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(54) **PROCESS AND DEVICE FOR CHLORINE-FREE SHRINKPROOF TREATMENT OF WOOL RAW MATERIAL AND ARTICLE THEREOF**

(57) The present invention relates to a process and a device for chlorine-free shrinkproof treatment of a wool raw material and an article thereof. In particular, the process of the present invention comprises the steps of a chlorine-free shrinkproof treatment, washing with water, protease inactivation, a softening treatment, dehydration, drying and the like, wherein a chlorine-free catalysis system consisting of a protease, a specific organic phosphine compound and the like is selected, removing the scale layer on the surface of wool fibres cooperatively and efficiently and modifying the scale layer so as to improve the shrinkproof performance of wool articles. The process of the present invention can completely replace the chloridisation shrinkproof method in the prior art, and is not only environmentally friendly, but also has low requirements for equipment, can be operated continuously and is suitable for large-scale industrial production.

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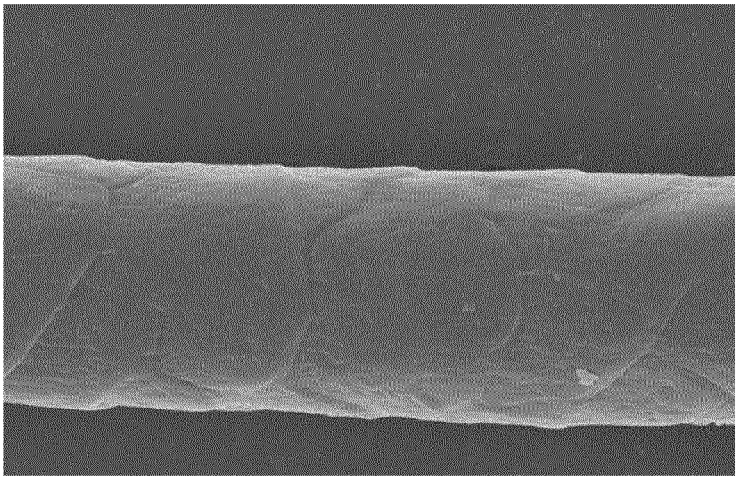

Figure 1

Description

Technical field

[0001] The present invention relates to wool product processing field, and particularly, to a process and device for chlorine-free shrinkproof treatment of wool raw material and article thereof, and more particularly to a chlorine-free continuous processing process and device for shrinkproof treatment of wool and wool article.

Background art

[0002] Wool is an important raw material of textile industry and has many excellent characteristics, such as good elasticity, strong hygroscopicity, not easy to stain, good warmth retention and soft luster. Wool, as a natural protein fiber, has a scale layer attached onto the surface thereof which is mainly composed of keratin and overlapped with each other as fish scales. Due to different friction coefficients along scale direction and against scale direction, under repeated external force, wool fibers will intersperse, entangle, wrap and felt with each other, thereby producing fulling. Although fulling makes wool fabric have effects such as beautiful appearance, rich and soft feel, and good warmth retention, it also makes wool fabric prone to size shrinkage and deformation in a washing process. Therefore, in order to improve shrinkproof properties of wool textile, surface modification treatment of wool fiber scale is necessary from the beginning so that the dimensional stability of wool fabric product is improved and the product can achieve "machine washable" effect.

[0003] At present, the main modification shrinkproof treatment methods of wool surface scale include: chlorination method, covering method, protease method and so on. The most extensive method is chlorination shrinkproof treatment method. However, organic halide AOX (which is absorbable organic halide) generated during the chlorination process will seriously pollute environment.

[0004] Chinese patent CN201010605809.9 has reported a shrinkproof scale-stripping process in which potassium permanganate and DCCA as a catalyst are added into water, and then chlorine gas is passed into so as to conduct a shrinkproof scale-stripping for wool tops. This method reduces 30% of chlorine usage on the basis of the original chlorine usage. Although this method has improved traditional chlorination method, but it still uses chlorine gas and causes serious environmental pollution. The covering method makes the wool surface scale voids filled by depositing a layer of resin film on surface of wool so as to make wool surface become smooth, thereby reducing surface friction effect of fibers. Although this treatment method can improve felting performance of fibers to a certain extent, it seriously affects the touching feel of wool fabric and has a shortage of poor durability. Protease method makes the scales and cell membrane complex etc. of wool partially dissolved by using protease hydrolysis of peptide bonds of macromolecules on wool fiber surface, so as to partially or totally remove the scales. This treatment method has advantages such as mild handling conditions, energy conservation and pollution reduction etc., and is an environmentally friendly wool shrinkproof treatment method. However, the shrinkproof effect obtained by using protease alone to treat wool is still unable to meet the actual requirements at present, so when protease is used for biological modification treatment of wool, in many cases, the wool firstly needs pretreatment (such as preoxidation by using strong oxidants such as potassium permanganate etc., or pretreatment by using a chloride solvent). The above-mentioned pretreatment methods have disadvantages such as the treatment time is too long, the enzyme is easy to inactivate, the treatment condition is difficult to control and so on.

[0005] In addition, although researchers have attempted to develop chlorine-free shrinkproof treatment processes for wool raw materials, those processes have the following disadvantages: (a) the treatment time is long (The time can not be shortened into 30 minutes or less if processing quality should be ensured); (b) the treatment capacity is limited and unsuitable for industrial applications; (c) the treatment quality is of high volatility and it is difficult to obtain wool processing products with uniform processing effect. Therefore, in major wool raw materials processing countries such as China, at present, no wool raw materials are processed with a chlorine-free shrinkproof treatment process in actual production.

[0006] In summary, there is an urgent need in the art to develop a wool shrinkproof treatment process which is environmentally friendly, simple and easy to control, of long-lasting anti-felting effect, of high (or fast) treatment efficiency and suitable for mass production.

SUMMARY OF THE INVENTION

[0007] The object of the present invention is to provide a wool shrinkproof treatment process which is environmentally friendly, simple and easy to control, of long-lasting anti-felting effect, of high (or fast) treatment efficiency and suitable for mass production.

[0008] In the first aspect of the present invention, a shrinkproof treatment agent for chlorine-free shrinkproof treatment is provided, and the shrinkproof treatment agent comprises: (a) an optional solvent; (b) a protease; and (c) an organic phosphine compound represented by formula A; and an optional inorganic salt;

$P\text{-}(X)_3$ A

wherein each X is independently selected from the group consisting of substituted or unsubstituted C1-C10 hydrocarbyl, wherein the term "substituted" refers to one or more substituents selected from the group consisting of -OH, -COOH (carboxy), C2-C8 ester group, -SH, -CN, C1-C3 alkyl, and C1-C3 alkoxy;
and at least one X is a substituted C1-C10 hydrocarbyl having a -OH or COOH substituent;
the weight ratio of the protease to the organic phosphine compound is (0.2 to 10) : (0.5 to 20);
and the protease in the shrinkproof treatment agent is selected from the group consisting of a neutral protease, an alkaline protease, and combinations thereof.

[0009] In another preferred embodiment, the chlorine-free treatment comprises descaling/shrinkproof treatment for a wool raw material and/or a wool product.

[0010] In another preferred embodiment, the wool raw material comprises wool top.

[0011] In another preferred embodiment, the weight ratio of the protease to the organic phosphine compound is (0.5 to 5): (1 to 10); and more preferably (1 to 5): (1 to 10).

[0012] In another preferred embodiment, the shrinkproof treatment agent further comprises a basic compound.

[0013] Preferably, the basic compound is selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal carbonates, alkaline earth metal carbonates, alkali metal bicarbonates, alkaline earth metal bicarbonate, and combinations thereof.

[0014] In another preferred embodiment, the basic compound is selected from the group consisting of NaOH, KOH, $Ca(OH)_2$, Na_2CO_3, K_2CO_3, and combinations thereof.

[0015] In another preferred embodiment, the "chlorine-free" means that the shrinkproof treatment agent does not contain an organochlorine compound and does not include a hypochlorous compound selected from the group consisting of: a compound containing ClO^- ion (root) and a compound which can produce ClO^- ion (such as chlorine gas).

[0016] In another preferred embodiment, in the shrinkproof treatment agent, the content of the hypochlorous compound is $\leq$ 0.05% by weight, preferably $\leq$ 0.01% by weight, more preferably $\leq$ 0.001% by weight, and most preferably about 0.

[0017] In another preferred embodiment, the shrinkproof treatment agent is a liquid (i.e., a treatment solution).

[0018] In another preferred embodiment, the solvent is selected from the group consisting of water or an aqueous solvent.

[0019] In another preferred embodiment, the shrinkproof treatment agent is a solid or semi-solid, and can be reconstituted into a treatment solution by adding a solvent (e.g., water) upon application.

[0020] In another preferred embodiment, in the treatment solution (or the reconstituted treatment solution), the concentration of the organic phosphine compound is from 1 to 10 g/L, preferably from 1.5 to 10 g/L, and more preferably from 5 to 10 g/L.

[0021] In another preferred embodiment, in the treatment solution (or the reconstituted treatment solution), the concentration of the protease is 0.1 to 25 g/L, preferably 0.2 to 10 g/L, and more preferably 0.5 to 5 g/L.

[0022] In another preferred embodiment, in the treatment solution (or the reconstituted treatment solution), the concentration of the inorganic salt is 0.01 to 10 g/L, preferably 0.05 to 5 g/L, and more preferably 0.1 to 2 g/L.

[0023] In another preferred embodiment, two X are identical.

[0024] In another preferred embodiment, three X are identical.

[0025] In another preferred embodiment, three X are different from each other.

[0026] In another preferred embodiment, each X is independently selected from the group consisting of substituted or unsubstituted C1-C6 hydrocarbyl.

[0027] In another preferred embodiment, the C1-C10 hydrocarbyl includes C1-C10 alkyl, C2-C10 alkenyl, C2-C10 alkynyl and C3-C8 cycloalkyl.

[0028] In another preferred embodiment, the C1-C10 hydrocarbyl includes C1-C10 alkyl and C3-C8 cycloalkyl.

[0029] In another preferred embodiment, when the shrinkproof treatment agent contains one or more components selected from the group consisting of a protease, an organic phosphine compound, an inorganic salt and a surfactant the contents thereof are as follows:

component	content	preferred content	more preferred content
protease	0.01 to 2.5wt% (or 0.1 to 25g/L)	0.02 to 1.0wt% (or 0.2 to 10g/L)	0.05 to 0.5wt% (or 0.5 to 5g/L)
organic phosphine compound	0.01 to 5.0wt% or 0.1 to 50g/L	0.05 to 2.0wt% or 0.5 to 20g/L	0.1 to 1.0wt% or 1 to 10g/L

(continued)

component	content	preferred content	more preferred content
inorganic salt	0.001 to 1.0wt% or 0.01 to 10g/L	0.005 to 0.5wt% 0.05 to 5g/L	0.01 to 0.2wt% 0.1 to 2g/L
surfactant	0.001 to 1.0wt% or 0.01 to 10g/L	0.005 to 0.5wt% 0.05 to 5g/L	0.01 to 0.2wt% 0.1 to 2g/L

[0030] In another preferred embodiment, in the shrinkproof treatment agent, the amount (wt) of the protease is less than or equal to (≤) the amount (wt) of the organic phosphine compound.

[0031] In another preferred embodiment, when the shrinkproof treatment agent is an aqueous solution or a reconstituted aqueous solution, pH thereof is from 6.5 to 12, preferably from 7 to 11.5, and more preferably from 7.5 to 10.5.

[0032] In another preferred embodiment, the protease is an alkaline protease.

[0033] In another preferred embodiment, the organic phosphine compound is a water-soluble aliphatic organic phosphine compound.

