inhibiting material as claimed in any of claims 1 to 10, comprising

the following stages:

- 5 a) Preparation of an aqueous suspension of the cellulose substrate together with the quaternary ammonium compound with formula (I) at an alkaline pH between 12 and 14, and constantly stirring the combination;
 b) Filtration and subjection of the resulting soaked cellulose material to a temperature between 60 °C and 110 °C;
 c) Washing the resulting material with water until a neutral pH is reached, and subsequent drying at a temperature between 60 °C and 80 °C.

10 **12.** Use of the material as claimed in any of claims 1 to 10 in order to inhibit colour transfer during the laundering of clothing.

13. A procedure for the laundering of textiles comprising the use of the material as claimed in any of claims 1 to 10.

14. A compound for the laundering of clothing comprising the material as claimed in any of claims 1 to 10.

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INTERNATIONAL SEARCH REPORT

International application No

PCT/ES2015/070018

A. CLASSIFICATION OF SUBJECT MATTER

INV. D06P5/22 D06M13/11 D06M13/463 C11D3/00 C11D3/22
 C11D11/00
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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)

D06P D06M C11D

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 4 380 453 A (CLAIBORNE J LYLE) 19 April 1983 (1983-04-19) cited in the application column 2, line 45 - column 3, line 28 claims	1-14

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No

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