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(71) Applicant: **AL.PRE.TEC. Srl**
Allergy Prevention Technology Italia
37128 Verona (VR) (IT)

(72) Inventor: **Montagner, Dino**
I-30027 S. Dona' DI Piave (VR) (IT)

(74) Representative: **Spagnolo, Chiara**
D'Agostini Group Srl
Corso G. Matteotti, 149
00041 Albano Laziale (RM) (IT)

(54) PROCESS FOR TREATING YARN, KNIT OR FABRIC WITH AN ANTIMICROBIAL AGENT OF NON-RELEASE TYPE

(57) Treating a fabric or a knit or yarns which can include, at least in part, silk, with a permanent or non-releasing antimicrobial agent of the quaternary ammonium-based type, with the following steps:
a) Fill a machine for finishing with water and load the fabric;
b) Bring the bath to a temperature of approx. 80°C;
c) Drain and fill with water at ambient temperature by adding antimicrobial agent, spin the fabric in the bath;
d) Drain and fill water, take process water to be used for the environmental impact test of the antimicrobial agent;
e) Acidifying the bath; add a percentage of antimicrobial agent, at the end of which take process water to be used for the test in point d);
f) Increase the temperature, adding Solvay soda and maintain the bath conditions for a few minutes;
g) Take other process water and carry out the test again; If shows complete exhaustion of the antimicrobial agent, drain the bath without rinsing;
h) Centrifuge and dry the fabric.

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Description

[0001] The present invention relates to a process for carrying out an antimicrobial treatment, on a fabric, a non-woven fabric or on a knit or spun fibre, which can include, at least in part, silk, and independently of the type of construction, be it pique, jersey, rib and stretch, where said fabric or knit is in the form of a semi-finished product or a finished article.

FIELD OF APPLICATION OF THE INVENTION

[0002] In the literature, for example, the proteinic properties of silk are known. It is a fibre of animal origin, which has been used for millennia to obtain manufactured articles, not least in the clothing sector, also for underwear and also accessories for clothing and home furnishings.
It is also known that, relatively recently, some have intended to treat the fibre, the semi-finished product or the article itself, with antimicrobial components, this, for example, because many subjects suffer from skin diseases, of which dermatitis are a possible typical pathology. In this case, the subjects who unfortunately suffer from it, who have to wear conventional untreated articles of clothing, may be subject to a skin irritation, which, sometimes, can be localized, while in as many circumstances it is also widespread, up to affect almost the entire body. It is certainly one of the many non-negligible problems, since it is understandable that the part of the body affected by the disease is not only usually treated with adequate drugs, but it will also have to be protected in the best possible way. Protection and generally, care, thus becomes an essential aspect, not only to favour the regeneration of the skin, but above all to prevent the phenomenon from worsening or worse from reappearing. Moreover, it can happen that due to inadequate protection, bacterial colonies may originate, causing repeated and annoying and dangerous infections which slow down the course of the disease. It must be also remembered that, as anticipated, skin infections are one of the most recurrent pathologies as a consequence, for example, of dermatitis. These are only elementary examples, indeed, the same can be observed in other diseases, such as, always in the literature, the diabetic foot, or even more so in the case of the treatment of burns. Ultimately, in these ones and other circumstances, always with the same protective purpose, it is necessary to proceed by wearing or applying special, adequate articles of clothing, bandages or also just coverings.
[0003] Some apparently decisive hypotheses have been undertaken in the past, although in relation to fabrics which did not involve the use of fibres of animal origin, for example, CN1044964 (Wang). More specifically, it dealt with the problem of transmission of dermatitis through contact with fabrics, creating a non-woven fabric which uses acrylic fibres modified through a chemical treatment, aimed at obtaining a uniform, antiseptic and anti-odour fibre combined with a polyester fibre, viscose and polypropylene fibre, subsequently structured as a net and then involving acrylate latex. According to the extender, this fabric would be particularly suitable for making sanitary napkins, with anti-inflammatory, anti-itch properties, and with health protection functions from skin softening, dermatitis and other skin disorders. A further example, which can be cited mostly for information purposes, is given by the document CN1211652 (Yutang) that is a fabric to prevent allergic asthma caused by dust mites. In short, the fabric, without specifying what type, was treated with an anti-mite emulsion, adhesive and water.