[0034] In another preferred embodiment, the water-soluble refers to solubility of the organic phosphine compound in 100 g of water at 25 °C is ≥ 0.1g, preferably ≥ 0.5g, and more preferably ≥ 2g, such as 0.1 to 10g or 0.5 to 5g.

[0035] In another preferred embodiment, the organic phosphine compound has the following structure formula:

$$P\text{-}(R_1\text{-}R_2)_3 \qquad I$$

wherein,

R_1 is substituted or unsubstituted C2-C8 alkylene (preferably C1-C6 alkylene); and/or
R_2 is selected from the group consisting of -OH, -COOH, C2-C8 ester group, alkali metal, and alkaline earth metal.

[0036] In another preferred embodiment, in the compound of formula I,

R_1 is unsubstituted C1-C6 alkylene; and/or
R_2 is selected from the group consisting of -OH and -COOH.

[0037] In another preferred embodiment, R_1 is selected from the group consisting of methylene, ethylene, propylene, butylene, pentylene, hexylene, and combinations thereof.

[0038] In another preferred embodiment, the aliphatic organic phosphine compound is selected from the group consisting of tris(3-hydroxypropyl)phosphine, tris(3-carboxypropyl)phosphine, tris(2-hydroxyethyl)phosphine, tris(4-carboxybutyl)phosphine, and combinations thereof.

[0039] In another preferred embodiment, the inorganic salt is selected from the group consisting of Ca salts, Mg salts, Na salts, Zn salts, Al salts, Ba salts, and combinations thereof.

[0040] In another preferred embodiment, the inorganic salt is selected from the group consisting of hydrochlorate, sulfate, carbonate, bicarbonate, nitrate, nitrite, phosphate, monohydrogen phosphate, dihydrogen phosphate, and combinations thereof.

[0041] In another preferred embodiment, the inorganic salt is selected from the group consisting of $Mg(NO_3)_2$, sodium phosphate, calcium hydrogen phosphate, $CaCl_2$, and combinations thereof.

[0042] In another preferred embodiment, the surfactant is selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, and combinations thereof.

[0043] In another preferred embodiment, the shrinkproof treatment agent further comprises a pH buffer.

[0044] In another preferred embodiment, the amount of the pH buffer is from 0.1 to 10 g/L, and preferably from 0.2 to 5 g/L.

[0045] In another preferred embodiment, the pH buffer is selected from the group consisting of disodium hydrogen phosphate - sodium dihydrogen phosphate buffer (PBS), $NaHCO_3$-Na_2CO_3 buffer, and combinations thereof.

[0046] In another preferred embodiment, the shrinkproof treatment agent is liquid at 25 to 80 °C.

[0047] In another preferred embodiment, the shrinkproof treatment agent is liquid at an application temperature of from 30 to 70 °C, preferably from 40 to 60 °C, and more preferably from 45 to 55 °C.

[0048] In another preferred embodiment, in the chlorine-free treatment, the size of wool tops to be treated is 10-30 g/m/piece, and preferably 20 to 25 g/m/piece.

[0049] In another preferred embodiment, in the chlorine-free treatment, n pieces of wool tops are treated in parallel

and simultaneously, wherein n is from 10 to 100, from 20 to 70, and preferably from 30 to 60.

[0050] In the second aspect of the present invention, a shrinkproof treatment device for chlorine-free wool tops or wool products is provided, which comprises:

a multiple padding apparatus which comprises n independent, continuously arranged padding machines, and every padding machine comprises a soaking tank and a rolling roller, wherein the soaking tank is used for placing a shrinkproof treatment agent for chlorine-free shrinkage treatment and the wool tops or the wool products to be treated are immersed in the treatment agent; and the rolling roller is used for rolling soaked wool tops or wool product, and the wool tops or wool product rolled by rolling rollers upstream enters into the soaking tank and the rolling roller of the padding machine downstream in turn, thereby repeating the soaking and rolling treatment, wherein n is a positive integer of 2 to 20;

a water washing apparatus for water washing the padded wool tops or wool products to form washed wool tops or wool products;

an enzyme inactivation apparatus for alkaline inactivation treatment of residual protease in the washed wool tops or wool products to form an enzyme-inactivated wool tops or wool products;

an optional soft processing apparatus for soft processing the enzyme-inactivated wool tops or wool products to form a softened wool tops or wool products; and

an optional dryer used to dry the softened wool tops or wool products obtained in the previous step.

[0051] In the third aspect of the present invention, it provides a chlorine-free shrinkproof treatment method for wool tops or wool products, which comprises the following steps:

(a) providing chlorine-free wool tops or wool products to be treated, and a shrinkproof treatment agent for chlorine-free wool tops or wool products according to the first aspect of the present invention;

(b) padding the chlorine-free wool tops or wool products to be treated with the shrinkproof treatment agent for n times, thereby obtaining padded wool products, wherein n is a positive integer of 2 to 20;

(c) water washing the padded chlorine-free wool tops or wool products, thereby obtaining water washed chlorine-free wool tops or wool products; and

(d) conducting an enzyme inactivation treatment of the water washed chlorine-free wool tops or wool products, thereby obtaining shrinkproof treated chlorine-free wool tops or wool products.

[0052] In another preferred embodiment, n is a positive integer of 3 to 10.

[0053] In another preferred embodiment, during and/or after the padding treatment for n times, a treatment agent containing only the protease but not the organic phosphine compound may be additionally used to treat.

[0054] In another preferred embodiment, total time T of the padding treatment of step (b) is $\leq$ 15 minutes, preferably $\leq$ 10 minutes, more preferably $\leq$ 5 minutes, and most preferably $\leq$ 3 minutes.

[0055] In another preferred embodiment, the chlorine-free wool tops or wool products to be treated in step (a) is flattened.

[0056] In another preferred embodiment, the wool tops has a component selected from the group consisting of wool, cashmere, and a combination thereof.

[0057] In another preferred embodiment, the wool tops has a size of 40 to 150 branches, preferably 40 to 120 branches, and more preferably 56 to 100 branches.

[0058] In another preferred embodiment, in step (b), the temperature for the padding treatment is 5 to 80 °C, preferably 10 to 60 °C, more preferably 25 to 50 °C, and most preferably 40 to 50 °C.

[0059] In another preferred embodiment, in step (b), total time for the padding treatment is not particularly limited, and is usually 1 to 20 minutes, preferably 1 to 10 minutes, and more preferably 1 to 5 minutes.

[0060] In another preferred embodiment, in step (c), the temperature for the water washing is not particularly limited and is usually from 5 to 60 °C, preferably from 10 to 50 °C, more preferably from 20 to 40 °C, and most preferably from 20 to 30 °C.

[0061] In another preferred embodiment, in step (c), time for the water washing is not particularly limited and is usually 30 seconds to 120 minutes, preferably 1 minute to 60 minutes, and more preferably 2 to 30 minutes.

[0062] In another preferred embodiment, the enzyme inactivation treatment uses conventional inactivation conditions as long as the residual protease is inactivated or substantially inactivated.

[0063] In another preferred embodiment, no hypochlorous compound is used in the method.

[0064] In another preferred embodiment, in step (b), ratio of the volume of the shrinkproof treatment agent to the weight of the wool products to be treated is not particularly limited as long as the wool tops or wool products to be treated can be wetted.

[0065] In another preferred embodiment, in step (b), times of the padding may be the same or different, and preferably the same.

[0066] In another preferred embodiment, in step (b), the times of the padding is 3 to 15 times, preferably 4 to 12 times, and more preferably 5 to 10 times.

[0067] In another preferred embodiment, treatment time of the padding in step (b) is 3 to 1000 s, preferably 5 to 800 s, more preferably 8 to 600 s, and most preferably 10 to 300 s.

[0068] In another preferred embodiment, the padded wool products obtained in step (b) has a liquid-containing rate of 50 to 160 wt%, preferably 60 to 150 wt%, and more preferably 80 to 140 wt%.

[0069] In another preferred embodiment, before step (c), step (b) is repeated, and repetition times is 3 to 15 times, preferably 4 to 12 times, and more preferably 5 to 10 times.

[0070] In another preferred embodiment, before repeating step (b) for every time, it further comprises a step of replacing the shrinkproof treatment agent.

[0071] In another preferred embodiment, in step (c), the temperature of water used for the water washing is 10-40 °C, and preferably 20 to 30 °C.

[0072] In another preferred embodiment, pH of water used for the water washing is 6.5-7.5, preferably 7.

[0073] In another preferred embodiment, in step (c), the padded wool products obtained in step (b) is water washed with a certain amount of water.

[0074] In another preferred embodiment, in step (c), the water washing is conducted 1 to 6 times, preferably 2 to 4 times.

[0075] In another preferred embodiment, the time for the water washing in step (c) is 1 to 60 minutes, preferably 1 to 30 minutes, and more preferably 1 to 10 minutes.

[0076] In another preferred embodiment, before step (d), step (c) is repeated and repetition times are 1 to 6 times, preferably 2 to 4 times.

[0077] In another preferred embodiment, in step (d), the inactivation treatment is carried out by using a method selected from the group consisting of hot water inactivation, hydrogen peroxide (H_2O_2) inactivation, and combination thereof.

[0078] In another preferred embodiment, the temperature of hot water used in the hot water inactivation is 85 to 100 °C, preferably 90 to 98 °C, and more preferably 92 to 96 °C.

[0079] In another preferred embodiment, treatment time of the hot water inactivation is from 5 to 300 s, preferably from 8 to 200 s, more preferably from 10 to 100 s.

[0080] In another preferred embodiment, in step (d), treatment time of the hydrogen peroxide inactivation treatment is from 5 to 300 s, preferably from 8 to 200 s, and more preferably from 10 to 100 s.

[0081] In another preferred embodiment, after step (d), it optionally further comprises following steps:

5) soft processing the product obtained in step (d), thereby obtaining a desired wool product; and
6) optionally dewatering and/or drying the product obtained in the previous step, thereby obtaining a desired wool product.

[0082] In another preferred embodiment, the soft treatment in step 5) is to soak the product obtained in step (d) with a soft treatment agent.

[0083] In another preferred embodiment, in step 5), a ratio of the product obtained in step (d) to the soft treatment agent is a conventional ratio.

[0084] In another preferred embodiment, the soft treatment in step 5) has a soaking time in the treatment agent of 5 to 200 s, preferably 8 to 100 s, and more preferably 10 to 50 s.

[0085] In another preferred embodiment, the soft treatment in step 5) has a frequency of 1 to 10 times, preferably 2 to 5 times, and more preferably 3 to 4 times.

[0086] In another preferred embodiment, the treatment agent employed in the soft treatment in step 5) has a temperature of from 25 to 65 °C, and preferably from 30 to 50 °C.

[0087] In another preferred embodiment, pH of the treatment agent employed in the soft treatment in step 5) is from 5 to 8, and preferably from 5.5 to 7.5.

[0088] In another preferred embodiment, concentration of the treatment agent used in the soft treatment in step 5) is from 5 to 100 g/L, preferably from 10 to 50 g/L, and more preferably from 15 to 30 g/L.

[0089] In another preferred embodiment, the treatment agent used in the soft treatment in step 5) is selected from the group consisting of wool smoothing agents, wool softening agents, and combinations thereof.

[0090] In another preferred embodiment, treatment temperature for the drying treatment in step 6) is 60 to 100 °C, preferably 70 to 90 °C.

[0091] In another preferred embodiment, in step 6), drying treatment time at the treatment temperature is from 1 to 30 minutes, and preferably from 3 to 15 minutes.

[0092] In the fourth aspect of the present invention, it provides a shrinkproof chlorine-free wool product in which there is no residual organic chlorine.

