

A Fibre Coating Process

Technical Field

The present invention relates to a process for coating keratinous fibres with a reduced keratinous protein.

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Background of the Invention

Current processes for imparting shrink resistance to proteinaceous fibres such as wool rely on pre-chlorination (e.g the chlorine Hercosett process) in order to enable treatment polymers to be applied. This process suffers from the disadvantage that chlorination by-products may be released into waste water streams. Wool textiles treated in this manner, or indeed not treated at all, generally dye or print to yield colour depth that is not as vibrant as that obtained with cotton or synthetic textiles.

There is therefore a need for a treatment process that eliminates the requirement for pre-chlorination treatment of proteinaceous fibres, while at the same time provides improved shrink resistance and may provide an additional advantage of improved colour depth upon dyeing or printing.

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Summary of the Invention

In a first aspect the present invention provides a process for coating a proteinaceous fibre with a keratinous protein said process comprising:

- (a) pre-treating the proteinaceous fibre;
- (b) applying a reduced form of a keratinous protein to the proteinaceous fibre;

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The proteinaceous fibre may be wool or any mammalian fibre, or silk or other insect derived fibre. The proteinaceous fibre may be a keratinous fibre. The keratinous fibre may be derived from an animal, or reconstituted from animal fibre.

In one embodiment, pre-treatment step (a) may be performed by contacting the proteinaceous fibre with a reducing agent or an enzyme.

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In an alternative embodiment, pre-treatment step (a) may be performed by contacting the proteinaceous fibre with an oxidising agent, followed by contacting the proteinaceous fibre with a reducing agent.

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The reducing agent may be any agent capable of cleaving the disulfide bonds of cystine residues in the proteinaceous fibre. The reducing agent may be selected from the group consisting of: sulfite, bisulfite, metabisulfite, thiols such as mercaptoethanol, dithiothreitol, thioglycollate and phosphine.

The enzyme may be any enzyme capable of cleaving the peptide bonds of cystine residues in the proteinaceous fibre. The enzyme may be a protease, for example Esperase L, papain, Bactosol SI or Biopraxe APL-30.

5 The oxidising agent may be selected from the group consisting of: permonosulfuric acid, and salts thereof, hydrogen peroxide and monoperoxyphthalic acid, and salts thereof.

In a further embodiment, a surfactant may be added in pre-treatment step (a). The surfactant may be a cationic quaternary ammonium compound, for example Arquad MCB50 or Gardiquat 1450. Alternatively, the surfactant may be a non-ionic surfactant, for example Triton X-100. In another embodiment, the surfactant may be an anionic surfactant, for example sodium dodecyl benzene sulfonate.

In yet another embodiment, step (b) may be repeated.

In a second aspect, the present invention provides proteinaceous fibre when coated by the process of the first aspect.

15 In a third aspect, the present invention provides proteinaceous fibre coated with reduced keratinous protein, wherein said proteinaceous fibre and said keratinous protein are crosslinked.

In a fourth aspect, the present invention provides the use of the proteinaceous fibre of the second or third aspect as a printing medium.

20 In a fifth aspect, the present invention provides a process for dyeing proteinaceous fibre, said process comprising exposing the proteinaceous fibre of the second or third aspects to a dye.

In a sixth aspect, the present invention provides a dyed proteinaceous fibre prepared in accordance with the process of the fifth aspect.

25 In a seventh aspect, the present invention provides a garment comprising proteinaceous fibre of the second, third or sixth aspects.

In an eighth aspect, the present invention provides a proteinaceous fibre according to the second, third or sixth aspects, wherein said proteinaceous fibre has improved shrink-resistance.

30 **Definitions**

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated step or element or integer or group of steps or elements or integers, but not the exclusion of any other step or element or integer or group of elements

or integers. Thus, in the context of this specification, the term “comprising” means “including principally, but not necessarily solely”.

The term “keratinous proteins” or “keratinaceous proteins” refers to proteins derived from keratin.

5 **Detailed Description of the Preferred Embodiments**

Keratinous proteins

Keratin is a naturally occurring protein found in keratin-containing materials including feather, wool and hair. One preferred source of keratinous proteins is feather, such as chicken and/or turkey feather. Another suitable source is wool.