STATE OF THE ART RELATIVE TO THE INVENTION

[0004] In IT1334384 (Montagner), a process is described for obtaining a manufactured article, particularly of silk, suitable for the treatment of skin diseases of the human body, in which the following treatment phases with antimicrobial agent are provided:

- realization of the manufactured article, carrying out the working with silk;
- immersion of the manufactured article thus obtained in a bath which provides a quaternary ammonium-based composition, bonded with a catalyst which polymerizes on the fibres;
- drying;

and in which the manufactured article consists of an article of clothing, particularly suitable for children, in the form of a therapeutic small overall suit, in silk knit, integrating portions of knit which cover the ends of the upper and lower limbs, which provides, in correspondence with said ends, slot-like openings for the temporary exit of hands and feet.
The use is also suggested in US6120587 (Elfersy et al.) of an antimicrobial composition formed by mixing an organosilane, optionally having a non-hydrolyzable organic group, but having one or more hydrolyzable groups, with a polyol containing at least two hydroxy groups, wherein at least two of the hydroxy groups are separated by no more than two intervening atoms. Water-stabilized organosilane compounds. A water stable composition based on polyol and organosilane or compound and water. A method for treating a substrate by mixing or contacting the substrate with the product compound, or composition of the present invention for a period of time sufficient for the treatment of the substrate. A treated substrate which has adhered to the product, to the compound or to the composition of the present invention. A method for dyeing

and treating a substrate. A method for antimicrobial treatment of a food item. A method for antimicrobial coating of a container for fluids. A method for antimicrobial coating of a latex medical article. A method for producing a siloxane in the presence of a stabilizer.

Finally, US2002141959 (Perterson et al.) was found which describes a method for applying on the skin aqueous compositions containing antimicrobial organosilane quaternary ammonium compounds, which remain on the skin, are substantial to it and reduce or eliminate bacteria, viruses and the fungi which are present and prevent future contamination due to their presence and substantial character. All formulations are aqueous solutions which can be scented and/or coloured and all contain a water-soluble organosilicon quaternary ammonium compound or a mixture thereof; in particular 3-(trimethoxysilyl)-propyloctadecyl-dimethyl ammonium chloride or 3-(trimethoxysilyl)propyldidecylmethyl ammonium chloride and its derivatives trisilanol, polysiloxanol and polysiloxane which are soluble in water.

DRAWBACKS

[0005] Although, in the past, the antimicrobial function of quaternary ammonium is known, and its use for example of the type AEGIS Dow Corning 5700 (3-trimethoxysilylpropyldimethyloctadecyl ammonium chloride) marketed by AEGIS Environmental Management, Inc., on the other hand it appears explicitly in IT1334384 (Montagner), which describes the treatment of application of the antimicrobial agent and indicates in the main phase of preparation of the fabric, exclusively the use, or the intended purpose of the antimicrobial agent related to fabrics or natural, raw, degummed silk fibre. It is also true that, always in IT1334384 it is stated that results can be also obtained using raw materials other than silk, such as non-woven fabric, synthetic, natural or artificial fibres and blends, however the adopted process is not described at all, nor are the measures suggested regarding how to carry out a correct process also aimed at constantly verifying the complete and uniform absorption of the antimicrobial agent used.

[0006] From a practical point of view, the start of similar treatments carried out particularly on blended fabrics, did not allow to detect the presence in a stable and uniform way of the properties found due to the treatment of the fabric with the antimicrobial agent as suggested in IT1334384 (Montagner). As a consequence, where said procedure is used for fabrics of the blended type, the reasonable loss or non-homogeneity of the antimicrobial function was observed, therefore, for example, not acquiring the characteristic hypoallergenic function with the ability not to irritate which is typical in the case of use of silk alone, as the barrier effect to skin irritation and abrasions disappears as it is unable to effectively protect and from a substantial point of view, that is the possibility of infections remaining almost unchanged. Finally, making the blended fabric and possible manufactured article not particularly suitable for the care and treatment of dermatitis, burns, in women's underwear, or for the treatment of skin symptoms caused by diabetes. Consequently, there is a limited and possible use to only certain types of clothing.

[0007] It should also be pointed out that also in the case of use of silk fibroin (100%) alone in a fabric, a certain difficulty was encountered in effectively binding the antimicrobial agent, which in many cases was not completely absorbed, and so as to be still present, in certain quantities, in process waters at the end of the process indicated in IT1334384 (Montagner). The consequence, also in this case, is therefore to obtain a manufactured article which does not completely fulfil the barrier function suitable for inhibiting the growth of bacteria.

