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(54) **ORGANIC ANTIMICROBIAL TEXTILE**

(57) The present invention relates to a method of rendering a textile antimicrobial by treating the textile in a liquor application process with at least one amino acid and/or at least one amino acid derivative, and to a wash-durable antimicrobial textile obtained by the method.

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## Description

### Field of the invention

**[0001]** The present invention relates to a method of rendering a textile antimicrobial by treating the textile in a liquor application process with at least one amino acid and/or at least one amino acid derivative. The obtained textile is equipped with a high antimicrobial performance, which is durable over multiple washing cycles.

### Background of the invention

**[0002]** Disinfectants are extensively used in everyday life to prevent microbial spread and microbial infections, such as in the health care sector, the food industry, agriculture, or in common household products.

**[0003]** However, one major problem arising from the extensive use of disinfectants is the continuous contamination of the environment with these disinfectants. Usually, disinfectants are provided in solution and applied directly onto contaminated surfaces, such as in hospitals or of laboratory equipment, or skin wounds. In case these disinfectants are not neutralized, such as by autoclaving, or cannot be easily neutralized, they finally accumulate in the waste water. Likewise, materials equipped with biocidal functionalities, such as antimicrobial plastics, coatings, or textiles, e.g. in the food packaging industry, wound dressings or functional wear, accumulate in the environment, and, furthermore, the antimicrobials used in these materials can leach out constantly. Such contamination may ultimately result in the emergence of microbial strains that are resistant to commonly used antimicrobial agents.

**[0004]** In the prior art, several methods for preparing antimicrobial textile materials are known. However, these methods mostly rely on the use of synthetic antimicrobial agents that cannot be easily degraded in the environment. Moreover, many antimicrobial agents known in the prior art are not approved for use as food additives or preservatives, and, in consequence, cannot be used in combination with food packaging.

**[0005]** Therefore, there is a need for a method for rendering a textile antimicrobial, which makes use of environmentally friendly chemical agents. The agents conferring antimicrobial functionality to the textile are preferably natural, organic compounds. Such compounds are usually biodegradable, thereby reducing the risk of accumulation and contamination of the environment. The obtained antimicrobial textile should be well tolerated by living tissues and could be used, for example, for sensitive applications such as preservative packaging for food or as wound dressing. Moreover, the production of such antimicrobial textile should be cost-efficient, in particular in terms of the costs for the chemical agents used.

### Brief description of the invention

**[0006]** The present invention solves the shortcomings of the state of the art by providing in a 1st embodiment of the invention a method for rendering a textile antimicrobial, comprising a main process cycle comprising the steps of:

- treating the textile in a main liquor application process such as padding or preferably exhaustion, the liquor of the main liquor application process comprising at least one amino acid and/or at least one amino acid derivative,
- subjecting the treated textile to a heat treatment,
- optionally washing the heat-treated textile, and
- optionally drying the washed textile,

and the method preferably comprising a secondary process cycle being performed after the steps of the main process cycle and comprising the steps of:

- treating the textile using a secondary liquor application process, such as an exhaust or preferably a padding process, wherein the liquor of the secondary liquor application process comprises at least one amino acid, at least one amino acid derivative, and/or at least one antimicrobial agent;
- subjecting the treated textile to a heat treatment,
- optionally washing the heat-treated textile, and
- optionally drying the washed textile.

**[0007]** The main liquor application process in combination with the heat treatment allows the production of a textile with durable antimicrobial properties. While the main liquor application process may be a padding process or any other liquor application process, preferably exhaustion is used, as such process allows that the amino acid and/or at amino acid derivative are substantially uniformly dispersed across the cross section of the textile. The secondary process, which may be in particular a padding process, can enhance the overall antimicrobial activity of the textile. The at least one amino acid and/or at least one amino acid derivative of the secondary process cycle may be different from the at

least one amino acid and/or at least one amino acid derivative of the main process cycle.

**[0008]** According to a 2nd embodiment, in the 1st embodiment, the amino acid and/or amino acid derivative comprised in the liquor of the main and/or secondary liquor application process has an isoelectric point equal to or above 7, preferably equal to or above 8, more preferably equal to or above 8.5, and/or has a pH-independent positive charge.

**[0009]** The use of amino acids and/or amino acid derivatives with an isoelectric point above 7 allows that the acids and/or amino acid derivatives carry a positive net charge at any pH value below the isoelectric point. Thus, the higher the isoelectric point, the larger is the range of pH values suitable for providing a positive net charge. Alternatively or in addition, amino acids or amino acid derivatives, such as quaternary ammonium comprising amino acid derivatives, may have a constant positive charge, which is pH independent. It has been found that a positive charge of the amino acid and/or amino acid derivative applied to the textile enhances the overall antimicrobial activity, in particular against gram-positive and gram-negative bacteria. Positive charges are believed to adhere to the negatively charged membranes of microorganisms and to disrupt the membrane integrity, thereby acting biocidal.

**[0010]** According to a 3rd embodiment, in any one of the preceding embodiments, the at least one amino acid comprised in the liquor of the main and/or secondary liquor application process is selected from the group consisting of natural amino acid, unnatural amino acid, non-proteinogenic amino acid, and/or wherein the at least one amino acid derivative is selected from the group consisting of peptide and quaternary ammonium comprising amino acid derivative.

**[0011]** The inventors have found that common amino acids, peptides and quaternary ammonium comprising amino acid derivatives can be adhered to a textile to provide an unexpectedly high antimicrobial activity to the textile. In contrast, when they are diluted in solution or suspension, these compounds do not act as efficient antimicrobial agents. Therefore, the antimicrobial activity of these compounds is neutralized when washed off the textile.

**[0012]** According to a 4th embodiment, in any one of the preceding embodiments, the natural, unnatural or non-proteinogenic amino acid is in L configuration, and/or wherein the peptide is a L-peptide.

**[0013]** The L-enantiomers of amino acids and peptides can be easily obtained from cultures, e.g. of *E. coli, L. lactis* or *S. cerevisiae*, rendering a complicated, cost-inefficient chemical synthesis unnecessary.

**[0014]** According to a 5th embodiment, in any one of the preceding embodiments, the peptide is a dipeptide or a polypeptide, wherein the polypeptide preferably contains 3 to 50 amino acids.

**[0015]** According to a 6th embodiment, in any one of the preceding embodiments, the at least one amino acid comprised in the liquor of the main and/or secondary liquor application process is lysine, arginine, or histidine, preferably arginine.

**[0016]** The naturally occurring amino acids lysine, arginine, or histidine are environmentally friendly, as they can be obtained from common biological cultures. Moreover, these amino acids can be used as food additives or preservatives in the context of finishing textiles used in the food industry, as they are non-toxic to living tissues. Arginine is one of the preferred amino acids because it is available at comparatively low costs.

**[0017]** According to a 7th embodiment, in any one of the preceding embodiments, the at least one amino acid derivative comprised in the liquor of the main and/or secondary liquor application process is a lantibiotic, preferably nisin.

**[0018]** Nisin is commonly used as a food preservative, and, thus, can be also used for the finishing of textiles used in the food industry.

**[0019]** According to an 8th embodiment, in any one of the preceding embodiments, the at least one amino acid derivative comprised in the liquor of the main and/or secondary liquor application process is carnitine or betaine, preferably carnitine.

**[0020]** Carnitine and betaine are naturally occurring amino acid derivatives, which comprise quaternary ammonium groups that are positively charged in a pH-independent manner. In particular carnitine has proven to have an adequate antimicrobial activity upon adherence to a textile.

**[0021]** According to a 9th embodiment, in any one of the preceding embodiments, at least arginine and carnitine are comprised in the liquor of the main and/or secondary liquor application process.

**[0022]** The combination of arginine and carnitine confers a particularly high antimicrobial activity to a textile, e.g. against both gram-negative and gram-positive bacteria.

**[0023]** According to a 10th embodiment, in any one of the preceding embodiments, the at least one amino acid or amino acid derivative in the liquors of all process cycles together is applied to the textile in an amount of at least 0.1 % by weight, preferably at least 0.2%, more preferably at least 0.5%, or at least 1%, at least 2%, at least 3%, or at least 4%, based on the weight of the textile.

**[0024]** According to a 11th embodiment, in any one of the preceding embodiments, the at least one amino acid or amino acid derivative in the liquors of all process cycles together is applied to the textile in an amount of at most 15% by weight, preferably at most 12%, or at most 10%, or at most 5%, or at most 4%, based on the weight of the textile.

**[0025]** According to a 12th embodiment, in any one of the preceding embodiments, preparing the liquor of the main and/or secondary liquor application process comprises the following steps:

- preparing an aqueous reaction mixture comprising the at least one amino acid and/or amino acid derivative,
- incubating the reaction mixture for at least 10 minutes, preferably at least 20 minutes, more preferably at least 30 minutes, even more preferably at least 40 minutes, and most preferably at least 50 minutes, wherein the temperature

of the reaction mixture during incubation is preferably at least 30 °C, more preferably at least 40 °C, even more preferably at least 50 °C, and most preferably at least 60 °C.

**[0026]** It was found that the incubation step of the amino acid and/or amino acid derivative in the reaction mixture, preferably at a pH below 6.5, preferably below 6.0, more preferably below 5.5, even more preferably below 5.0, most preferably to a pH of about 4.5, allows a further increase in antimicrobial activity of the finished textile.

**[0027]** According to a 13th embodiment, in any one of the preceding embodiments, the liquor of the main and/or secondary liquor application process comprises glucosamine and/or polyglucosamine.

**[0028]** The combination of polyglucosamine (chitosan) and one or more amino acids and/or amino acid derivatives allows for a synergistic increase in antimicrobial performance of the treated textile.

**[0029]** Preferably, polyglucosamine is non-animal derived. For example, non-animal derived polyglucosamine can be isolated from fungi, such as mucorales.

**[0030]** Preferably at most 0.8%, more preferably at most 0.1% of the amine groups of polyglucosamine are functionalized with the at least one amino acid, and/or amino acid derivative.

**[0031]** It was found that a complicated coupling of the amino acids or amino acid derivatives to polyglucosamine in terms of a peptide bond between the carboxy groups of the amino acids or amino acid derivatives and the amine groups of polyglucosamine is not required to achieve a high antimicrobial activity. Rather, the compounds may be simply combined in the liquor or in a reaction mixture without performing a crosslinking or condensation reaction. Further, it was found that an ester bond between the hydroxy groups of chitosan and carboxy groups of the amino acids and or amino acid derivates can be formed in an acidic solution, which allows that the amine groups of polyglucosamine, the amine groups of the amino acids and/or amino acid and potential further functional groups are non-functionalized and can carry positive charges, e.g. in a solution of neutral pH.

**[0032]** According to a 14th embodiment, in any one of the preceding embodiments, the polyglucosamine and/or glucosamine is in a water-soluble form.

**[0033]** A water-soluble form of polyglucosamine can be provided by dissolving a powder or flakes comprising polyglucosamine in an acidic medium. By using a water-soluble form in the liquor, polyglucosamine can be well dispersed throughout the cross-section of the textile.

**[0034]** According to a 15th embodiment, in the 14th embodiment, polyglucosamine and/or glucosamine is provided as a concentrated solution or suspension of at most 50% polyglucosamine and/or glucosamine, preferably at most 40%, more preferably at most 30%, most preferably at most 20%, and/or of at least 1%, preferably at least 5%, more preferably at least 10%, and most preferably at least 15%.

**[0035]** According to a 16th embodiment, in the 15th embodiment, the pH of the concentrated solution or suspension is adjusted to a pH below 6.5, preferably below 6.0, more preferably below 5.5, even more preferably below 5.0, most preferably to a about 4.5.

**[0036]** According to a 17th embodiment, in the 16h embodiment, the pH of the concentrated solution or suspension is adjusted by using an organic acid, more preferably a monocarboxylic acid, even more preferably acetic acid, lactic acid, formic acid, propionic acid, p-toluenesulfonic acid or a combination thereof.

