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(54) COATED TEXTILE OBTAINABLE BY A DIPPING PROCESS

(57) The present invention pertains to a method of coating a textile with a polyurethane dispersion by a dipping process, a coated textile obtained by the method and the use of the coated textile as part of a clothing or a shoe.

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Description

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[0001] The present invention pertains to a method of coating a textile by a dipping process, a coated textile obtained by the method and the use of the coated textile as part of a clothing or a shoe.

[0002] In the recent years the use of waterproof clothing and shoes became increasingly popular. Commonly waterproof and breathable shoes based on technologies such as GoreTex® are manufactured from flat "2D" materials. Therefore, GoreTex® "2D laminate" is cut into the right shape, and then sewn to the 3D inner shoe. Subsequently, the seam needs to be sealed with a waterproof tape.

[0003] Since the seam can lead to an uncomfortable wear comfort or even to injuries of the foot of the wearer, there is a need for different solutions to obtain water proof textile, in particular inner shoes. An option could be to coat a single textile before bringing it into the desired shape. However, in case of a shoe the waterproof coating has to be between the inner and the outer shoe. An inner shoe coated on the inside would as well not be comfortable for the wearer. Therefore, the aim is to essentially coat only one side of a textile. However, commonly used textiles are hydrophilic and soak up water based dispersions, which leads to an impregnation of both sides.

[0004] Thus, the object is to provide a method, which essentially coats only one side of a textile. Additionally, to be employed in clothing or shoes, the coating needs to be breathable, flexible and stable toward hydrolysis.

[0005] The inventors of the present invention have surprisingly found that this object can be solved by the specific method of coating a textile by a dipping process according to the present invention, a coated textile obtained by the method and the use of the coated textile of the present invention as part of a clothing or a shoe. Surprisingly, the method of the present invention provides lower manufacturing costs and an easier automatization due to the avoidance of the additional sealing step of the seam.

[0006] Therefore, in a first aspect the present invention pertains to a method of coating a textile, comprising the steps of:

i) providing a textile;

ii)

- a) dipping at least one surface of the textile into an aqueous solution comprising 1 to 40 wt.-% of at least one inorganic salt; or
- b) spraying an aqueous solution comprising 0.2 to 85 wt.-% of at least one inorganic salt onto at least one surface of the textile; or
- c) spraying at least one inorganic salt as a powder onto at least one surface of the textile, preferably a preheated textile;
- iii) removing the textile of step ii) from the aqueous solution if step ii) a) is performed and optionally allowing the excess aqueous solution to flow off and/or optionally drying the textile; or
- optionally allowing the excess aqueous solution to flow off and/or optionally drying the textile if step ii) b) is performed; iv) dipping the surface(s) which was (were) brought into contact with the at least one inorganic salt of the textile of step ii) c) or iii) into a polyurethane based dispersion;
- v) removing the textile of step iv) from the dispersion and optionally allowing the excess dispersion to flow off and/or drying the textile obtained in step iv) thereby obtaining a coated textile.

[0007] Furthermore, in a second aspect the present invention relates to a coated textile, preferably a coated jacket or inner shoe, which is obtainable by the method according to the present invention.

[0008] Moreover, the present invention in a third aspect pertains to the use of the coated textile of the present invention as part of a clothing, preferably a jacket or a shoe, preferably an inner shoe.

[0009] "At least one", as used herein, means one or more, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9 or more of the referenced species. Similarly, "one or more", as used herein, relates to at least one and comprises 1, 2, 3, 4, 5, 6, 7, 8, 9 or more. In connection with a given species, the term does not relate to the total number of molecules, but rather to the type of species. "At least one inorganic salt", for example, thus means that one type of inorganic salt or two or more different types of inorganic salts may be present. In connected with amounts, the term relates to the total amount of the referenced species. In case of the inorganic salt, for example, this means that the given amount is the total amount of all inorganic salts in the aqueous solution.

[0010] "About", as used herein, relates to \pm 20 %, preferably \pm 10 % of the numerical value to which it refers. "About 200" thus relates to 200 \pm 40, preferably 200 \pm 20.

⁵ [0011] All percentages given herein in relation to the compositions or formulations relate to weight % relative to the total weight of the respective composition or formula, if not explicitly stated otherwise.

[0012] In the present specification, the terms "a" and "an" and "at least one" are the same as the term "one or more" and are used interchangeably.

[0013] The term "essentially free" within the context of this invention is to be interpreted as the respective compound is contained in the composition in an amount of less than 5 wt.-%, 4 wt.-%, 3 wt.-%, 2 wt.-%, 1.5 wt.-%, 1 wt.-%, 0.75 wt.-%, 0.5 wt.-%, 0.25 wt.-%, or 0.1 wt.-%, based on the total weight of the composition, wherein the amounts are respectively more preferred in descending order. For example, 4 wt.-% is more preferred than 5 wt.-% and 3 wt.-% is more preferred than 4 wt.-%.

[0014] If reference is made herein to a molecular weight, this reference refers to the average number molecular weight M_n , if not explicitly stated otherwise. The number average molecular weight M_n can be calculated based on end group analysis via OH numbers according to DIN 53240-1:2013-06, in the present invention referred to as OH group titration as well, or can be determined by gel permeation chromatography according to DIN 55672-1:2007-08 with THF as the eluent. If not stated otherwise, all given molecular weights are those determined by gel permeation chromatography. The weight average molecular weight M_w can be determined by GPC, as described for M_n .

[0015] The NCO value is measured according to DIN EN ISO 11909:2007-05 if not explicitly stated otherwise.

[0016] The present invention in particular pertains to:

- 1. Method of coating a textile, comprising or consisting of the steps of:
 - i) providing a textile;

ii)

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- a) dipping at least one surface, preferably only one surface, of the textile into an aqueous solution comprising 0.2 to 85 wt.-%, preferably 1 to 40 wt.-%, more preferably 2 to 20 wt.-%, of at least one inorganic salt; or
- b) spraying an aqueous solution comprising 0.2 to 85 wt.-%, preferably 1 to 40 wt.-%, more preferably 2 to 20 wt.-%, of at least one inorganic salt onto at least one surface of the textile; or
- c) spraying at least one inorganic salt as a powder onto at least one surface of the textile, preferably a preheated textile;

iii) removing the textile of step ii) from the aqueous solution if step ii) a) is performed and optionally allowing the excess aqueous solution to flow off and/or optionally drying the textile; or

optionally allowing the excess aqueous solution to flow off and/or optionally drying the textile if step ii) b) is performed;

iv) dipping the surface(s) which was (were) brought into contact with the at least one inorganic salt of the textile of step ii) c) or iii) into a polyurethane based dispersion;

- v) removing the textile of step iv) from the dispersion and optionally allowing the excess dispersion to flow off and/or drying the textile obtained in step iv) thereby obtaining a coated textile.
- 2. The method according to item 1, wherein the textile is a woven, knitted or nonwoven textile, preferably based on polyamide fibers, polyester fibers, polyurethane fibers, in particular polyurethane elastic fibers, natural fibers, like cotton; preferably the textile is based on polyamide fibers, polyester fibers or polyurethane fibers and/or
- the textile is a clothing or an inner shoe, more preferably an inner shoe and/or the part of the textile, upon which the coating contains no seam.
- 3. The method according to item 1 or 2, wherein the inorganic salt of the aqueous solution contains multivalent cations, preferably selected from Ca^2+ , Mg^{2+} , Sr^{2+} , Al^{3+} , Fe^{2+} , Fe^{3+} or mixtures thereof, preferably Ca^{2+} , Mg^{2+} or mixtures thereof, more preferably Ca^{2+} and/or

anions selected from NO₃²⁻, F⁻, Cl⁻, SO₄³⁻, CO₃²⁻, PO₄³⁻ or mixtures thereof, preferably NO₃²⁻, F⁻, Cl⁻, SO₄³⁻ or mixtures thereof, more preferably NO₃²⁻.