[0008] In conclusion, although not optimized, the following can be considered as generally known:

- the use, with antimicrobial function, of quaternary ammonium with a relative binder from the family of silicone softening agents;
- the execution of a process to apply said antimicrobial agent, on silk fibroin (100%) as well as, possibly, on non-woven fabrics, synthetic, natural or artificial fibres and blends;
- where said process involves the following phases: i) realization of the manufactured article, of silk; ii) immersion in a bath which includes a composition based on quaternary ammonium, bound with a catalyst which polymerizes on the fibres; iii) drying;
- the aims of the previous solutions, such as an article of clothing with hypoallergenic properties and with a barrier function against skin irritation and abrasions being capable of effectively protecting the skin in case of bacterial proliferation.

[0009] In the context of the solutions mentioned above, solutions are not found or suggested which are intended to more effectively treat fabrics or knits made, also in blends, of silk fibroin and non-woven fabric, synthetic, natural or artificial fibres and blends, in such a way as to ensure on the whole the complete exhaustion of the antimicrobial agent in the fabric or knit.

[0010] An essential aim of the present invention is also to obviate the aforementioned drawbacks.

BRIEF DESCRIPTION OF THE INVENTION

[0011] This and other aims are achieved with the present innovation according to the characteristics of the appended claims, solving the problems set forth by means of a process for treating a fabric or a knit and yarns with a permanent or non-releasing antimicrobial agent, which process requires the following steps:

a) Fill a machine of the type for finishing with water at ambient temperature and load the fabric into it; if the fabric is silk fibroin fabric, of schappe type, for whitening, add hydrogen peroxide and anhydrous sodium pyrophosphate;
b) Bring the bath to a temperature of approx. 80°C and maintain for approx. 60 minutes, performing the washing continuously for a total of three cycles;
c) Drain the bath and fill with new water at ambient temperature by adding a percentage of antimicrobial agent of the AEM5772 type, gradually over approx. 15 minutes, once the introduction is complete, spin the fabric in the bath for approx. 30 minutes for a total of approx. 45 minutes, in order to eliminate any possible anionic residues from previous working;
d) Drain the bath and fill with new water at ambient temperature and take process water to be used later also for the environmental impact test of the antimicrobial agent;
e) Continue by acidifying the bath to a pH of approx. = 5.5; add a percentage of antimicrobial agent over 15 minutes, at the end of which take other process water to be used later for the test referred to in point d);
f) Then increase the temperature gradually, until reaching the temperature of approx. T = 60°C adding Solvay soda to increase the pH up to approx. 8 and maintain the bath conditions for a few minutes (pH = 8 and T = 60°C);
g) Take other process water and carry out the test again to verify the absence of environmental impact of the antimicrobial agent on the samples taken; If the test shows complete exhaustion of the antimicrobial agent, drain the bath without rinsing;
h) Centrifuge the fabric and dry the fabric.

ADVANTAGES

[0012] In this way, through the considerable creative contribution whose effect constitutes an immediate technical progress, certain aims and advantages are achieved.

[0013] By way of example, through said process, it is possible to achieve in an optimal manner the antimicrobial treatment relative to fabrics which are not only made of 100% silk fibroin, but which can also be of the blended type, such as for example in a non-woven fabric, also with natural or artificial synthetic fibres and blends.

[0014] Another possible use of the process provides for the possibility of carrying out the same treatment not only of 100% silk fibroin knitted fabrics or in combination with other microfibers (natural, synthetic, artificial and elastane), but also on non-woven fabrics (TNT) and natural, artificial and synthetic fabrics but without silk fibroin, while ensuring at the same time the absorption of the antimicrobial agent in an almost stable way over time.

[0015] Furthermore, the process described is also ideally suited only for the treatment of the single yarn which is thus ennobled with the antimicrobial agent and is particularly useful in the production of articles of clothing and accessories manufactured by machines which use the thread, such as, for example in the production of gloves, stockings, pants, tubular socks, seamless knitwear and the like; these articles are made of 100% silk fibroin, or in combination with other microfibres (natural, synthetic, artificial and elastane also known as spandex). In the same way, using the already ennobled yarn, non-woven fabrics (TNT) and natural, artificial and synthetic fabrics can be produced.