[0093] In another preferred embodiment, the wool product is shrinkproof treated by the shrinkproof treatment process (method) of the present invention.

[0094] In another preferred embodiment, the wool product is shrinkproof treated with the shrinkproof treatment agent for chlorine-free wool tops or wool products according to the first aspect of the present invention.

[0095] In another preferred embodiment, the wool product is chlorine-free treated by using the shrinkproof treatment device according to the second aspect of the present invention.

[0096] In another preferred embodiment, after treated by the shrinkproof treatment method, a scale layer removal rate of wool surface layer of the treated chlorine-free wool product is 80 to 100%, preferably from 90 to 100%, more preferably from 95 to 100%, such as from 99 to 100%, when it is compared with that of the wool product to be treated.

[0097] In another preferred embodiment, after treated by the shrinkproof treatment method, the absolute value of shrinkage rate of the treated chlorine-free wool product is ≤ 10%, preferably ≤ 8%, preferably ≤ 6%, more preferably ≤ 5%, and most preferably ≤ 3% when it is compared with that of the wool product to be treated, wherein measurement method thereof is TWC.TM31 test method of the International Wool Bureau.

[0098] In another preferred embodiment, after treated by the shrinkproof treatment method, the strength retention of the treated chlorine-free wool product is ≥ 80%, preferably ≥ 82%, more preferably ≥ 84% when it is compared with that of the wool product to be treated.

[0099] In another preferred embodiment, after treated by the shrinkproof treatment method, the elongation retention of the treated chlorine-free wool product is ≥ 70%, preferably ≥ 75%, and more preferably ≥ 80% when it is compared with that of the wool product to be treated.

[0100] In another preferred embodiment, the drip diffusion time of the treated chlorine-free wool product is ≤ 30 s, preferably ≤ 15 s, and more preferably ≤ 10 s.

[0101] In the fifth aspect of the present invention, an article is provided, and the article comprises the wool product or is made up of the wool product according to the fourth aspect of the present invention.

[0102] In another preferred embodiment, the article comprises a wool tops, a wool blanket and a garment.

[0103] In the sixth aspect of the present invention, it provides a use of the shrinkproof treatment agent according to the first aspect of the present invention in the chlorine-free shrinkproof treatment of a wool top or a wool product.

[0104] In the seventh aspect of the present invention, a shrinkproof treatment agent for chlorine-free wool tops and wool products is provided, and main components thereof comprises: a protease, a water-soluble aliphatic trisubstituted organic phosphine compound, and an inorganic salt, wherein the water-soluble aliphatic trisubstituted organic phosphine compound has a structure of $P-(R-S)_3$, wherein R is hydrocarbyl containing 1 to 6 carbon, S is hydroxyl or carboxyl and derivatives thereof; and mass concentration thereof is 1 to 10 g/L; the inorganic salt is calcium chloride, and has a concentration of 0 to 2g/L.

[0105] In another preferred embodiment, the trisubstituted organic phosphine compound is at least one of tris(3-hydroxypropyl)phosphine, tris(3-carboxypropyl)phosphine, tris(2-hydroxyethyl)phosphine and tris(4-carboxybutyl) phosphine.

[0106] In the eighth aspect of the present invention, a continuous processing process of shrinkproof treatment of chlorine-free wool tops and wool products is provided, which comprises the following steps:

1) shrinkproof treatment: wool tops and wool products are arranged, and uniformly transported with a roller (or rollers) into a number of tanks filled with shrinkproof treatment agent and subjected to an alternate soaking and rolling treatment for 3 to 10 times, wherein process conditions comprise: pH of the shrinkproof treatment agent is 7 to 10.5, temperature is 40 to 50 °C; a rolling liquid-containing rate is 60% to 150%; process delivery speed is 3 to 15 m/min, and total time of soaking and rolling is 1 to 5 minutes;
2) water washing: the treated wool tops obtained in the previous step are transported by rolling into one to four water tanks for multiple washing, thereby removing residual biological enzyme activator and enzyme preparation to prevent them from continuously eroding wool;
3) inactivation of protease: the washed wool tops are evenly and quickly passed through a hot water tank filled with hot water having a temperature of 85 to 95 °C or a solution containing 0 to 1 g/L of hydrogen peroxide, thereby inactivating any protease which is not completely washed out;
4) soft treatment: the inactivated wool tops are soaked into a tank filled with a conventional wool smoothing agent or organosilicon softening-agent, and a common soft treatment is conducted to improve feel of wool fabric;
5) dehydration and drying;
wherein the shrinkproof treatment agent mainly contains:

trisubstituted organic phosphine, with a concentration is 1 to 10g/L;
calcium chloride, with a concentration is 0.3 to 2g/L;
protease, with a concentration is 0.5 to 5 g/L;
and the rest is water;
wherein the trisubstituted organic phosphine is at least one of tris(3-hydroxypropyl)phosphine, tris(3-carboxypropyl)phosphine, tris(2-hydroxyethyl)phosphine and tris(4-carboxybutyl)phosphine.

[0107] In another preferred embodiment, the soaking and rolling (or extruding) treatment is repeated for 3 to 10 times; total time for the padding treatment is 1-5 minutes; and process delivery speed is 3 to 8 m/min.

[0108] In another preferred embodiment, the wool tops are wool or cashmere of 56 to 100 branches.

[0109] It should be understood that in the present invention, any of the technical features specifically described above and below (such as in the Examples) can be combined with each other, thereby constituting new or preferred technical solutions which will not redundantly be described one by one herein.

DESCRIPTION OF FIGURES

[0110]

Figure 1 is an effect graph of wool fiber after scales are stripped in Example 1 of the present invention.
Figure 2 is an effect graph of wool fiber after scales are stripped in Example 2 of the present invention.
Figure 3 is an effect graph of wool fiber after scales are stripped in Example 3 of the present invention.
Figure 4 is an effect graph of wool fiber after scales are stripped in Example 4 of the present invention.
Figure 5 is an effect graph of wool fiber after scales are stripped in Example 5 of the present invention.
Figure 6 is a flow chart of a process example of the present invention.
Figure 7 is a schematic diagram of a chlorine-free treatment device of the present invention.

DETAILED DESCRIPTION OF INVENTION

[0111] Through extensive and intensive long research, the inventors have unexpectedly prepared a descaling shrinkproof process and a corresponding shrinkproof treatment agent and a device for chlorine-free wool tops and wool products. The process and the shrinkproof treatment agent of the invention can efficiently and rapidly remove the scale layer on the surface of the wool fiber under chlorine-free condition and modify the scale layer, thereby improving felting property of the wool product and dimensional stability of product. On this basis, the inventors have completed the present invention.

[0112] Specially, a continuous processing process of shrinkproof treatment of chlorine-free wool tops and wool products is provided in the invention. It comprises shrinkproof treatment, water washing, protease inactivation, soft treatment, dehydration and drying steps. According to a characteristic that the wool fiber is a protein fiber, a highly efficient integrated catalytic system composed of a protease, an activator of a water-soluble aliphatic trisubstituted organic phosphine structure, a metal salt and non-ionic surfactant is selected, which can synergistically and efficiently remove the scale layer on the surface of wool fiber and modify the scale layer, thereby improving felting property of the wool product and dimensional stability of product and conferring the fabric with anti-pilling characteristics and smooth feel. The invention can completely replace the chlorination shrinkproof method in the art, and avoid the environmental pollution caused by the chlorination method. The present invention is a cleaning treatment process which meets the environmental requirements, and has no problem of chlorination pollution. The method has following advantages such as: reagent usage amount is small, the cost is low, the process is simple, the requirement for equipment is low, it can be continuously conducted, and it can realize industrial production.

TERMS

[0113] As used herein, the term "wool raw material" includes wool, wool top, or semi-finished products thereof without subjecting to a descaling shrinkproof treatment. In addition, the term may also include wool raw material which has been subjected to descaling shrinkproof treatment, but has not completely been descaled.

[0114] As used herein, the terms "wool top/wool product" and "wool top and/or wool product" can be used interchangeably and refer to wool top, or wool product, or a combination thereof. The term may include both the wool top/ wool product to be treated and the treated or being treated wool top/ wool product.

[0115] As used herein, the terms "chlorine-free product of the present invention" and "chlorine-free wool top/ wool article of the present invention" can be used interchangeably and refer to the wool top/ wool product obtained by the chlorine-free descaling shrinkproof treatment process of the present invention. Since the chlorine-free descaling shrinkproof treatment process of the present invention does not use any organochlorine compound and does not use any hypochlorous compound (i.e., a compound containing ClO^- ion or a compound capable of producing ClO^- ion), the chlorine-free wool products (including wool tops/ wool products) have excellent safety.

[0116] As used herein, the terms "shrinkproof agent (or liquid) of the present invention", "descaling shrinkproof agent (or liquid) of the present invention", "the chlorine-free shrinkproof treatment agent (or liquid)" and "the chlorine-free descaling shrinkproof treatment agent (or liquid) " can be used interchangeably and refer to the shrinkproof treatment agent (or liquid) for the chlorine-free wool top/ wool product in the present invention.

SHRINKPROOF TREATMENT AGENT FOR CHLORINE-FREE WOOL TOP/ WOOL PRODUCT

[0117] A descaling shrinkproof treatment agent for the chlorine-free wool top/ wool product of the present invention is provided in the present invention. The descaling shrinkproof treatment agent of the present invention may be solid or liquid. When the chlorine-free shrinkproof agent of the present invention is solid, it can be reconstituted into a corresponding shrinkproof treatment liquid used for a chlorine-free wool top/ wool product by adding water (or an aqueous solvent).

[0118] In addition, in the present invention, every combination may have been mixed together (i.e. in a mixed form), or the components of the agent may also be present in an unmixed form and are mixed into a formulation *in situ* when one need to use such agent.

[0119] In a preferred embodiment, main components of a shrinkproof treatment liquid for chlorine-free wool top and wool product comprise a protease, a water-soluble aliphatic trisubstituted organic phosphine compound, and an inorganic salt. The structure of the water-soluble aliphatic trisubstituted organic phosphine is $P\text{-}(R\text{-}S)_3$, wherein R is hydrocarbyl containing 1 to 6 carbons, S is hydroxyl or carboxyl and derivatives thereof; and mass concentration thereof is 1 to 10 g/L. The inorganic salt is calcium chloride, and the concentration thereof is 0 to 2 g/L.

[0120] In the present invention, the preferred trisubstituted organic phosphine includes (but is not limited to): tris(3-hydroxypropyl)phosphine, tris(3-carboxypropyl)phosphine, tris(2-hydroxyethyl)phosphine, tris(4-carboxybutyl)phosphine, or combinations thereof.

[0121] In another preferred embodiment, the protease includes a neutral protease, an alkaline protease, or a combination thereof.

[0122] In another preferred embodiment, the neutral protease refers to a protease whose optimal pH is neutral (e.g. about 6.8 to 7.0), and molecular weight thereof is generally from 35 to 40 kD. Neutral proteases suitable for use in the present invention include neutral proteases that are commercially available or prepared by conventional methods, such as neutral proteases from microorganisms, Neutrase, or combinations thereof.

[0123] In another preferred embodiment, the alkaline protease refers to a protease whose optimal pH is alkaline (e.g. about 9 to 11), and molecular weight thereof is generally from 26 to 34 kD. Alkaline proteases suitable for use in the present invention include alkaline proteases that are commercially available or prepared by conventional methods, such as alkaline proteases from *Bacillus licheniformis* (a protease belong to serine-type endoprotease and having a molecular weight of about 27300), alkaline proteases from *Streptomycetes*, 2709 alkaline protease, Novo protease, Carsberg protease and the like.