- 4. The method according to any of the preceding items, wherein the drying step of step iii) is active or passive drying, preferably an active drying with a dryer, more preferably selected from ovens convection ovens, radiation sources like IR, NIR and microwaves, by reduction of ambient pressure or vacuum, air flow as well as combination thereof and/or the drying in step iii) is performed until the textile obtained after step ii) is dry.
- 55 5. The method according to any of the preceding items, wherein the polyurethane based dispersion comprises polymers with a weight average molecular weight of 10,000 to 500,000 g/mol, preferably 20,000 to 100,000 g/mol, more preferably 40,000 to 50,000 g/mol.

- 6. The method according to any of the preceding items, wherein the polyurethane based dispersion comprises polymers with a number average molecular weight of 1,000 to 25,000 g/mol, preferably 1,500 to 20,000 g/mol, more preferably 2,000 to 15,000 g/mol.
- 7. The method according to any of the preceding items, wherein the polyurethane based dispersion comprises polymers with a polydispersity of 1.0 to 50.0, preferably 2.5 to 40.0, more preferably 5.0 to 30.0.
 - 8. The method according to any of the preceding items, wherein the dispersion is a polyurethane based dispersion, preferably in which the polyurethane polymers are based on more than 20 wt.-% polyol, preferably more than 40 wt.-% polyol.
 - 9. The method according to any of the preceding items, wherein the drying step of step v) is active or passive drying, preferably an active drying with a dryer and/or
- the drying in step v) is performed until the textile obtained after step iv) is dry.
 - 10. The method according to any of the preceding items, wherein the coating of the coated textile has a coating weight of 5.0 to 1,000 g/m², preferably 100 to 600 g/m², more preferably 150 to 450 g/m².
- 20 11. The method according to any of the preceding items, wherein the coated textile is completely or partly coated, preferably completely.
 - 12. The method according to any of the preceding items, wherein the coated textile has a water column > 1 m, preferably > 3 m, more preferably > 5m, preferably measured according to ISO 811:2018.
 - 13. The method according to any of the preceding items, wherein the coated textile has a breathability of more than 50 g/dm², preferably more than 100 g/dm², more preferably more than 150 g/dm², even more preferably more than 250 g/dm², preferably measured according to DIN 53122-1:2001-08
- 30 14. A coated textile, preferably a coated jacket or inner shoe, which is obtainable by the method according to any of items 1 to 13.
 - 15. Use of the coated textile of item 14 as part of a clothing, preferably a jacket or a shoe, preferably an inner shoe.
- In one embodiment, the method of coating a textile, comprises or consists of the steps of:
 - i) providing a textile;

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- ii) dipping at least one surface, preferably only one surface, of the textile into an aqueous solution comprising 0.2 to 85 wt.-%, preferably 1 to 40 wt.-%, more preferably 2 to 20 wt.-%, of at least one inorganic salt, whereby the textile is preferably a preheated textile;
- iii) removing the textile of step ii) from the aqueous solution and optionally allowing the excess aqueous solution to flow off and/or drying the textile;
- iv) dipping the surface(s) which was (were) brought into contact with the at least one inorganic salt of the textile of step iii) into a polyurethane based dispersion;
- v) removing the textile of step iv) from the dispersion and optionally allowing the excess dispersion to flow off and/or drying the textile obtained in step iv) thereby obtaining a coated textile.
 - [0018] In another embodiment, the method of coating a textile, comprises or consists of the steps of:
- i) providing a textile;
 - ii) spraying an aqueous solution comprising 0.2 to 85 wt.-%, preferably 1 to 40 wt.-%, more preferably 2 to 20 wt.-%, of at least one inorganic salt onto at least one, preferably only one, surface of the textile, preferably a preheated textile:
 - iii) optionally allowing the excess aqueous solution of step ii) to flow off and/or drying the textile;
- iv) dipping the surface(s) which was (were) brought into contact with the at least one inorganic salt of the textile of step iii) into a polyurethane based dispersion;
 - v) removing the textile of step iv) from the dispersion and optionally allowing the excess dispersion to flow off and/or drying the textile obtained in step iv) thereby obtaining a coated textile.

[0019] In another embodiment, the method of coating a textile, comprises or consists of the steps of:

i) providing a textile;

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- ii) spraying at least one inorganic salt as a powder onto at least one, preferably only one, surface of the textile, preferably a preheated textile;
- iv) dipping the surface(s) which was (were) brought into contact with the at least one inorganic salt of the textile of step ii) into a polyurethane based dispersion;
- v) removing the textile of step iv) from the dispersion and optionally allowing the excess dispersion to flow off and/or drying the textile obtained in step iv) thereby obtaining a coated textile.

[0020] If the textile is treated in step ii) by spraying at least one inorganic salt as a powder onto at least one surface of the textile, preferably a preheated textile, it is not necessary to remove the textile from an aqueous solution and/or to allow the excess aqueous solution to flow off and to dry the textile. By employing this embodiment, a less time consuming and more cost efficient method can be provided.

- **[0021]** The coating in the present invention is formed by a polyurethane based dispersion.
- [0022] In a preferred embodiment the dispersion is a polyurethane based dispersion.
- [0023] As coating dispersions any known polyurethane based dispersions are suitable.
- **[0024]** Polyurethane based dispersions are in general based on at least one NCO-containing compound and at least one compound which can react with the NCO-group, preferably an OH-containing compound. Furthermore, the dispersion can contain at least one additive.
- **[0025]** The pH of the polyurethane dispersions is preferably less than 9.0, more preferably less than 8.5, particularly preferably less than 8.0, most preferably 6.0 to 8.0.
- **[0026]** The at least one NCO-containing compound is preferably a polyisocyanate or a polyurethane-prepolymer or a mixture of both.
- [0027] The polyisocyanates may be the aromatic, araliphatic, aliphatic or cycloaliphatic polyisocyanates having an NCO functionality of 2 or more which are known per se to the person skilled in the art.
 - **[0028]** Examples of suitable polyisocyanates are hydrogenated methylene diphenyl isocyanate MDI (HMDI or H12MDI), saturated MDI (SMDI), or reduced MDI (RMDI), 1,4-butylene diisocyanate, 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 2,2,4- and/or 2,4,4-trimethylhexamethylene diisocyanate, 1,4-cyclohexylene diisocyanate, 1,4-phenylene diisocyanate, 2,2'- and/or 2,6-tolylene diisocyanate, 1,5-naphthylene diisocyanate, 2,2'- and/or 2,4'-and/or 4,4'-diphenylmethane diisocyanate, 1,3- and/or 1,4-bis(2-isocyanatoprop-2-yl)benzene (TMXDI), 1,3-bis(isocyanatomethyl)benzene (XDI), and alkyl 2,6-diisocyanatohexanoates (lysine diisocyanates) containing C1-C8-alkyl groups. Besides the above-mentioned polyisocyanates, it is also possible to employ proportionately modified diisocyanates having a uretdione, isocyanurate, urethane, allophanate, biuret, iminooxadiazinedione and/or oxadiazinetrione structure and unmodified polyisocyanates containing more than 2 NCO groups per molecule, for example 4-isocyanatomethyloctane 1,8-diisocyanate (nonane triisocyanate) or triphenylmethane 4,4',4"-triisocyanate.