[0016] Whether it is fabrics or thread, which are so ennobled, the semi-finished product obtained is particularly useful for the manufacture of sweaters and other articles of clothing, suitable for sports, wellness and fitness sectors, since, unlike the known technical fabrics, it does not impoverish the skin and performs, on the one hand, the function of preventing irritation but also infections of the skin, and on the other hand it achieves a good capacity to reduce and absorb odours.

[0017] A further possible intended purpose, through the use of fabrics treated with the described process, may concern the subsequent manufacture of textile medical devices, such as, for example, in the form of plasters, gauze, tampons, bandages with or without compression, tubular socks and sheets, masks included, all able to prevent irritation and at the same time able to offer an effective antimicrobial protection, a barrier, of the "non-release" type.

[0018] To sum up, it should be noted that in addition to respecting the environment, the proposed solution is particularly suitable for use in the medical field since it eliminates microbial superinfections in contact without chemical release. It also favours its use in sports and wellness, since it reduces or eliminates microbial colonization (bacteria and fungi) on the fabrics, giving them longer durability, shorter washing cycles, absence of bad odours, no release of chemicals on the skin, which instead happens in the case of the use of silver, heavy metals, chitosan, triclosan and sanitized. Finally, no release into water during washings, which are vice-versa frequent.

[0019] The process thus carried out, if it is carried out in a punctual way, also allows to ensure a uniform, homogeneous and stable treatment, in correspondence with all the fibres of the fabric or thread, and, at the same time, it allows through the multiple test phases, to verify the complete absorption of the amount of antimicrobial agent poured into the bath, stabilizing it in an optimal way, and at the same time avoiding to pour into the waste water of the baths even minimal amounts of antimicrobial agent, which, vice-versa, would require subsequent purification treatments to be properly disposed of, finally taking advantage of a significant reduction in the working costs and also of a real reduction in environmental impact. It should be noted that with the third taking of water referred to in phase h) there is the absence of antimicrobial agent in the water, so as to ensure the complete exhaustion of it in the fabric, knit or yarn, and the purity of the drain water which does not require purification.

[0020] Finally, a further advantageous aspect derives from the extreme versatility of the process, which, alternatively or simultaneously, allows to effectively treat fabrics which are natural or of synthetic or artificial fibres, also in blends, or the thread alone, so that through the two prescribed washing phases with the enrichment of antibacterial, the ionic charge precipitates of the fabric capable of receiving the cationic antimicrobial.

[0021] In this regard, tests were also carried out, in particular with the collaboration of the University of Bologna, Department of Haematology, Microbiology and Oncology, aimed at an in vitro evaluation of the bioactivity of different fabrics for underwear, taking into account the Lactobacillus acidophilus, Staph. Epidermidis, Staph. Aureus and Candida albicans.

As part of this assessment, the following types of fabrics available on the market were taken and a test fabric referred to in no. 8 called Dermasilk (of the 100% fibroin type) treated as per the process described above, in relation to which the comparative test was performed:

Table 1: tested Bio-Functional underwear available in the market

1. DERMASMART: polyester with Silver ions
2. PLATATEX: 50% cotton, 42% polyamide, 8% Silver
3. PADYCARE: 82% polyamide, 18% lycra with, 20% Silver filaments
5. SANITIZED T99-19: polyamide with T 99-19
6. CRABYON: chitosan and viscose
7. TRICLOSAN/SANITIZED: polyamide with TRICLOSAN (SANITIZED)
8. DERMASILK: pure silk (100% fibroine, without sericine) with AEM 5772/5
9. COTTON: 100% without antimicrobial treatment

10 ECZEMACLOTHING: 100% cotton with Silver ions

[0022] The analysis, in a quantitative evaluation, of the antimicrobial activity released by the fabrics after 24 hours of incubation in PBS (a balanced salt solution), showed that all the fabrics analysed exerted an antimicrobial activity ranging from 18% to 100% on an average basis of 24 hours of incubation, with the following results:

Antimicrobial activity released by textiles

Quantitative evaluation after 24 hours of incubation in PBS

[0023]

Textiles	Antimicrobial agent	% reduction			
		Lactobacillus Acidophilus (ATCC11975)	Staphylo coccus epidermidis (ATCC 1228)	Staphylo coccus aureus (ATCC 700698)	Candida albicans (ATCC 10261)
DERMAS MART	Ag*ions	100,0	98,11	100,0	100,0
ECZEMAC LOTHING	Ag*ions	100,0	96,07	98,38	86,84
PLATATEX	Pure Ag	94,82	100,0	100,0	100,0
PADYCARE	Ag filaments	96,66	100,0	95,00	100,0