10 The term keratinous protein is used in the broadest sense to encompass any one or more of the keratinous proteins obtained from keratinous materials, or fragments or derivatives thereof. Such fragments and derivatives thereof include keratinous proteins that have been subjected to chemical modifications such as functionalisation to introduce desired functional groups to provide additional desired properties. Any modification
15 retains the backbone of the keratin or keratin derivative. Examples of chemical modifications include hydrolysis, halogenation, oxidation, reduction, alkylation, amination, carboxylation, addition of aromatics or alkyl groups or the addition/substitution of any other (positively or negatively) charged or neutral functional groups.

20 Functional groups that may be added to the keratinous proteins may be any one or more groups selected from hydrogen, alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino,
25 alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, benzylthio, acylthio, siloxanes, polyethers and phosphorus-containing groups.

30 *Preparation of reduced keratinous proteins*

In the following, some suitable techniques for extracting the keratinous proteins from the keratin containing raw materials are described. One particular procedure involves the following steps:

- i. subjecting the keratin-containing material to reduction in a liquid medium to solubilise the keratinous proteins (suitably under conditions that minimise hydrolysis of the keratinous proteins), to yield a solution of keratinous proteins and undissolved solids;
- 5 ii. separating the solution of keratinous proteins from the undissolved solids.

However, it is noted that any other procedure known or disclosed in the art for removing keratinous proteins from keratinous materials may be used in place of the following procedure.

10 *Exemplified Extraction Technique*

(1) Raw Material Preparation

The keratinous raw material is advantageously washed and optionally fragmented into smaller particles to be in a suitable form for subjecting to the reduction step (see (2) below). In the case of non-feather materials, the preparation advantageously includes
15 scouring and washing to remove extraneous materials, greases and lipids. In materials such as wool, fragmentation may not generally be necessary, although there may be some practical or economical advantages for using short wool. According to one suitable embodiment, the keratinous material is washed with warm water containing a suitable surfactant and rinsed with water. The keratinous material may be dried if it is not
20 intended to be processed immediately after the washing stage.

In the case of feathers, these are advantageously washed and fragmented into smaller fragments to aid digestion. The washing may be conducted by washing in surfactant-containing water, as described above. Thereafter, the washed feathers may be fragmented by mincing and/or milling. Similarly, dry feathers may also be fragmented by
25 mincing or milling prior to digestion in the reduction stage. Fragmenting may be effected in any suitable apparatus, such as a mincing machine of a type used by butchers, or a rotary blade (eg Wiley) mill. Fragmentation enables a greater amount of keratin to be extracted from the feather material.

(2) Reduction

30 The keratin-containing material is suitably subjected to reduction in a liquid medium to solubilise the keratinous proteins. This stage may be referred to as "digestion". The reduction step effects reduction of the disulfide bonds in the cystine residues of the keratins in the keratin-containing material to cysteine (containing terminal thiol groups) to break the linked keratin protein fragment into smaller fragments. In the
35 case of feather keratins, the smaller fragment length is around 10.4 kDa, although some

larger fragments may remain, but preferably the majority of the product is the 10.4 kDa product. In the case of wool keratins, there are a variety of proteins of differing molecular weights. A great majority, above about 94% of these, are greater than 11 kDa. About 6% of the proteins, known as the “high Gly/Tyr” proteins, have a molecular weight of between 9-13 kDa, and thus a very minor percentage (less than 6%) of the reduced proteins will include some protein of between 9-11 kDa in molecular weight. Visual assessment of gel electrophoresis results will however reflect that the principal molecular weight fraction is above the 10 kDa level.