[0029] Preferably polyisocyanates or polyisocyanate mixtures of the above-mentioned type contain exclusively aliphatically and/or cycloaliphatically bonded isocyanate groups and have an average NCO functionality of the mixture of 2 to 4, preferably 2 to 2.6 and particularly preferred 2 to 2.4.

- **[0030]** Particularly, preferred polyurethane based dispersions of the present invention comprise a hydrophilic polycarbodiimide. In certain embodiments, the hydrophilic polycarbodiimide comprises an aqueous aliphatic polycarbodiimide dispersion. As will be appreciated, and as used herein, the term polycarbodiimide refers to a compound containing two or more carbodiimide units, that is, units of the structure: -N=C=N-.
- [0031] Polycarbodiimides can be prepared by condensation reaction of a polyisocyanate in the presence of a suitable catalyst to form a polycarbodiimide having terminal isocyanate groups. The polycarbodiimides used in certain embodiments of the dispersions are aliphatic. As a result, they are derived from one or more aliphatic polyisocyanates. Suitable aliphatic polyisocyanates include, for example, 4,4'-dicyclohexylmethane diisocyanate (also known as PICM, hydrogenated methylene diphenyl isocyanate MDI (HMDI or H12MDI), saturated MDI (SMDI), or reduced MDI (RMDI), 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 1,4-cyclohexane diisocyanate (CIIDI), 1,3-bis(isocyanatomethyl)cyclohexane (H-XDI), m-tetramethylxylene diisocyanate (m-TMXDI), and mixtures thereof.
- [0032] The preferred polycarbodiimide based dispersion suitable for use in the present invention can be modified to be hydrophilic. This can be accomplished by reacting the terminal isocyanate groups with one or more hydrophilic active-hydrogen compounds, such as monothiols, monoamines, and/or mono alcohols, such that the resulting polycarbodiimide contains substantially no remaining isocyanate functionality. In certain embodiments, the hydrophilic active-hydrogen compound comprises one or more monoalcohols. Examples of monoalcohols that are suitable for use in preparing the aqueous aliphatic polycarbodiimide dispersion include, without limitation, aliphatic monoalcohols having 1 to 18 carbon atoms, specific examples of which include, but are not limited to, ethanol, n-butanol, 2-ethylhexanol, 1-octanol, 1-dodecanol, 1-hexadecanol, as well as poly(alkylene oxide) monoalkyl ethers, such as, for example, poly(ethylene oxide)

monomethyl ethers. As will be appreciated, two or more of the foregoing monoalcohols can be used.

[0033] The solids content of the aqueous polycarbodiimide based dispersion is, in certain embodiments, at least 25% by weight, such as at least 30 or, in some cases, at least 35% by weight and/or no more than 65% by weight, such as no more than 50 or, in some cases, no more than 45% by weight, based on the total weight of the dispersion.

[0034] One example of an aqueous aliphatic polycarbodiimide dispersion that is suitable for use in the coating compositions of the present invention is Desmodur® XP 2802, a waterborne dispersion of a hydrophilically modified, aliphatic polycarbodiimide, 40% by weight resin solids in water from Covestro AG, Leverkusen, Germany.

[0035] The term polyol component comprises polyester polyols as well.

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[0036] It is possible that this polyester polyol is the sole polyol of the polyol component.

[0037] Examples for aliphatic dicarboxylic acids include tetrahydrophthalic acid, hexahydrophthalic acid, cyclohexanedicarboxylic acid, adipic acid, azelaic acid, sebacic acid, glutaric acid, maleic acid, fumaric acid, itaconic acid, malonic acid, suberic acid, 2-methylsuccinic acid, 3,3-diethylglutaric acid and/or 2,2-dimethylsuccinic acid. The corresponding anhydrides can also be used as acid source. The aliphatic dicarboxylic acids may be used in the form of one or more of their corresponding diester derivatives, particularly their dimethanol or diethanol ester derivatives.

[0038] Examples for linear aliphatic diols include 1,2-ethanediol (i.e., ethylene glycol), 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol and 1,3-butanediol. Preferably, linear aliphatic diols are selected from the group consisting of 1,3- and 1,4-butanediol, 1,6-hexanediol and/or 1,8-octanediol.

[0039] Examples for branched aliphatic diols include neopentyl glycol, 1,2-propanediol, 2-methyl-1,2-propanediol, 2-methyl-1,3-propanediol, 1,2-butanediol, meso-2,3-butanediol, 2,3-dimethyl-2,3-butanediol (pinacol), 1,2-pentanediol, 2,3-pentanediol, 2,4-pentanediol, 1,4-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 1,3-hexanediol, 1,4-hexandiol, 1,5-hexanediol, 2,5-hexanediol, 2,5-hexanediol, 1,3-cyclobutanediol, 2,2,4,4-tetramethylcyclobutanediol, 1,2-cyclopentanediol, 1,3-cyclopentanediol, 1,3-cyclopentanediol, 1,3-cyclohexanediol, 1,4-cyclohexanediol and 1,4-dimethylolcyclohexane. Preferably, branched aliphatic diols are selected from the group consisting of neopentyl glycol, 2-methyl-1,3-propanediol and/ or 2,2,4-trimethyl-1,3-pentanediol.

[0040] Suitable polyesters are cyclic polyester polyols having a number average molecular of 500 to 5,000 g/mol, preferably 850 to 2,500 g/mol. The number average molecular weight is determined according to OH titration.

[0041] The polyester polyol can preferably be based on a cyclic polyester chain containing at least any one of a cyclohexane ring, a cyclohexene ring, a bicyclo[4.4.0]decane ring and a bicyclo[4.4.0]decadiene ring and can be prepared, for example, by the method described below.

