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(54) **Crease-resistant linen slivers and yarns**

(57) The present invention relates to modified linen slivers and yarns characterized by increased crease resistance while maintaining the allomorph I content, the strength and the beautiful appearance of the natural fibers.

In particular, the cross-linked linen slivers and yarns according to the invention have an allomorph I content

measured by solid state ^{13}C NMR of at least 40%, preferably at least 45%, and a solubility in cuproethylendiamine (Cued) 0.5 M lower than 1.4 g/l.

The low solubility in Cued indicates the presence of cross-linking between cellulose chains which is stable to the strong basic conditions of Cued.

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DescriptionField of the invention

[0001] The present invention relates to modified linen fibers, in particular modified linen slivers and yarns, having an allomorph I content of at least 40% and a solubility in cuproethylenediamine (Cued) 0.5 M lower than 1.4 g/l, as well as to a process for their preparation.

Background of the invention

[0002] The main constituent of linen fibers is cellulose I. From a chemical point of view, cellulose is a beta-1,4-linked polymer of D-glucopyranose and it occurs in several distinct crystalline forms known as allomorphs, such as for instance cellulose I, II, III and IV [see A. Sarko in New developments of industrial polysaccharides, page 87, Ed. V. Crescenzi, I.C.M.]. Cellulose allomorphs can be identified by a variety of analytical techniques, such as spectroscopic (IR, Raman or solid state ^{13}C -NMR spectroscopy) and diffractive (electron, neutron or x-ray diffraction) techniques.

[0003] Cellulose I and cellulose II are the commercially dominant allomorphs of cellulose.

[0004] Cellulose I ("native cellulose") is the naturally occurring form in nearly all plants while cellulose II, also known as "hydrate" cellulose, is mainly produced by treatment of cellulose I with strong basic agents such as concentrated aqueous potassium or sodium hydroxides. Such a treatment, known as mercerization, is commonly used for removing the non-cellulosic components, such as lignin and hemicelluloses, from raw materials containing cellulose. It causes the irreversible transition of cellulose I to the thermodynamically more stable cellulose II.

[0005] Fibers made of cellulose I are characterized, in the dry state, by a greater breaking load resistance and, most of all, by a typical brightness and luster that are particularly appreciated in the textile field.

[0006] On the contrary, mercerized cellulose fibers and fabrics are deprived of the beauty and resistance of natural materials.

[0007] Nevertheless natural cellulose I fibers show a significant drawback, that is they lose much of their strength when wet. In fact the hydrogen bonds between hydroxyls of neighboring fibers, which are very strong in a dry state, are considerably weakened by water. This inconvenient can limit the applicability of natural fibers, especially in those fields in which a high breaking resistance, even in a wet state, is required.

[0008] Furthermore another aspect of the same problem is represented by the low wet and dry crease resistance of linen.

[0009] In this case, linen fabrics do not spontaneously recover the initial arrangement after washing and drying and, unavoidably, an additional ironing step is required in order to return to the original shape.

[0010] With the aim to improve wet strength and crease recovery of raw cellulosic materials, and optionally, to confer new additional advantageous properties, some cross-linking processes are performed on natural fibers, in particular etherification reactions.

[0011] The known processes for preparing cellulose ethers are generally carried out in two stages, with the preparation of the "alkali cellulose" taking place first followed by its etherification. Alkali cellulose is, in turn, prepared by mixing cellulose, as homogeneously as possible, with water and alkali metal hydroxides in suitable industrial units. The etherification stage is usually carried out by reacting the alkali cellulose produced in the first stage together with an etherifying agent (United States patent n. 5,493,013 - Hoechst Aktiengesellschaft).

[0012] Etherification cross-linking processes, by linking together hydroxyl groups of different cellulose chains with strong covalent bonds instead of weak hydrogen bonds, can improve several properties of the final products, such as wet strength or crease resistance. Nevertheless, the rather drastic aqueous alkaline conditions can irreversibly alter the appearance and the crystalline structure of cellulosic materials and, therefore, not always, they apply to textiles.