The reduction stage is suitably conducted under conditions that minimise the hydrolysis of the keratinous proteins. In other words, the reduction conditions effect breaking of the disulfide bonds, but are not so severe as to cause hydrolysis of the keratinous proteins. The extent of hydrolysis of the keratinous proteins can be measured by reference to the molecular weight of the keratinous proteins following the reduction stage. If the molecular weight of the protein product is below the levels indicated above for the particular keratin types, then the reduction conditions have not been such as to minimise hydrolysis of the keratinous proteins. In particular, if the majority of the keratinous proteins have a molecular weight below 10.4 kDa for feather, or a majority of the keratinous proteins are below 10.4 kDa (or more specifically 11 kDa) for wool (noting that some wool proteins will be in the 9-13 kDa range when the conditions are as required), the reduction conditions are too harsh. Under typical conditions, at least 95% of the keratinous protein product is 10.4 kDa or higher, and usually more than 99%. Due to contaminating material from harvested feathers, such as fragments or adhering flesh tissue and blood in the quill, the product may not be 100% free from lower molecular weight material.

The protein size is generally assessed qualitatively using polyacrylamide gel electrophoresis (PAGE) of the extracted feather protein. In a qualitative PAGE run on a feather keratin product, there is observed a heavy band corresponding to 10.4 kDa, and light bands at around 25 kDa, 35 kDa and 50 kDa. No significant bands can be detected below the 10.4 kDa band. For a wool keratin product, the bands will generally reflect the constituent keratinous protein fractions of wool that are able to be solubilised, which are as follows:

| Soluble Protein Fraction | Low sulfur | High sulfur | Ultrahigh sulfur | High Gly/Tyr |
|---------------------------------|------------|-------------|------------------|--------------|
| Amount (%) | 58% | 18% | 8% | 6% |

| | | | | |
|---------------------------|---------|-------|----|---------|
| Sulfur Content (%) | 1.5-2.0 | 4-6 | 8 | 0.5-2.0 |
| Mol Mass (Kda) | 45-50 | 14-28 | 28 | 9-13 |

Reference: Wool Science-The Chemical Reactivity of the Wool Fibre. John A McLaren and Brian Milligan, Science Press (1981) page 13.

To minimise hydrolysis of the keratinous proteins, an appropriate balance between reduction time and temperature should be sought. Generally, in the case of feather keratins, the reduction time should be 1 hour or less for reaction temperatures of 50°C or less, and for example is suitably 45°C for a digestion lasting about 45 minutes typically at atmospheric pressure. However, should the reduction temperature be 25°C or less, the reduction stage may be conducted over a period of up to 1.5 hours or more. In the case of wool keratins, the reduction time may be from 1 hour to 72 hours at 25°C, with lower temperatures enabling the longer reduction times, and higher temperatures enabling shorter reduction times, and for example is suitably 45°C for a digestion lasting about 45 minutes at atmospheric pressure.

The reduction stage may be conducted in an air or oxygen-containing atmosphere, or may alternatively be conducted in an oxygen-reduced or oxygen-free atmosphere.

Suitably, the reduction may be conducted in an inert gas atmosphere, for instance in a nitrogen gas atmosphere.

The reducing agent may be any suitable reducing agent that effects digestion of the keratinous proteins, whilst minimising hydrolysis thereof. According to one example, the reducing agent is an alkali metal sulfide, such as sodium or potassium sulfide. In the case of alkali metal sulfide reducing agents, these are suitably used in an amount of from 5 parts per 100 parts to 1000 parts per 100 parts, depending on the nature of the keratin containing material (eg feather or wool), the temperature, pressure, pH and time conditions.

An appropriate balance can be determined by reasonable trial and error, using the molecular weight information from the reduced product as a guide. In general, the conditions will be more severe for wool-based keratinous materials.

Preferably, the reduction stage is conducted in the presence of an alkali, and more preferably an alkali metal hydroxide. Suitable examples of alkalis include sodium and potassium hydroxide.

It is also possible for further additives to be used in the reduction stage. Suitable additives include surfactants and so forth. The addition of surfactants including anionic,

cationic and non-ionic surfactants in various stages during production in some cases may be used to improve the characteristics of the final keratinous protein product.

According to one embodiment, the alkali is added in an amount sufficient to adjust the pH to 12.0-13.5. According to one preferred embodiment, the pH is adjusted to 13.0.

5 Reduction of the keratinous proteins will continue to occur after the material is discharged from the reduction vessel, unless the reduction is ended in the reduction vessel by adding a suitable reagent. Accordingly, the subsequent stages should be controlled to ensure that the continued reduction does not proceed to the extent that hydrolysis occurs.