[0042] An unsaturated fatty acid having from 2 to 4 (preferably 2) ethylenic double bonds or an ester thereof (first unsaturated fatty acid or ester thereof) and an unsaturated fatty acid having from 1 to 4 (preferably one or 2) ethylenic double bonds or an ester thereof (second unsaturated fatty acid or ester thereof) are subjected, for example, to transfer of the double bond and/or Diels-Alder reaction to be dimerized, thereby preparing a dimer acid having a cyclohexene ring or a bicyclo[4.4.0]decadiene ring. The resulting dimer acid is hydrogenated to prepare a dimer acid having a cyclohexane ring or a bicyclo[4.4.0]decane ring.

[0043] A reaction product (ester) of the dimer acid having any one of the cyclic structures described above with an alcohol, for example, methanol, is reduced to prepare a dimer diol having any one of the cyclic structures described above. **[0044]** Then, at least one of the dimer acid and dimer diol described above is incorporated into the polymerization component, and condensation polymerization between a dicarboxylic acid and a diol is performed to prepare a cyclic polyester chain containing at least one of a cyclohexane ring, a cyclohexene ring, a bicyclo[4.4.0]decane ring and a bicyclo[4.4.0]decadiene ring.

[0045] The unsaturated fatty acid having from 2 to 4 ethylenic double bonds or the ester thereof, which is used in the preparation of the dimer acid, is preferably an unsaturated fatty acid having from 12 to 24 carbon atoms or an ester thereof, and includes, for example, tetradecadienoic acid, hexadecadienoic acid, octadecadienoic acid (for example, linoleic acid), eidosadienoic acid, docosadienoic acid, octadecatrienoic acid (linolenic acid) and eicosatetraenoic acid (for example, arachidonic acid). The unsaturated fatty acid having one ethylenic double bond or the ester thereof, which is used in the preparation of the dimer acid, is preferably an unsaturated fatty acid having from 12 to 24 carbon atoms or an ester thereof, and includes, for example, tetradecenoic acid, hexadecenoic acid, octadecenoic acid (for example, oleic acid, elaidic acid or vaccenic acid), eicocenoic acid (for example, gadoleic acid) and dococenoic acid (for example, erucic acid)

[0046] The dimer acid obtained by the preparation method described above is ordinarily a mixture of plural kinds of dimer acids different in the chemical structure depending on the position of the double bond in the unsaturated fatty acid, which is used in the preparation of the dimer acid, and the degree of hydrogenation of the dimer acid, and also a mixture of dimer acid having a ring structure and a dimer acid having no ring structure. Moreover, there is a case in which a monomer acid and/or a trimer acid is mixed in the dimer acid obtained by the preparation method described above. **[0047]** Examples of the chemical structure of the dimer acid having a cyclohexane ring, a cyclohexene ring, a bicyclo[4.4.0]decane ring or a bicyclo[4.4.0]decadiene ring are shown below. In the structural formulae shown below, each

of a, b, c and d represents an integer, and total number of carbon atoms included in the molecule is, for example, from 24 to 48.

$$CH_{3} \xrightarrow{(CH_{2})_{c}} COOH$$

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[0048] According to an example of the exemplary embodiment, the cyclic polyester chain in the monomer unit having a cyclic polyester chain includes a cyclic polyester containing a structural unit obtained by polymerization of at least one selected from a dimer acid having a ring structure, which is a dimer acid obtained by dimerizing an unsaturated fatty acid having from 12 to 24 carbon atoms or an ester thereof, a hydrogenated dimer acid obtained by hydrogenating the dimer acid described above and a dimer diol derived from the dimer acid or the hydrogenated dimer acid described above. The ring structure described above is preferably at least any one of a cyclohexane ring, a cyclohexene ring, a bicyclo[4.4.0]decane ring or a bicyclo[4.4.0]decadiene ring.

[0049] Examples of commercially available product of the cyclic polyester derived from a dimer acid include, for example, Priplast 1901 (polyester diol having hydroxyl groups at both terminals, number average molecular weight according to OH titration: 2,000 g/mol), Priplast 3197 (polyester diol having hydroxyl groups at both terminals, number average molecular weight according to OH titration: 2,000 g/mol) and Priplast 3186 (polyester diol having hydroxyl groups at both terminals, number average molecular weight according to OH titration: 1,700 g/mol) produced by Croda.

[0050] Preferred polyurethane based dispersions of the present invention comprise a polyvinyl alcohol (PVA). A preferred polyvinyl alcohol has a viscosity in the range of from 10 to 80 cPs, more preferably 38 to 55 cPs. The cPs measurements given herein refer to 4% aqueous solution at 20° C. Suitable commercially available polyols are for example Mowiol 40-88 and Mowiol 18-88, both supplied by Kuraray Co., Ltd, Japan.

[0051] In various embodiments, the polyurethane based dispersion further comprises one or more additives selected from fillers, stabilizers, conservatives, antifoaming agents, emulsifiers, rheology modifiers, colorants, and mixtures thereof.

[0052] Optionally present nonionic surfactants may serve as an emulsifier and may be selected from the group consisting of alcohol ethoxylates (alkyl ethoxylates), alkylphenol ethoxylates, phenol ethoxylates, amide ethoxylates, glyceride ethoxylates, fatty acid ethoxylates, fatty amine ethoxylates, and mixtures thereof, preferably alkyl ethoxylates, such as polyethylene glycol C8-20 alkyl ether, more preferably PEG 2-10 lauryl ether.

[0053] Optionally present filler may be selected from all known fillers suitable for polyurethane based dispersions. Preferred fillers are fumed silicas.

[0054] Known antifoaming agents that may be used in accordance with the invention included organo-modified polysi-

loxanes.

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[0055] Furthermore, preferred polyurethane based dispersions of the present invention comprise one or more rheology modifiers as additive. Examples of rheology modifiers include associated hydrophilic polyurethanes, such as DSX1415 from Cognis Corp., BorchiGel L75N from Borchers, or alkali-swellable thickeners such as UCAR Polyphobes 102 and 106 from Dow Chemical.

[0056] The preparation of the polyurethane dispersions can be carried out in one or more steps in a homogeneous or multistep reaction, some in the disperse phase. After complete or partial polyaddition a dispersion, emulsification or dissolution step is carried out. If desired, a further polyaddition or modification in the disperse phase is subsequently carried out. All processes known from the prior art, such as, for example, the prepolymer mixing process, acetone process or melt dispersal process, can be used here. The acetone process is preferably used.

[0057] For preparation by the acetone process, the component(s) which can react with the NCO-group and the NCO-component(s) are usually initially introduced for the preparation of an isocyanate-functional polyurethane prepolymer and optionally diluted with a solvent which is miscible with water, but inert to isocyanate groups and heated to temperatures in the range from 50 to 120 °C. In order to accelerate the isocyanate addition reaction, the catalysts known in polyurethane chemistry can be employed.

[0058] Suitable solvents are the conventional aliphatic, keto-functional solvents, such as acetone, 2-butanone, which can be added not only at the beginning of the preparation, but, if desired, can also partly be added later. Preference is given to acetone and 2-butanone.

[0059] Other solvents, such as xylene, toluene, cyclohexane, butyl acetate, ethyl acetate, methoxypropyl acetate, N-methylpyrrolidone, N-ethylpyrrolidone, solvents containing ether or ester units, may additionally be employed and distilled off in full or part or, in the case of N-methylpyrrolidone, N-ethylpyrrolidone, remain completely in the dispersion. However, other solvents apart from the conventional aliphatic, keto-functional solvents are preferably not used.

