(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 444 546 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.04.2012 Bulletin 2012/17

(21) Application number: **10188180.3**

(22) Date of filing: **20.10.2010**

(51) Int Cl.:
D06M 15/15 *(2006.01)* ***D06M 16/00*** *(2006.01)*
D06M 23/06 *(2006.01)* ***D06H 1/00*** *(2006.01)*
G01N 33/36 *(2006.01)*

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(71) Applicants:
- **Centro Tessile Cotoniero e Abbigliamento S.p.A.**
  21052 Busto Arsizio (VA) (IT)
- **Felli Color S.p.A.**
  24057 Martinengo (BG) (IT)
- **Stazione Sperimentale per la Seta**
  20133 Milano (IT)
- **Linificio e Canapificio Nazionale S.p.A.**
  20121 Milano (IT)

(72) Inventors:
- **Donelli, Ilaria**
  I-20099, Sesto San Giovanni, MILANO (IT)
- **Rosace, Giuseppe**
  I-24044, Dalmine, BERGAMO (IT)
- **Rondi, Giorgio**
  I-24018, Villa d'Almè, BERGAMO (IT)
- **Isella, Francesca**
  I-20045, Besana Brianza, MONZA E BRIANZA (IT)
- **Alberti Fusi, Gabriella**
  I-22100, COMO (IT)
- **Calleri, Sergio**
  I-24057, Martinengo, BERGAMO (IT)
- **Freddi, Giuliano**
  I-20133, MILANO (IT)

(74) Representative: **Long, Giorgio et al**
Jacobacci & Partners S.p.A.
Via Senato 8
20121 Milano (IT)

(54) Method for biomarking textile materials

(57) The present invention describes a process designed to integrate biomarkers into textile substrates. The invention is directed to any kind of textile materials in form of loose fibres, tops, tow, sliver, yarn, fabric (woven, knitted, nonwoven, braided, etc.), garment. Textile materials can be made of natural or man-made fibres (artificial, synthetic) or their blends. The biomarkers of the invention are proteins, preferably endowed with biocatalytic activity. The biomarker carrier media include aqueous solutions of textile auxiliaries and finishes. The presence of the biomarker is detected by means of specific activity tests by applying the concept of biosensing. Visual inspection is generally sufficient to authenticate the biomarker.

EP 2 444 546 A1

Description

Field of the invention

[0001] The present invention relates to the field of textile materials and provide a method for biomarking such materials in order to allow identification, authentication or tracking of the materials and their manufacturers.

Background art

[0002] Nowadays, the problem of identification, authentication or tracking of textile products, including the important issue of counterfeit, is strongly felt in the textile production and trade sectors. One important point is the ability to make distinguishable textile products in order to allow brand and product tracking, to determine origin and authenticity thereof, to provide protection against counterfeits, to detect frauds and to stop the flow of wrongly labelled textile goods.

[0003] . The problem of identification, authentication or tracking of textile materials exists not only for finished articles and clothes, but also for intermediates and semi-finished products. The structure of the textile sector is formed by SMEs (>95%), the majority of which are commission companies specialised in one or few processes, receiving textile materials (yarns and/or fabrics and/or garments), applying the requested treatment and then sending the treated textiles back to their clients or, more often, to the next component of the textile and clothing supply chain, i.e. a weaver, dyer, printer, finisher, or to an end-user, i.e. garment maker, distributor, retailer, etc.

[0004] The number of claims involving a supplier and its client or an end-user in the textile chain is very high and often results in loss of time and money. The possibility of identifying, authenticating or tracking textile materials with a high degree of reliability and possibly at a cost as low as possible would bring strong contribution of transparency in many transactions involving members of the textile supply chain, as well as end-users and consumers.

[0005] Application of labels to textile goods to identify a non counterfeit item often fails to obtain the desired results since the label can be detached, replaced or counterfeited. To face these problems, more sophisticated labels have been developed incorporating DNA (Deoxyribonucleic acid) or RFId (Radio Frequency Identification) anti-counterfeiting technology, but their use is under scrutiny because production of labels at affordable cost is still a challenge. Moreover, this approach does not work for some intermediate and semi-finished products.