**[0037]** According to a 18th embodiment, in any one of the preceding embodiments 13 to 17, the glucosamine and/or polyglucosamine in the liquors of all process cycles together is applied to the textile in an amount of at least 0.1%, preferably at least 0.2%, more preferably at least 0.3%, or at least 0.7% or at least 1%, based on the weight of the textile.

**[0038]** According to a 19th embodiment, in any one of the preceding embodiments 13 to 18, the glucosamine and/or polyglucosamine in the liquors of all process cycles together is applied to the textile in an amount of at most 5% by weight, preferably at most 4% by weight, more preferably at most 3% by weight, even more preferably at most 2%, and most preferably at most 1.6% or at most 1%, based on the weight of the textile material.

**[0039]** According to a 20th embodiment, in any one of the preceding embodiments, preparing the liquor of the main and/or secondary liquor application process comprises the following steps:

- providing the at least one amino acid and/or amino acid derivative in powder or liquid form,
- providing the glucosamine and/or polyglucosamine in powder or liquid form,
- preparing a preferably aqueous reaction mixture comprising the at least one amino acid and/or amino acid derivative, and glucosamine and/or polyglucosamine, and
- incubating the reaction mixture for at least 10 minutes, preferably at least 20 minutes, more preferably at least 30 minutes, even more preferably at least 40 minutes, and most preferably at least 50 minutes, wherein the temperature of the reaction mixture during incubation is preferably at least 30 °C, more preferably at least 40 °C, even more preferably at least 50 °C, and most preferably at least 60 °C.

**[0040]** The preparation of the reaction mixture of polyglucosamine and the amino acid and/or amino acid derivate and the incubation step allows for a further increase in antimicrobial activity. The inventors believe that in the reaction mixture,

polyglucosamine molecules react with the amino acid and/or amino acid derivate, such that an ester bond is formed. This new product can further react with the textile during the liquor application process, for example via free hydroxyl groups of polyglucosamine molecules. A temperature of the reaction mixture of at least 30 °C, more preferably at least 40 °C, even more preferably at least 50 °C, and most preferably at least 60 °C was found to foster the reaction in the incubation step.

**[0041]** According to a 21st embodiment, in the preceding embodiments 12 or 20, the temperature of the reaction mixture during incubation is at most 95 °C, preferably at most 90 °C, more preferably at most 85 °C, even more preferably at most 80 °C, and most preferably at most 75 °C.

**[0042]** According to a 22nd embodiment, in the 12th, 20th or 21st embodiment, the reaction mixture is stirred during the incubation step, preferably at a rotation speed of at least 10 rpm.

**[0043]** According to a 23rd embodiment, in any one of the preceding 12th or 20th to 22nd embodiments, the pH of the reaction mixture is below 6.5, preferably below 6.0, more preferably below 5.5, even more preferably below 5.0, most preferably about 4.5.

**[0044]** An acidic pH improves the solubility of polyglucosamine in the concentrated solution and/or aqueous reaction mixture.

**[0045]** According to a 24th embodiment, in the preceding embodiment, the pH is adjusted by using an organic acid, more preferably a monocarboxylic acid, even more preferably acetic acid, lactic acid, formic acid, propionic acid, p-toluenesulfonic acid or a combination thereof.

**[0046]** These acids have proven compatible with the overall textile finishing as explained in further detail below.

**[0047]** According to a 25th embodiment, in any one of the preceding embodiments, in the main and/or secondary liquor application process, at least 50%, preferably at 70%, more preferably at least 80%, even more preferably at least 90%, and most preferably at least 95% of the at least one amino acid, amino acid derivative and/or polyglucosamine bound to the textile are not bound to cellulose molecules dispersed or dissolved in the liquor.

**[0048]** According to a 26th embodiment, in any one of the preceding embodiments, the liquor of the main and/or secondary process cycle comprises one, two, three, or all four of the antimicrobial agents selected from the group consisting of azole based compound, silver ions, polyhexamethylene biguanide, quaternary ammonium organosilane.

**[0049]** These antimicrobial agents are not biodegradable. In certain applications it may nevertheless be desirable to add them because they increase the overall antimicrobial activity of the textile. The inventors found that these antimicrobial agents can be well combined with amino acids and/or amino acid derivatives.

**[0050]** According to a 27th embodiment, in the preceding 26th embodiment, the azole based compound is propiconazole.

**[0051]** According to a 28th embodiment, in any one of the 26th or 27th embodiments, the quaternary ammonium organosilane is a hydrophilic quaternary ammonium organosilane, preferably an organomethoxysilane compound, more preferably N-trimethoxysilylpropyl-n,n,n-trimethylammonium chloride.

**[0052]** According to a 29th embodiment, in any one of the 26th to 28th embodiments, the quaternary ammonium organosilane compound in the liquors of all process cycles together is applied to the textile in an amount of at least 0.1% by weight, preferably at least 0.2% by weight, more preferably at least 0.25% by weight, and most preferably at least 0.3% by weight, based on the weight of the textile material.

**[0053]** According to a 30th embodiment, in any one of the 26th to 29th embodiments, the quaternary ammonium organosilane compound in the liquors of all process cycles together is applied to the textile in an amount of at most 5% by weight, preferably at most 1.5% by weight, more preferably at most 1.2% by weight, in particular at most 1.0% by weight, and most preferably at most 0.8% by weight, based on the weight of the textile material.

**[0054]** According to a 31st embodiment, in any one of the 26th to 30th embodiments, the silver cations or silver cations trapped in an inorganic or organic matrix in the liquors of all process cycles together are applied to the textile in an amount of at most 0.1% by weight, preferably at most 0.05% by weight, more preferably at most 0.02% by weight, and most preferably at most about 0.01% by weight, based on the weight of the textile material.

**[0055]** According to a 32nd embodiment, in any one of the 26th to 31st embodiments, the silver cations or silver cations trapped in an inorganic or organic matrix in the liquors of all process cycles together are applied to the textile in an amount of at least 0.001% by weight, preferably at least 0.002% by weight, more preferably at least 0.003% by weight, and most preferably at least about 0.005% by weight, based on the weight of the textile material.

**[0056]** According to a 33rd embodiment, in any one of the 26th to 32nd embodiments, polyhexamethylene biguanide in the liquors of all process cycles together is applied to the textile in an amount of at most 0.5% by weight, preferably at most 0.4% by weight, more preferably at most 0.3% by weight, and most preferably at most 0.2% by weight, based on the weight of the textile material.

**[0057]** According to a 34th embodiment, in any one of the 26th to 33rd embodiments, polyhexamethylene biguanide in the liquors of all process cycles together is applied to the textile in an amount of at least 0.03% by weight, preferably at least 0.05% by weight, or at least 0.10% by weight, preferably at least 0.15% by weight, based on the weight of the textile material.

**[0058]** According to a 35th embodiment, in any one of the 26th to 34th embodiments, the azole-based compound in

the liquors of all process cycles together is applied to the textile in an amount of at most 0.6% by weight, preferably at most 0.5% by weight, more preferably at most 0.4% by weight, and most preferably at most 0.3% by weight, based on the weight of the textile material.

**[0059]** According to a 36th embodiment, in any one of the 26th to 35th embodiments, the azole-based compound in the liquors of all process cycles together is applied to the textile in an amount of at least 0.05% by weight, preferably at least 0.10% by weight, more preferably at least 0.15% by weight, and most preferably at least 0.20% by weight, based on the weight of the textile material.

**[0060]** According to a 37th embodiment, in any one of the preceding embodiments, the liquor of the main and/or secondary liquor application process comprises water, preferably water and isopropanol, more preferably wherein isopropanol is contained in the liquor at a concentration of between 0.05 and 2 wt.%, preferably between 0.1 and 1 wt.%, more preferably between 0.2 and 0.6 wt.%.

**[0061]** Isopropanol reduces the surface tension of water, thereby facilitating the penetration of the amino acids and/or amino acid derivatives into the fibers of the textile. Isopropanol evaporates during the liquor application process and/or heat treatment.

**[0062]** According to a 38th embodiment, in any one of the preceding embodiments, the pH of the liquor of the main and/or secondary liquor application process is equal to or below 6.5, preferably equal to or below 6.0, more preferably equal to or below 5.5, even more preferably equal to or below 5.0, most preferably about 4.5.

**[0063]** An acidic pH can catalyze the reaction between the amino acids and/or amino acid derivatives with the textile, in particular when the reaction is an esterification reaction.

**[0064]** According to a 39th embodiment, in the preceding 38th embodiment, the pH of the liquor of the main and/or secondary liquor application process is adjusted by an organic acid, preferably a monocarboxylic acid, in particular acetic acid, lactic acid, formic acid, propionic acid, p-Toluenesulfonic acid or a combination thereof.

**[0065]** Organic acids are compatible with most textile materials, such as viscose or cotton whereas HCl for example may impair the textile. In particular monocarboxylic acids can be used in the liquor application processes, as these acids do not influence the overall charge of the textile after application of the amino acids and/or amino acid derivatives. In contrast, multifunctional acids, such as di- or tricarboxylic acids, e.g. citric acid, can increase the overall negative charge of the textile, in case of binding to the textile via one of the functional groups.

**[0066]** According to a 40th embodiment, in any one of the preceding embodiments, the liquor comprises a cross linking reagent, preferably an isocyanate cross linking agent or an acrylic crosslinker, more preferably a blocked isocyanate cross linking agent.

**[0067]** Cross linking agents are typically not biodegradable. In certain applications it may nevertheless be desirable to add them because they can covalently bind to the amino acids and/or amino acid derivatives and to functional groups of the textile, thereby increasing the wash-resistance of the antimicrobial properties of the obtained textile.

**[0068]** According to a 41st embodiment, in any one of the preceding embodiments, during an exhaust process, the liquor has a temperature of at least 40 °C, in particular at least 45 °C, preferably at least 50 °C, more preferably at least 55 °C, even more preferably at least 60 °C, most preferably at least about 65 °C.

**[0069]** According to a 42nd embodiment, in any one of the preceding embodiments, during an exhaust process, the liquor has a temperature below boiling temperature, preferably at most 95 °C, more preferably at most 90 °C, particularly at most 85 °C, and most preferably at most about 80 °C.

**[0070]** According to a 43rd embodiment, in any one of the preceding embodiments, the exhaust time of an exhaust process is at least 30 minutes, preferably at least 40 minutes, more preferably at least 50 minutes, particularly at least 55 minutes, and most preferably at least about 60 minutes, and/or at most 120 minutes, in particular 90 minutes, preferably at most 80 minutes, more preferably at most 75 minutes, even more preferably at most 70 minutes, even more preferably at most 65 minutes, most preferably at most about 60 minutes.

**[0071]** According to a 44th embodiment, in any one of the preceding embodiments, the heat treatment of the main and/or secondary process cycle comprises drying and/or curing.

**[0072]** According to a 45th embodiment, in the preceding 44th embodiment, drying is conducted at an ambient temperature of at most 190 °C, preferably at most 180 °C, more preferably at most 170 °C, and/or at an ambient temperature of at least 60 °C, preferably at least 80 °C, more preferably at least 100 °C, and most preferably at least about 120 °C.

**[0073]** According to a 46th embodiment, in any one of the preceding 44th or 45th embodiments, curing is conducted at least partially at an ambient temperature of at least 150 °C, preferably at least 160 °C, more preferably at least 170 °C, particularly at least 175 °C, and most preferably at least about 180 °C, and/or at an ambient temperature of at most 205 °C, preferably at most 195 °C, more preferably at most 190 °C, particularly at most 185 °C, and most preferably at most about 180 °C.

**[0074]** The curing temperature is adapted to promote the (covalent) binding of the amino acids and/or amino acid derivatives to the textile.

**[0075]** According to a 47th embodiment, in any one of the preceding embodiments, the starting textile comprises hydroxyl, peptide and/or carbonyl groups, in particular hydroxyl and/or peptide groups.

**[0076]** These groups enable fixing, bonding, attaching or adhering of one or more amino acids and/or amino acid derivatives to the textile. In exemplary embodiments, the starting textile material comprises peptide and/or hydroxyl groups, in particular hydroxyl groups.