[0013] For instance, a cellulose cross-linking process that provides superabsorbent articles is described in the International patent application WO96/15154 [The Procter & Gamble Company]. However the reported reaction conditions, that confer good absorbing properties to those cellulose materials, would not be usable in the textile field in that they would spoil the look and the resistance of cellulose natural fibers.

[0014] A cellulose cross-linking process carried out in organic solvents which prevents the original compact and rigid structure of native cellulose is described in the International patent application WO89/09643 [Grandics]. However, the patent does not mention the possible application of the process to substrates different from microcrystalline cellulose.

[0015] There are a few examples of cross-linking reactions performed on fabrics and, very often, they use formaldehyde as cross-linking agent. For instance, a cross-linking treatment of cellulose fabrics with formaldehyde is claimed in the United States patent n. 3,663,974 [Toyo Spinning Co Ltd.]. Nevertheless a significant drawback of those derivatives is the scarce stability of the resultant bonds that slowly degrade and release formaldehyde.

[0016] Some different cross-linking reagents for cellulose textiles have been investigated but they generally require high temperatures or aqueous basic conditions that can damage the native structure of cellulose [see, as an example,

the cross-linking process claimed in US 6,036,731 in the name of Ciba SC Holding AG].

[0017] It would be highly desirable to provide modified linen fibers in which the allomorph I content, the strength and the beautiful appearance of the natural fibers are maintained and the crease resistance increased.

Description of the invention

[0018] We have now surprisingly found that it is possible to increase crease resistance while maintaining the allomorph I content, the strength and the beautiful appearance of the natural fibers by a cross-linking process on linen slivers and yarns.

[0019] In particular, the cross-linked linen slivers and yarns according to the invention have an allomorph I content measured by solid state ^{13}C NMR of at least 40%, preferably at least 45%, and a solubility in cuproethylendiamine (Cued) 0.5 M lower than 1.4 g/l.

[0020] The low solubility in Cued indicates the presence of cross-linking between cellulose chains which is stable to the strong basic conditions of Cued. Untreated linen slivers and yarns have a solubility in Cued 0.5 M much higher than 1.4 g/l, since Cued is able to destroy the chain to chain interactions present in linen fibers. If the cross-linking is obtained by formation of an ester bond, the cross-linked cellulose is also dissolved in Cued because of the hydrolysis of the ester bonds under these conditions. However, basic conditions are also applied in standard laundry washings. This is why fibers cross-linked by formation of ester bonds lose their crease-resistance properties in time. On the contrary, the low solubility of the products according to the invention proves that they do not hydrolyze in the presence of bases and, consequently, are likely to have increased crease resistance even after repeated washes.

[0021] Another object of the present invention is a process for preparing modified linen slivers and yarns, by reacting linen slivers and yarns with a cross-linking agent in the presence of a base in a non-aqueous medium

[0022] In a preferred embodiment, the cross-linking reaction is performed by formation of an ether bond between the hydroxyls of cellulose chains.

[0023] Preferably, the number of hydroxyls per glucose unit of cellulose that can be cross-linked ranges from 0.0001 to 3, more preferably from 0.001 to 1; most preferably, from 0.005 to 0.15.

[0024] As far as the position of hydroxyls of cellulose involved in the cross-linking process is concerned, any possible isomer is encompassed within the scope of the present invention.

[0025] In addition, as the present cross-linking reaction is an heterogeneous reaction, the final distribution of cross-linking can be irregular. In particular the extent of cross-linking could be higher on the surface of the fiber and negligible inside. However it is within the scope of the present invention any composition comprising modified linen slivers and yarns, having allomorph I content of at least 40% and a solubility in cuproethylendiamine (Cued) 0.5 M lower than 1.4 g/l, optionally together with not modified linen slivers and yarns.

[0026] Preferred cross-linking reagents suited for the present process include compounds of formula



wherein

[0027] X and X' are reactive groups, i.e. moieties capable of reacting with hydroxyl groups of cellulose, rather than undergoing self-polymerization.

[0028] Such reactive groups include, for example, detachable groups, activated unsaturated groups, formyl, aziridino and epoxy groups.