(3) Separation of Undissolved Solids

10 The keratinous proteins are suitably separated from the undissolved solids using techniques that avoid excessive gel formation. Gel formation occurs via aggregation of the keratinous proteins.

With small scale processing, the separation of the solubilised protein from undissolved solids can be performed by centrifugation followed by rapid vacuum
15 filtration to remove the remaining fine particulate matter. For larger scale processing, vacuum or pressure filtration apparatus can be used. Such apparatus encompasses rotary drum filters and continuous belt filters, and all other filters that continuously or semi-continuously present a fresh filtration surface to the feed material being subjected to separation. A suitable apparatus tested is a filter press. The preferred type of filter press
20 is a membrane filter press - either of the mixed plate or full plate type. A large range of filters in this class are available commercially and are described for example in the *Filters and Filtration Handbook*, Third Edition (1994) Christopher Dickenson, Elsevier Advanced Technology.

If a continuous decanting centrifuge is used, it is desirable for the G forces to be
25 sufficiently high to achieve a high degree of separation of solids from the protein solution, to avoid the need for further separation stages to remove residual material.

The separation step may be conducted prior to aggregation of the stabilised keratinous proteins. Preferably, the solid separation is conducted within a period not greater than 4 hours after the reduction step.

30 According to one suitable example, the separation step is commenced within a period of 1 hour after the completion of the reduction step, and the undissolved solids separated are subjected to a second stage of reduction. This second stage of reduction, like the first stage, is advantageously conducted in a liquid medium to solubilise the keratinous proteins therein under conditions that minimise hydrolysis of the keratinous
35 proteins, to yield a solution of keratinous proteins of similar qualities to those yielded in

the first stage. The solids remaining from the second stage of reduction can be considered to be waste undissolved solids.

The secondary stage of reduction/digestion may be conducted under the same conditions as the first or primary stage, or under modified conditions, to recover further
5 keratinous protein for further processing. The “secondary solution” of keratinous proteins may be combined with the “primary solution”, or may be kept separate. One reason for keeping the secondary solution of keratinous proteins separate from the primary solution is due to the fact that the amount of protein and the molecular weight of the extracted
10 protein from the secondary reduction/digestion may be variable (and generally lower than the primary stage). During alkaline digestion of keratins, especially in the presence of sulfides, there is progressive conversion of disulfide bonds to lanthionine and lysinoalanine residues that are not then able to be cleaved by additional reducing reagent, such as sulfide.

Preferably, if conducted, the secondary reduction/digestion is conducted within a
15 period not greater than four hours following completion of the primary reduction stage of step (i). If the solids are left in alkaline conditions for greater than four hours before further digestion, the amounts of lanthionine and lysinoalanine residues have a significant effect on the secondary yields.

(4) Solids Treatment

20 Any undissolved solids not subjected to secondary reduction/digestion, or following secondary reduction/digestion may be sent to waste. For the avoidance of any confusion, it is noted that the “solids” referred to here are not precipitated keratins, but are the solids remaining after extraction of the keratins therefrom. Although these waste solids may contain some residual keratinous proteins, they may conveniently be referred to as “non-
25 keratinous solids”. These waste solids may be treated to eliminate remaining sulfide, neutralised, and supplied as an additive for feedstock or fertiliser manufacture.

(5) Desalting

The salt-containing protein solution may be used in some applications without further processing. However, the procedure may further comprise the step of:

30 iii. desalting the solution of keratinous proteins.

Desalting refers to the removal of salts.

One particularly suitable technique for desalting the keratinous protein solution is desalting by diafiltration using ultrafiltration technology.

Diafiltration is effective in separating proteins of around 1 kD-1000 kDa from
35 small peptides and salts. The diafiltration is conducted using a cross-flow ultrafiltration

membrane. Three or more volume exchanges of deionised water or buffer solution may be used to remove excess salts. However, five or more volume exchanges of deionised water or buffer yield higher purity product. Currently, about 10 volume exchanges are being used.

5 During diafiltration deionised water or a weak buffer solution in water may be introduced to replace the salts in the starting solution. Diafiltration against deionised water or buffer solution adjusts the pH of the protein solution to typically between pH 7-10.