**[0077]** According to a 48th embodiment, in any one of the preceding embodiments, the starting textile is a cellulosic textile material, an animal-derived textile material, a synthetic textile material, or a blend comprising a cellulosic, animal-derived and/or a synthetic textile material.

**[0078]** According to a 49th embodiment, in the 48th embodiment, the cellulosic textile comprises one or more selected from the group consisting of cotton, viscose, rayon, linen, hemp, ramie, jute, and combinations (blends) thereof. In particular, the cellulose textile comprises at least 50%, preferably at least 60%, more preferably at least 70% viscose.

**[0079]** According to a 50th embodiment, in the 48th embodiment, the animal-derived textile comprises one or more selected from the group consisting of wool and silk.

**[0080]** According to a 51st embodiment, in the 48th embodiment, the synthetic textile comprises one or more selected from the group consisting of polyester, polyamide (nylon), acrylic polyester, spandex (elastane, Lycra), aramids, modal, sulfar, polylactide (PLA), lyocell, polybutyl tetrachloride (PBT), and combinations (blends) thereof.

**[0081]** According to a 52nd embodiment, in any one of the preceding 47th to 51st embodiment, at least 90%, preferably at least 95%, more preferably at least 98%, even more preferably at least 99%, and most preferably about 100% of the starting textile is made from a renewable raw material, and/or is biodegradable and/or natural and organic.

**[0082]** According to a 53rd embodiment, in any one of the preceding embodiments, the textile is selected from the group consisting of woven, knitted, crocheted, bonded, warp knitted, and non-woven fabrics, preferably wherein the antimicrobial textile is a woven fabric.

**[0083]** The preferred textiles are multifilament fabrics, i.e. fabrics made of multifilament yarns. Fabrics are preferred because their treatment is significantly cheaper than the treatment of yarns or even fibers. Fabrics made of multifilament yarns are preferred over fabrics made of monofilament yarns because they are stronger, have a higher surface area, and can be blended.

**[0084]** According to a 54th embodiment, the present invention further relates to an antimicrobial textile obtainable by any one of the preceding embodiments, preferably wherein the at least one amino acid and/or amino acid derivative is (are) adhered or bound or covalently bound to the textile, and/or, if present, preferably wherein also the glucosamine, polyglucosamine and/or further antimicrobial agent(s) is (are) adhered or bound or covalently bound to the textile.

**[0085]** According to a 55th embodiment, in the 54th embodiment, the amino acid, amino acid derivative, glucosamine, polyglucosamine and/or further antimicrobial agent (s) adhered or bound or covalently bound to the textile have an individual weight as defined for the respective antimicrobial agents in any one of embodiments 10, 11, 18, 19, 29 to 36.

**[0086]** According to a 56th embodiment, in the 54th or 55th embodiment, the antimicrobial textile exhibits a reduction value of P. aeruginosa ATCC 9027 and/or Staphylococcus aureus ATCC 6538, measured in accordance with AATCC test method 100-2012, of at least 99%, preferably at least 99.9%, more preferably at least 99.99%, most preferably at least 99.999%, within 24 hours of contact time, preferably within 6 hours of contact time, more preferably within 1 hour of contact time, even more preferably within 15 minutes of contact time, particularly within 10 minutes of contact time.

**[0087]** According to a 57th embodiment, in the 56th embodiment, the reduction value is achieved even after at least 10 laundry washes in a laundry washing machine at 40 °C for 20-40 minutes, preferably using brand name non-antimicrobial, non-ionic and non-chlorine containing laundry detergent, preferably followed by a standard rinse cycle.

**[0088]** According to a 58th embodiment, in any one of the 54th to 57th embodiments, the antimicrobial textile exhibits a zero growth of microbes when tested in accordance with AATCC Test Method 30-2013 Part III (Agar Plate, Aspergillus Niger or Candida albicans).

**[0089]** According to a 59th embodiment, in the 58th embodiment, the zero growth value is achieved even after at least 10 laundry washes in a laundry washing machine at 40°C for 20-40 minutes, preferably using brand name non-antimicrobial, non-ionic and non-chlorine containing laundry detergent, preferably followed by a standard rinse cycle.

**[0090]** According to a 60th embodiment, in any one of the 54th to 59th embodiments, at least 90%, based on weight, preferably at least 95%, more preferably at least 98%, even more preferably at least 99%, particularly 99.5%, and most preferably about 100% of all antimicrobial agents adhered to or comprised by the textile are biodegradable and/or natural and organic.

**[0091]** All percentages hereinafter refer to weight unless otherwise indicated. "% owf" or "% o.w.f." stands for "of weight fabric" and is the weight percentage of the uptake of the antimicrobial agent in relation to the fabric, "gpl" or "GPL" stands for "grams per liter". "R.t." stands for "room temperature", which is a temperature in the range of 15 to 35 °C.

**[0092]** The term "antimicrobial" as used in the context of the present invention relates to the ability to kill at least some types of microorganisms, or to inhibit the growth or reproduction of at least some types of microorganisms. Said term relates to any compound, agent, product or process that is harmful to one or more "microorganism" as used in the context of the present invention. Preferably, the one or more "microorganism" gets killed by the "antimicrobial" product or process.

**[0093]** The term "antimicrobial agent" as used herein means any chemical compound that acts antimicrobial against at least some types of microorganisms. Exemplary antimicrobial agents are chitosan, quaternary ammonium organosi-

lane, silver cations, polyhexamethylene biguanide (PHMB), and propiconazole. Amino acids and/or amino acid derivatives are not antimicrobial agents *per se*, but become antimicrobial upon adherence and/or binding to the textile. Therefore, in the context of amino acids and/or amino acid derivates adhered to the textile, these compounds are also to be understood as antimicrobial agents.

**[0094]** The terms "microorganism" and "microbe", which are used interchangeably in the context of the present invention, are defined to comprise any organism too small to be seen by the unaided eye, such as, especially, single-celled organisms. In particular, the terms "microorganism" and "microbe" cover prokaryotes including bacteria and archaea, eukaryotes including protists, animals like dust mites or spider mites, fungi, and plants like green algae, as well as viruses.

**[0095]** The term "textile" as used herein means a textile or textile material in any form and includes fibers, yarns, threads, ply yarns, fabrics produced from fibers and/or yarns, and the finished products produced from fibers, yarns, and/or fabrics. The textile can be woven, knitted, crocheted, bonded and/or non-woven fabric. It can be spun, electrospun, drawn or extruded.

**[0096]** The term "biodegradable" as used herein refers to any form of textile, amino acid, amino acid derivative, chitosan, antimicrobial agent or other chemical compounds, which can be decomposed by living cells, such as bacteria.

**[0097]** The term "natural and organic" as used herein refers to organic compounds that may by produced by living organisms. For example, all amino acids that are synthesized by biological cells or chitosan are natural and organic compounds.

## Detailed description of the invention

**[0098]** Preferred embodiments and examples of the invention will be described in the following detailed description. It is emphasized, however, that the present invention is not limited to these embodiments.

**[0099]** The present invention relates to a method for rendering a textile antimicrobial. Advantageously, the method allows the use of naturally occurring functional agents, such as amino acids or peptides, or a combination of these compounds with chitosan for the finishing of a textile.

**[0100]** The inventors have discovered that the deposition of positive surface charges on a textile, such as by (covalently) binding the amino acid arginine and/or the amino acid derivative carnitine to the textile, confers a high antimicrobial activity to the textile. While not wishing to be bound by theory, it is believed that a high density of positive charges of the amino acid and/or amino acid derivative disrupts the cellular membrane of microorganisms, e.g. of gram-negative or gram-positive bacteria.

**[0101]** The obtained antimicrobial textile is environmentally friendly, as the antimicrobial agents, such as natural amino acids, are biodegradable. Moreover, the use of amino acids and/or amino acid derivatives as antimicrobial agents lowers the production costs for the antimicrobial textile, e.g. in comparison to antimicrobial textiles comprising chitosan only.

*Liquor application process:*

**[0102]** The method according to the invention comprises a liquor application process, in particular an exhaust process, for the application of the amino acids and/or amino acid derivatives. As is known in the art, during an exhaust process, a textile material is brought in contact with a liquor which comprises ingredients which are transferred to the article during the exhaust process. This can be achieved by guiding the textile material through a container filled with the liquor. Yarn and fabrics are typically treated with exhaust processes. During a common exhaust process, chemicals to be applied to a textile material are dissolved or dispersed in a solvent, e.g. water, according to the required material to liquor ratio, which describes the ratio between the weight of the textile to be treated and the weight of the liquor. For example, if the desired material to liquor ratio is 1:2, there would be 600 kg of liquor for 300 kg of textile material to be exhausted. Following, the textile material is brought in contact with the liquor, for example by immersing it into the liquor, whereby the chemicals preferably contact the fibers and more preferably enter the fibers. For obtaining proper diffusion and penetration of the chemicals in the fiber, a respective liquor temperature and respective exhaustion time are set, such that kinetic and thermodynamic reactions take place as desired. As the textile material and its fibers absorb the chemicals, the concentration thereof in the liquor decreases. As is known in the art, the degree of liquor exhaustion as a function of elapsed time is termed extent of the exhaust process. The percentage of the chemicals initially present in the liquor which is exhausted onto the textile at the end of the process is called exhaustion rate or exhaust rate.

**[0103]** In an exhaust process, the textile opens up and the fibers are individually exposed to penetration by the amino acids and/or amino acid derivatives. This is particularly true for multifilament yarns or fabrics made out of them, which are preferred for most applications because they are stronger, have a higher surface area, and can be blended. Thus, by use of an exhaust process, the agents can diffuse into the fibers and do not occupy the surface space of the fibers to the same extent as it is the case in more superficial liquor application processes like padding or spraying. Therefore, the use of an exhaustion process in the main process cycle allows to improve the antimicrobial performance by a secondary antimicrobial process cycle, in particular by a secondary process cycle in which a padding process is used,

or to apply other functional agents to the textile in a further process cycle. In contrast, repeated superficial liquor applications like repeated padding applications will not improve performance, or at least not improve performance to the same extent. Furthermore, the inventors found that leaching is at lowest values only when exhaustion is used in the main process cycle. On the other hand, in the case of non-woven fabrics, exhaustion may not be preferred because non-woven fabrics can oftentimes not withstand the forces applied by exhaustion machines like jiggers.

**[0104]** Exhaustion may be performed by any suitable technique, and on any suitable machine, like a yarn dying machine, a beam machine, a winch machine, a jet-dyeing machine, a continuous dyeing range (CDR), continuous bleaching range (CBR), or a jigger machine.

**[0105]** The exhaustion allows for evenly spreading the liquor across the entire cross section of the textile material, such that preferably no spot of the textile material is left untouched by the liquor. As a result, interactions and/or bonds may be created between the textile material and one or more amino acids and/or amino acid derivatives at this time. Preferably most of the agents of the liquor are exhausted evenly onto the entire cross section of the textile material. Preferably, an exhaustion rate of the exhaust process is at least 75%, more preferably at least 85%, more preferably at least 90%, and most preferably at least 95%, such that the textile material picks up most preferably about 95% of the amino acids, amino acid derivatives or antimicrobial agents contained in the exhaust liquor. This exhaustion rate allows for reducing costs, as most of the ingredients of the liquor are exhausted by the textile material. It is also more ecological than processes with lower pickup rates.

**[0106]** In general, more heat on the fabric is better for bonding. Therefore, preferably, the temperature of the liquor during the exhaust process is sufficiently high and the exhaust time is sufficiently long such that the one or more antimicrobial agents in the liquor are substantially uniformly dispersed across the cross section of the textile material as a result of the exhaust process. Thus, the temperature of the liquor should be sufficiently high and the exhaust time should be sufficiently long such that preferably the textile material is well impregnated and the antimicrobial agents are dispersed throughout the entire textile material. Preferably, the exhaust time is sufficiently long and the temperature of the liquor during the exhaust process is sufficiently high such that the textile material can achieve the desired antimicrobial performance after a respective curing process, as will be outlined below.