[0029] Example of detachable groups, also known as leaving groups, are halogens, cyano, triflate, mesylate, tosylate, trifluoroacetate, ammonium, sulphate, p-nitrobenzoate, phosphato, acetoxy, propionyloxy and the like. Halogens are preferred leaving groups. Chloro is particularly preferred.

[0030] Activated unsaturated groups are for example vinyl, halovinyl, styryl, acryloyl or methacryloyl groups.

[0031] Further reactive groups according to the present invention are formyl, comprising masked formyls, aziridino and epoxy groups, such as for instance ethylene or propylene oxides, and the like. Preferred cross-linking reagents contain glycidyl residues.

[0032] A is a bivalent bridging radical comprising from 1 to 100 carbon atoms and, optionally, from 1 to 50 heteroatoms selected among halogens, oxygen, nitrogen, sulfur, boron, phosphorus and silicon.

[0033] With the term "a bivalent bridging radical A" an aliphatic, aromatic or heteroaromatic radical linking X and X' is intended.

[0034] The bivalent radical A includes linear, branched or cyclic aliphatic radicals such as methylene, ethylidene, propylidene, isopropylidene, butylidene, pentylidene, hexylidene, heptylidene, octylidene, nonylidene, decylidene, dodecylidene, tetradecylidene, hexadecylidene, heptadecylidene, octadecylidene, cyclohexylidene and the like. Preferred bivalent aliphatic radicals A are $\text{C}_1\text{-C}_{18}$ aliphatic linear radicals.

[0035] Radical A may optionally include double or triple bonds and from 1 to 50 heteroatoms selected from halogens, oxygen, nitrogen, sulphur, boron, phosphorus and silicon. These heteroatoms can alternate with carbon atoms along the bridging chain or can represent side functional groups linked to the bridging chain. Examples of heterogroups linked to the bridging chain are halogens, amino or hydroxyl groups.

[0036] Examples of preferred heteroatom-containing radicals A are poly(oxyethylene), poly(oxypropylene), poly(vinylchloride), poly(ethyleneimine), poly(propyleneimine), optionally substituted by one or more hydroxyl groups.

[0037] Bivalent radicals A comprising aromatic systems, such as benzene, naphthalene, anthracene, phenantrene, fluorene and the like, or heterocyclic rings such as furan, pyrrole, thiophene, pyrazole, imidazole, triazole, thiazole, isothiazole, oxazole, isoxazole, pyridine, pyrimidine, pyrazine, pyridazine, quinoline, isoquinoline, tetrahydrofuran, dioxane, tetrahydropyran, piperidine, dihydropyran, dihydropyridine, optionally benzo-condensed, and the like are also included in the present invention.

[0038] A preferred group of cross-linking reagents comprises compounds in which A is selected among poly(oxyethylene), poly(oxypropylene), poly(ethyleneimine) or poly(propyleneimine).

[0039] When X and X' are identical, they are preferably selected from 1,2-epoxyethyl, vinyl and chloro.

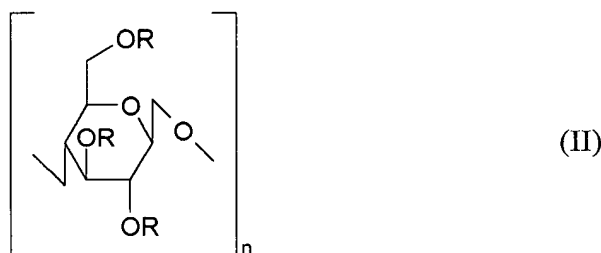
[0040] A preferred group of cross-linking reagents according to the present invention is represented by diglycidyl reagents.

[0041] A particularly preferred reagent is poly(propylene glycol)diglycidyl ether.

[0042] Other preferred cross-linking reagents have X different from X', in particular X is a halogen and X' is 1,2-epoxyethyl.

[0043] Among these reagents epichlorohydrin is particularly preferred.

[0044] By the use of cross-linking agents of formula (I), the obtained cross-linked linen fibers have the following formula (II):



wherein

n is an integer from 100 to 100,000

R is a hydrogen, a group of formula AR" in which A is a bivalent bridging radical comprising from 1 to 100 carbon atoms and, optionally, from 1 to 50 heteroatoms selected from halogens, oxygen, nitrogen, sulphur, boron, phosphorus and silicon, and

R" is an O-cellulose I radical derived from formula II;

provided that AR" groups are present in a AR"/n ratio from 0.0001 to 3.