[0060] In the preparation of the polyurethane prepolymer from the molar ratio of isocyanate groups to isocyanate-reactive groups is preferably 1.05 to 3.5, more preferably 1.1 to 3.0, particularly preferably 1.15 to 2.5.

[0061] The conversion into the prepolymer is carried out in part or full, but preferably in full. Thus, polyurethane prepolymers which contain free isocyanate groups are obtained as such or in solution.

[0062] It is possible to add a neutralization step, if desired. In the neutralization step for the partial or complete conversion of potentially anionic groups into anionic groups, bases, such as tertiary amines, for example trialkylamines having 1 to 12 C atoms, preferably 1 to 6 C atoms, particularly preferably 2 to 3 C atoms, in each alkyl radical or alkali metal bases, such as the corresponding hydroxides, are employed.

[0063] Examples thereof are trimethylamine, triethylamine, methyldiethylamine, tripropylamine, N-methylmorpholine, methyldiisopropylamine, ethyldiisopropylamine and diisopropylethylamine. The alkyl radicals may also carry, for example, hydroxyl groups, as in the case of the dialkylmonoalkanolamines, alkyldialkanolamines and trialkanolamines. Neutralizers which can be employed, if desired, are also inorganic bases, such as aqueous ammonia solution or sodium hydroxide or potassium hydroxide.

[0064] Preference is given to ammonia, triethylamine, triethanolamine, dimethylethanolamine or diisopropylethylamine, as well as sodium hydroxide and potassium hydroxide, particularly preferably sodium hydroxide and potassium hydroxide. The molar amount of the bases is 50 to 125 mol %, preferably between 70 and 100 mol %, of the molar amount of the acid groups to be neutralized. The neutralization can also be carried out simultaneously with the dispersion if the dispersion water already comprises the neutralizer.

[0065] In a further optional process step, the resultant prepolymer is subsequently dissolved, if this has not already taken place or has only taken place in part, with the aid of aliphatic ketones, such as acetone or 2-butanone.

[0066] In an optional chain extension step, NH_2 - and/or NH-functional components are reacted in part or full with the remaining isocyanate groups of the prepolymer. The chain extension/termination is preferably carried out after the dispersion in water. If the partial or complete chain extension is carried out using anionic or potentially anionic hydrophilizing agents containing NH_2 or NH groups, the chain extension of the prepolymers is preferably carried out prior to the dispersion.

[0067] In another embodiment of the dispersion the NCO-reactive component further comprises a polyamine chain extender. These are preferably aliphatic or cycloaliphatic diamines, although it is also possible, if needed, to use trifunctional polyamines or polyfunctional polyamines in order to achieve specific properties. In general, it is possible to use polyamines containing additional functional groups, such as, for example, OH groups. Examples of suitable aliphatic polyamines are ethylenediamine, 1,2- and 1,3-propylenediamine, 1,4-tetramethylenediamine, 1,6-hexamethylenediamine, isophorone diamine, the isomer mixture of 2,2,4- and 2,4,4-trimethylhexamethylenediamine, 2-methylpentamethylenediamine and diethylenetriamine. Preferred amounts of the polyamine chain extender are > 1 wt.-% to < 10 wt.-%, based on the total weight of the NCO-reactive component.

[0068] In addition, compounds which, besides a primary amino group, also contain secondary amino groups or, besides an amino group (primary or secondary), also contain OH groups can also be added. Examples thereof are primary/secondary amines, such as diethanolamine, 3-amino-1-methylaminopropane, 3-amino-1-ethylaminopropane, 3-amin

cyclohexylaminopropane, 3-amino-1-methylaminobutane, and alkanolamines, such as N-aminoethylethanolamine, ethanolamine, 3-aminopropanol, and neopentanolamine.

[0069] Furthermore, monofunctional isocyanate-reactive amino compounds, such as, for example, methylamine, ethylamine, propylamine, butylamine, octylamine, laurylamine, stearylamine, isononyloxypropylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, N-methylaminopropylamine, diethyl(methyl)aminopropylamine, morpholine, piperidine, or suitable substituted derivatives thereof, amidoamines made from diprimary amines and monocarboxylic acids, monoketimes of diprimary amines, primary/tertiary amines, such as N,N-dimethylaminopropylamine, can also be added.

[0070] The dispersion is preferably carried out before the chain extension, if a chain extension took place. To this end, the dissolved polyurethane prepolymer is either introduced into the dispersion water, optionally with high shear, such as, for example, vigorous stirring, or conversely the dispersion water is stirred into the polyurethane prepolymer solutions. The polyurethane prepolymer is preferably added to the water. Optionally present additives can be added at this process step.

[0071] The solvent still present in the dispersions after the dispersion step is usually subsequently removed by distillation. Removal during the dispersion is likewise possible. The residual content of organic solvents in the polyurethane dispersions is preferably less than 1.0 % by weight, based on the entire dispersion.

[0072] The pH of the polyurethane dispersions is preferably less than 9.0, more preferably less than 8.5, particularly preferably less than 8.0, most preferably 6.0 to 8.0. The solids content of the polyurethane dispersions is preferably 30 to 60 % by weight, more preferably 35 to 50 % by weight.

[0073] The polyurethane dispersion, preferably comprises 30 to 60 % by weight, more preferably 35 to 50 % by weight solids (as, for example, determined by drying loss measurements at 150°C for 30 minutes to evaporate the water/solvents), with the solids being mainly composed of the polyurethane polymer particles of a preferred diameter between 30 and 1000 nm, preferably between 50 and 500 nm, more preferably between 80 and 250 nm (as determined by dynamic light scattering (DLS) according to ISO 22412:2017).

[0074] The liquid phase of the dispersion comprises or consists of water, and may, in certain embodiments, also include minor amounts of organic solvents or other liquid components, although it is preferred that it consists essentially of water, i.e. to about 95 vol.%. In the polyurethane dispersion, the liquid phase preferably makes up 40 to 70 % by weight, more preferably 40 to 65 % by weight.