[0124] In the shrinkproof agent of the present invention, the concentration of protease is generally 0.1 to 25 g/L, preferably 0.2 to 10 g/L, and more preferably 0.5 to 5 g/L. According to international units (IU), the amount (or concentration) of protease is generally 1×10^4-1×10^8U/L, preferably 5×10^4-5×10^7U/L, and more preferably 1×10^5-1×10^7U/L.

[0125] In another preferred embodiment, the shrinkproof treatment liquid of the present invention further comprises a nonionic surfactant (e.g. JFC) or an anionic surfactant. Representative non-ionic surfactants include (but are not limited to): polyoxyethylene type surfactants such as alkylphenol polyoxyethylene ether (APEO), fatty acid polyoxyethylene esters (AE), fatty acid methyl ester ethoxylates (FMEE), and polyol type surfactants (such as sorbitan esters, including Tween and Span), or combinations thereof. Representative examples include Tween, Span, JFC, or combinations thereof. Representative anionic surfactants include (but are not limited to): sodium dodecylbenzenesulfonate, sodium dodecyl sulfate (SDS), hexadecylsulfonate, or combinations thereof.

[0126] In general, the concentration of surfactant is 0.001 to 1.0 wt% or 0.01 to 10 g/L, and preferably 0.1 to 2 g/L.

[0127] Preferably, the pH of the shrinkproof treatment liquid of the present invention is from 7 to 10.5.

[0128] In another preferred embodiment, a shrinkproof treatment liquid for chlorine-free wool tops and wool products is provided in the present invention, which has main components in mass as follows:

trisubstituted organic phosphine, with a concentration of 1 to 10g/L;
calcium chloride, with a concentration of 0 to 2g/L;
protease, with a concentration of 0.5 to 5 g/L;
and the rest is water.

[0129] The shrinkproof treatment agent (liquid) of the present invention can directly treat the wool top/ wool product to obtain a descaling shrinkproof wool top/ wool product.

[0130] Compared with the chlorine-containing shrinkproof treatment solution in the prior art, the shrinkproof treatment liquid of the present invention contains neither an organochlorine compound nor a hypochlorous compound (i.e., a compound containing ClO^- ion or a compound capable of producing ClO^- ion such as Cl_2). The organochlorine compounds include DCCA, chloroform, carbon tetrachloride, TCCA and the like.

[0131] In another preferred embodiment, the main components of the shrinkproof treatment liquid of the chlorine-free wool top and wool product of the present invention are protease, water-soluble aliphatic trisubstituted organic phosphine

compound and inorganic salt.

[0132] In which, the water-soluble aliphatic trisubstituted organic phosphine has a structure of P-(R-S)$_3$, wherein R is a hydrocarbyl having 1 to 6 carbon (C), and S is hydroxyl (-OH) or carboxyl (-COOH) and derivatives thereof. The usage amount is 1g~10g/L. The inorganic salts are calcium chloride etc., and usage amount thereof is 0g/L ~ 2g/L.

[0133] The trisubstituted organic phosphine is at least one of tris(3-hydroxypropyl)phosphine, tris(3-carboxypropyl)phosphine, tris(2-hydroxyethyl)phosphine and tris(4-carboxybutyl)phosphine.

[0134] The protease is a neutral protease, an alkaline protease and the like, and the concentration of protease is 0.5 g/L to 5 g/L.

[0135] The pH of the shrinkproof treatment liquid is 7 to 10.5.

[0136] In another preferred embodiment, the main components of the shrinkproof treatment liquid in mass comprises:

trisubstituted organic phosphine, with a concentration of 1 to 10g/L;
calcium chloride, with a concentration of 0 to 2g/L;
protease, with a concentration of 0.5 to 5 g/L; and
the rest is water.

SHRINKPROOF TREATMENT METHOD (PROCESS) FOR CHLORINE-FREE WOOL TOP OR WOOL PRODUCT

[0137] A shrinkproof treatment method for chlorine-free wool top or wool product is also provided in the present invention, in which the wool top/ wool product is treated with the chlorine-free descaling shrinkproof treatment liquid of the present invention, thereby obtaining a wool top/ wool product with excellent shrinkproof properties. It should be understood that although the shrinkproof treatment liquid and method of the present invention can achieve a sufficient descaling to obtain a fully descaled wool product, the method of the present invention can also be used to produce a wool product that is not fully descaled (i.e. partially descaled).

[0138] As shown in Figure 6, in a preferred embodiment, a continuous processing process of shrinkproof treatment of chlorine-free wool top and wool product is provided in the invention, and comprises the following steps:

1) descaling shrinkproof treatment: wool tops/wool products are arranged, and uniformly transported into one or more tanks filled with shrinkproof treatment agent and subjected to an alternate soaking and rolling treatment (e.g. 3 to 10 times), wherein process conditions comprise: pH of the shrinkproof treatment agent is 7 to 10.5, temperature is 40 to 50 °C; and total time of soaking and rolling is 1 to 5 minutes;
preferably, wool tops are arranged in order, and uniformly transported into a number of tanks filled with a shrinkproof treatment agent and subjected to an alternate soaking and rolling treatment for 3 to 10 times, wherein process conditions comprise: pH of the shrinkproof treatment agent is 7 to 10.5, temperature is 40 to 50 °C; a rolling liquid-containing rate is 60% to 150%; a process delivery speed is 3 to 15 m/min (preferably 3 to 8 m/min), and total time of soaking and rolling is 1 to 5 minutes;
2) water washing: the treated wool tops obtained in the previous step are transported by rolling into one to four water tanks for multiple washing, thereby removing residual biological enzyme activator and enzyme preparation to prevent them from continuously eroding wool;
3) inactivation of protease: the washed wool tops are quickly passed through a hot water tank filled with hot water having a temperature of 85 to 95 °C or a solution containing 0.1 to 1 g/L of hydrogen peroxide, thereby inactivating any protease which is not completely washed out;
4) soft treatment: the inactivated wool tops are soaked in a tank filled with a conventional wool smoothing agent or organosilicon softening-agent, and a common soft treatment is conducted to improve feel of wool fabric;
5) dehydration and drying;
wherein the shrinkproof treatment agent mainly contains:

trisubstituted organic phosphine in a concentration of 1 to 10g/L;
calcium chloride in a concentration of 0.3 to 2g/L;
protease in a concentration of 0.5 to 5 g/L;
and the rest is water;
the trisubstituted organic phosphine is at least one of tris(3-hydroxypropyl)phosphine, tris(3-carboxypropyl)phosphine, tris(2-hydroxyethyl)phosphine and tris(4-carboxybutyl)phosphine.

[0139] In another preferred embodiment, the immersion (or soaking) and rolling operation may be repeated for a plurality of times, for example, 3 to 10 times.

[0140] In the present invention, the total time of the soaking and rolling treatment is not particularly limited, and is usually 0.5 to 20 minutes, preferably 1 to 10 minutes, and more preferably 1 to 5 minutes.

[0141] The present invention requires only a very short total time for the soaking / rolling operation, since the chlorine-free descaling shrinkproof treatment agent of the present invention can descale very efficiently and with almost no damage.

[0142] In another preferred embodiment, the chlorine-free shrinkproof treatment process of the present invention is continuous, wherein the delivery speed in the continuous process may be from 0.5 to 20 m/min, and preferably from 1 to 10 m/min.

[0143] In a preferred embodiment of the present invention, the process comprises:

1) shrinkproof treatment. The wool tops are subjected to a descaling treatment using an integrated protease catalytic system. In the case when every wool top has no tension, the wool tops are arranged in order, and uniformly transported with roller into an high-efficient catalytic system composed of a protease, a water-soluble aliphatic trisubstituted organic phosphine biological enzyme activator and inorganic salt catalyst. A conventional non-ionic surfactant as auxiliary penetrant can also be added, pH is 7 to 10.5, and temperature of the catalytic system is 40 to 50 °C, when the wool tops are completely (soaking and exchange rate between wool fibers and the surrounding treatment fluid can be accelerated by using a suction roller or other equipments), and the wool tops are squeezed with rollers so that a liquid-containing rate is 60% to 150%. Then, they are transferred again into a catalytic system having a temperature of 40 to 50 °C, and after being immersed, the wool tops are squeezed with rollers, and this soaking and rolling treatment is repeated. The process speed is controlled between 3 to 15 m/min (optionally 3 to 8 m/min). According to different wool branches and product quality requirements, in the treatment solution of the same integrated catalytic system and under the same treatment conditions, the treatment is conducted for 1 to 5 minutes and for 3 to 10 times, and finally the obtained wool tops are transported into a follow-up processing tank, thereby achieving continuous automation effects.

2) water washing. The treated wool tops obtained in the previous step are transported by roller into one to four water tanks for multiple washing, thereby removing residual biological enzyme activator and enzyme preparation to prevent them from continuously eroding wool.

3) inactivation of protease. The washed wool tops obtained in step 2) are evenly and quickly passed through a boiling water tank or a solution containing 0 to 1 g/L of hydrogen peroxide, thereby inactivating any protease that is not completely washed out.

4) soft treatment. The inactivated wool tops are soaked in a conventional wool smoothing agent or organosilicon softening-agent (that is, in a soft treatment tank, a general soft treatment is carried out, and the soft agent is a hydrogen-containing silicone oil, an amino silicone oil, and a modified silicone oil or an emulsion thereof), so as to improve feel of wool fabric.

5) dehydration and drying (conventional methods can be used).

CHLORINE-FREE TREATMENT DEVICE

[0144] A chlorine-free treatment device for use in the method of invention is also provided in the present invention.

[0145] A typical treatment device is shown in Figure 7. The device comprises:

a multiple padding apparatus 10, which comprises n independent, continuously arranged padding machines (not shown), and every padding machine comprises a soaking tank and a rolling roller, wherein the soaking tank is used for placing a shrinkproof treatment agent for chlorine-free shrinkage treatment and the wool top or the wool product to be treated is immersed in the treatment agent; and the rolling roller is used for rolling the soaked wool top or wool product, and the wool top or wool product rolled by rolling rollers upstream enters into the soaking tank and the rolling roller of the padding machine downstream in turn, thereby repeating the soaking and rolling treatment, wherein n is a positive integer of 2 to 20;

a water washing apparatus 20 for water washing the padded wool tops or wool products to form washed wool tops or wool products;

an enzyme inactivation apparatus 30 for alkaline inactivation treatment of residual protease in the washed wool tops or wool products to form an enzyme-inactivated wool tops or wool products;

an optional soft processing apparatus 40 for soft processing the enzyme-inactivated wool tops or wool products to form a softened wool tops or wool products; and

an optional dryer 50 used to dry the softened wool tops or wool products obtained in the previous step.

[0146] In another preferred embodiment, the multiple padding apparatus, the water washing apparatus, the enzyme inactivation apparatus, the optional soft processing apparatus and the optional dryer are arranged in sequence.

[0147] In another preferred embodiment, one or more auxiliary padding machines are further set between or behind every padding machine of the multiple padding apparatus, and every auxiliary padding machines independently com-

prises an auxiliary soaking tank and an auxiliary rolling roller, wherein the auxiliary soaking tank is filled with a protease treatment solution containing no organic phosphine compound and/or an organic phosphine compound treatment liquid containing no protease.

[0148] In another preferred embodiment, the auxiliary soaking tank is an enzyme treatment tank.

[0149] In another preferred embodiment, the enzyme treatment bath is located after the second, third, fourth or fifth padding machine.

[0150] In another preferred embodiment, n is 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20, preferably 3 to 15, and more preferably 4 to 10.

[0151] In another preferred embodiment, the shape and size of every padding machine may be the same or different.

[0152] In another preferred embodiment, every padding machine is arranged in sequence.