[0045] The present process is particularly mild and a relevant advantage is that it does not significantly alter the appearance, the strength and the allomorph I content of starting linen slivers and yarns.

[0046] In a preferred embodiment the process for preparing cross-linked linen sliver and yarns comprises the steps of:

- a) applying an cross-linking reagent to linen sliver and yarns and
- b) treating with a base in a non-aqueous medium.

[0047] It is possible to apply the two steps in any order, i.e. first step a) and then step b) or first step b) followed by step a). The linen slivers and yarns, starting materials used in the present invention, contain an average content of water of about 14% and according to the present process, linen slivers and yarns do not generally need any previous dehydrating step, but can be used as such.

[0048] The application of the cross-linking reagent generally comprises the imbibition of the linen slivers and yarns, with the commercial grade reagent, and the removal of the exceeding reagent by centrifugation or squeeze.

[0049] The cross-linking reagent can be used as such or can be previously dissolved in a suitable solvent.

[0050] The imbibition of step a) of the present process is generally performed at a mild temperature and for the time

needed to saturate the starting material.

[0051] Step b) of the process, according to the present invention, comprises the treatment of linen slivers and yarns, previously processed according to step a), with a base in a non-aqueous medium.

[0052] With the term "base" any basic reagent which is able to activate the hydroxyl groups of cellulose towards cross-linking etherification is meant. Suitable bases are both organic and inorganic bases. Examples of organic base are nitrogen-containing compounds such as amines, pyridines and the like. Examples of inorganic bases are alkaline hydroxides and ammonia. Other suitable basic reagents are, for instance, quaternary ammonium hydroxides, alkaline alcoholates or carbanions. They are commercially available or can be prepared by known methods.

[0053] Preferred bases for the process of the present invention are alkaline hydroxides and alcoholates. Among them sodium and potassium hydroxide, sodium methoxide and ethoxide are the most preferred.

[0054] As already stated, step b) of the process, according to the present invention, comprises the treatment of linen slivers and yarns previously processed according to step a), with a base in a non-aqueous medium.

[0055] With the term "non aqueous medium" a polar solvent with a low content of water is intended. The absence of water is important for the present process, however commercially available "pure grade" solvents can successfully be used without any further dehydrating treatment.

[0056] Polar solvents suitable for the present process are able to dissolve or to suspend the base without giving side reactions or irreversibly altering the cellulose crystalline structure.

[0057] However, it is also possible to add a suitable dissolving agent in order to dissolve the selected base, such as for instance a phase transfer catalyst and the like.

[0058] Solvents particularly suited for the present purpose are, for instance, alcohols, such as methanol, ethanol, n-propanol, i-propanol, n-butanol, ter-butanol and the like.

[0059] Methanol, ethanol and i-propanol are preferred. I-propanol is particularly preferred from an industrial point of view.

[0060] The base is usually dissolved in the selected solvent and then the resultant solution is used in step b). The concentration of non-aqueous basic solutions used in step b) of the present invention can vary. Suitable values of concentration are those sufficient to activate hydroxyl groups of cellulose towards cross-linking etherification. Examples of usable ranges of concentration are 1-30% (w/v) for alkaline hydroxides and 0.01-5M for alcoholates.

[0061] In a preferred embodiment, the linen slivers and yarns processed according to step a), are dipped into the non-aqueous basic solution above described, at a temperature and for a time needed to complete the reaction.

[0062] After completion of the cross-linking reaction, the linen slivers and yarns are repeatedly washed, at first with the same solvent selected for step b) and then with water up to neutral pH.

[0063] In another preferred embodiment, the process comprises a step b) of the process, according to the present invention, followed by a step a) of the process, according to the present invention.

[0064] According to the process of the present invention, it is possible to improve the properties of linen slivers and yarns without losing the qualities of native cellulose.

[0065] In particular the modified linen slivers and yarns of the present invention maintain the allomorph I content, the strength and the beautiful appearance of the natural fibers and increase the crease resistance.