30 Examples:

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Used compounds:

[0075] White hydrophilic textile LJ A 3411 AD from Jade Long John,

Dipping body consisting of aluminum with a diameter d=11 cm,

Desmodur XP 2802 (aliphatic polycarbodiimide, approx. 40 %) from Covestro,

Mowiol 18-88 from Kuraray,

Borchi®Gel L75N (approx. 50%) from Borchers,

Luconyl NG green 8730 (Z-average diameter of 136 nm, polydispersity index (Pdi) of 0.18) from BASF,

40 Calcium nitrate tetrahydrate from VWR Chem (CAS 13477-34-4).

Synthesis of Polyurethane 1

[0076] For synthesis, 1573.52 g of Priplast 1901 (Croda), 60.00 g of Carbowax 1450 (Dow) and 40.00 g of DMPA (2,2-bis(hydroxymethyl) propionic acid) were weighted into a 5 L three-neck flask. The flask was provided with an inlet for vacuum or nitrogen application, KPG stirrer shaft and glass stopper for dehydration. Polyols were heated to 85 °C (bath temperature) and dehydrated by less than 1 mbar. Subsequently, the flask was aired with dry nitrogen. A reflux condensator and an internal contact thermometer were added to the flask via a double-neck unit. 326.48 g of isophorone diisocyanate were added to the mixture at 68 °C. The flask was rinsed with 50 g of dried acetone in order to make sure that the complete amount of isocyanate was in the flask. Afterwards, it was catalyzed with 1.00 g of Borchi®Kat 0761 (in 50 % acetone solution) and a temperature increase of 4 °C was monitored. After 4 hours at 85 °C, an NCO value of 1.91 wt.-% was measured by titration according to Spiegelberger (DIN EN ISO 11909:2007-05). For further catalysis, further 1,00 g of Borchi®Kat 0761 (in 50 % acetone solution) were added. After another hour, the NCO value was 1.70 wt.-%. The resulting prepolymer was dissolved in 2000 g of dry acetone.

For emulsifying, 3500 g of water, 23.86 g of NaOH (50 %) and 2 droplets of Tego Antifoam 2291 were heated to 40 °C. The prepolymer/acetone mixture was added by stirring with a stirrer from Ultraturrax at 10,000 U/min. After 10 minutes, 47.68 g of isophorone diamine were added as a solution into 238.45 g of water. Subsequently, acetone was distilled using a device from Rotavapor and the dispersion was filtered through a Perlon sieve bag (80 μm).

Dynamic light scattering (DLS) according to Malvern:

[0077] Z-average diameter of 103 nm Pdi of 0.12 FG of 40 %

Synthesis of Polyurethane 2

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[0078] For synthesis, 1573.52 g of Priplast 1901 (Croda), 60.00 g of Carbowax 1450 (Dow) and 40.00 g of DMPA (2,2-bis(hydroxymethyl) propionic acid) were weighted into a 5 L three-neck flask. The flask was provided with an inlet for vacuum or nitrogen application, KPG stirrer shaft and glass stopper for dehydration. Polyols were heated to 85 °C (bath temperature) and dehydrated by less than 1 mbar. Subsequently, the flask was aired with dry nitrogen. A reflux condensator and an internal contact thermometer were added to the flask. 326.48 g of isophorone diisocyanate were added to the mixture at 69 °C. The flask was rinsed with 50 g of dry acetone in order to make sure that the complete isocyanate was in the flask. Afterwards, it was catalyzed with 1.00 g of Borchi®Kat 0761 (in 50 % acetone solution) and a temperature increase of 5°C was monitored. After 5 hours at 85 °C, an NCO value of 1.68 wt.-% was measured by titration according to Spiegelberger (DIN EN ISO 11909:2007-05). The resulting prepolymer was dissolved in 2000 g of dry acetone.

For emulsifying, 3500 g of water, 23.86 g of NaOH (50 %) and two droplets of Tego Antifoam 2291 were heated to 40 °C. The prepolymer/acetone mixture was added by stirring with a stirrer from Ultraturrax at 10,000 U/min. After 10 minutes, 47.68 g of isophorone diamine were added as a solution into 238.42 g of water. Subsequently, acetone was distilled using a device from Rotavapor and the dispersion was filtered through a Perlon sieve bag (80µm).

DLS according to Malvern:

[0079] Z-average diameter of 80 nm Pdi of 0.14 FG of 40%

30 Synthesis of Polyurethane 3

[0080] For synthesis, 1573.79 g of Priplast 1901 (Croda), 60.00 g of Pluriol E 1500 (BASF) and 40.00 g of DMPA (2,2-bis(hydroxymethyl) propionic acid) were weighted into a 5 L three-neck flask. The flask was provided with an inlet for vacuum or nitrogen application, KPG stirrer shaft and glass stopper for dehydration. Polyols were heated to 85 °C (bath temperature) and dehydrated using a pressure less than 1 mbar. Subsequently, the flask was aired with dry nitrogen. A reflux condensator and an internal contact thermometer were added to the double-neck flask. 326.21 g of isophorone diisocyanate were added to the mixture at 70 °C. The flask was rinsed with 100 g of dry acetone in order to make sure that the complete amount of isocyanate was in the flask. Afterwards, it was catalyzed with 1.00 g of Borchi®Kat 0761 (in 50 % acetone solution) and a temperature increase of 2 °C was monitored. After 3.5 hours at 85 °C, an NCO value of 1.69 wt.-% was measured by titration according to Spiegelberger (DIN EN ISO 11909:2007-05). The resulting prepolymer was dissolved in 2000 g of dry acetone.

For emulsifying, 3500 g of water, 23.86 g of NaOH (50%) and two droplets of Tego Antifoam 2291 were heated to 40 $^{\circ}$ C. The prepolymer/acetone mixture was added by stirring with a stirrer from Ultraturrax at 10,000 U/min. After 10 minutes, 47.68 g of isophorone diamine were added as a solution into 238.42 g of water. Subsequently, acetone was distilled using a device from Rotavapor and the dispersion was filtered through a Perlon sieve bag (80 μ m).

DLS according to Malvern:

[0081] Z-average diameter of 105 nm Pdi of 0.12 FG of 41%

Aqueous solutions:

55 [0082]

Mowiol 18-88 (10 90 g of deionized water were added to a beaker glass and 10 g Mowiol were added during stirring %): with a dumbbell-shaped magnetic stir bar. The mixture was heated to a temperature of 90-95 °C

with a dumbbell-shaped magnetic stir bar. The mixture was heated to a temperature of 90-95 °C and mixed until the Mowiol was dissolved completely. The mixture was allowed to cool down,

while it was further stirred, to avoid skin formation.

Calcium nitrate The calculated amounts are related to water free calcium nitrate. 463.14 g of calcium nitrate x

(20 %) 4H₂O were dissolved in 1145.92 g of deionized water by stirring.

Borchi®Gel L75N (25 %) 3 g Borchi®Gel were mixed with 3 g of deionized water.

Preparation example for a polyurethane dispersion (PUD)

[0083] 15.1 g of Desmodur XP 2802 were added to 500 g of Polyurethane 1 and Polyurethane 2 (mixed in a ratio of 1:1; solid content =38.94 %, viscosity of 60 mPas, spindle No. 4, 10 rpm, 0.4 %, 22.4 °C) by stirring for 10 minutes. The viscosity was adjusted with 7.8 g of Mowiol 18-88 solution (10 %) and 0.68 g of Borchi®Gel L75N solution (25 %) within 2 h by stirring at 300 rpm. Finally, 0.29 g (approx. 6 droplets) of Luconyl green were added and it was stirred for further 5 minutes

[0084] The obtained polyurethane dispersion had a viscosity of about 1320 mPas.