**[0107]** However, too much heat causes yellowness and weakens the fabric. Therefore, preferably, the temperature of the liquor during the exhaust process is sufficiently low and/or the exhaust time is sufficiently short such that the textile material does not discolor and/or turn yellow and/or its breaking (tensile) strength is not reduced by more than 15%, preferably not more than 10%, more preferably not more than 7%, and most preferably not more than 5%, as a result of the exhaust process. As is known in the art, excessive heat leads to yellowing of the textile material, which may be undesirable. Accordingly, the temperature of the liquor should not be too high. At too high temperatures, too much steam forms, reducing the efficiency of the process. Furthermore, if the temperature of the liquor is too high, turbulences can occur within the liquor bath and the textile material may get harmed. Further, with increasing exhaust time, the textile material may become weaker, i.e. its breaking strength may decrease.

**[0108]** The term exhaust time when used in the context of the present invention is preferably defined as the period starting when at least part of the entire batch of textile material first comes into contact with the liquor and lasting until the last part of the batch is taken out of the liquor. For a given application, the ideal exhaust time can vary significantly. In case the textile is a fabric, it will depend on the type of machine, the size of the liquor bath, and the length and weight of the fabric. For example, if the ideal exhaust time for a fabric of a length of 1,500 meters is 60 minutes, the ideal exhaust time for a fabric of a length of 3,000 meters may be 100 minutes under otherwise identical conditions. Whenever an exhaust time is specified herein, it refers to the time which is equivalent to the exhaust time of a fabric of 1,500 meters in length and 200 g/m$^2$ in weight on a standard jigger machine (e.g. model number Y1100 manufactured by Yamuda) being operated at a standard fabric speed (e.g. 50 meters/minute). For any given textile material and exhaustion machine, the skilled person, using common general knowledge, will be able to determine the exhaust time which is equivalent to an exhaust time specified for the above-mentioned parameters.

**[0109]** Accordingly, with the exhaust process, one or more amino acids and/or amino acid derivatives, and preferably antimicrobial agents are substantially uniformly dispersed across the cross section of the textile material.

**[0110]** The exhaust process is followed by a heat treatment. In the case that there is only one process cycle, the heat treatment may comprise drying and curing. Curing, which takes place at high temperatures, preferably 180 °C, is necessary to fully bind the amino acids and/or amino acid derivatives to the textile material in a non-leaching or substantially non-leaching manner. Prior to curing, the textile must be dried because the temperature of the textile cannot exceed 100 °C until the water in the textile is evaporated. In the case that the main process cycle is followed by further process cycles, be it a secondary process cycle as described herein below, or a process cycle which imparts other properties like hydrophilicity or hydrophobicity to the textile, there is preferably no curing at this stage, i.e. in the main process cycle. This is for economic reasons, but also because curing may close up or seal the textile so that treatments in further process cycles become less effective. In the case of a further process cycle, the textile should be dried because otherwise it would not absorb the liquor of the further process cycle. Drying could be performed by low temperatures such as room temperature. However, to speed up the manufacturing process, drying it is preferably performed by a heat treatment.

Also, the heat treatment can achieve basic bonding of the agents to the textile so that they are not washed out in a subsequent washing step.

**[0111]** The drying can be performed by using normal heat setting processes, depending on the actually used textile material. Preferably, the drying of the textile material is conducted at least partially at a temperature of at least 60 °C, more preferably at least 100 °C, even more preferably at least 110 °C, and most preferably at least about 120 °C. Lower temperatures would require longer dwell time, which is disadvantageous because a longer dwell time has a negative impact on the textile in terms of yellowing and also strength of the fabric.

**[0112]** Preferably, the drying of the textile material is conducted at a temperature of at most 190 °C, more preferably at most 180 °C, particularly at most 170 °C. Even more preferably, the drying of the textile material is conducted at a temperature of at most 150°C, more preferably at most 140 °C, particularly at most 130 °C, and most preferably at most about 120 °C.

**[0113]** Preferably, the drying time at the temperatures given above is of at least 30 seconds, preferably at least 40 seconds, more preferably at least 50 seconds, and most preferably at least about 60 seconds, per 100 g of fabric weight per m2 (in case the textile material is a fabric). Further preferably, the drying is performed over a period of at most 120 seconds, preferably at most 90 seconds, more preferably at most 75 seconds, most preferably at most about 60 seconds, per 100 g of fabric weight per m2 (in case the textile material is a fabric). It will be appreciated that the drying times increase with increasing fabric weight (per $m^2$). The skilled person understands that similar drying times apply if the textile material is a yarn, and understands to choose respective drying times which then depend on the yarn diameter.

**[0114]** The drying process can be typically conducted by passing the textile material through a stenter or stenter frame (sometimes also referred to as a "tenter") or similar drying machine. By drying the textile material, preferably excess moisture is removed.

**[0115]** The drying process may be followed by a curing process if there are no further process cycles. In this case, the curing process can be as described below. However, while in the secondary process cycle the curing process is preferably carried out together with drying process in one single pass through the stenter, there are preferably two separate passes through the stenter for drying and curing in case there is only one process cycle. This is because if there is only one process cycle, the textile is typically wetter, and therefore the drying process can be better controlled if it is performed in a separate pass through the stenter.

**[0116]** On the other hand, if there is a further liquor application process cycle, drying may be followed by a washing step. During washing, the textile material is preferably washed in water, further preferably without using detergents. Preferably, the textile material is washed in a bath, such as e.g. a water bath, having a temperature between 30 °C and 50 °C, further preferably between 35 °C and 45 °C. The washing time is preferably at least 35 minutes and more preferably at least 40 minutes.

**[0117]** After the main process cycle, the resulting textile material already features antimicrobial properties. However, they can be further improved by conducting an optional secondary process cycle, such as padding. Other liquor application processes can be used in the alternative, such as e.g. an exhaust process, coating process or spraying process. However, a padding process has proven to be particularly advantageous because it is less time consuming and therefore less expensive than exhaustion, it provides for a more even distribution of the liquor than spraying (and unlike spraying can be applied on both sides of a fabric at the same time), and it yields better results in terms of non-leaching properties than coating because a coating paste typically contains ingredients which tend to leak.

**[0118]** Any suitable technique can be utilized for performing padding, in which preferably a respective liquor (which may or may not be the same liquor as the one of exhaust process 11 and will be detailed further below) is prepared and fed through a pump to a respective padding mangle. Accordingly, padding process 15 preferably comprises applications of one or more rolls to obtain optimum wet pickup of the liquor on the textile material. The appropriate padding mangle pressure is typically predetermined, depending on the quality of the textile material, and it is in general set such that the wet pickup of the antimicrobial agents is optimized. The liquor may be at room temperature or it may be heated during the padding process.

**[0119]** Preferably, the padding process is performed in a padding mangle at a pressure of 0.5 to 4 bars, more preferably 1.0 to 3.0 bars, even more preferably 1.5 to 2.5 bars, most preferably about 2 bars. The pick-up rate (or "wet pick-up") specifies the amount of liquor applied and is defined as a percentage on the weight of the dry untreated textile as follows:% pick-up rate = weight of liquor applied x 100 / weight of dry textile. For example, a pick-up rate of 65% means that 650 grams of liquor are applied to 1 kg of textile. The pick-up rate of the padding process according to the invention is preferably at least 40%, more preferably at least 50%, even more preferably at least 55, particularly at least 60%, and most preferably at least about 65%. It is preferably at most 90%, more preferably at most 80%, even more preferably at most 75%, particularly at most 70%, and most preferably at most about 65%.

**[0120]** After padding, a heat treatment comprising drying and curing may be performed. Curing may be defined as heat treatment, at temperatures as mentioned in the present application, of the textile material in the dry state, wherein dry means that the textile is 99% devoid of moisture. Typically, a stenter may be used for the curing.

**[0121]** Curing is preferably conducted at least partially at a curing temperature of at least 150 °C, preferably at least

160 °C, more preferably at least 170 °C, even more preferably at least 175 °C, and most preferably at least about 180 °C. Preferably, curing is conducted at a temperature of at most 205 °C, preferably at most 195 °C, more preferably at most 190 °C, even more preferably at most 185 °C, and most preferably at most about 180 °C. Thus, the preferred curing temperature is about 180 °C.

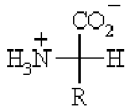
**[0122]** Preferably, curing is performed at the temperature discussed above over a period of at least 20 seconds, preferably at least 24 seconds, more preferably at least 28 seconds, and most preferably at least about 30 seconds per 100 g of the fabric weight per m2 (in case the textile material is a fabric). Preferably, the time period during which this temperature is applied is at most 50 seconds, preferably at most 45 seconds, more preferably at most 40 seconds, even more preferably at most 35 seconds, and most preferably at most about 30 seconds per 100 g of fabric weight per m2 (in case the textile material is a fabric). Thus, in the most preferred embodiment, a curing temperature of about 180 °C is applied for about 30 seconds per 100 g of fabric weight per m2. However, in case of heavy fabrics, the preferred curing time is longer, namely 45 seconds at the temperature discussed above for fabrics of 350 to 500 g/$m^2$, and 60 seconds for fabrics of more than 500 g/$m^2$. This is because with increasing thickness of the fabric, heat waves will take more time to get to the core of the fabric. It will be appreciated that modified temperatures are applied in case that the textile material is a yarn, and the dwell times and curing temperatures then depend on the yarn diameter. Since the curing temperature is substantially independent from the textile material, only the curing time (and drying time) have to be adjusted when using different textile materials. The inventors found that the curing time, or dwell time, increases about linearly with increasing weight of the textile material.

**[0123]** Preferably, curing immediately follows drying. Thus, the textile material preferably does not substantially cool down between the drying and the curing. Accordingly, when performing the drying and curing directly one after the other, both steps are preferably performed over a total period of at least 45 seconds, preferably at least 50 seconds, more preferably at least 55 seconds, and most preferably at least about 60 seconds per 100 g of fabric weight per m2 (in case the textile material is a fabric). Further preferred, the drying and curing are performed over a total period of at most 75 seconds, preferably at most 70 seconds, more preferably at most 65 seconds, and most preferably at most about 60 seconds per 100 g of fabric weight per m2 (in case the textile material is a fabric).

*Functional agents:*

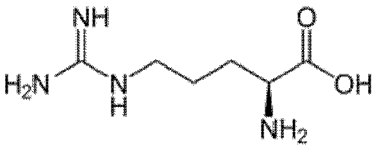
**[0124]** The liquor of the main liquor application cycle, and optionally the liquor of the secondary process cycle comprises at least one amino acid and/or at least one amino acid derivative.