(continued)

Textiles	Antimicrobial agent	% reduction			
		Lactobacillus Acidophilus (ATCC11975)	Staphylo coccus epidermidis (ATCC 1228)	Staphylo coccus aureus (ATCC 700698)	Candida albicans (ATCC 10261)
	Ag fibers	100,0	100,0	100,0	100,0
SANITIZED T99-19	T99-19	96,72	98,0	96,36	56,09
TRICLOSAN/SANITIZED	Triclosan	96,36	98,07	100,0	17,64
CRABYON	Chitosan	98,33	100,0	100,0	34,37
DERMASILK	AEM 5772/5	1,69	0	0	0
COTTON	-	0	0	0	6,25
Negative control (no textile)	-	0	0	0	0

[0024] Most fabrics, therefore, showed a marked increase in the antimicrobial activity related to the incubation time, reaching the highest rate of reduction in a time variable between 6 and 22 hours of incubation. The only material which has shown to exert its maximum antimicrobial activity in a short time (within the first 60 minutes) was Dermasilk. The evaluation of the antimicrobial activity released by the fabrics after 24 hours of incubation in PBS showed that all fabrics released varying levels of antimicrobial molecules in the incubation medium with the only exception of pure cotton and Dermasilk (pure silk, 100% fibroin, deficient sericin, treated with AEGIS AEM5772 / 5).
Conclusion: All the fabrics evaluated had an ability to kill microbes when in close contact with microorganisms in a warm and humid environment. This inhibiting activity was released in varying degrees in the incubation medium by all the fabrics, but Dermasilk showed no release into the environment. The release of antimicrobial chemicals into the environment could cause concern for the onset of allergies and skin damage. Furthermore, the antimicrobial activity of Dermasilk was very rapid, being the highest level, reached within 1 hour of incubation, this because action takes place by contact and not by release and subsequent accumulation. These, but also other advantages or purposes will appear from the following detailed description of at least one preferred embodiment with the help of the attached table whose execution details are not to be intended as limiting but only as examples.

CONTENT OF THE DRAWINGS

[0025] **Figure 1** is a block diagram of the process described.

PRACTICAL DESCRIPTION OF REALIZATION OF THE INVENTION

[0026] The process in question first requires the preparation of the semi-finished product to be treated and which, in principle, can consist of for example fabric, raw fabric, not excluding non-woven fabrics, but also only the thread, or both, be them in fibre of animal origin, such as for example 100% silk fibroin, wool, or cashmere, synthetic or natural or artificial and blends. In the case of fabrics, as well as non-woven fabrics and thread, they can also be of the blended type, thus fibres of animal origin with those of the synthetic type being combined to varying degrees.

[0027] A condition for being able to correctly carry out said process is the possibility of using common finishing machines, without special precautions, such as those of the "overflow" type.

[0028] These machines are usually used for dyeing fabrics, they consist of a large tank, obtained inside a containment compartment, which can be isolated from the outside to allow access during the loading phase of the semi-finished product, which last being immersed in a bath, in a given phase, allows the mixing of the semi-finished products. In some cases, the mixing of the semi-finished products introduced can also take place with the help of a mixer, which can sometimes cooperate with the movement of the tank, depending on the type of machine, for example of the type oval paddle dyeing machine. Furthermore, said machines can also provide an integrated drying function, whose phase can

be managed independently or provided separately in a tumbler within a finishing cycle.

[0029] In a possible application, assuming the need to treat approx. 80 kg of semi-finished product, be it fabric, raw fabric, not excluding non-woven fabrics, for example 100% silk fibroin fabric (Pique, Jersey, rib and stretch construction), dressing and blended fabrics (for example 37% silk and 63% polypropylene), the finishing machine is loaded for example of the overflow type. Once loaded, the procedure, in sequential order, is as described below:

a) Fill said machine with water, approx. 2500 litres at ambient temperature (~20/25°C); only in the case of silk fibroin of schappe type, for the whitening, add hydrogen peroxide (20 g/L) and anhydrous sodium pyrophosphate 3 g/L, bring the bath to T = 80°C and maintain for 60 minutes. Wash continuously for 10 minutes, then do two more washings with ambient temperature water.
b) Drain the bath from said machine and fill with new water at ambient temperature, then add 1.5% of antimicrobial agent, of the type EC Number 248-595-8 and CAS Number 27688-52-6, gradually over 15 minutes, once the introduction is complete, spin the fabric in the bath for 30 minutes (total 45 minutes), in order to eliminate any possible anionic residues from previous working.
c) Drain the bath and fill with new water at ambient temperature and take 10 ml of water to be used later for a first environmental impact test of the antimicrobial agent.
d) Continue by acidifying the bath to pH = 5.5 (tolerance $\pm$ 0.5); add 9% of antimicrobial agent over 15 minutes, at the end of which take another 10 ml of process water to be used later for a second environmental impact test of the antimicrobial agent.
e) Then increase the temperature until reaching the temperature of T = 60°C, adding
Solvay soda to increase the pH up to 8 (tolerance $\pm$ 0.2) and maintain the bath conditions (pH = 8 and T = 60°C) for 20 minutes;
f) Take another 10 ml of process water and carry out the third BPB test to verify the absence of environmental impact of the antimicrobial agent on the three samples taken. If the test shows complete exhaustion of the antimicrobial agent, drain the bath without rinsing; Centrifuge in the same or another machine, ensuring to carefully clean the centrifuge basket so that it is perfectly clean for a subsequent working cycle.
g) Dry the fabric in a special machine
h) Carry out the BPB test on a dried piece of fabric to check the correct outcome of the antimicrobial treatment and record the result.

[0030] During the execution of phases c), d) and f), during which the first, second and third environmental impact tests are carried out, it is appropriate to specify that it allows immediate verification of the absence of environmental impact of the antimicrobial treatment with the substance identified with EC Number 248-595-8 and CAS Number 27668-52-6 carried out on fabric or thread, before the process water is drained into the sewer, thus ensuring on the one hand total protection of the environment, without pollution for the water supply network and the organisms contained in it, but above all on the other hand, to verify whether the treatment of exhaustion, that is the application of the antimicrobial agent in the fabric or thread, took place completely and therefore the chemical substance was completely absorbed and is no longer present in the process water.

[0031] This test includes the following phases:

1) Prepare a 0.001% Bromophenol Blu (BPB) solution as follows:

- dilute 0.1 ml of 4% liquid BPB in 400 ml of tap water. Mix for 15 minutes until the solution is completely homogenized;

2) Take 10 ml of water from the process bath before adding the antimicrobial agent and dilute it with 1 ml of 0.001% BPB solution prepared as in point 1) The solution formed becomes of indigo colour;
3) 5 minutes after the introduction of the antimicrobial substance into the machinery used for the antimicrobial application process and before raising the temperature and pH of the processing bath, take 10 ml of water from the bath and dilute it with 1 ml of 0.001% BPB. The solution changes colour and becomes light-blue due to the presence of the antimicrobial agent identified with EC Number 248-595-8 and CAS Number 27668-52-6;
4) Once all the steps of the antimicrobial application process are completed, take 10 ml of water from the processing bath and add 1 ml of 0.001% BPB previously prepared. The solution formed becomes of indigo colour again due to the absence of the antimicrobial.

The antimicrobial exhaustion treatment is considered complete when it is exhausted, that is totally bound to the fibres, therefore it is no longer present in the process bath water: indeed the BPB test demonstrates that the colour of the water returns to be the same as before the introduction of the antimicrobial substance identified with EC Number 248-595-8

and CAS Number 27668-52-6. Said process ends only once the exhaustion treatment is completed, otherwise the working continues, thus ensuring that the water drained into the water supply network is always free of antimicrobial agents.

[0032] In a further preferential solution, it was tested that said antimicrobial substance identified with EC Number 248-595-8 and CAS Number 27668-52-6 can be combined with a sulphonamide. By way of example, the proportions which can be used in the compound fall within a percentage ranging from 2% to 15% of a sulphonamide diluted in water, which to treat approximately 80 kg of silk, require approx. 2500 litres of water, together with the quaternary silane in the quantity of about 10%. The compound thus originated allows, following the described working, the achievement of results almost close to 100% of antibacterial activity. In this regard, some initial kill tests were carried out on Arthrobacter of the strain (IAI-3), an organism which forms a biofilm, comparing two 0.1% organosilane antimicrobial agents on 100% polyester in two moments. After 1 hour of contact, the long-chain SiC18Q was 99.9% effective while the sulphonamide accelerator showed a complete killing of 99.9999% after one hour and three hours. Finally, after a long incubation, the quat (that is the quaternary silane) showed complete killing after 3 hours. No stress test was performed prior to the microbial test.