[0006] The use of markers directly integrated into the textile substrates (either fibres, yarns, fabrics or garments), either applied on a predetermined area or homogeneously distributed in all their parts, is probably a more attractive and effective approach to solve the above mentioned problems. The markers used for textile substrates must not degrade their properties, must be easy to apply, not detectable under normal visual or hand inspection but unequivocally detectable by means of appropriate portable or laboratory tools to allow goods being identified with certainty.

[0007] Fluorescent or phosphorescent organic and inorganic dyes and pigments, ultraviolet emitting, near/mid infrared detectable compounds, magnetic or reflective nano-particles comprising metal tracers are some of the anti-counterfeit markers proposed for use onto textile substrates. These markers can be added to polymer melt or dope before spinning the fibres. Thus, intrinsically marked synthetic fibres can be produced and then transformed into yarns and fabrics to manufacture 100% marked textile goods, or blended in different proportions with other natural or synthetic fibres to manufacture textile goods containing variable proportions of marked fibres.

[0008] Alternatively, already made natural and synthetic fibres can be treated at different processing stages (from sorting, carding, spinning to dyeing, printing and finishing) with suitable processing aids containing the marker in order to obtain an homogeneous distribution of the same onto the textile substrate and, consequently, onto the textile good produced therefrom. Interference with conventional textile auxiliaries, dyes, and finishing products must be avoided as it may impair aesthetic and functional properties of textile goods.

[0009] Bio-based approaches have been proposed to produce counterfeit-proof textile products, to investigate frauds in the textile market (from fibres to garments), and to determine the authenticity as well as the origin of the textile materials. For example, immunological techniques can be used to qualitatively and quantitatively identify the presence of different animal fibres in an article. The method is based upon the production and use of monoclonal antibodies to recognize the species specific sequences of the primary structure of keratin for identifying fibres from the different animal species (EP 1 847 831 A1).

[0010] DNA technology is currently being pursued to mark textiles for authenticating purposes. Appropriately selected DNA markers can be directly incorporated into various kinds of processing media and then applied onto textile substrates by means of conventional textile technologies to obtain marked textile products to be manufactured into different goods (WO 2004/094713 A2; WO 2007/035581 A2). A method for authenticating textile articles by labelling with an optical reporter marker linked to a nucleic acid tag, detecting the optical reporter and then characterizing or verifying the nucleic acid sequencing, genotyping or like techniques has also been reported (US 20080299559). The marker could be either solid or liquid and applied to a predetermined area of the garment. Textiles may have a label with the manufacturer name on it and may also be used as a region of the garment which the optical reporter marker is placed.

Summary of the invention

[0011] The present invention describes a process designed to integrate biomarkers into textile substrates. The stage of application and related application conditions are selected so as to ensure stability and durability of the biomarker activity for the required shelf life and life time span.

[0012] The biomarkers of the invention are proteins, preferably endowed with biocatalytic activity. Their presence is detected by means of specific activity tests resulting, more often but non exclusively, in colour changes of a solution containing a compound acting as substrate of the biocatalyst. Visual inspection of the reaction is generally sufficient as identification or authentication tool, but specific instruments, i.e. a UV/Vis spectrophotometer, can also be used to detect the presence of the biomarker.

[0013] The biomarker carrier media can include aqueous solutions of polymers, adhesives, binders, cross-linking agents, textile auxiliaries, softeners, lubricants, textile finishes (antistatic, water-proof, softening, antimicrobial agents or the like). Application of the biomarker can be made preferably but not exclusively during finishing, more generally at any processing stage where a treatment under wet conditions can be carried out.