**[0125]** Both the amino acid and the amino acid derivative contain at least two functional groups, one of them being a carboxy group, and the other one being an amine group or quaternary amine group. Unless otherwise indicated, the carboxy group and the amino group are not derivatized, e.g. with crosslinking agents. The amino acid may be an alpha-amino acid, as represented by the following structural formula:

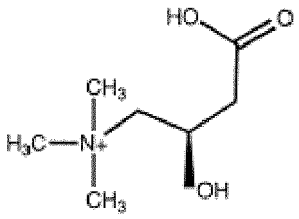


**[0126]** In other embodiments, the amino acid may be a beta-, gamma- or delta-amino acid.

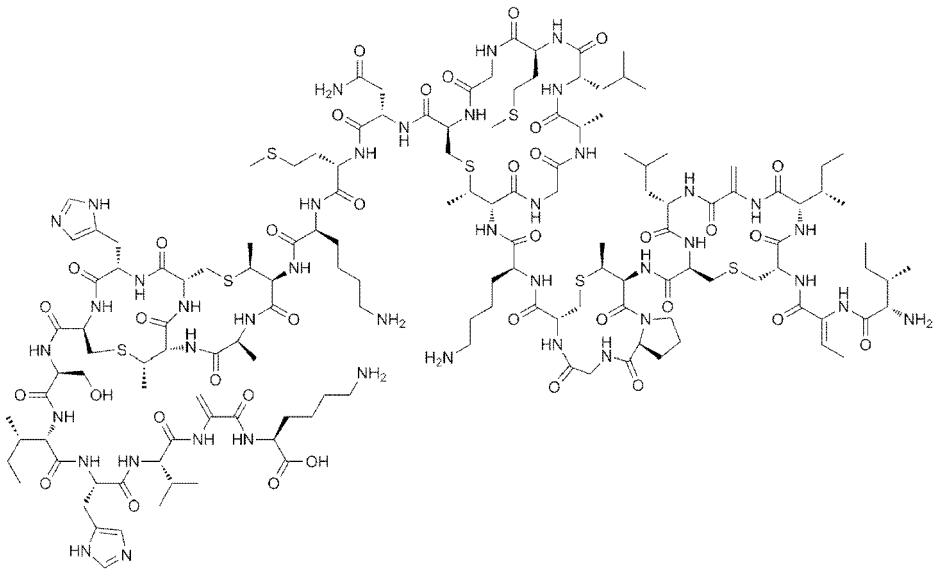
**[0127]** The exemplary proteinogenic amino acid L-arginine is represented by the following structural formula:



**[0128]** The exemplary non-proteinogenic amino acid derivative L-carnitine is represented by the following structural formula:

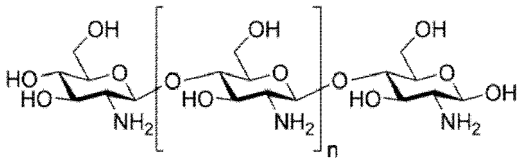


**[0129]** Nisin is a lantibiotic with the following structure:

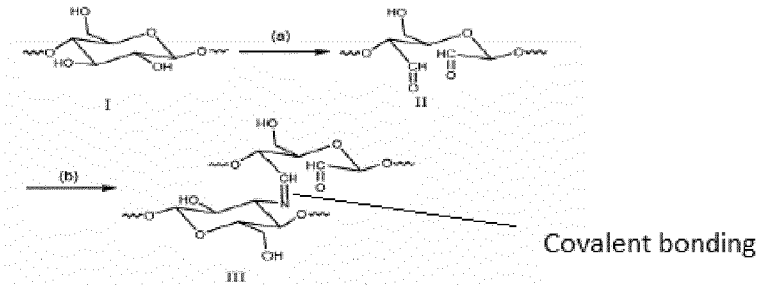


**[0130]** Under the reaction conditions according to the method of the present invention, R'-COOH groups of amino acids and/or amino acid derivatives may react with R"-OH groups of cellulose by forming an ester bond R'-COO-R".

**[0131]** In some embodiments of the invention, polyglucosamine (chitosan) is applied to the textile. Chitosan has a structure as shown hereinafter, wherein n indicates the number of monomer units as known in the art:



**[0132]** Under the reaction conditions disclosed herein, chitosan can react with functional groups of cellulosic materials resulting in covalent bonds as shown below.




Chitosan treated cellulosic molecule

**[0133]** When the amino acids and/or amino acid derivatives are used in combination with chitosan, under the reaction conditions disclosed herein, R'-COOH groups of amino acids and/or amino acid derivatives may react with R"-OH groups of chitosan by forming an ester bond R'-COO-R'.

## Examples

**[0134]** The invention will be further described by the following examples which illustrate the preparation of textile materials, without limiting the invention.

### *AATCC 100-2012 test method for antimicrobial performance:*

**[0135]** Antimicrobial performance of antimicrobial textiles according to the invention were performed following the AATCC 100-2012 test method. The AATCC 100-2012 test procedure for antimicrobial performance is described in detail in AATCC Technical Manual 2013, p. 166-168.

**[0136]** Briefly, 3 circular swatches of 48 mm diameter were prepared from autoclaved (121 °C, 15 min) textile samples, and a defined number of swatches was added to a 250 ml Erlenmeyer flask. 1 ml of prepared inoculum (in phosphate buffered water) was spot onto the swatches. The test inoculum was *P. aeruginosa* ATCC 9027 or S. aureus ATCC 6538 ($10^7$ CFU/ml), and the inoculum load was 1% BSA. Contact times were varied between o mins, 10 mins, 30 mins, and 1 hour. The o minute contact time was immediately analyzed after inoculation. For the other contact times, the Erlenmeyer flask was sealed immediately after inoculation and incubated at 37 °C for the respective contact times.

**[0137]** After the defined contact time, 100 ml of Dey-Engley Neutralizing broth was added to each flask, and the flask was shaken for one minute by hand. A dilution series was prepared and each dilution sample was plated on a nutrient agar. Agar plates were incubated at 37 °C for 24 and 48 hours.

**[0138]** The Log Reduction (R) of bacteria was calculated by:

B [log(number bacteria recovered from the inoculated treated test specimen swatches in the jar immediately after inoculation, i.e. at o contact time)] - A [log(number of bacteria recovered from the inoculated treated test specimen swatches in the jar incubated over the desired contact period)].

### *AATCC TM-30 (Part III) test method for antimicrobial performance:*

**[0139]** The antifungal activity of the textile according to the invention was tested following standard test method "AATCC test method 30-2013" and with *Aspergillus Niger* or *Candida albicans* as test organisms ("Test III" of the standard test method).

**[0140]** A 48 hours old culture of *C. albicans* or *A. niger* was used for testing. The grown culture was scrapped from a Sabouraud dextrose agar medium containing 3% glucose and inoculated in 50 mL sterile distilled water with glass beads. The flask was shaken to make a suspension and the final density was maintained at $2\times10^6$ CFU/ml. The test medium (15 mL) was poured onto the sterile petri dish and allowed to solidify. 1 ml of inoculum was spread over the surface.

**[0141]** A textile sample (3.8 $\pm$ 0.5 cm discs, autoclaved prior to testing at 121 °C, 15 mins) was placed onto the agar surface and 0.2 mL of inoculum was added over each sample. The plates were incubated at 28 °C for 4-5 days. At the end of the incubation period, the plates were examined for yeast/fungal growth according to the following rating:

| Growth on specimen | Rating |
|---|---|
| No growth | o |
| Trace of growth ($\leq$ 10%) | 1 |
| Light growth (10-30%) | 2 |
| Medium Growth (30-60%) | 3 |
| Heavy Growth (60% to complete coverage) | 4 |

### *Chemicals*

**[0142]** The following chemicals were used in the experiments described hereafter:

L-arginine is known in the art and commercially available, e.g. by Sciencelab. In the following examples, L-arginine was provided as a powder with 100% by weight.

L-carnitine was provided by Lonza Specialty Chemicals Switzerland as a powder with > 98% by weight.

**[0143]** Chitosan was provided in a stock solution by Go Yen Chemical (Goyenchem-102), Taiwan. Measurements conducted by the inventors showed that this stock solution contains about 8% active ingredient, i.e. 8% of chitosan.

**[0144]** Propiconazole is known in the art and commercially available, e.g. Utconazol (manufactured by Utpan Chempro). Propiconazole can be bound to the textile material using a crosslinking agent, in particular a preferably blocked isocyanate compound, which results in urethane bonds, or an acrylate based-product. When using propiconazole, it is preferred to use a crosslinking agent in the liquor, in particular the exhaust liquor. It is even more preferred that the formulation of propiconazole contains the cross-linking agent or the cross-linking agent is part of the propiconazole formulation. In the following examples, propiconazol (Utpan Chempro) was provided as a 25% stock solution.

**[0145]** The quaternary ammonium organosilane can comprise an organomethoxysilane, preferably N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride, as provided by Gelest Inc. as a 50% stock solution.

**[0146]** Polyhexamethylene biguanide is known in the art and commercially available. In the following examples, polyhexamethylene biguanide (PHMB, Thor GmbH) was provided as a 20% stock solution.

**[0147]** An antimicrobial agent can comprise silver cations. In particular embodiments, the silver cations are trapped in an inorganic or organic matrix. Preferably, the inorganic matrix is an aluminosilicate. Preferably, the organic matrix is a polymeric matrix. Such silver-containing microbial agents are known in the art and available on the market. In the following examples, Silvadur 930 Flex (0.17% silver cations trapped in a polymeric matrix) was provided by Dow Chemical Company.

**[0148]** As a cross-linker, blocked polyisocyanate, e.g. oxime-blocked polyisocyanate, can be used. Oxime-blocked polyisocyanate is, for example, provided by Schoeller Technologies AG.

***Textiles***

**[0149]** The following textiles were used in the experiments described hereafter:

- 100% viscose: 117 grams per square meter (GSM), yarn count/construction of 30*30/68*64
- 100% cotton: 40's cotton, 140 GSM
- 50% cotton/50% viscose (CVC blend): 140 GSM
- 65% polyester/35% cotton (PC blend): 165 GSM

***Liquor application processes***

**[0150]** Unless otherwise specified in the examples below, the liquor application processes were conducted as follows:

In a first step ("liquor preparation"), a liquor was prepared in a reaction mixture comprising the amino acid(s)/amino acid derivative(s), and/or antimicrobial agents, and water. The pH of the reaction mixture was adjusted as specified in the examples by application of an acid. The reaction mixture was stirred for a specified time and temperature.

**[0151]** Following the liquor preparation, the liquor was used undiluted in the main liquor application process, being either an exhaustion or a padding process, with the specified parameters. In some examples, the main liquor application process was followed by a secondary application process, being a padding process.

**[0152]** Some of the fabrics were produced using a jigger machine for exhaustion (Yamuna, model number Y1100), and others were produced under laboratory conditions which closely simulated this process. The inventors estimate that the amount of chemicals added to the textile in the exhaust process corresponded to the amount of chemicals comprised in a wet pickup of about 100%. Thus, where an agent was comprised in the liquor, e.g., at a concentration of 30 gpl (grams per liter), the amount of the agent on the textile after the exhaust process was about 3% on-weight-fabric. The padding process was carried out with a wet pickup of about 65%. Thus, where an agent was comprised in the liquor, e.g., at a concentration of 30 gpl, the amount of the agent added to the textile in the padding process was about 1.95% on-weight-fabric.

***Drying and curing***

**[0153]** Between the main liquor application process and a secondary liquor application process, the textile was dried, sometimes dried and cured. Following the last liquor application process, the textile was dried and cured. Unless otherwise specified below, drying was performed for 2 minutes at 120 °C, and curing was performed for 2 minutes at 180 °C.

***Washing***

**[0154]** In some examples, the cured textile was washed several times, as indicated in the examples, under the following conditions: The temperature in the washing cycles was 40 °C, and Clax 200s (Johnson Wax Professional) was used as a soap in normal dosage. After each washing cycle, the textile was rinsed for 10 minutes with 0.05% citric acid.

***Example 1:*** *Viscose textile treated with L-arginine*

**[0155]** A 100% viscose textile was treated with L-arginine in a two-cycle process, comprising in the main liquor application cycle an exhaustion process, and in the secondary process cycle a padding process.

**[0156]** A liquor for both the exhaust and the padding processes was prepared containing 30 or 40 grams L-arginine per liter (gpl). The pH was adjusted to pH 4.5 using citric acid. The liquor was stirred at 70 °C for 1 hour.

**[0157]** The exhaustion process was carried out with a wet pickup of about 100%, resulting in an on-weight-fabric L-arginine add-on of 3.0/4.0%. Exhaustion was performed with the undiluted liquor for 1 hour at 60 °C, followed by drying at 120 °C.

**[0158]** Padding was performed with an L-arginine concentration of 10 gpl in the liquor. The padding pickup rate was about 65%. Thus, the total amount of L-arginine added to the textile in the exhaust and padding processes together can be estimated to be 3.0/4.0% + 0.65% = 3.65/4.65% o.w.f.

**[0159]** After padding, the textiles were dried at 120 °C and cured at 180 °C. The cured samples were washed 10 times in a laboratory washing machine using the non-ionic detergent Clax 200 S.