10 Diafiltration of the protein produced according to the procedure described above has been found to proceed with excellent yields, and with minimal blocking of the filtration membrane.

(6) Concentration

15 The desalted keratinous protein solution is optionally subjected to concentration. Concentration may be effected by any suitable method. Ultrafiltration is one such method. Specifically, ultrafiltration apparatus may be used to remove or separate some water from the keratinous protein solution to thereby concentrate the solution.

(7) Ultrafiltration Technology

20 Larger scale ultrafiltration apparatus is available, and is in use in the dairy industry. Such ultrafiltration apparatus may be used for the desalting and concentration stage. Membrane cartridges or cassettes are available from various suppliers such as Millipore which are capable of effecting the required separation and concentration in such ultrafiltration apparatus. The cut-off molecular weight of these membranes are typically somewhat below the 10.4 kDa level of the reduced keratins of the exemplified keratin extraction procedure. Usual cut-off values for membranes are less than 10 kDa but more
25 than 5 kDa.

The diafiltration and concentration in the ultrafiltration stage can be conducted continuously or semi-continuously, or in batches. Semi-continuous processing is particularly appropriate, to enable multiple passing of a quantity of solution through the apparatus prior to treatment of the next quantity.

(8) Optional Keratinous Protein Modifications

30 Following production of a desalted, and optionally concentrated reduced keratinous protein solution by the procedure, it is possible to conduct side protein chain additions or modifications, as desired to give any additional performance qualities. Such modifications may be performed on keratinous proteins extracted by any other suitable

techniques known in the art. As a consequence, the procedure may further comprise the step of:

iv. modifying the keratinous protein to produce a modified keratin-based product.

5 By way of example, the keratinous protein can be chemically modified by the introduction of carboxyl, amide, hydroxyl, aryl, alkyl or aromatic groups, either separately or in combination. Depending on the type of modification made, the modified keratin-based products should remain soluble, or substantially soluble in water.

(9) Optional Drying

10 The solution of keratinous proteins produced by the procedure may optionally be dried. This drying step is suitably conducted following desalting and concentration of the keratinous protein solution. The dried keratinous proteins may be used in the dried state, or may be used in a reconstituted solution form.

Suitable techniques for drying the protein include freezing and spray drying. Spray drying is a preferred method due to economic reasons. Nevertheless, large scale freeze drying equipment is commercially available, and can process around 1,000 litres of solution in 24-36 hours.

Pre-treating of proteinaceous fibres

20 Step (a) of the process may be carried out by exposing the proteinaceous fibre, for example wool fabric, to a solution of a reducing agent, such as sodium metabisulfite (between about 0.5 to 50g/L, or between about 5 and 30g/L, or between about 10 and 25 g/L or between about 15 and 25 g/L, or between about 17 and 22 g/L, or about 19g/L), at room temperature for about 1 to 4 hours with agitation. Other reducing agents that may be used include any reducing agents capable of cleaving the peptide bonds of cystine residues in the proteinaceous fibre, for example thiols such as mercaptoethanol, dithiothreitol, thioglycollate and phosphine.

In an alternative embodiment, step (a) may be performed by exposing the proteinaceous fibre to a solution of an oxidising agent, for example permonosulfuric acid, or salts thereof, hydrogen peroxide or monoperoxyphthalic acid, or salts thereof, followed by exposing the proteinaceous fibre to a solution of a reducing agent.

30 The oxidation step may be performed by exposing the proteinaceous fibre, for example wool fabric, to a solution comprising between 0.5 to 20 g/L, or between about 1 and 10 g/L, or between about 1.5 and 5 g/L, or about 2 g/L of permonosulfate, for between about 10 minutes to 1 hour at room temperature. The fabric may then be washed with water, and exposed to a solution of a reducing agent, such as sodium sulfite.

A surfactant may optionally be added to the solution of the reducing agent and/or the solution of the oxidising agent in order to alter the charge characteristics of the protein/fibre interaction. The surfactant may be a cationic surfactant, for example quaternary ammonium compounds, Arquad MCB50 or Gardiquat 1450. Alternatively, 5 the surfactant may be an anionic surfactant, for example sodium dodecyl benzene sulfonate. In another embodiment, the surfactant may be a non-ionic surfactant, for example Triton X-100.