[0014] The invention is directed to any kind of textile materials in form of loose fibres, tops, tow, sliver, yarn, fabric (woven, knitted, nonwoven, braided, etc.), garment. Textile materials can be made of natural or man-made (artificial, synthetic) fibres or their blends. End uses of biomarked textile products may comprise apparel, household, decoration, furnishing, industrial and technical textiles.

[0015] Further characteristics and the advantages of this invention will be better understood from the following detailed description of some embodiments thereof, which are provided by way of non-limiting examples wherein:

Figure 1 shows a flow sheet of the typical working operations in a supply chain of textile materials.

Detailed description of the invention

[0016] The present invention relates to a method for biomarking a textile material, comprising the step of putting the said textile material into contact with an aqueous solution containing a biomarker substance for a time and in conditions sufficient to allow the said biomarker substance to be retained by the said textile material in a detectable amount, wherein the said biomarker substance is a protein that is preferably able to interact with a substrate that can undergo a detectable reaction upon contact with such a protein.

[0017] The method of the invention is used to mark textile materials in any form and at any processing stage where a treatment under wet conditions can be carried out. Non limiting examples will be given herein below, which include textile materials from sliver to yarn, fabric and garment.

[0018] The biomarker will be made to intimately adhere to the individual fibres constituting the textile material by means of current textile technologies. The intermediate and semi-finished biomarked textile materials of the invention thus obtained can be used to manufacture fully biomarked textile items or can be blended or otherwise included into other textile and non textile products thus endowing them with an effective biomarking function. End uses of biomarked textile materials can be apparel, household, decoration, furnishing, industrial and technical textiles.

[0019] The steps leading to biomarking textile materials are as follows:

- Selection of the processing step for the application of the biomarker,
- Selection of the biomarker,
- Preparation of the processing medium containing the biomarker,
- Application of the medium containing the biomarker to the textile material, and finally, by the end user,
- Detection of biomarker activity.

[0020] The biomarker of the invention is a protein preferably endowed with biocatalytic activity. Protein biocatalysts typically belong to the following classes: oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases.

[0021] Biocatalysts are commercially available products supplied in form of granules, powder or aqueous solution. Before use, the biocatalyst activity is tested as received by means of specific testing methods provided by the supplier or available from the scientific and technical literature. This allows determining the activity per unit weight or volume necessary to define the biomarkers concentration in the application medium.

[0022] The biomarker is selected as a function of the kind of textile material to be treated (the biocatalyst must be inert against the polymeric textile material), of the processing step identified for its application (application conditions - i.e. pH, solvent, time, temperature, etc. - must not impair the biocatalyst activity), and taking into account the compatibility with other components of the application medium, i.e. textile auxiliaries and finishing products.

[0023] Typical non compatible biocatalyst/textile combinations are: proteases on protein fibres (eg. wool and silk); cellulases on cellulosic fibres (cotton, linen, hemp, viscose, lyocell, etc.); lipases and esterases on polyester fibres;

proteases and amidases on polyamide fibres; nitrilases on acrylic fibres. Under suitable ambient conditions (i.e. temperature, humidity) all these biocatalysts are able to hydrolyze the respective polymeric material constituting the fibres, thus leading to fibre degradation. Accordingly oxidoreductases, such as laccases and other polyphenol oxidases able to use air oxygen as co-substrate, must be avoided because their activation and reaction with the textile substrate may lead to colour change (more or less extensive browning of fibres).

[0024] Biocatalysts suffer from exposition to high temperatures and/or extreme acidic or alkaline pHs for long times. To avoid any risk of loosing totally or partially the biocatalyst activity during application to textiles, the processing conditions under which the biomarker can be safely applied to the textile material are as follows:

- temperature ≤ 100°C, preferably ≤ 80°C (pad-drying conditions), and ≤ 70°C, preferably ≤ 50°C (exhaust conditions);
- pH 4 to 10, preferably 6 to 8;
- time ≤ 5 min, preferably ≤ 2.5 min (pad-drying conditions), and ≤ 40 min, preferably ≤ 20 min (exhaust conditions).