**[0160]** The finishing method and the test results are summarized in the following **table 1.**

**Table 1:** 100% Viscose finishing with L-arginine

| Sample ID | Arg 30 gpl | Arg 40 gpl |
|---|---|---|
| **Liquor preparation** | | |
| Arginine | 30 gpl | 40 gpl |
| Liquor pH | 4.5 | 4.5 |
| pH adjustor chemical | citric acid | citric acid |
| Liquor temp | 70 °C | 70 °C |
| Stirring time | 1 hour | 1 hour |
| **Main process cycle** | | |
| Exhaust time | 1 hour | 1 hour |
| Exhaust temp | 60 °C | 60 °C |
| Drying temp | 120 °C | 120 °C |
| **Secondary process cycle** | | |
| Arginine | 10 gpl | 10 gpl |
| Padding bath temperature | room temperature | room temperature |
| Curing temp | 180 °C | 180 °C |
| **Washing** | | |
| Number of washes | 10 | 10 |
| **Antimicrobial activity (AATCC 100-2012)** | | |
| **Log Reduction (R) [Log cfu/ml] after 10 min** | | |
| S. aureus | 0.53 | 0.76 |
| P. aeruginosa | 2.76 | 2.76 |
| **Log Reduction (R) [Log cfu/ml] after 30 min** | | |
| S. aureus | 0.86 | 0.88 |
| P. aeruginosa | 2.82 | 2.92 |

(continued)

| Log Reduction (R) [Log cfu/ml] after 1 hour | | |
|---|---|---|
| S. aureus | 0.86 | 1.03 |
| P. aeruginosa | 3.82 | 3.82 |

**[0161]** As can be derived from **table 1,** L-arginine confers a significant antimicrobial performance against gram negative *P. aeruginosa* of 2.76 log (i.e. > 99% reduction) already after 10 minutes. The antimicrobial performance against gram-positive *S. aureus* is about 1 log after 1 hour (i.e. about 90% reduction). The overall antimicrobial performance is not influenced by washing the textile in a detergent, rendering it washable and reusable. Such a wash-durability could not be achieved in experiments conducted by the inventors using only a padding process and no exhaust process. The wash-resistance indicates that the amino acid is covalently bound to the textile. Without wishing to be bound by theory, it is believed that the process conditions, including exhaustion at elevated temperature and at a low pH, as well as curing at a high temperature, during which water is evaporated, facilitate an esterification reaction between the carboxy group of L-arginine and the hydroxyl group of the cellulose molecules comprised in the viscose textile. Finally, the data indicate a positive correlation between the L-arginine concentration used in the liquor and the antimicrobial efficiency.

*Colorimetric test for the detection of L-arginine:*

**[0162]** A modified Sakaguchi test was established for detecting and quantifying L-arginine on the textile samples of **table 1.** An adapted Sakaguchi reagent was used, which consists of 1-Naphthol and a drop of sodium hypochlorite solution (2.5%). The procedure for the modified Sakaguchi test was as follows:

*Preparation of four reagents:*

**[0163]**

(1)500 mg of 1-Naphthol (N100-10G, Sigma-Aldrich) in 100 ml Ethanol, corresponds to a 0.5% 1-Naphthol solution in EtOH (each time fresh preparation)
(2) 5 g NaOH in 100 ml deion. water, corresponds to a 5% NaOH solution
(3) Javelle, corresponds to 2.5% NaOCl solution
(4) 5 g Urea in 100 ml deion. water, corresponds to a 5% urea solution in water

*Protocol:*

**[0164]**

- submit textile sample on a petri dish
- textile sample is provided with 1 ml of reagent (1)
- textile sample is provided with 1 ml of reagent (2)
- textile sample is provided with 1 ml of reagent (3)
- textile sample is provided with 1 ml of reagent (4)

**[0165]** A red coloration indicates the presence of L-arginine.

**[0166]** In a first step, a dilution series of L-arginine was tested to estimate the limit for the detection. In this series, 1 ml of a 1% L-arginine, 0.1% L-arginine, 0.01% L-arginine and 0.001% L-arginine solution were each applied to a 6x6 cm fabric (mass = 408 mg), and each fabric was subjected to the Sakaguchi reaction. Coloration could be observed for 0.01% L-arginine solutions and higher concentrated solutions. As 1 ml of a 0.01% L-arginine solution corresponds to 0.1 mg of L-arginine, applied to 408 mg of fabric, the detection limit was estimated to be about 0.025% arginine o.w.f.

**[0167]** The washed textiles of **table 1** were tested according to the Sakaguchi test, and the obtained colorations compared to the dilution series. The o.w.f. concentration of L-arginine of the sample "Arginine 30 gpl" could be estimated to be between 0.25-2.5% of arginine on viscose, and the o.w.f. concentration of L-arginine of the sample "Arginine 40 gpl" could be estimated to be higher than 2.5% of arginine on viscose.

**[0168]** The Sakaguchi test confirmed that L-arginine was stably bound to the textile samples in a wash-durable manner.

***Example 2:*** *Viscose textiles treated with L-carnitine*

**[0169]** A 100% viscose textile was treated with L-carnitine in a two-cycle process, the main process cycle comprising an exhaust process and the secondary process cycle comprising a padding process.

**[0170]** A liquor was prepared by dissolving in water 40 gpl L-carnitine provided as powder, and adjusting the pH to pH 4.5 with citric acid. The liquor was stirred for 30 minutes at 60 °C before being applied to the textile samples by means of exhaustion, followed by drying at 120 °C, and padding.

**[0171]** The exhaustion process was carried out with a wet pickup of about 100%, resulting in an on-weight-fabric L-carnitine add-on of 4.0%. The padding pickup rate was about 65%. Thus, the total amount of L-carnitine added to the textile in the exhaust and padding processes together can be estimated to be 4.0% + 2.6% = 6.6% o.w.f.

**[0172]** After padding, the textile was dried at 120 °C and cured at 180 °C for 2 minutes. After curing, one treated sample was tested directly for antimicrobial activity, whereas a second treated sample was washed 10 times, as described above, before testing the antimicrobial activity.

**[0173]** The prepared textile samples were tested according to AATCC 100-2012 as described above. Further, the prepared textile samples were tested according AATCC TM-30 (Part III) against *Candida albicans* ATCC10231 as described above.

**Table 2:** 100% Viscose finishing with L-carnitine, wash-performance

| Sample ID | Carnitine, unwashed | Carnitine, washed |
|---|---|---|
| **Liquor preparation** | | |
| L-Carnitine | 40 gpl | 40 gpl |
| Liquor pH | 4.5 | 4.5 |
| pH adjustor chemical | citric acid | citric acid |
| pH adjusting dosage | 1 gpl | 1 gpl |
| Liquor temp | 60 °C | 60 °C |
| Stirring time | 30 min | 30 min |
| **Main process cycle** | | |
| Exhaust time | 1 hour | 1 hour |
| Exhaust temp | 60 °C | 60 °C |
| Drying temp | 180 °C | 180 °C |
| **Secondary process cycle** | | |
| Padding bath temperature | 60 °C | 60 °C |
| Number of nib and dip into padding bath | 20 | 20 |
| Curing temp | 180 °C | 180 °C |
| **Washing** | | |
| Number of washes | 0 | 10 |
| **Antimicrobial activity (AATCC 100-2012)** | | |
| **Log Reduction (R) [Log cfu/ml after 10 min** | | |
| S. aureus | 0.13 | 0.13 |
| P. aeruginosa | 0.12 | 0.1 |
| **Log Reduction (R) [Log cfu/ml after 30 min** | | |
| S. aureus | 0.27 | 0.23 |
| P. aeruginosa | 2.9 | 2.82 |
| **Log Reduction (R) [Log cfu/ml after 60 min** | | |
| S. aureus | 0.45 | 0.44 |

(continued)

| | | |
|---|---|---|
| **Main process cycle** | | |
| P. aeruginosa | 3.61 | 3.54 |
| **Antimicrobial activity (AATCC TM-30 (Part III))** | | |
| C. albicans - 48 hours contact | Moderate resistant (rating:3) | Very mild resistant (rating:1) |

**[0174]** As can be derived from **table 2,** L-carnitine confers a high antimicrobial performance against *P. aeruginosa* of 2.82 log (i.e. > 99% reduction) after 30 minutes of incubation. On the other hand, the antimicrobial performance against *S. aureus* is significantly lower. The overall antimicrobial performance is not influenced by washing the textile at 40 °C in a detergent, showing that it is wash-durable and reusable. Such a wash-durability could not be achieved in experiments conducted by the inventors using only a padding process and no exhaust process. The wash-resistance indicates that L-carnitine can also be covalently bound to the textile, possibly in terms of an ester group between the carboxy group of L-carnitine and the hydroxyl group of the cellulose molecules comprised in the viscose textile. Furthermore, the test results regarding *C. albicans* demonstrate that textiles treated with L-carnitine have an antifungal activity.

***Example 3:*** *Viscose textiles treated with combinations of L-arginine and chitosan*

**[0175]** A 100% viscose textile was treated with chitosan or with L-arginine and chitosan in a two-cycle process, comprising in the main liquor application cycle an exhaust step, and in the secondary process cycle a padding step.

**[0176]** A liquor for the exhaustion step was prepared containing 40 grams chitosan stock solution (8%) per liter or 40 grams of chitosan stock solution and 60 grams of L-arginine per liter. The pH was adjusted to pH 4.5 using citric acid or acetic acid. The liquor was stirred at 70 °C for 1 hour. The exhaustion process was carried out with a wet pickup of about 100%, resulting in a chitosan add-on of 0.32% o.w.f. and an L-arginine add-on (where applicable) of 6% o.w.f. Exhaustion was performed for 1 hour at 60 °C, followed by drying at 120 °C.

**[0177]** The liquor used in the padding process contained 10 grams chitosan stock solution (8%) per liter or 10 grams of chitosan stock solution and 30 grams of L-arginine per liter. Padding pickup rate of the secondary process cycle was about 65%. Thus, the total amount of chitosan added to the textile in the exhaust and padding processes together can be estimated to be 0.32% + 0.052% = 0.372% o.w.f. The total amount of L-arginine added to the textile in the exhaust and padding processes together (where applicable) can be estimated to be 6% + 1.95% = 7.95% o.w.f.

**[0178]** After padding, the textiles were dried and cured at 180 °C. The cured samples were washed 10 times in a laboratory washing machine using the non-ionic detergent Clax 200 S.

**[0179]** The finishing method and the test results are summarized in the following **table 3.**

**Table 3:** 100% Viscose finishing with L-arginine or L-arginine and chitosan

| **Sample ID** | **Chit** | **Chit + Arg** |
|---|---|---|
| **Liquor preparation** | | |
| Arginine | - | 60 gpl |
| Chitosan stock solution | 40 gpl | 40 gpl |
| Liquor pH | 4.5 | 4.5 |
| pH adjustor chemical | citric acid | acetic acid |
| Liquor temp | 70 °C | 70 °C |
| Stirring time | 1 hour | 1 hour |
| **Main process cycle** | | |
| Exhaust time | 1 hour | 1 hour |
| Exhaust temp | 60 °C | 60 °C |
| Drying temp | 120 °C | 120 °C |
| **Secondary process cycle** | | |
| Arginine | - | 30 gpl |

(continued)

| | | |
|---|---|---|
| **Secondary process cycle** | | |
| Chitosan stock solution | 10 gpl | 10 gpl |
| Padding bath temperature | room temperature | room temperature |
| Curing temp | 180 °C | 180 °C |
| **Washing** | | |
| Number of washes | 10 | 10 |
| **Antimicrobial activity (AATCC 100-2012)** | | |
| **Log Reduction (R) [Log cfu/ml] after 10 min** | | |
| S. aureus | 0.8 | 2.47 |
| oP. aeruginosa | 2.71 | 2.92 |
| **Log Reduction (R) [Log cfu/ml] after 30 min** | | |
| S. aureus | 1.11 | 5.17 |
| P. aeruginosa | 3.52 | 4.82 |
| **Log Reduction (R) [Log cfu/ml] after 1 hour** | | |
| S. aureus | 1.13 | 5.17 |
| P. aeruginosa | 4.82 | 4.82 |

**[0180]** As can be derived from **table 3,** the combination of L-arginine and chitosan confers an extraordinary high antimicrobial performance against *P. aeruginosa* of at least 2.47 log (i.e. > 99% reduction) after 10 minutes of incubation, and against *S. aureus* of at least 2.92 log. After 30 minutes of incubation, the reduction rate increases to 5.17 log and 4.82 log. Such high performances could not be achieved using the antimicrobial agent chitosan only.