Example 1

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The textile was dipped with calcium nitrate solution:

[0085] The dipping body was covered crease-free with the textile and the textile was fixed with two rubber bands. Subsequently, it was heated to 50 °C for 30 minutes in a drying cabinet with circulating air. Afterwards, the textile covered dipping body was shortly dipped in a calcium nitrate solution (20 %) at 50 °C. The excess solution is allowed to flow off by holding out the submersible body diagonally downwards until nothing drips anymore. Finally, the textile was completely dried for 60 minutes at 50°C in the drying cabinet with circulating air.

Afterwards, the textile was coated with Polyurethane dispersion 1:

[0086] The prepared dipping body, after dipping into the calcium nitrate solution and subsequent drying, was dipped into the dispersion, with the provision that only the outer surface of the textile was in contact with the aqueous liquid, and was directly taken out again. The dispersion was allowed to flow off for 5 seconds, excess dispersion was shortly shaken off three times and the dipping body was hold out diagonally downwards until nothing drips anymore. The textile was dried for 45 minutes at 90°C. Subsequently, after cooling down to room temperature, the dipping body was removed and it was controlled, whether the dispersion shows bledding through the textile, which is not desired. The textile was washed for 30 seconds in deionized water at room temperature and thereafter, the textile was dried for 30 minutes at 70 °C.

[0087] The experiment was repeated twice (Ex.1.2 and Ex 1.3).

[0088] All coatings were visually assessed by microscope.

Determination of the water column:

[0089] According to ISO 811:2018; Device: Textest FX3000; test surface 10 cm²; gradient: 0.612 mWS/min; criterion to stop: 3rd droplet (Ex 1.1: >15 mWS; Ex.1.2: >15 mWS; Ex.1.3: >15 mWS).

Determination of the coating weight:

[0090] Three circular samples each (d=3.5 cm) of treated and untreated textiles were cut out by a circular knife from Karl Schröder and weighted.

Calculation: (average value sample-average value (blind value (BW)))*1000=coating weight in g/m²

| | | 1. Sample (g) | 2. Sample (g) | 3. Sample (g) | Average value (g) | Coating weight (g/m ²) |
|----|---------|---------------|---------------|---------------|-------------------|------------------------------------|
| 55 | Ex. 1.1 | 0.6272 | 0.5672 | 0.5512 | 0.5819 | 366.2 |
| | Ex. 1.2 | 0.6478 | 0.5646 | 0.6617 | 0.6247 | 409 |

(continued)

| | | 1. Sample (g) | 2. Sample (g) | 3. Sample (g) | Average value (g) | Coating weight (g/m²) |
|--|----------------------------|---------------|---------------|---------------|-------------------|-----------------------|
| | Ex. 1.3 | 0.6911 | 0.6344 | 0.6188 | 0.6481 | 432.4 |
| | Long John, white untreated | 0.2151 | 0.2169 | 0.2151 | 0.2157 | |
| | | | | | | Ø 402.5 |

[0091] All Examples 1.1 to 1.3 showed a coating solely on one side. The other (inner) side did not show any signs of a coating by visual inspection. The examples showed a breathability of about 192 g/d*m².

Example 2

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Used materials:

[0092] LJ A 3411 AD is a white, hydrophilic textile from Jade Long John. The textile was stitched with a polyester yarn to form a small tube, which is closed at one end.

[0093] The dipping body was a test tube (d=2 cm, l=18 cm) filled with sand.

[0094] Polyurethane polymer 3 (FG=36.2 %, viscosity: 60 mPas (Sp.4, 10 rpm, 0.3 %, 22.6 °C) Mowiol 18-88 from Kuraray,

Borchi®Gel L75N (50 %) from Borchers,

Luconyl NG green 8730 from BASF (Z-average: 136 nm diameter, Pdi: 0.18),

Calcium nitrate tetrahydrate from VWR Chem (CAS: 13477-34-4).

Prepared aqueous solutions:

[0095]

| 30 | Mowiol 18-88 (10 %): | 90 g of deionized water were added to a beaker glass and 10 g Mowiol were added during stirring with a dumbbell-shaped magnetic stir bar. The mixture was heated to a temperature of 90-95°C and mixed until the Mowiol was completely dissolved. The mixture was allowed to cool down while it was stirred to avoid skin formation. |
|----|-------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 35 | Calcium nitrate (20 %) | The calculated amounts are related to water free calcium nitrate. 463.14 g of calcium nitrate x 4H ₂ O were dissolved in 1145.92 g of deionized water by stirring. |

Borchi®Gel L75N (25 %) 3 g Borchi®Gel were mixed with 3 g of deionized water.

Preparation example for a Polyurethane dispersion 2:

[0096] Viscosity of Polyurethane polymer 3 (500 g) was adjusted to 1120 mPas (spindle No. 4, 10 rpm). Firstly, 7.5 g of Mowiol 18-88 solution (10 %) were added and subsequently, the solution was mixed for 25 minutes at 300 rpm. Thereafter, 2.53 g of Borchi®Gel L75N solution were added within 3 hours. Finally, 0.32 g (approx. 6 droplets) Luconyl green were added and subsequently, the solution was mixed for further 5 minutes at 300 rpm. The polyurethane dispersion had a viscosity of about 1320 mPas.

The textile was dipped with calcium nitrate solution:

- [0097] The test tube was covered by the sewn textile in finger form and the textile was fixed with two rubber bands. Subsequently it was heated to 50 °C for 30 minutes in the drying cabinet with circulating air. Afterwards, it was shortly dipped into the calcium nitrate solution (20 %, 50 °C). The solution was allowed to flow off and the sewn textile was subsequently completely dried at 50 °C for 60 minutes in the drying cabinet with circulating air.
- Afterwards, the textile was coated with Polyurethane dispersion 2:

[0098] The sewn textile was dipped deep in the coating dispersion (7 cm) with the provision that only the outer surface

of the textile was in contact with the aqueous liquid. Subsequently, it was allowed to dry for 45 minutes at 90°C. After cooling down to room temperature, the submersible body was removed and it was controlled, if the dispersion shows bleeding through the textile, which is not desired. Then, the textile was washed in deionized water at room temperature for 30 seconds and subsequently, the textile was dried for 30 minutes at 70 °C.

[0099] All coatings were visually assessed by microscope.

[0100] The experiment was repeated once. Experiment 2.1 and 2.2 showed a coating mainly on one side, minor, hardly noticeable bleeding, was partly present around the seam.

10 Claims

- 1. Method of coating a textile, comprising or consisting of the steps of:
 - i) providing a textile;

ii)

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- a) dipping at least one surface of the textile into an aqueous solution comprising 0.2 to 85 wt.-%, preferably 1 to 40 wt.-%, more preferably 2 to 20 wt.-%, of at least one inorganic salt; or
- b) spraying an aqueous solution comprising 0.2 to 85 wt.-%, preferably 1 to 40 wt.-%, more preferably 2 to 20 wt.-%, of at least one inorganic salt onto at least one surface of the textile; or
- c) spraying at least one inorganic salt as a powder onto at least one surface of the textile, preferably a preheated textile;
- iii) removing the textile of step ii) from the aqueous solution if step ii) a) is performed and optionally allowing the excess aqueous solution to flow off and/or optionally drying the textile; or
- optionally allowing the excess aqueous solution to flow off and/or optionally drying the textile if step ii) b) is performed;
- iv) dipping the surface(s) which was (were) brought into contact with the at least one inorganic salt of the textile of step ii) c) or iii) into a polyurethane based dispersion;
- v) removing the textile of step iv) from the dispersion and optionally allowing the excess dispersion to flow off and/or drying the textile obtained in step iv) thereby obtaining a coated textile.
- 2. The method according to claim 1, wherein the textile is a woven, knitted or nonwoven textile, preferably based on polyamide fibers, polyester fibers, polyurethane fibers, in particular polyurethane elastic fibers, natural fibers, like cotton; preferably the textile is based on polyamide fibers, polyester fibers or polyurethane fibers and/or

the textile is a clothing or an inner shoe, more preferably an inner shoe.