In another embodiment, mixtures of anionic, cationic and non-ionic surfactants may be added to the solution of the reducing agent and/or the solution of the oxidising agent.

10 The amount of surfactant added may be between about 0.05 to 3g/L, or between about 0.5 to 2.5 g/L, or between about 1.5 and 2.5 g/L, or about 2g/L.

Following the treatment of the proteinaceous fibre with the solution of the reducing agent, the proteinaceous fibre may be drained prior to coating with the keratinous protein (step (b)).

15 In an alternative embodiment, step (a) may be carried out by exposing the proteinaceous fibre to an enzyme at a temperature between room temperature and about 50 °C for between about 5 minutes and about 3 hours in a suitable buffer solution such as phosphate or Tris at concentrations appropriate for the enzyme used. The enzyme may be any enzyme capable of cleaving peptide bonds of cystine residues in the proteinaceous 20 fibre. The enzyme may be a protease, for example Esperase L, papain, Bactosol SI or Bioprase APL-30. A cationic, anionic or non-ionic surfactant and/or other additives may be added to the aqueous buffer solution.

Examples of other additives are fabric softeners, such as ethers and polyglycol esters, oxiethylates, paraffins and fats, sulforicinate, amine-esters, amino-amides, 25 polysiloxanes, *N*-methylol derivatives of fatty amides or urea.

Application of a keratinous protein to the proteinaceous fibre

Once pre-treatment step (a) has been completed, the proteinaceous fibres can be coated with keratinous protein as per step (b). Step (b) may be carried out by making up an aqueous solution (volume of between about 5 to 30 w/v of fibre) of reduced keratinous 30 protein (as obtained by the procedures described above) and soaking the pre-treated proteinaceous fibre therein for about 15 minutes. Following this treatment, the coated proteinaceous fibre may be typically pad mangled to remove excess solution and dried at room temperature, or in an oven up to a temperature of about 120 °C for a period of a few hours or overnight.

The application of the keratinous protein coating according to the present process provides a chlorine-free method for achieving shrink-resistance and improved wash-fastness of materials comprising proteinaceous fibres. The keratinous protein coating is also naturally occurring and biodegradable.

5 The keratinous protein coatings have been found to be highly receptive to inks and dyes, and as such proteinaceous fibres coated with the keratinous protein coating show improved colour depth compared to proteinaceous fibres that have not been so coated.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications. The
10 invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations or any two or more of said steps or features.

Examples

15 **Example 1 – Extraction of keratinous proteins from keratinous materials**

Poultry feathers were used as the keratinous protein source. 10 kg of feathers were washed and scoured in a washing apparatus (a stainless steel tumbling vessel of 250 L capacity manufactured by Dose GmbH) using water and surfactant Baymol A™ from Bayer. The washed feathers were dried and milled, and the milled product transferred to
20 a rotary drum mixer. In the rotary drum mixer, the milled feathers were digested with a solution of 320 grams of sodium sulfide (calculated as 100% Na₂S) in 100 L of water at 45 °C. The pH of the reduction mixture was adjusted to pH 13 with sodium hydroxide.

The milled feathers were subjected to digestion over a period of 45 minutes. Following digestion, the product was immediately transferred to a filtration apparatus,
25 typically a centrifuge, in which the solids were separated from the solution containing keratinous proteins. The separation stage was conducted over a period of 1 hour.

Example 2 - Pre-treatment of wool fabric (oxidation followed by reduction)

Wool fabric is oxidized with potassium permonosulfate (PSA, 2g/L) in the presence
30 of an non-ionic surfactant (eg Triton X-100, 2 mL/L) for 15 min at room temperature, rinsed in water three times over a total of five min, and reduced with sodium sulfite (10 g/L, adjusted to pH 8.5 with 2 M sulfuric acid) for 15 min at room temperature, followed by rinsing in water before proceeding to coating with a feather keratin solution (2%,

reduced form). In both cases of PSA and sulfite treatments, the fabric:liquid ratio is 40:1 on weight of fabric (w/v).