[0066] A further advantage of the present process is that it can be performed as a continuous process.

[0067] All these aspects make the present invention particularly attractive from an industrial viewpoint.

[0068] In order to better illustrate the present invention, without limiting it, the following examples are now given.

Evaluation methods

[0069] The allomorph I content of the samples was evaluated by solid state ^{13}C -NMR spectroscopy (CP/MAS and MAS techniques).

[0070] The solubility in cuproethylendiamine 0.5M was measured in the following way: 70 mg of linen sample are dipped in 25 ml of distillate water for 1 hour, then 25 ml of cuproethylendiamine 1M are added with a burette and finally mixed for 4 hours. At the end of this procedure the sample is visually observed. The presence of undissolved linen fibers indicates solubility in Cued 0.5 M lower than 1.4 g/l. Complete dissolution of the sample implies solubility in Cued 0.5 M equal to or higher than 1.4 g/l

[0071] Breaking-load test (g/tex) was performed according to ASTM D 1445/2524.

General procedure 1

[0072] A linen sliver was dipped in the selected cross-linking reagent for a proper time (contact time) and at a suitable temperature. It was then centrifuged for about 10 minutes at 1000 r.p.m. The procedure can be repeated twice (double imbibition).

[0073] The sliver was then dipped into a non-aqueous basic solution, at the reported temperature, and left for the

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indicated contact time. The final product was washed first with the same solvent used for the basic solution and then with water up to neutral pH.

Example 1. Cross-linking reaction with epichlorohydrin

[0074] Experiments 3-4 (table 1) were carried out according to the general procedure 1. Epichlorohydrin (Aldrich) was used as cross-linking reagent. Step a) was performed at 50°C and for a contact time of 30 minutes while step b) at 50°C and for a contact time of 60 minutes.

[0075] Comparative experiment 1 represents the unmodified linen sliver.

[0076] Comparative experiment 2 is a cross-linking reaction according to general procedure 1 but performed in an aqueous base.

Table 1

Exp. n.	<u>Step B</u>			Solubility in Cued 0.5M (g/l)	Resistance g/tex	Allomorph I content (%)
	Base	Solvent	Conc.			
1 (comp.)	-	-	-	≥ 1.4	29	58
2 (comp.)	NaOH	H ₂ O	24%	< 1.4	14	n. d.
3	CH ₃ ONa	CH ₃ OH	0.2M	< 1.4	28	57
4	CH ₃ ONa	CH ₃ OH	1.0M	< 1.4	29	56
n. d.= not detectable						

Example 2. Alkylating reaction with poly(propylene glycol)diglycidyl ether

[0077] The experiments (table 2) were carried out according to general procedure 1.

[0078] Poly(propylene glycol)diglycidyl ether (Aldrich, average molecular weight by number ~380) was used as cross-linking reagent. Step a) was performed at 50°C and for a contact time of 30 minutes while step b) at 50°C and for a contact time of 60 minutes.

[0079] Comparative experiment 1 represents the unmodified linen sliver.

[0080] Comparative experiment 5 is a cross-linking reaction according to general procedure 1 but performed in an aqueous base.

Table 2

Exp. n.	<u>Step B</u>			Solubility in Cued 0.5M (g/l)	Resistance g/tex	Allomorph I content (%)
	Base	Solvent	Conc.			
1(comp.)	-	-	-	≥ 1.4	29	58
5 (comp.)	NaOH	H ₂ O	24%	< 1.4	12	n. d.
6	CH ₃ ONa	CH ₃ OH	0.2M	< 1.4	26	57
7*	CH ₃ ONa	CH ₃ OH	0.2M	< 1.4	25	62
8	CH ₃ ONa	CH ₃ OH	1M	< 1.4	29	57

* double imbibition n. d.= not detectable

General procedure 2

[0081] A linen sliver or yarn is dipped into a non-aqueous basic solution, at the reported temperature, and left for the indicated contact time.

[0082] The sliver or yarn is then dipped in the selected cross-linking reagent for a proper time (contact time) and at a suitable temperature. The final product is washed first with the same solvent used for the basic solution and then with water up to neutral pH.