3. The method according to claim 1 or 2, wherein the inorganic salt of the aqueous solution contains multivalent cations, preferably selected from Ca²⁺, Mg²⁺, Sr²⁺, Al³⁺, Fe²⁺, Fe³⁺ or mixtures thereof, preferably Ca²⁺, Mg²⁺ or mixtures thereof, more preferably Ca²⁺

and/o

anions selected from NO3²⁻, F⁻, Cl⁻, SO₄³⁻, CO₃²⁻, PO₄³⁻ or mixtures thereof, preferably NO₃²⁻, F⁻, Cl⁻, SO₄³⁻ or mixtures thereof, more preferably NO₃²⁻.

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4. The method according to any of the preceding claims, wherein the optional drying step of step iii) is active or passive drying, preferably an active drying with a dryer, more preferably selected from ovens convection ovens, radiation sources like IR, NIR and microwaves, by reduction of ambient pressure or vacuum, air flow as well as combination thereof and/or the drying in step iii) is performed until the textile obtained after step ii) is dry.

- **5.** The method according to any of the preceding claims, wherein the polyurethane based dispersion comprises polymers with a weight average molecular weight of 10,000 to 500,000 g/mol, preferably 20,000 to 100,000 g/mol, more preferably 40,000 to 50,000 g/mol.
- 6. The method according to any of the preceding claims, wherein the polyurethane based dispersion comprises polymers with a number average molecular weight of 1,000 to 25,000 g/mol, preferably 1,500 to 20,000 g/mol, more preferably 2,000 to 15,000 g/mol.

- 7. The method according to any of the preceding claims, wherein the polyurethane based dispersion comprises polymers with a polydispersity of 1.0 to 50.0, preferably 2.5 to 40.0, more preferably 5.0 to 30.0.
- 8. The method according to any of the preceding claims, wherein the dispersion is a polyurethane based dispersion, preferably in which the polyurethane polymers are based on more than 20 wt.-% polyol, preferably more than 40 wt.-% polyol.
 - 9. The method according to any of the preceding claims, wherein the drying step of step v) is active or passive drying, preferably an active drying with a dryer and/or
 - the drying in step v) is performed until the textile obtained after step iv) is dry.

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- 10. The method according to any of the preceding claims, wherein the coating of the coated textile has a coating weight of 5.0 to 1,000 g/m², preferably 100 to 600 g/m², more preferably 150 to 450 g/m², preferably determined after drying the coated sample for 1 hour at 90°C and allowing to rest at 25°C for day.
- 11. The method according to any of the preceding claims, wherein the coated textile is completely or partly coated, preferably completely.
- 20 12. The method according to any of the preceding claims, wherein the coated textile has a water column > 1 m, preferably > 3 m, more preferably > 5m, preferably measured according to ISO 811:2018.
 - 13. The method according to any of the preceding claims, wherein the coated textile has a breathability of more than 50 g/dm², preferably more than 100 g/dm², more preferably more than 150 g/dm², even more preferably more than 250 g/dm², preferably measured according to DIN 53122-1:2001-08.
 - 14. A coated textile, preferably a coated jacket or inner shoe, which is obtainable by the method according to any of claims 1 to 13.
- 30 15. Use of the coated textile of claim 14 as part of a clothing, preferably a jacket or a shoe, preferably an inner shoe.



EUROPEAN SEARCH REPORT

Application Number

EP 18 20 0115

| des | brevets | | | 10 20 011 |
|----------|-------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|-----------------------------------------------|
| | DOCUMENTS CONSID | ERED TO BE RELEVANT | |] |
| Category | Citation of document with i | ndication, where appropriate, | Relevant to claim | CLASSIFICATION OF THE APPLICATION (IPC) |
| X | [DE]; COVESTRO POLY 1 March 2018 (2018- * page 1, paragraph | (COVESTRO DEUTSCHLAND AG /MERS CHINA CO LTD [CN]) -03-01) | | INV. D06M15/564 D06M11/00 D06N3/14 |
| | * page 7, paragraph * page 13, step c) | ns 3,4,5 * | | |
| X | 31 October 2013 (20 * paragraphs [0001] [0014], [0015], | | 1-15 | |
| | 1,2; examples * | | | TECHNICAL FIFLING |
| | | | | TECHNICAL FIELDS SEARCHED (IPC) D06M D06N |
| | | | | |
| | | | | |
| | | | | |
| 2 | The present search report has | <u> </u> | | |
| 1001) | Place of search The Hague | Date of completion of the search 17 April 2019 | Bla | Examiner s, Valérie |
| X: part | ATEGORY OF CITED DOCUMENTS ticularly relevant if taken alone ticularly relevant if combined with anot ument of the same category | T : theory or principle E : earlier patent doc after the filing date b : document cited in L : document cited fo | underlying the in ument, but publis the application r other reasons | nvention shed on, or |
| <u> </u> | A: technological background O: non-written disclosure B: intermediate document A: technological background A: member of the same pate document | | | |

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

EP 18 20 0115

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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 The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-04-2019

| 10 | Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|----|----------------------------------------|------------------|-----------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| 15 | WO 2018037039 A | 1 01-03-2018 | CN 107780230 A TW 201840927 A WO 2018037039 A1 | 09-03-2018 16-11-2018 01-03-2018 |
| 15 | US 2013288551 A | 1 31-10-2013 | AU 2011249947 A1 BR 112012028562 A2 DK 2567019 T3 EP 2567019 A1 | 06-12-2012 26-07-2016 05-05-2014 13-03-2013 |
| 20 | | | ES 2458426 T3 HK 1182150 A1 HR P20140366 T1 JP 5730988 B2 JP 2013528713 A | 05-05-2014 25-09-2015 23-05-2014 10-06-2015 11-07-2013 |
| 25 | | | KR 20130063511 A PT 2567019 E TW 201215738 A US 2013288551 A1 WO 2011138284 A1 ZA 201208196 B | 14-06-2013 22-04-2014 16-04-2012 31-10-2013 10-11-2011 29-01-2014 |
| 30 | | | | |
| 35 | | | | |
| 40 | | | | |
| 45 | | | | |
| 50 | 89 | | | |
| 55 | FORM P0459 | | | |

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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.

Non-patent literature cited in the description

• CHEMICAL ABSTRACTS, 13477-34-4 [0075] [0094]