***Example 4:*** *Viscose textiles treated with combinations of L-arginine, L-carnitine and chitosan*

**[0181]** A 100% viscose textile was treated with combinations of L-arginine, L-carnitine and chitosan in a one-cycle exhaustion process. Chitosan was provided as aqueous stock solution comprising 8% water-soluble chitosan.

**[0182]** The concentrations of actives in the exhaust liquor resulted in a concentration of 0/0.56% chitosan o.w.f., 7% L-arginine o.w.f., and 7% L-carnitine o.w.f. After exhaustion, the textiles were dried at 120 °C and cured at 180 °C for 2 minutes.

**[0183]** The thus prepared textile samples were washed and tested according to AATCC 100-2012 as described above for example 1.

**Table 4:** 100% Viscose finishing with L-arginine and L-carnitine, or L-arginine, L-carnitine, chitosan

| **Sample ID** | **L-arginine, L-carnitine** | **L-arginine, L-carnitine, chitosan** |
|---|---|---|
| **Liquor preparation** | | |
| Chitosan stock solution | 0 gpl | 70 gpl |
| Carnitine | 70 gpl | 70 gpl |
| Arginine | 70 gpl | 70 gpl |
| Liquor pH | 4.5 | 4.5 |
| pH adjustor chemical | Acetic acid | Acetic acid |
| Liquor temp | 50 °C | 50 °C |
| Stirring time | 1 hour | 1 hour |
| **Main process cycle** | | |
| Exhaust time | 1 hour | 1 hour |

(continued)

| | | |
|---|---|---|
| **Main process cycle** | | |
| Exhaust temp | 50 °C | 50 °C |
| Curing temp | 180 °C | 180 °C |
| **Washing** | | |
| Number of washes | 10 | 10 |
| **Testing results 30 Mins(AATCC-100): Log Reduction (R) [Log cfu/ml]** | | |
| S. aureus | 3.47 | 4.47 |
| P. aeruginosa | 2.15 | 4.06 |

**[0184]** The combination of L-carnitine and L-arginine in the exhaust process results in a significant increase in antimicrobial activity compared to the use of only one of L-carnitine and L-arginine against *S. aureus.* The further addition of chitosan again significally increases the antimicrobial activity, to at least 4 log (i.e., > 99.99% reduction) after 30 min contact time.

***Example 5:*** *Different textiles treated with combinations of L-arginine, carnitine, chitosan, and optionally silver cations*

**[0185]** Different textiles were treated according to the invention, namely a textile consisting of 100% viscose, a textile consisting of 100% cotton, a textile consisting of a blend of 50% cotton and 50% polyester (CVC), and a textile consisting of a blend of 65% polyester and 35% cotton (PC).

**[0186]** A liquor comprising 120 gpl chitosan stock solution (8%), 70 gpl L-arginine and 70 gpl L-carnitine, and optionally 10 gpl Silvadur 930 Flex was applied to the respective textile material in a main process cycle comprising exhaustion, drying at 120 °C and curing at 180 °C, followed by a secondary process cycle comprising padding, drying at 120 °C and curing at 180 °C, using the same liquor as for the exhaustion process.

**[0187]** The concentrations of actives in the liquor resulted in an estimated add-on of 1.584% chitosan o.w.f, 11.55% L-arginine o.w.f., 11.55% L-carnitine o.w.f., and 0.002805% silver o.w.f (where applicable).

**[0188]** The prepared textile samples were tested according to AATCC 100-2012 as described above.

**Table 5:** 100% Viscose or 100% cotton finishing with combinations of L-arginine, L-carnitine, chitosan and silver ions

| **Sample ID** | **100% viscose** | **100% viscose, +Ag** | **100% cotton** | **100% cotton, +Ag** |
|---|---|---|---|---|
| **Liquor preparation** | | | | |
| Chitosan stock solution | 120 gpl | 120 gpl | 120 gpl | 120 gpl |
| Carnitine | 70 gpl | 70 gpl | 70 gpl | 70 gpl |
| Arginine | 70 gpl | 70 gpl | 70 gpl | 70 gpl |
| Silvadur 930 Flex | 0 gpl | 10 gpl | 0 gpl | 10 gpl |
| Liquor pH | 4.5 | 4.5 | 4.5 | 4.5 |
| pH adjustor chemical | Acetic acid | Acetic acid | Acetic acid | Acetic acid |
| Liquor temp | 50 °C | 50 °C | 50 °C | 50 °C |
| Stirring time | 1 hour | 1 hour | 1 hour | 1 hour |
| **Main process cycle** | | | | |
| Exhaust time | 1 hour | 1 hour | 1 hour | 1 hour |
| Exhaust temp | 70 °C | 70 °C | 70 °C | 70 °C |
| Curing temp | 180 °C | 180 °C | 180 °C | 180 °C |
| **Secondary process cycle** | | | | |
| Padding bath temperature | 50 °C | 50 °C | 50 °C | 50 °C |
| Curing temp | 180 °C | 180 °C | 180 °C | 180 °C |

(continued)

| | | | | |
|---|---|---|---|---|
| **Washing** | | | | |
| Number of washes | 10 | 10 | 10 | 10 |
| **Testing results 30 Mins(AATCC-100): Log Reduction (R) [Log cfu/ml]** | | | | |
| S. aureus | 5.34 | 5.64 | 4.83 | 5 |
| P. aeruginosa | 4.91 | 4.91 | 4.91 | 4.91 |

**Table 6:** CVC and PC finishing with combinations of L-arginine, L-carnitine, chitosan and silver ions

| **Sample ID** | **CVC** | **CVC, +Ag** | **PC** | **PC, +Ag** |
|---|---|---|---|---|
| **Liquor preparation** | | | | |
| Chitosan stock solution | 120 gpl | 120 gpl | 120 gpl | 120 gpl |
| Carnitine | 70 gpl | 70 gpl | 70 gpl | 70 gpl |
| Arginine | 70 gpl | 70 gpl | 70 gpl | 70 gpl |
| Silvadur 930 Flex | 0 gpl | 10 gpl | 0 gpl | 10 gpl |
| Liquor pH | 4.5 | 4.5 | 4.5 | 4.5 |
| pH adjustor chemical | Acetic acid | Acetic acid | Acetic acid | Acetic acid |
| Liquor temp | 50 °C | 50 °C | 50 °C | 50 °C |
| Stirring time | 1 hour | 1 hour | 1 hour | 1 hour |
| **Main process cycle** | | | | |
| Exhaust time | 1 hour | 1 hour | 1 hour | 1 hour |
| Exhaust temp | 70 °C | 70 °C | 70 °C | 70 °C |
| Curing temp | 180 °C | 180 °C | 180 °C | 180 °C |
| **Secondary process cycle** | | | | |
| Padding bath temperature | 50 °C | 50 °C | 50 °C | 50 °C |
| Curing temp | 180 °C | 180 °C | 180 °C | 180 °C |
| **Washing** | | | | |
| Number of washes | 10 | 10 | 10 | 10 |
| **Testing results 30 Mins(AATCC-100): Log Reduction (R) [Log cfu/ml]** | | | | |
| S. aureus | 3.83 | 4.05 | 3.12 | 3.88 |
| P. aeruginosa | 4.91 | 4.91 | 4.91 | 4.91 |

**[0189]** As can be derived from the above **tables 5** and **6,** all four textile materials that were tested exhibited high antimicrobial performances, of at least 3 log (i.e. > 99.9% reduction) after 30 min contact time after 10 washes in nonionic detergent Clax 200 S. The addition of silver ions further increased the antimicrobial action against *S. aureus.* Overall, treated viscose textiles exhibited a higher antimicrobial activity than other textile materials. The antimicrobial performance decreased in the following order: viscose > cotton > CVC blend > PC blend. In view of the decreasing concentration of cellulose molecules, and thus of reactive hydroxyl groups, with respect to the CVC blend and the PC blend, it may be possible that the functional groups of the textiles are decisive for a stable binding of L-arginine, L-carnitine and chitosan.

**[0190]** Finally, sample "PC, +Ag" showed to be partially resistant against *A. niger*, when tested according to AATCC-30 (7 days contact time) (not shown in the tables).

***Example 6:*** *100% viscose textiles treated with combinations of L-arginine and chitosan in different types of acids*

**[0191]** 100% viscose textile samples were treated with L-arginine and chitosan in a two-cycle process, comprising in the main liquor application cycle an exhaust step, and in the secondary process cycle a padding step. The pH of the liquor was adjusted either with acetic acid, citric acid or hydrochloric acid.

**[0192]** A liquor comprising 40 gram per liter (gpl) chitosan stock solution (concentration: 8%) and 60 gpl L-arginine was applied in a main process by exhaustion, resulting in a concentration of about 0.32% chitosan o.w.f. and 6% L-arginine o.w.f. Exhaustion was followed by drying at 120 °C. A secondary liquor application cycle comprised padding, drying at 120 °C and curing at 180 °C. The padding liquor comprised 10 gram per liter (gpl) chitosan stock solution and 30 gpl L-arginine, resulting in an additional add-on of 0.052% chitosan o.w.f. and 1.95% L-arginine o.w.f. Total actives add-on in both process cycles together was therefore 0.372% chitosan o.w.f. and 7.95% L-arginine o.w.f.

**[0193]** Exhaustion was followed by drying at 120 °C. After drying, the samples were washed 30 times at 40 °C with Clax 200 S before testing the antimicrobial activity.

**Table 7:** Combinations of L-arginine and chitosan with different acids

| Sample ID | Chit-Arg acetic acid | Chit-Arg citric acid | Chit-Arg HCl |
|---|---|---|---|
| **Liquor preparation** | | | |
| Chitosan stock solution | 40 gpl | 40 gpl | 40 gpl |
| Arginine | 60 gpl | 60 gpl | 60 gpl |
| Liquor pH | 4.5 | 4.5 | 4.5 |
| pH adjustor chemical | Acetic acid | Citric acid | HCl |
| Ph adjusting dosage | 26 gpl | 30 gpl | 33 gpl |
| Liquor temp | 70 °C | 70 °C | 70 °C |
| Stirring time | 1 hour | 1 hour | 1 hour |
| **Main process cycle** | | | |
| Exhaust time | 1 hour | 1 hour | 1 hour |
| Exhaust temp | 60 °C | 60 °C | 60 °C |
| Drying temp | 120 °C | 120 °C | 120 °C |
| **Secondary process cycle** | | | |
| Chitosan stock solution | 10 gpl | 10 gpl | 10 gpl |
| Arginine | 30 gpl | 30 gpl | 30 gpl |
| Padding bath temperature | r.t. | r.t. | r.t. |
| Curing temp | 180 °C | 180 °C | 180 °C |
| **Washing** | | | |
| Number of washes | 30 | 30 | 30 |
| **Antimicrobial activity (AATCC 100-2012)** | | | |
| **Log Reduction (R) [Log cfu/ml] after 10 Mins** | | | |
| S. aureus | 2 | 1.5 | 0.57 |
| P. aeruginosa | 2.1 | 1.74 | 0.85 |
| **Log Reduction (R) [Log cfu/ml] after 30 Mins** | | | |
| S. aureus | 3.8 | 2.55 | 1.1 |
| P. aeruginosa | 3.5 | 3.15 | 1.42 |
| **Log Reduction (R) [Log cfu/ml] after 60 Mins** | | | |
| S. aureus | 4.3 | 2.89 | 1.8 |

(continued)

| Log Reduction (R) [Log cfu/ml] after 60 Mins | | | |
|---|---|---|---|
| P. aeruginosa | 4 | 3.5 | 2.45 |

**[0194]** The results of **table 7** show that the highest antimicrobial performance could be obtained using acetic acid for adjusting the pH of the liquor. Citric acid performs slightly worse, which may be due to the build-up of free carboxylic groups, i.e. negative charges on the textile. On the other hand, hydrochloric acid may affect the textile, in particular cellulosic textiles.