Example 3. Cross-linking reaction with epichlorohydrin / i-propanol 1/1 (v/v)

[0083] The following experiments were carried out on linen sliver (table 3) and on linen yarn (table 4) according to general procedure 2. Epichlorohydrin (Aldrich) was used as cross-linking reagent. It was previously dissolved in i-propanol achieving a ratio epichlorohydrin / i-propanol 1/1 (v/v). Step a) and step b) were performed at 50°C and for a contact time of 15 minutes. Young module was measured to test crease resistance of the yarn. The values of untreated yarn are reported as comparative experiment 11 in table 4. The sharp reduction of Young module of the cross-linked sample is an indication of an improvement in crease resistance.

Table 3

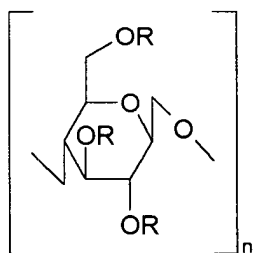
Exp. n.	<u>Step B</u>			Solubility in Cued 0.5M (g/l)	Resistance g/tex	Allomorph I content (%)
	Base	Solvent	Conc.			
9	NaOH	CH ₃ OH	24%	< 1.4	26	59
10	KOH	i-C ₃ H ₇ OH	8%	< 1.4	26	50

Table 4

Exp. n.	<u>Step B</u>			Solubility in Cued 0.5M (g/l)	Young Module (N/tex)	Allomorph I content (%)
	Base	Solvent	Conc.			
11 (comp.)	-	-	-	≥ 1.4	16.1	57
12	KOH	i-C ₃ H ₇ OH	8%	< 1.4	5.4	49

Claims

1. Modified linen slivers and yarns, having an allomorph I content measured by solid state ¹³C NMR of at least 40% and **characterized by** a solubility in cuproethyldiamine (Cued) 0.5 M lower than 1.4 g/l.
2. Modified linen sliver and yarns according to claim 1 wherein the linen are cross-linked by formation of an ether bond between the hydroxyls groups of cellulose chains.
3. Modified linen sliver and yarns according to claim 1 wherein the allomorph I content is at least 45%.
4. Modified linen sliver and yarns according to claims 1-3 having the following formula:



(II)

wherein

n is an integer from 100 to 100,000

R is a hydrogen or a group of formula AR" in which A is a bivalent bridging radical comprising from 1 to 100 carbon atoms and, optionally, from 1 to 50 heteroatoms selected among halogens, oxygen, nitrogen, sulfur, boron, phosphorus and silicon, and R" is an O-cellulose I radical derived from formula I; provided that

AR" groups are present in a AR"/n ratio from 0.0001 to 3.

5. Modified linen sliver and yarns according to claim 4 wherein A is a C₁-C₁₈ linear aliphatic radical, optionally substituted by one or more hydroxyl groups.

6. Modified linen sliver and yarns according to claim 4 wherein A is poly(oxyethylene), poly(oxypropylene), poly(ethyleneimine) and poly(propyleneimine), optionally substituted by one or more hydroxyl groups.

7. A process for preparing modified linen slivers and yarns comprising the steps of:

- a) applying a cross-linking reagent to linen slivers and yarns and
- b) treating with a base in a non-aqueous medium.

8. A process according to claim 7 wherein step a) is performed before step b).

9. A process according to claim 7 wherein step b) is performed before step a).

10. A process according to claims 7-9 wherein the cross-linking reagent is a compound of formula



X and X' are reactive groups, i.e. moieties capable of reacting with hydroxyl groups of cellulose, rather than undergoing self-polymerization; A is a bivalent bridging radical comprising from 1 to 100 carbon atoms and, optionally, from 1 to 50 heteroatoms selected from halogens, oxygen, nitrogen, sulfur, boron, phosphorus and silicon



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EUROPEAN SEARCH REPORT

Application Number
EP 01 13 0848

DOCUMENTS CONSIDERED TO BE RELEVANT			
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The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7) D06M C08B
Place of search THE HAGUE		Date of completion of the search 30 August 2002	Examiner Lensen, H
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			

EPO FORM 1503 03 82 (P04001)

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

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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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