[0153] In another preferred embodiment, the soaking tank is filled with the shrinkproof treatment agent (or liquid) according to the first aspect of the present invention.

[0154] In another preferred embodiment, the soaking tank is a suction roller tank.

[0155] In another preferred embodiment, the soaking tank is independently equipped with or without a heating apparatus or a temperature control apparatus.

[0156] In another preferred embodiment, every heating apparatus or every temperature control apparatus controls the temperature in a range of 25 to 80 °C by, preferably 30 to 70 °C, more preferably 40 to 60 °C, and most preferably 45 to 55 °C.

[0157] In another preferred embodiment, the water washing apparatus comprises m water scrubbers, wherein m is a positive integer of 1 to 10, preferably 1 to 6, and preferably 2 to 4.

[0158] In another preferred embodiment, every water scrubber is filled with a solvent of water.

[0159] In another preferred embodiment, in every water scrubber, temperature of the solvent water is 10-40 °C, preferably 20 to 30 °C.

[0160] In another preferred embodiment, in every water scrubber, pH of the solvent water is 6.5-7.5, preferably 7 ± 0.2.

[0161] In another preferred embodiment, the enzyme inactivation apparatus is a high temperature inactivation tank and/or a hydrogen peroxide inactivation tank.

[0162] In another preferred embodiment, in the enzyme inactivation apparatus, the temperature of the solvent water is from 85 to 100 °C, preferably from 90 to 98 °C, and more preferably from 92 to 96 °C.

[0163] In another preferred embodiment, the enzyme inactivation apparatus is filled with a H_2O_2 solution.

[0164] In another preferred embodiment, in the enzyme inactivation apparatus, the concentration of the H_2O_2 in the solution is 0.01 to 50 g/L, preferably 0.05 to 30 g/L, and more preferably 0.1 to 10 g/L.

[0165] In another preferred embodiment, the soft treatment apparatus is filled with the soft treatment agent selected from the group consisting of: wool smoothing agents, wool softening agents, or combinations thereof.

[0166] In another preferred embodiment, in the soft treatment apparatus, the soft treatment agent has a concentration of about 1 to 50 g/L, preferably 2 to 40 g/L, and more preferably 5 to 25 g/L.

[0167] In another preferred embodiment, the wool softening agent includes an organic silicon softening agent.

[0168] In another preferred embodiment, the organic silicon softening agent is selected from the group consisting of: silicone oil, hydrogen silicone oil, amino silicone oil, modified silicone oil, or combinations thereof.

CHLORINE-FREE WOOL TOP/WOOL PRODUCT

[0169] Shrinkproof chlorine-free wool top/wool product with little or no organochlorine residue obtained with the chlorine-free shrinkage treatment process of invention is also provided in the present invention.

[0170] As used herein, the term "ecoshine" or "ecoshine product" refers to a shrinkproof chlorine-free wool top/ wool product with little or no organochlorine residue obtained with the chlorine-free shrinkage treatment process of the present invention.

[0171] The chlorine-free treated wool tops or wool products (i.e. ecoshine product) of the present invention have excellent properties including (but not limited to):

(a) a high scale layer removal rate: the scale layer removal rate of wool surface layer of the treated wool product is from 80 to 100%, preferably from 90 to 100%, and more preferably from 95 to 100% (such as from 99 to 100%), when it is compared with that of the wool product to be treated.

(b) a low shrinkage rate: the absolute value of shrinkage rate of the treated wool product is $\leq$ 10%, preferably $\leq$ 8%, preferably $\leq$ 6%, more preferably $\leq$ 5%, and most preferably $\leq$ 3%, when it is compared with that of the wool product to be treated, wherein the measurement method thereof is TWC.TM31 test method of the International Wool Bureau.

(c) high strength retention: after treated by the shrinkproof treatment method, strength retention of the treated wool product is $\geq$ 80%, preferably $\geq$ 82%, and more preferably $\geq$ 84%, when it is compared with that of the wool product to be treated.

(d) high elongation retention: after treated by the shrinkproof treatment method, elongation retention of the treated wool product is ≥ 70%, preferably ≥ 75%, and more preferably ≥ 80%, when it is compared with that of the wool product to be treated.

(e) excellent wetting and penetration performance: drip diffusion time (according to GB/T21655.1-2008) is increased from ≥ 10 minutes (before treatment) to ≤ 10 seconds.

TREATMENT MECHANISM AND ADVANTAGES

[0172] The present inventors provides the following mechanism for the purpose of facilitating understanding of the present invention. However, it should be understood that the invention is not limited by this mechanism.

[0173] The present inventors have found that there are some specific structures and substances in the scale layer of the wool surface, such as disulfide bond-containing cystine and lipids and so on, which make it difficult for the protease to efficiently digest and decompose the high-sulfur protein on the surface of the scale and therein. However, in the presence of the organic phosphine compound represented by formula A of the present invention, by using the multiple padding process of the present invention, on the one hand, the structure of the scale layer on the surface of the wool can be effectively altered, which makes that proteins such as high-sulfur protein are more prone to be decomposed by protease, and on the other hand, the vitality of the protease can be maintained or enhanced, thereby achieving descaling and shrinkproof treatment of wool with very high efficiency and high speed.

[0174] In the preferred treatment agent of the present invention, the action of the protease is mainly to degrade the scale on the surface of wool fiber by hydrolysis; on the one hand, the water-soluble aliphatic trisubstituted organic phosphine rapidly reduces a large number of disulfide bond existed in the scale and activates the reaction substrate by its unique effect on the disulfide bonds in the wool so as to facilitate the reaction between the protease and wool macromolecule. Furthermore, it has good stabilizing effect on the activity of the protease, and can effectively reduce the decline of protease activity in the integrated catalytic system, while at the same time it is also able to further activate the catalytic action of protease, resulting in a rapid reaction effect. In addition, the main role of the inorganic salt catalyst is to further activate the protease; and the main role of the surfactant is to assist treatment solution to wet and infiltrate the surface of wool fiber as soon as possible.

[0175] In the process of the present invention, multiple padding or repeated padding is also a necessary condition for the present invention to achieve a rapid process. During the process of repeated padding, rapid contact and interaction between the protease, the activator and wool fiber surface are realized compulsively, and it is helpful to clear the reactants and hydrolyzes so as to facilitate further reaction.

[0176] Compared with the prior art, the present invention has following main advantages:

(1) It is environmentally friendly since no chlorine-containing organic matter or chlorine gas is used. The present invention uses the high-efficiency catalytic system mainly composed of the protease and the activator of water-soluble organic phosphine structure as a treatment liquid to treat wool. By using a synergistic effect therefrom, one can achieve the mercerizing shrinkproof continuous processing of the chlorine-free wool tops, and no toxic and hazardous substances is produced during the process. It solves fundamentally environment pollution caused by the chlorinated mercerization, and is in concord with the "ecologic textiles" concept because it does not cause environmental pollution.

(2) The process is simple and easy to control.

(3) High processing efficiency and rapid processing speed. Compared with the known protease shrinkproof process, the method of invention is fast, and shrinkproof treatment of wool can be completed in 1 to 5mins, and it can ensure its mechanical properties within the acceptable range.

(4) The anti-felting effect is long and lasting.

(5) It is suitable for large-scale production. The process of the invention has low requirement for equipment, can be continuously conducted, and is conducive to realize the industrial production.

[0177] The present invention will be further illustrated below with reference to the specific examples. It should be understood that these examples are only to illustrate the invention but not to limit the scope of the invention. The experimental methods with no specific conditions described in the following examples are generally performed under the conventional conditions, or according to the manufacture's instructions. Unless indicated otherwise, parts and percentage are calculated by weight.

[0178] The reagents involved in the examples are commercially available, unless specifically described.

[0179] The treatment liquid of the present invention is prepared by weighing the protease, the water-soluble aliphatic trisubstituted organic phosphine compound, the inorganic salt and the surfactant according to the amount of the main formula and using the general mass concentration (g/L) preparation method. The organic phosphine compound were purchased from TianJin Littoral Orient Technology Co., Ltd..

Example 1

[0180] In the present example, the wool tops were subjected to a chlorine-free shrinkproof treatment using a continuous process having five-multiple padding.

[0181] Full wool tops to be treated had a specification of 70. The process comprised the following steps:

The first tank contained a padding treatment solution. The tank had a width of 1 m and a volume of 360 liters and was equipped with a suction roller tank having a circumference of 1 meter (general apparatus). The suction roller tank had an automatic heating apparatus (general apparatus) inside, and the tank was filled with a high efficiency catalytic solution mainly composed of alkali protease 3g/L and tris(3-hydroxypropyl)phosphine 3g/L (nonionic surfactant JFC 1g/L was added) , and pH thereof was 9 (using disodium hydrogen phosphate and sodium dihydrogen phosphate as a pH regulator), and temperature thereof was controlled at 50 °C.

[0182] The wool tops were evenly arranged side by side on the roller and uniformly transported into the treatment liquid at a speed of 8 m/min, so that the wool tops were completely wet to ensure that the surface of every fiber of the wool tops was evenly and thoroughly treated. Then the wool tops were squeezed by the pressure roller to ensure that the liquid-containing rate of the wool tops was about 135%. Afterwards, the wool tops containing the enzyme fluid entered into the second treatment tank at a speed of 8 m/min. It took 15 seconds from the time when the wool tops entered into the first tank treatment liquid to the time when the wool tops entered into the second tank treatment liquid.

[0183] The second tank: padding treatment solution. They are the same as those for the first tank.

[0184] The third tank: padding treatment solution. They are the same as those for the first tank. The fourth tank: padding treatment solution. They are the same as those for the first tank.

[0185] The fifth tank: padding treatment solution. They are the same as those for the first tank. It took 15 seconds x 5 = 75 seconds from the beginning of first tank to the end of the fifth tank.

[0186] The sixth tank: water washing. The wool tops were rolling washed by rolling, so that the reagents, enzymes and degraded products attached on the surface of the wool fiber were cleaned. The water temperature was room temperature, and pH was 7.0.

[0187] The seventh tank: the second water washing. They are the same as those for the sixth tank.

[0188] The eighth tank: water washing at high temperature. It played a role of enzyme inactivation, so as to prevent subsequent continuous erosion of wool fibers. Temperature was 95 °C and time was 15 seconds.

[0189] The ninth tank: conventional soft treatment. The wool fiber were softened to achieve soft effect and to improve the feel. Afterwards, the wool tops were subjected to conventional dehydration and drying (for example: drying process conditions: drying temperature was 70 to 90 °C, and drying time was 3 to 10 minutes).

[0190] The process speed was 8 m/min, and number of padding in the treatment liquid was 5 times in total. After treated by this process, the scale stripping effect of the wool fiber was shown in Figure 1.

[0191] The strength retention of the wool treated by this process was 85% and elongation retention thereof was 83%, compared with those of the untreated wool.

[0192] According to the TWC.TM31 test method of International Wool Bureau, the wool treated by this process had a 5×5A test results of -4.86%.

[0193] Chlorine content of the treated wool was measured, and no residual chlorine component (organic substance) was detected.

Example 2

[0194] In the present example, the wool tops were subjected to a chlorine-free shrinkproof treatment using a continuous process having six-multiple padding.

[0195] Full wool tops to be treated had a specification of 56. The process comprised the following steps:

The first tank contained padding treatment solution. The tank had a width of 1 m and a volume of 360 liters and was equipped with a suction roller tank having a circumference of 1 meter. The suction roller tank had an automatic heating apparatus inside, and the tank was filled with a high efficiency catalytic solution containing alkali protease 3g/L and tris(3-hydroxypropyl)phosphine 3g/L, and pH thereof was 10.5, and temperature thereof was controlled at 50 °C.