[0033] A variant of the process described above is provided in the case in which it is necessary to proceed with the treatment of articles made of 100% silk fibroin thread or blended. In this hypothesis, the procedure is as follows:

a) Fill the appropriate machinery with water at ambient temperature (~20/25°C) and load the loose thread or in skein; add 1.5% of antimicrobial agent gradually over 15 minutes, once the introduction is complete, spin the goods in the bath for 30 minutes (total 45 minutes), in order to eliminate any possible anionic residues from previous working;
b) Drain the bath and fill with new water at ambient temperature and take 10 ml of water to be used later for the first environmental impact test of the antimicrobial agent;
c) Continue by acidifying the bath to pH = 5.5 (tolerance ± 0.5); add 9% of antimicrobial agent over 15 minutes, at the end of which take another 10 ml of process water to be used later for the second environmental impact test of the antimicrobial agent;
d) Then increase the temperature until reaching the temperature of T = 60°÷70°C
adding Solvay soda to increase the pH up to 8 (tolerance ± 0.2) and maintain the bath conditions (pH and temperature) for 20 minutes;
e) Take another 10 ml of process water and carry out the third BPB test to verify the absence of environmental impact of the antimicrobial agent on the three samples taken. If the test shows complete exhaustion of the antimicrobial agent, drain the bath without rinsing;
f) Perform the drying in a tumbler or in a hot air oven. Carry out the BPB test on a dried item to check the correct outcome of the antimicrobial treatment and record the result.

[0034] Also in this hypothesis, the environmental impact test required in phases b), c) and e), will be of the type described above. It must be said, in principle, that the number of repeated tests, in the different phases of treatment of the fabric or thread, may vary according to the needs, provided that the threshold of complete exhaustion is reached of the antimicrobial substance identified with EC Number 248-595-8 and CAS Number 27668-52-6.

Claims

1. Process for carrying out an antimicrobial treatment of the quaternary ammonium-based type, on a fabric or on a knit or a thread which can include, at least in part, silk, and independently of the type of construction, be it pique, jersey, rib and stretch, where said fabric or knit is in the form of a semi-finished product or a finished article, said process which requires a finishing machine, **characterized in that** at least the following steps are required:

   a) Fill said machine with water at ambient temperature (~20/25°C) and load the thread, or the fabric, or the knit; add 1.5% of antimicrobial agent gradually over 15 minutes, once the introduction is complete, spin the goods in the bath for at least 30 minutes, in order to eliminate any possible anionic residues from previous working;
   b) Drain the bath and fill with new water at ambient temperature and take a few millilitres of water to be used later for the first environmental impact test of the antimicrobial agent;
   c) Continue by acidifying the bath to pH = 5.5 (tolerance ± 0.5); add 9% of antimicrobial agent over 15 minutes, at the end of which take another 10 ml of process water to be used later for the second environmental impact test of the antimicrobial agent;
   d) Then increase the temperature until reaching the temperature of T = 60° ÷ 70°C
   adding Solvay soda to increase the pH up to 8 (tolerance ± 0.2) and maintain the bath conditions (pH and temperature) for approx. 20 minutes;

e) Take other millilitres of process water and carry out the third BPB test to verify the absence of environmental impact of the antimicrobial agent on the three samples taken. If the test shows complete exhaustion of the antimicrobial agent, drain the bath without rinsing;
f) Perform the drying in a tumbler or in a hot air oven.