Example 3 -Pre-treatment of wool fabric by reduction

5 Wool fabric is reduced with sodium metabisulfite (1.9g/L) in the presence of a cationic surfactant (eg Arquad MCB50, 2 mL/L) for 180 min at room temperature, the fabric:liquid ratio is 50:1 w/v. After draining and removing excess liquid, a coating with a reduced keratin solution (1-2%) is applied. The fabric is then dried at 100°C for 2 hours. A second coat of protein solution should also be applied.

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Example 4 - Feather keratin coating

After pre-treatment, wool fibre or fabric is coated with a solution of reduced keratinous protein having a concentration of up to 10% w/v by padding or soaking. The solution of the reduced keratinous protein has a pH between about 9.5-10. The coated fabric or fibre is dried at room temperature or in an oven (up to 120°C) for up to overnight.

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Example 5 – Shrink-Resistance Testing

Fabric pretreated according to methods described in either of Examples 2 or 3 was coated with keratin according to Example 4. Following application of the feather keratin coating, the fabric was washed according to a protocol similar to Woolmark test TM31. Five wash cycles were completed with fabric shrinkage being recorded as typically less than 2% of fabric area.

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Example 6 - Pre-treatment and coating of wool fabric for printing

25 Wool fabric is pre-treated with an aqueous solution of sodium metabisulfite (1.9g/L) in the presence of a cationic surfactant (Gardiquat 1450, 2 mL/L) for 60 min at room temperature. The fabric:liquid ratio is 50:1 w/v. The pre-treated wool fabric is drained, pad mangled dry and then coated with reduced keratinous solution (1-2%), wherein the keratinous protein is obtained from feathers. The fabric is then dried at 30 100°C for 2 hours.

The claims defining the invention are as follows:

1. A process for coating a proteinaceous fibre with a keratinous protein said process comprising:
 - (a) pre-treating the proteinaceous fibre;
 - 5 (b) applying a reduced form of a keratinous protein to the proteinaceous fibre;
2. The process of claim 1, wherein the proteinaceous fibre is a keratinous fibre.
3. The process of claim 1, wherein the proteinaceous fibre is a mammalian fibre.
4. The process of claim 1, wherein the proteinaceous fibre is a silk or other insect derived fibre.
- 10 5. The process of claim 2, wherein the keratinous fibre is wool.
6. The process of any one of claims 1 to 5, wherein step (a) is performed by contacting the proteinaceous fibre with a reducing agent or an enzyme.
7. The process of claim 6, wherein the reducing agent is selected from the group consisting of: sulfite, bisulfite, metabisulfite, thiols such as mercaptoethanol,
15 dithiothreitol, thioglycollate and phosphine.
8. The process of claim 6, wherein the enzyme is a protease.
9. The process of claim 8, wherein the protease is selected from the group consisting of: Esperase L, papain, Bactosol SI and Biopraxe APL-30.
10. The process of claim 6 or claim 7, wherein step (a) comprises contacting the
20 proteinaceous fibre with an oxidising agent, followed by contacting the proteinaceous fibre with the reducing agent or the enzyme.
11. The process of claim 10, wherein the oxidising agent is selected from the group consisting of: permonosulfuric acid and salts thereof, hydrogen peroxide and monoperoxyphthalic acid, and salts thereof.
- 25 12. The process of any one of claims 1 to 11, wherein a surfactant is added in step (a).
13. The process of any one of claims 1 to 12, wherein step (b) is repeated.
14. Proteinaceous fibre when coated by the process of any one of claims 1 to 13.
15. Proteinaceous fibre coated with reduced keratinous protein, wherein said
30 proteinaceous fibre and said keratinous protein are crosslinked.
16. Use of the proteinaceous fibre of claim 14 or claim 15 as a printing medium.
17. A process for dyeing proteinaceous fibre, said process comprising exposing the proteinaceous fibre of claim 14 or claim 15 to a dye.
18. A dyed proteinaceous fibre prepared in accordance with the process of claim
35 17.

19. A garment comprising the proteinaceous fibre of any one of claims 14, 15 or 18.
20. A proteinaceous fibre according to any one of claims 14, 15 or 18, wherein the proteinaceous fibre has improved shrink-resistance.