[0196] The wool tops were evenly arranged side by side on the roller and uniformly transported into the treatment liquid at a speed of 3.8 m/min, so that the wool tops were completely wet to ensure that the surface of every fiber of the wool tops was evenly and thoroughly treated; and then the wool tops were squeezed by the pressure roller to ensure that the liquid-containing rate of the wool tops was 130%. Afterwards, the wool tops containing the enzyme fluid entered

into the second treatment tank at a speed of 3.8 m/min. It took 31.5 seconds from the time when the wool tops entered into the first tank treatment liquid to the time when the wool tops entered into the second tank treatment liquid.

[0197] The second tank: padding treatment solution. They are the same as those for the first tank.

[0198] The third tank: padding treatment solution. They are the same as those for the first tank.

[0199] The fourth tank: padding treatment solution. They are the same as those for the first tank.

[0200] The fifth tank: padding treatment solution. They are the same as those for the first tank.

[0201] The sixth tank: padding treatment solution. They are the same as those for the first tank. It took 31.5 seconds x 6 = 189 seconds from the beginning of first tank to the end of the sixth tank.

[0202] The seventh tank: water washing. The wool tops were rolling washed by rolling, so that the reagents, enzymes and degraded products attached on the surface of the wool fiber were cleaned. The water temperature was room temperature, and pH was 7.0.

[0203] The eighth tank: the second water washing. They are the same as those for the seventh tank.

[0204] The ninth tank: water washing at high temperature. It played a role of enzyme inactivation, so as to prevent subsequent continuous erosion of wool fibers. Temperature was 95 °C and time was 15 seconds.

[0205] The tenth tank. The wool tops were padded in a solution containing 20g/L of wool softener, and the wool fiber were softened to achieve soft effect and to improve the feel. Temperature of the softener solution was 40 °C, and pH thereof was 7.0, and time was 15 seconds. Afterwards, the wool tops were subjected to dehydrate and dry.

[0206] The process speed was 3.8 m/min, and number of padding in the treatment liquid was 6 times in total. After treated by this process, the scale stripping effect of the wool fiber was shown in Figure 2.

[0207] The strength retention of the wool treated by this process was 83% and elongation retention thereof was 72%, compared with those of the untreated wool.

[0208] According to the TWC.TM31 test method of International Wool Bureau, the wool treated by this process had a 5×5A test results of -3.82%.

[0209] Chlorine content of the treated wool was measured, and no residual chlorine component (organic substance) was detected.

Example 3

[0210] In the present example, the wool tops were subjected to a chlorine-free shrinkproof treatment using a continuous process having five-multiple padding.

[0211] Full wool tops to be treated had a specification of 90. The process comprised the following steps:

The first tank contained padding treatment solution. The tank had a width of 1 m and a volume of 360 liters and was equipped with a suction roller tank having a circumference of 1 meter. The suction roller tank had an automatic heating apparatus inside, and the tank was filled with a high efficiency catalytic solution composed of alkali protease 3g/L, tris(3-carboxypropyl)phosphine 3g/L and anhydrous calcium chloride 0.3g/L (nonionic surfactant JFC 1g/L was further added), and pH thereof was 8.5 (pH was adjusted with appropriate amount of sodium carbonate or sodium hydroxide solution), and temperature thereof was controlled at 50 °C.

[0212] The wool tops were evenly arranged side by side on the roller and uniformly transported into the treatment liquid at a speed of 3.8 m/min, so that the wool tops were completely wet to ensure that the surface of every fiber of the wool tops was evenly and thoroughly treated. Then the wool tops were squeezed by the pressure roller to ensure that the liquid-containing rate of the wool tops was 130%. Afterwards, the wool tops containing the enzyme fluid entered into the second treatment tank at a speed of 3.8 m/min. It took 31.5 seconds from the time when the wool tops entered into the first tank treatment liquid to the time when the wool tops entered into the second tank treatment liquid.

[0213] The second tank: padding treatment solution. They are the same as those for the first tank.

[0214] The third tank: padding treatment solution. They are the same as those for the first tank.

[0215] The fourth tank: padding treatment solution. They are the same as those for the first tank.

[0216] The fifth tank: padding treatment solution. They are the same as those for the first tank. It took 31.5 seconds x 5 = about 158 seconds from the beginning of the first tank to the end of the fifth tank.

[0217] The sixth tank: water washing. The wool tops were rolling washed by rolling, so that the reagents, enzymes and degraded products attached on the surface of the wool fiber were cleaned. The water temperature was room temperature, and pH was 7.0.

[0218] The seventh tank: the second water washing. They are the same as those for the sixth tank.

[0219] The eighth tank: water washing at high temperature. It played a role of enzyme inactivation, so as to prevent subsequent continuous erosion of wool fibers. Temperature was 95 °C, and time was 15 seconds.

[0220] The ninth tank: the wool tops were padded in a solution containing 20g/L of wool softener, and the wool fiber were softened to achieve soft effect and to improve the feel. Temperature of the softener solution was 40 °C, and pH

thereof was 6.0, and time was 15 seconds. Afterwards, the wool tops were subjected to dehydrate and dry.

[0221] The process speed was 3.8 m/min, and number of padding in the treatment liquid was 5 times in total. After treated by this process, the scale stripping effect of the wool fiber was shown in Figure 3.

[0222] The strength retention of the wool treated by this process was 81% and elongation retention thereof was 80%, compared with those of the untreated wool.

[0223] According to the TWC.TM31 test method of International Wool Bureau, the wool treated by this process had a 5×5A test results of -2.98%.

[0224] Chlorine content of the treated wool was measured, and no residual chlorine component (organic substance) was detected.

Example 4

[0225] In the present example, the wool tops were subjected to a chlorine-free shrinkproof treatment using a continuous process having five-multiple padding.

[0226] Full wool tops to be treated had a specification of 80. The process comprised the following steps:

The first tank contained padding treatment solution. The tank had a width of 1 m and a volume of 360 liters and was equipped with a suction roller tank having a circumference of 1 meter. The suction roller tank had an automatic heating apparatus inside, and the tank was filled with a high efficiency catalytic solution mainly composed of alkali protease 3g/L, tris(2-hydroxyethyl)phosphine 3g/L and anhydrous calcium chloride 0.3g/L (nonionic surfactant JFC 1g/L was further added), and pH thereof was 7.5. Temperature was controlled at 50 °C.

[0227] The wool tops were evenly arranged side by side on the roller and uniformly transported into the treatment liquid at a speed of 4.5 m/min, so that the wool tops were completely wet to ensure the surface of every fiber of the wool tops was evenly and thoroughly treated; and then the wool tops were squeezed by the pressure roller to ensure that the liquid-containing rate of the wool tops was 130%. Afterwards, the wool tops containing the enzyme fluid entered into the second treatment tank at a speed of 4.5 m/min. It took 26.7 seconds from the time when the wool tops entered into the first tank treatment liquid to the time when the wool tops entered into the second tank treatment liquid.

[0228] The second tank: padding treatment solution. They are the same as those for the first tank.

[0229] The third tank: padding treatment solution. They are the same as those for the first tank. The fourth tank: padding treatment solution. They are the same as those for the first tank.

[0230] The fifth tank: padding treatment solution. They are the same as those for the first tank. It took 26.7 seconds x 5 = about 134 seconds from the beginning of the first tank to the end of the fifth tank.

[0231] The sixth tank: water washing. The wool tops were rolling washed by rolling, so that the reagents, enzymes and degraded products attached on the surface of the wool fiber were cleaned. The water temperature was room temperature, and pH was 7.0.

[0232] The seventh tank: the second water washing. They are the same as those for the sixth tank.

[0233] The eighth tank: water washing at high temperature. It played a role of enzyme inactivation, so as to prevent subsequent continuous erosion of wool fibers. Temperature was 95 °C, and time was 15 seconds.

[0234] The ninth tank: the wool tops were padded in a solution containing 20g/L of wool softener, and the wool fiber were softened to achieve soft effect and to improve the feel. Temperature of the softener solution was 40 °C, and pH was 6.0, and time was 15 seconds. Afterwards, the wool tops were subjected to dehydrate and dry.

[0235] The process speed was 4.5 m/min, and number of padding in the treatment liquid was 5 times in total. After treated by this process, the scale stripping effect of the wool fiber was shown in Figure 4.

[0236] The strength retention of the wool treated by this process was 82% and elongation retention thereof was 81%, compared with those of the untreated wool.

[0237] According to the TWC.TM31 test method of International Wool Bureau, the wool treated by this process had a 5×5A test results of -3.56%.

Example 5

[0238] In the present example, the wool tops were subjected to a chlorine-free shrinkproof treatment using a continuous process having seven-multiple padding.

[0239] Full wool tops to be treated had a specification of 70. The process comprised the following steps:

The first tank contained padding treatment solution. The tank had a width of 1 m and a volume of 360 liters and was equipped with a suction roller tank having a circumference of 1 meter. The suction roller tank had an automatic heating apparatus inside, and the tank was filled with a high efficiency catalytic solution mainly composed of alkali

protease 2g/L, tris(4-carboxybutyl)phosphine 3g/L and anhydrous calcium chloride 0.3g/L (optionally, nonionic surfactant JFC 1g/L or anionic surfactant was further added), and pH thereof was 8, and temperature thereof was controlled at 50 °C.

[0240] The wool tops were evenly arranged side by side on the roller and uniformly transported into the treatment liquid at a speed of 6 m/min, so that the wool tops were completely wet to ensure the surface of every fiber of the wool tops was evenly and thoroughly treated. Then the wool tops were squeezed by the pressure roller to ensure that the liquid-containing rate of the wool tops was 130%. Afterwards, the wool tops containing the enzyme fluid entered into the second treatment tank at a speed of 6 m/min. It took 20 seconds from the time when the wool tops entered into the first tank treatment liquid to the time when the wool tops entered into the second tank treatment liquid.

[0241] The second tank: padding treatment solution. They are the same as those for the first tank.

[0242] The third tank: padding treatment solution. They are the same as those for the first tank.

[0243] The fourth tank: padding treatment solution. They are the same as those for the first tank.

[0244] The fifth tank: padding treatment solution. They are the same as those for the first tank.

[0245] The sixth tank: padding treatment solution. They are the same as those for the first tank.

[0246] The seventh tank: padding treatment solution. They are the same as those for the first tank. It took 20 seconds x 7 = 140 seconds from the beginning of first tank to the end of the seventh tank.

[0247] The eighth tank: water washing. The wool tops were rolling washed by rolling, so that the reagents, enzymes and degraded products attached on the surface of the wool fiber were cleaned. The water temperature was room temperature, and pH was 7.0.

[0248] The ninth tank: the second water washing. They are the same as those for the eighth tank.

[0249] The tenth tank: water washing at high temperature. It played a role of enzyme inactivation, so as to prevent subsequent continuous erosion of wool fibers. Temperature was 95 °C, and time was 15 seconds.

[0250] The eleventh tank: the wool tops were padded in a solution containing 20g/L of wool softener, and the wool fiber were softened to achieve soft effect and to improve the feel. Temperature of the softener solution was 40 °C, and pH thereof was 6.0, and time was 15 seconds. Afterwards, the wool tops were subjected to dehydrate and dry.

[0251] The process speed was 6 m/min, and number of padding in the treatment liquid was 7 times in total. After treated by this process, the scale stripping effect of the wool fiber was shown in Figure 5.

[0252] The strength retention of the wool treated by this process was 82% and elongation retention thereof was 80%, compared with those of the untreated wool.

[0253] According to the TWC.TM31 test method of International Wool Bureau, the wool treated by this process had a 5×5A test results of -3.01%.