***Example 7:*** *100% Polyethylene textiles treated with combinations of L-arginine, L-carnitine, chitosan and further antimicrobial agents*

**[0195]** A thin fabric was prepared by the method according to the present invention.

**[0196]** A 100% polyester textile (22 GSM) was treated with L-arginine in a one-cycle process, comprising a padding process only.

**[0197]** The liquor for the padding processes was prepared containing 5 gpl each of L-arginine and L-carnitine. Furthermore, the liquor contained 1 gpl of a 25% propiconazole stock solution, 1.5 gpl of a 25% PHMB stock solution, 25 gpl of an 8% chitosan stock solution, and 8% of Silvadur 930 Flex (comprising 0.17% of silver). The pH was adjusted to pH 6.5 using acetic acid. Furthermore, the liquor comprised 4 gpl of isopropanol. The liquor was stirred at 50 °C for 1 hour.

**[0198]** The padding process was carried out with a wet pickup of about 50%. The resulting add-ons of chemicals can be gathered from the table below. Padding was followed by drying at 100 °C for 3 minutes and curing at the same temperature for 2 minutes.

**[0199]** The cured samples were tested for antimicrobial performance, and the test results are compiled in **table 8.**

**Table 8:** Combinations of L-arginine, L-carnitine and chitosan with further antimicrobial agents

| | | | | | |
|---|---|---|---|---|---|
| **Fabric details:** | Plain dotted 100% PE<br>Total meter: 1000<br>GSM: 22<br>GLM: 30.8<br>Width, meter: 1.4<br>Total weight, kg: 31 | | | | |
| **Process parameters** | Total pad liquor lit: 15<br>%pickup, padding: 50%<br>Pad (2 dip--> 2 nip) ---> dry at 100 °C for 3 min ---> cure at 100 °C for 2 min | | | | |
| **Padding liquor** | **Chemicals (stock solution or powder)** | **gm/lit** | **Quantity, kg** | **% actives** | **Add mg/sq -on, .meter** |
| Pad application only | Propiconazol | 1 | 0.015 | 25% | **3.8500** |
| | Polyhexamethylene biguanide | 1.5 | 0.023 | 20% | **4.6200** |
| | Chitosan | 25 | 0.385 | 8% | **30.8000** |
| | Silvadur 930 Flex | 8 | 0.123 | 0.17% | **0.2094** |
| | L-arginine | 5 | 0.077 | 100.00% | **77.0000** |
| | L-carnitine | 5 | 0.077 | 100.00% | **77.0000** |
| | Isopropanol | 4 | | | 0.0000 (evaporates) |
| | Acetic acid (pH adjustment to pH 6.5) | 0.3 | 0.005 | 100% | 0.0000 |
| | | | Total add-on, mg/sq. mtr | | 195.4794 |

(continued)

| | | | | | |
|---|---|---|---|---|---|
| **Antimicrobial activity (AATCC 100-2012)** | | | | | |
| **Log Reduction (R) [Log cfu/ml] after 10 Mins** | | | | | |
| S. aureus | | | | | 2.35 |
| E. coli | | | | | 1.5 |
| **Log Reduction (R) [Log cfu/ml] after 4 hours** | | | | | |
| S. aureus | | | | | 4.15 |
| E. coli | | | | | 4.78 |
| **Log Reduction (R) [Log cfu/ml] after 8 hours** | | | | | |
| S. aureus | | | | | 5.39 |
| E. coli | | | | | 5.54 |
| **Log Reduction (R) [Log cfu/ml] after 24 hours** | | | | | |
| S. aureus | | | | | 5.24 |
| E. coli | | | | | 4.09 |

**[0200]** Although the textile was only treated with padding and, because of its low weight, was cured only at 100 °C, the antimicrobial performance was found to be high.

***Example 7:*** *100% viscose textiles treated with combinations of L-arginine and chitosan by padding*

**[0201]** 100% viscose textile samples were treated with L-arginine and chitosan in a one-cycle process, comprising in the main liquor application cycle a padding step, and in the secondary process cycle a padding step. The pH of the liquor was adjusted to pH 7 with hydrochloric acid.

**[0202]** The padding liquor comprised 40 gram per liter (gpl) chitosan stock solution (concentration: 8%) and 5 gpl L-arginine, resulting in an additional add-on of 0.052% chitosan o.w.f. and 0.325% L-arginine o.w.f.

**[0203]** The padding bath temperature was kept at room temperature. After padding, the textile samples were dried at 150°C for 2 minutes and cured at 180°C for 2 minutes. In the following the textiles were washed 5 times in water, each washing cycle performed over 10 minutes at 27°C, and tested according to AATCC 100-2012, as described above. The process parameters and test results are summarized in **table 9.**

**Table 9:** Wash-durability after padding

| **Sample ID** | **Chit-Arg unwashed** | **Chit-Arg washed** |
|---|---|---|
| **Liquor preparation** | | |
| Chitosan stock solution | 40 gpl | 40 gpl |
| Arginine | 60 gpl | 60 gpl |
| Liquor pH | 7 | 7 |
| pH adjustor chemical | HCl | HCl |
| **Main process cycle** | | |
| Padding bath temperature | r.t. | r.t. |
| Curing temp | 180 °C | 180 °C |
| **Washing** | | |
| Number of washes | 0 | 5 |
| **Antimicrobial activity (AATCC 100-2012)** | | |
| **Log Reduction (R) [Log cfu/ml] after 30 Mins** | | |
| S. aureus | 1.99 | 3.29 |

(continued)

| Log Reduction (R) [Log cfu/ml] after 60 Mins | | |
|---|---|---|
| S. aureus | 4.28 | 4.28 |

**[0204]** The results according to **table 9** indicate that a padding process allows the production of an antimicrobial textile with wash-durable performance to a certain extent. However, the performance decreases slightly upon washing the textile, while an exhaustion process renders textiles highly wash-durable and reusable as antimicrobial textile, as described above. Therefore, application of an exhaust process in the main process cycle is currently preferred.

## Claims

**1.** A method for rendering a textile antimicrobial, comprising a main process cycle comprising the steps of:

- treating the textile in a main liquor application process such as padding or preferably exhaustion, the liquor of the main liquor application process comprising at least one amino acid and/or at least one amino acid derivative, wherein the amino acid and/or amino acid derivative has an isoelectric point equal to or above 7, preferably equal to or above 8, more preferably equal to or above 8.5, and/or has a pH-independent positive charge
- subjecting the treated textile to a heat treatment,
- optionally washing the heat-treated textile, and
- optionally drying the washed textile,

and the method preferably comprising a secondary process cycle being performed after the steps of the main process cycle and comprising the steps of:

- treating the textile using a secondary liquor application process, such as an exhaust or preferably a padding process, wherein the liquor of the secondary liquor application process comprises at least one amino acid, at least one amino acid derivative, and/or at least one antimicrobial agent;
- subjecting the treated textile to a heat treatment,
- optionally washing the heat-treated textile, and
- optionally drying the washed textile.

**2.** The method of claim 1, wherein the at least one amino acid comprised in the liquor of the main and/or secondary liquor application process is selected from the group consisting of natural amino acid, unnatural amino acid, non-proteinogenic amino acid, and/or wherein the at least one amino acid derivative is selected from the group consisting of peptide and quaternary ammonium comprising amino acid derivative, preferably wherein the natural, unnatural or non-proteinogenic amino acid is in L configuration, and/or wherein the peptide is a L-peptide.

**3.** The method of claim 1 or 2, wherein the at least one amino acid comprised in the liquor of the main and/or secondary liquor application process is lysine, arginine, or histidine, preferably arginine;
and/or wherein the at least one amino acid derivative comprised in the liquor of the main and/or secondary liquor application process is a lantibiotic, preferably nisin;
and/or wherein the at least one amino acid derivative comprised in the liquor of the main and/or secondary liquor application process is carnitine or betaine, preferably carnitine.

**4.** The method of any one of claims 1 to 3, wherein the at least one amino acid or amino acid derivative in the liquors of all process cycles together is applied to the textile in an amount of at least 0.1 % by weight, preferably at least 0.2%, more preferably at least 0.5%, or at least 1%, at least 2%, at least 3%, or at least 4%, based on the weight of the textile; and /or wherein the at least one amino acid or amino acid derivative in the liquors of all process cycles together is applied to the textile in an amount of at most 15% by weight, preferably at most 12%, or at most 10%, or at most 5%, or at most 4%, based on the weight of the textile.

**5.** The method of any one of claims 1 to 4, wherein the liquor of the main and/or secondary liquor application process comprises glucosamine and/or polyglucosamine.

**6.** The method of claim 5, wherein glucosamine and/or polyglucosamine in the liquors of all process cycles together

is applied to the textile in an amount of at least 0.1%, preferably at least 0.2%, more preferably at least 0.3%, or at least 0.7% or at least 1%, based on the weight of the textile; and/or wherein glucosamine and/or polyglucosamine in the liquors of all process cycles together is applied to the textile in an amount of at most 5%, preferably at most 4%, more preferably at most 3%, even more preferably at most 2%, and most preferably at most 1.6%, or at most 1%, based on the weight of the textile material.

**7.** The method of any one of claims 1 to 6, wherein the liquor of the main and/or secondary process cycle comprises one, two, three, or all four of the antimicrobial agents selected from the group consisting of azole based compound, silver ions, polyhexamethylene biguanide, quaternary ammonium organosilane.

**8.** The method of any one of claims 1 to 7, wherein the pH of the liquor of the main and/or secondary liquor application process is equal to or below 6.5, preferably equal to or below 6.0, more preferably equal to or below 5.5, even more preferably equal to or below 5.0, most preferably about 4.5.

**9.** The method of claim 8, wherein the pH of the liquor of the main and/or secondary liquor application process is adjusted by an organic acid, preferably a monocarboxylic acid, in particular acetic acid, lactic acid, formic acid, propionic acid, p-Toluenesulfonic acid or a combination thereof.

**10.** The method of any one of claims 1 to 9, wherein the heat treatment of the main and/or secondary process cycle comprises curing, wherein curing is conducted at least partially at an ambient temperature of at least 150 °C, preferably at least 160 °C, more preferably at least 170 °C, particularly at least 175 °C, and most preferably at least about 180 °C, and/or at an ambient temperature of at most 205 °C, preferably at most 195 °C, more preferably at most 190 °C, particularly at most 185 °C, and most preferably at most about 180 °C.

**11.** The method of any one of claims 1 to 10, wherein the starting textile comprises hydroxyl, peptide and/or carbonyl groups, in particular hydroxyl and/or peptide groups, preferably wherein the starting textile is a cellulosic textile material, an animal-derived textile material, a synthetic textile material, or a blend comprising a cellulosic, animal-derived and/or a synthetic textile material.

**12.** The method of claim 11, wherein at least 90%, preferably at least 95%, more preferably at least 98%, even more preferably at least 99%, and most preferably about 100% of the starting textile is made from a renewable raw material, and/or is biodegradable and/or natural and organic.

**13.** An antimicrobial textile obtainable by any one of the preceding claims 1 to 12, preferably wherein the at least one amino acid and/or amino acid derivative is (are) adhered or bound or covalently bound to the textile, and/or, if present, preferably wherein also the glucosamine, polyglucosamine and/or further antimicrobial agent(s) is (are) adhered or bound or covalently bound to the textile.

**14.** The antimicrobial textile of claim 13, exhibiting a reduction value of P. aeruginosa ATCC 9027 and/or Staphylococcus aureus ATCC 6538, measured in accordance with AATCC test method 100-2012, of at least 99 %, preferably at least 99.9%, more preferably at least 99.99%, most preferably at least 99.999%, within 24 hours of contact time, preferably within 6 hours of contact time, more preferably within 1 hour of contact time, even more preferably within 15 minutes of contact time, particularly within 10 minutes of contact time.

**15.** The antimicrobial textile of claim 14, wherein the reduction value is achieved even after at least 10 laundry washes in a laundry washing machine at 40 °C for 20-40 minutes, preferably using brand name non-antimicrobial, non-ionic and non-chlorine containing laundry detergent, preferably followed by a standard rinse cycle.

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# EUROPEAN SEARCH REPORT

Application Number
EP 18 16 2641

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