2. Process for carrying out a treatment, on a fabric or on a knit or a thread which can include, at least in part, silk, and independently of the type of construction, be it pique, jersey, rib and stretch, where said fabric o knit is in the form of a semi-finished product or a finished article, **characterized in that** it requires the following steps:

a) Fill a machine of the type for finishing with water at ambient temperature and load the fabric into it; if the fabric is a silk fibroin fabric, of schappe type, add hydrogen peroxide and anhydrous sodium pyrophosphate;
b) Bring the bath to a temperature of approx. 80°C and maintain for approx. 60 minutes, performing the washing continuously for a total of three cycles with water at ambient temperature;
c) Drain the bath and fill with new water at ambient temperature adding a percentage of antimicrobial agent, gradually over approx. 15 minutes, once the introduction is complete, spin the fabric in the bath for approx. 30 minutes for a total of approx. 45 minutes, in order to eliminate any possible anionic residues from previous working;
d) Drain the bath and fill with new water at ambient temperature and take process water to be used later also for the environmental impact test of the antimicrobial agent;
e) Continue by acidifying the bath to a pH of approx. = 5.5; add a percentage of antimicrobial agent over 15 minutes, at the end of which take other process water to be used later for the test referred to in point d);
f) Then increase the temperature gradually, until reaching the temperature of approx. T = 60°C;
adding Solvay soda to increase the pH up to approx. 8 and maintain the bath conditions for a few minutes (pH = 8 and T = 60°C);
g) Take other process water and carry out the test again to verify the absence of environmental impact of the antimicrobial agent on the samples taken; if the test shows complete exhaustion of the antimicrobial agent, drain the bath without rinsing;
h) Centrifuge the fabric and dry the fabric, subsequently, at the end of the procedure.

3. Process for carrying out a treatment, on a fabric or on a knit or on a thread, according to claims 1 and 2, **characterized in that** the antimicrobial agent is of the AEM5772 type, EC Number 248-595-8 and the CAS Number 27688-52-6.

4. Process for carrying out a treatment according to the previous claims, where a sulphonamide is added to said antimicrobial agent.

5. Process for carrying out a treatment, on a fabric or on a knit or on a thread, according to the previous claims, **characterized in that** said environmental impact test and product verification requires the following steps

- Prepare a 0.001% Bromophenol Blue (BPB) solution as follows:
- Dilute 0.1 ml of 4% liquid BPB in 400 ml of tap water. Mix for 15 minutes until the solution is completely homogenized;
- Take 10 ml of water from the process bath before adding the antimicrobial agent and dilute it with 1 ml of 0.001% BPB solution prepared as in point 1). The solution formed becomes of indigo colour;
- 5 minutes after the introduction of the antimicrobial substance into the machinery used for the process of application of the antimicrobial agent and before raising the temperature and pH of the working bath, take 10 ml of water from the bath and dilute it with 1 ml of 0.001% BPB. The solution changes colour and becomes light-blue for the presence of the antimicrobial agent identified with EC Number 248-595-8 and CAS Number 27668-52-6;
- Once all the steps of the procedure of application of the antimicrobial agent have been completed, take 10 ml of water from the working bath and add 1 ml of 0.001% BPB previously prepared: the solution formed becomes of indigo colour again for the absence of the antimicrobial agent.

a) If the whitening phase is required; fill a machine of the type for finishing with water at ambient temperature and load the fabric into it; if the fabric is a silk fibroin fabric, of schappe type, add hydrogen peroxide and anhydrous sodium pyrophosphate;

b) and bring the bath to a temperature of approx. 80°C and maintain for approx. 60 minutes, performing the washing, introducing water continuously for a total of three cycles with water at ambient temperature, replacing the water used and reducing the temperature;

c) Drain the bath and fill with new water at ambient temperature adding a percentage of antimicrobial agent of the AEM5772 type, gradually over approx. 15 minutes, once the introduction is complete, spin the fabric in the bath for approx. 30 minutes for a total of approx. 45 minutes, in order to eliminate any possible anionic residues from previous working;

d) Drain the bath and fill with new water at ambient temperature and take process water to be used later for the environmental impact test of the antimicrobial agent;

e) Continue by acidifying the bath to a pH of approx. = 5.5; add a percentage of antimicrobial agent over 15 minutes, at the end of which take other process water to be used later for the test referred to in point d);

f) Then increase the temperature gradually, until reaching the temperature of approx. T = 60°C;

g) Add Solvay soda to increase the pH up to approx. 8 and maintain the bath conditions for a few minutes (pH = 8 and T = 60°C);

h) Take other process water and carry out the test again to verify the absence of environmental impact of the antimicrobial agent on the samples taken; If the test shows complete exhaustion of the antimicrobial agent, drain the bath without rinsing;

i) Centrifuge and dry the fabric, thread or a knit

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EUROPEAN SEARCH REPORT

Application Number
EP 21 02 0016

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D06M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	29 July 2021	Fiocco, Marco

CATEGORY OF CITED DOCUMENTS

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