Example 6

[0254] In the present example, the wool products were subjected to a chlorine-free shrinkproof treatment using a continuous process having four-multiple padding.

[0255] The products to be treated were wool products (serge). Method was as follows:

Four groups of Kroy deepim reaction tank (each group had a depth of 1.5 m, a width of 1.8 m and a thickness of 0.4 m) were used and filled with the integrated protease catalytic treatment solution for padding. Main components of the treatment solution (efficient catalytic solution) comprised alkaline protease 1.8 g/L, tris(4-carboxybutyl)phosphine as a biological enzyme activator 3.0 g/L and anhydrous calcium chloride 0.3 g/L (nonionic surfactant JFC 1g/L was also optionally added), and pH thereof was 7.5, and temperature thereof was controlled at 50 °C. Serge to be treated in flat state was successively transported into the four groups of Kroy deepim reaction tanks and subjected a four-multiple padding uniformly at a rate of 6 m/min for two minutes. The liquid-containing rates among every two groups were controlled at 100%. Afterwards, water washing, inactivation, soft treatment and drying treatment were conducted.

[0256] After above treatment, wool products not only had good shrinkproof performance, especially the wetting properties and permeability were significantly improved, but also the drip diffusion time thereof (according to GB/T21655.1-2008) was increased from ≥ 10 minutes (before the treatment) to ≤ 10 seconds.

Comparative Example 1

Treatment by soaking method

[0257] Descaling shrinkproof treatment was conducted by using a conventional soaking method, and the method was

as follows:

Wool tops (70 branches, 20 g) were soaked into a soaking treatment solution for 20 minutes or 60 minutes (50 °C). After soaking treatment, it was subjected to a post-treatment (similar to that in Example 1) by a conventional method, which included water washing for three times, followed by enzyme inactivation treatment and soft treatment, and then followed by dehydration and drying.

[0258] The formulation of the soaking treatment liquid was as follows: alkaline protease (alkali protease) 3g/L, nonionic surfactant JFC 1g/L (pH = 8.5), and the solvent was water.

[0259] The results showed that, when soaking time was 20 minutes, partial wool was not fully descaled. When soaking time was 60 minutes, descaling effect of the wool was basically uniform, but there were still a small amount of wool not fully descaled. This showed that the soaking method was not suitable for large-scale production due to long treatment time and non-uniform treatment effects.

Comparative Example 2

Treatment by soaking-steaming method

[0260] This comparative example adopted a conventional batch type method, and descaling shrinkproof treatment was conducted by using a soaking-steaming method. Method was as follows:

Wool tops (70 branches, 20 g) was fully soaked with a soaking treatment solution (50 °C, liquid-containing rates of 120%) to carry out a pre-soaking treatment for about 1 minute and then steamed (50 °C) for 25 minutes in a steam box, and steam treatment liquid (The composition thereof was the same as that of the soaking treatment solution) was added at the 5th, 10th, 15th and 20th minute. Soaking-steaming treatment took 26 minutes totally.

[0261] After soaking-steaming treatment, it was subjected to a post-treatment (similar to that in Example 1) by using a conventional method, which included water washing for three times, followed by enzyme inactivation treatment and soft treatment, and then followed by dehydration and drying.

[0262] The formulation of the soaking treatment liquid was similar to that of the padding treatment solution in Example 1 except that tris(3-hydroxypropyl)phosphine was not contained. That is, the formulation was as follows: alkaline protease 3g/L, nonionic surfactant JFC 1g/L.

RESULT

[0263] After the above-mentioned shrinkproof treatment of the wool, corners of the scales on the surface of wool were substantially completely removed. But its uniformity was poor, in which the scales on the surface of the finer wool were very vague while the scale layer of the thicker wool was cut very thin, indicating that this treatment process had better stripping effect for scales of fine wool than that of coarse wool.

[0264] After treatment, the fiber strength was 10.34cN, the strength retention rate was 83.25%, the elongation rate was 32.30%, and the elongation retention rate was 64.77%. This indicated that the wool treated by this process could meet the shrinkproof requirement, and the loss of rupture strength was in the acceptable range, but the elongation loss was relatively high.

[0265] In addition, the entire soaking-steaming treatment took up to 26 minutes, but the treatment effect thereof was much worse than that in any of Examples 1-5. In contrast, the total time for multiple padding in Examples 1-5 of the present invention was very low ($\leq$ 5 minutes, more preferably $\leq$ 3 minutes), and the descaling effect was more uniform, and the shrinkproof properties was more excellent.

[0266] The present invention is characterized in that a chlorine-free and rapid continuous processing is provided to completely substitute chlorination shrinkproof method so as to improve the shortcomings when protease biological treatment process is used alone. It also improves the protease biological treatment method, and finally achieves the goal of the optimal treatment effect and improves the quality of the whole wool product.

[0267] All literatures mentioned in the present invention are incorporated by reference herein, as though individually incorporated by reference. Additionally, it should be understood that after reading the above teaching, many variations and modifications may be made by the skilled in the art, and these equivalents also fall within the scope as defined by the appended claims.

Claims

1. A shrinkproof treatment agent for chlorine-free shrinkproof treatment, wherein the shrinkproof treatment agent comprises: (a) an optional solvent; (b) a protease; and (c) an organic phosphine compound represented by formula A; and an optional inorganic salt;

$$P\text{-}(X)_3 \qquad A$$

wherein each X is independently selected from the group consisting of substituted or unsubstituted C1-C10 hydrocarbyl, wherein the term "substituted" refers to one or more substituents selected from the group consisting of -OH, -COOH (carboxy), C2-C8 ester group, -SH, -CN, C1-C3 alkyl, C1-C3 alkoxy; and at least one X is a substituted C1-C10 hydrocarbyl having a -OH or COOH substituent;
the weight ratio of the protease to the organic phosphine compound is (0.2 to 10) : (0.5 to 20);
and the protease in the shrinkproof treatment agent is selected from the group consisting of a neutral protease, an alkaline protease, and combinations thereof.

2. The shrinkproof treatment agent according to claim 1, wherein when the shrinkproof treatment agent is an aqueous solution or a reconstituted aqueous solution, pH thereof is from 6.5 to 12, preferably from 7 to 11.5, and more preferably from 7.5 to 10.5.

3. The shrinkproof treatment agent according to claim 1, wherein the organic phosphine compound is a water-soluble aliphatic organic phosphine compound.

4. The shrinkproof treatment agent according to claim 1, wherein the organic phosphine compound has the following structure formula:

$$P\text{-}(R_1\text{-}R_2)_3 \qquad I$$

wherein,

R_1 is substituted or unsubstituted C2-C8 alkylene (preferably C1-C6 alkylene); and/or
R_2 is selected from the group consisting of -OH, -COOH, C2-C8 ester group, alkali metal, and alkaline earth metal.

5. The shrinkproof treatment agent according to claim 1, wherein the organic phosphine compound is selected from the group consisting of tris(3-hydroxypropyl)phosphine, tris(3 -carboxypropyl)phosphine, tris(2-hydroxyethyl)phosphine, tris(4-carboxybutyl)phosphine, and combinations thereof.

6. A shrinkproof treatment device for chlorine-free wool tops or wool products, which comprises:

a multiple padding apparatus which comprises *n* independent, continuously arranged padding machines, and every padding machine comprises a soaking tank and a rolling roller, wherein the soaking tank is used for placing a shrinkproof treatment agent for chlorine-free shrinkage treatment and the wool tops or the wool products to be treated are immersed in the treatment agent; and the rolling roller is used for rolling soaked wool tops or wool products, and the wool tops or wool products rolled by a rolling roller upstream enter into the soaking tank and the rolling roller of the padding machine downstream in turn, thereby repeating the soaking and rolling treatment, wherein *n* is a positive integer of 2 to 20;
a water washing apparatus for water washing the padded wool tops or wool products to form washed wool tops or wool products;
an enzyme inactivation apparatus for alkaline inactivation treatment of residual protease in the washed wool tops or wool products to form an enzyme-inactivated wool tops or wool products;
an optional soft processing apparatus for soft processing the enzyme-inactivated wool tops or wool products to form a softened wool tops or wool products; and
an optional dryer used to dry the softened wool tops or wool products obtained in the previous step.

7. The shrinkproof treatment device according to claim 6, wherein one or more auxiliary padding machines are further set between or behind every padding machine of the multiple padding apparatus, and every auxiliary padding machines independently comprises an auxiliary soaking tank and an auxiliary rolling roller, wherein the auxiliary soaking tank is filled with a protease treatment solution containing no organic phosphine compound and/or an organic

phosphine compound treatment liquid containing no protease.

8. A shrinkproof treatment method for chlorine-free wool tops or wool products, which comprises the following steps:

(a) providing chlorine-free wool tops or wool products to be treated, and a shrinkproof treatment agent for chlorine-free wool tops or wool products according to claim 1;
(b) padding the chlorine-free wool tops or wool products to be treated with the shrinkproof treatment agent for *n* times, thereby obtaining padded wool products, wherein *n* is a positive integer of 2 to 20;
(c) water washing the padded chlorine-free wool tops or wool products, thereby obtaining water washed chlorine-free wool tops or wool products;
(d) conducting an enzyme inactivation treatment of the water washed chlorine-free wool tops or wool products, thereby obtaining shrinkproof treated chlorine-free wool tops or wool products..

9. The method according to claim 8, wherein total time T of the padding treatment of step (b) is ≤ 15 minutes, preferably ≤ 10 minutes, more preferably ≤ 5 minutes, and most preferably ≤ 3 minutes.

10. A shrinkproof chlorine-free wool product wherein there is no residual organic chlorine in the wool product and the chlorine-free wool product is chlorine-free treated using the shrinkproof treatment apparatus according to claim 6 or using the method according to claim 8.

11. The method according to claim 10, wherein the chlorine-free wool product has four or five characteristics selected from the group consisting of:

(a) after treated by the shrinkproof treatment method, scale layer removal rate of wool surface layer of the treated chlorine-free wool product is 80 to 100% compared with that of the wool product to be treated;
(b) after treated by the shrinkproof treatment method, the absolute value of shrinkage rate of the treated chlorine-free wool product is ≤ 5%, and most preferably ≤ 3% when it is compared with that of the wool product to be treated, wherein measurement method thereof is TWC.TM31 test method of the International Wool Bureau;
(c) after treated by the shrinkproof treatment method, strength retention of the treated chlorine-free wool product is ≥ 80% compared with that of the wool product to be treated;
(d) after treated by the shrinkproof treatment method, elongation retention of the treated chlorine-free wool product is ≥ 75% compared with that of the wool product to be treated;
(e) drip diffusion time of the treated chlorine-free wool product is ≤ 15 s.

12. An article, wherein the article comprises the wool product according to claim 10 or is made of the wool product according to claim 10.

13. A use of the shrinkproof treatment agent according to claim 1 in chlorine-free shrinkproof treatment of a wool top or a wool product.

14. A shrinkproof treatment agent for chlorine-free wool tops and wool products, wherein its main components comprise a protease, a water-soluble aliphatic trisubstituted organic phosphine compound, and an inorganic salt; and the water-soluble aliphatic trisubstituted organic phosphine has a structure of $P\text{-}(R\text{-}S)_3$, wherein R is hydrocarbyl containing 1 to 6 carbon, S is hydroxyl or carboxyl and derivatives thereof; and mass concentration thereof is 1 to 10 g/L; the inorganic salt is calcium chloride, and concentration thereof is 0 to 2 g/L.

15. The shrinkproof treatment agent according to claim 14, wherein the trisubstituted organic phosphine is at least one of tris(3-hydroxypropyl)phosphine, tris(3 -carboxypropyl)phosphine, tris(2-hydroxyethyl)phosphine and tris(4-carboxybutyl)phosphine.

16. A continuous processing process for shrinkproof treatment of chlorine-free wool tops and wool products, wherein it comprises following steps:

1) shrinkproof treatment: wool tops and wool products are arranged, and uniformly transported with a roller into a number of tanks filled with shrinkproof treatment agent and subjected to an alternate soaking and rolling treatment for 3 to 10 times, wherein process conditions comprising : pH of the shrinkproof treatment agent is 7 to 10.5, temperature is 40 to 50 °C; a rolling liquid-containing rate is 60% to 150%; process delivery speed is 3 to 15 m/min, and total time of soaking and rolling is 1 to 5 minutes;

2) water washing: the treated wool tops obtained in the previous step are transported by rolling into one to four water tanks for multiple washing, thereby removing residual biological enzyme activator and enzyme preparation to prevent them from continuously eroding wool;
3) inactivation of protease: the washed wool tops are evenly and quickly passed through a hot water tank filled with hot water having a temperature of 85 to 95 °C or a solution containing 0 to 1 g/L of hydrogen peroxide, thereby inactivating any protease which is not completely washed out;
4) soft treatment: the inactivated wool tops are soaked into a tank filled with a conventional wool smoothing agent or organosilicon softening-agent, and a common soft treatment is conducted to improve feel of wool fabric;
5) dehydration and drying;
wherein the shrinkproof treatment agent mainly contains:

trisubstituted organic phosphine, with a concentration of 1 to 10g/L;
calcium chloride, with a concentration of 0.3 to 2g/L;
protease, with a concentration of 0.5 to 5 g/L;
and the rest is water;
the trisubstituted organic phosphine is at least one of tris(3-hydroxypropyl)phosphine, tris(3 -carboxypropyl)phosphine, tris(2-hydroxyethyl)phosphine and tris(4-carboxybutyl)phosphine.

17. The process according to claim 16, wherein the soaking and rolling treatment or padding treatment is repeated for 3 to 10 times; total time for the padding treatment is between 1 and 5 minutes; and process delivery speed is 3 to 8 m/min.

18. The process according to claim 16, wherein the wool tops are wool or cashmere of 56 to 100 branches.

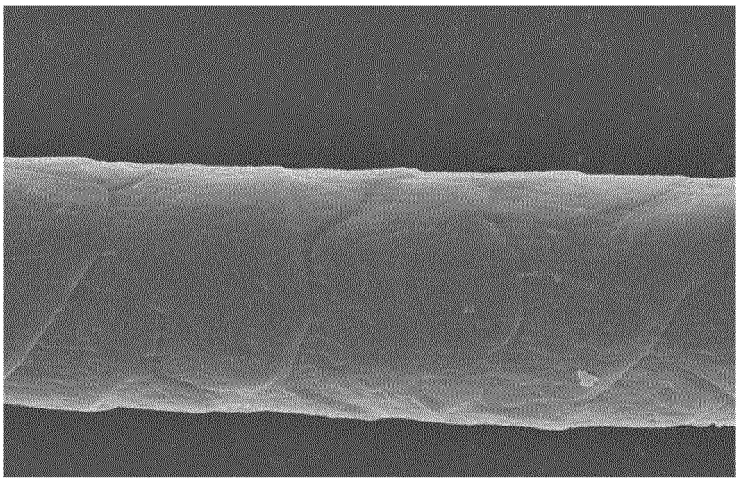

Figure 1

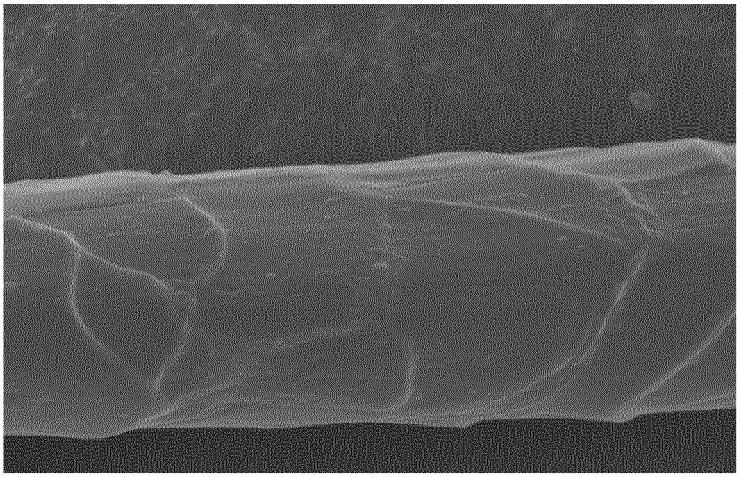

Figure 2

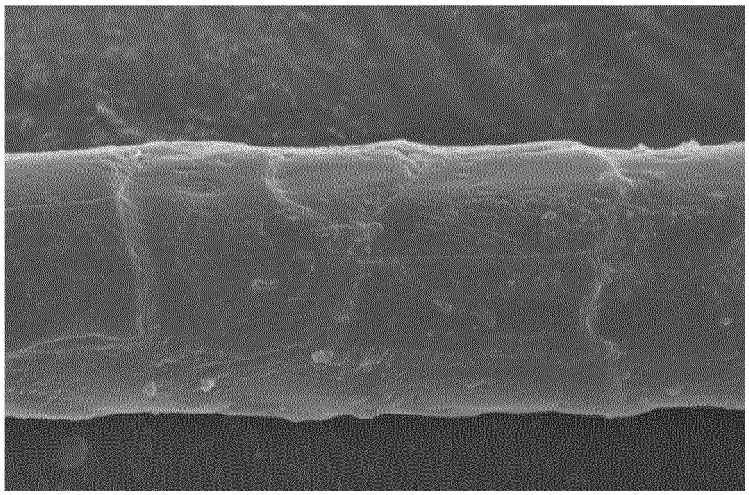

Figure 3

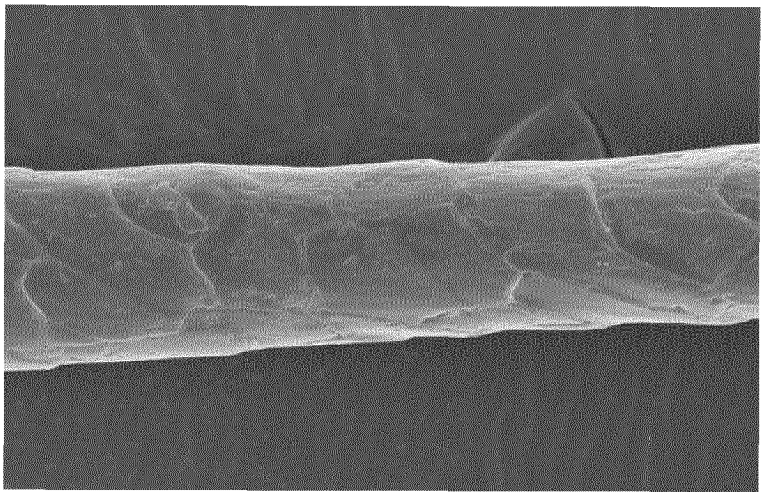

Figure 4

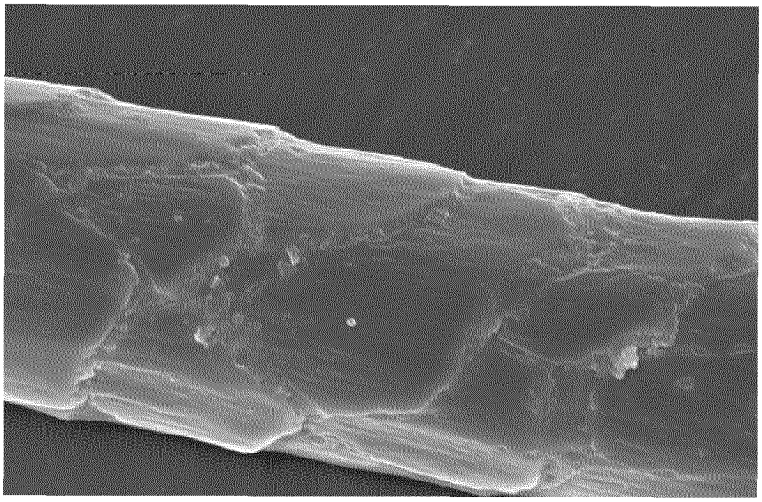

Figure 5

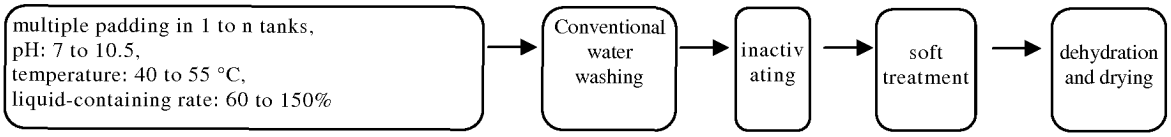

Figure 6

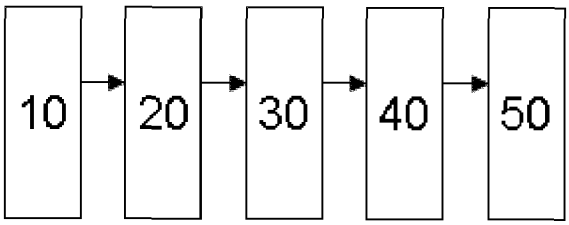

Figure 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2016/073835

A. CLASSIFICATION OF SUBJECT MATTER

D06M 16/00 (2006.01) i; D06M 13/285 (2006.01) i; D06M 11/155 (2006.01) i; D06L 1/16 (2006.01) i
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D06M; D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CNPAT, VEN, WPI, CNKI: Bacillus subtilis, protease, phosphorus, carboxybutyl phosphonium, ethoxyl phosphonium, hydroxypropyl phosphonium, proteolytic enzyme, sutilains, organic phosphine, carboxypropyl phosphonium, impregnation, padding, inactivated, killing enzyme, PHOSPHINE, ALKENZYME, (PROTEASE W ALKALINE), +ENZYME, WOOL, (PROTEIN 3W ENZYME), (PROTEASE W ENZYME), SHRINK W RESISTANCE, SHIRINK???, BACILLOPETIDASEA, BACILLOPETIDASEB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 11172580 A (NIPPON CHEMICAL IND et al.), 29 June 1999 (29.06.1999), description, paragraphs 0001-0081, and embodiment 1	1-18
X	CN 102965959 A (TIANJIN POLYTECHNIC UNIVERSITY et al.), 13 March 2013 (13.03.2013), description, paragraphs 0002-0025	1-18
A	JP 05272057 A (NIPPON CHEM IND CO., LTD. et al.), 19 October 1993 (19.10.1993), the whole document	1-18
A	CN 1070235 A (SCHOELLER HARDTURM AG), 24 March 1993 (24.03.1993), the whole document	1-18
A	CN 104153195 A (DONGHUA UNIVERSITY), 19 November 2014 (19.11.2014), the whole document	1-18
A	CN 103725810 A (HENAN PROSPER SKINS AND LEATHER ENTERPRISE CO., LTD.), 16 April 2014 (16.04.2014), the whole document	1-18

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

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 March 2016 (31.03.2016)	**22 April 2016 (22.04.2016)**
Name and mailing address of the ISA/CN: State Intellectual Property Office of the P. R. China No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088, China Facsimile No.: (86-10) 62019451	Authorized officer **FENG, Jie** Telephone No.: (86-10) **62084556**

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2016/073835

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
JP 11172580 A	29 June 1999	None	
CN 102965959 A	13 March 2013	CN 102965959 B	28 May 2014
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