[0025] The compatibility of the biocatalyst with the other components of the application medium, which may include textile auxiliaries (surfactants, wetting and levelling agents, salts, dyes, emulsifiers, lubricants, antifoam agents, etc.) and/or finishing products (softeners, antistatic, water-proof, soil release, antimicrobial, fire-proofing, agents; binders, polymers, cross-linking agents, etc.) is tested before application by mixing the required amount of biocatalyst with the other recipe components and then performing the activity testing procedure provided by the supplier or available from the scientific and technical literature. This allows determining the activity of the biomarker per unit weight or volume of application medium and, consequently, the amount of biomarker that will be transferred onto the textile material by pad-drying or exhaust processing conditions.

[0026] An important advantage of the method of the invention is that the wide range of commercial protein biocatalysts available allows setting up a large number of unique biomarker/textile material combinations endowed with high specificity, thus making counterfeit of the biomarking method and of the biomarked textile material very difficult from one side and identification or verification of the same more straightforward from the other side. Embodiments of the invention have the advantage that textile materials can be conveniently and unequivocally marked at a selected processing step with a solution containing the biomarker prepared on purpose. The costs related to the biomarking process are very low because the biomarker is applied in catalytic amounts. Another advantage is that biomarking can be repeated several times along the manufacturing chain to ensure the required durability. The intrinsic aesthetic and functional properties and performance of the textile material are not affected by the presence of the biomarker which is not visible at the naked eye. Authentication techniques apply the concept of biosensing.

[0027] Textile fibres that can be treated with the method of the invention include all natural (both plant and animal fibres, including but not limited to cotton, flax, hemp, wool, silk), man-made fibres (including but non limited to polyester, polyamide, acrylic, polyolefin, regenerated cellulose fibres) and their blends in any range of composition. Staple and continuous filament fibres are all included. Accordingly, two and three dimensional textile constructions obtained by carding, combing, spinning, weaving, knitting, nonwoven bonding, braiding, knotting, laying, and plating are possible materials for the inventive method.

[0028] Methods of application comprise all, but not exclusively, the currently available technologies which bring fluids in close contact with the individual fibres forming the textile material thus favouring adsorption, adhesion and/or physical and/or chemical bonding of the active ingredients contained in the fluid onto the fibre surface or diffusion, penetration and anchoring in the fibre bulk. These technologies include but are not limited to batch processes, where both the fluid and the textile material move with respect to one another or only one of them (the fluid or the textile material) is moving and the other is stationary, as well as continuous processes generally comprising the impregnation of the textile material with a high concentrated solution of the processing aids made by padding, coating or spraying, followed by drying and fixation/curing steps.

[0029] . For illustrative purposes only, examples of application of the biomarking method of the invention are given herein considering different processing steps and different shapes of the textile material.

[0030] *Biomarking textile materials in sliver or rove form*

[0031] EXAMPLE 1

[0032] Natural and man-made staple fibres and their blends undergo a series of operations, such as opening, carding, combing, roving before being fed to the spinning machine to make the yarn. All these processes are performed under dry conditions, but wetting the fibrous materials with an aqueous solution containing auxiliaries like lubricating, softening, and antistatic agents may be required to lower the negative effects of fibre-fibre and fibre-machine friction and to reduce electrostatic charge building under the strong mechanical stresses caused by the process.

[0033] In an embodiment of this invention, spraying heads mounted on a drawing frame of a combing machine are fed with an aqueous solution containing the lubricant/antistatic agent and the biomarker. As a specific example, to an aqueous solution of 10-50 g/L, preferably 20-30 g/L, of a non-ionic fatty acid polyglycol ester with softening/lubricating/antistatic activity a peroxidase biomarker (EC 1.11.1.7) is added in an amount of 1-10 g/L, preferably 3-6 g/L. The solution

is buffered at pH 6 with 0.1 M phosphate buffer. Then the running sliver is sprayed at room temperature in such a way that the wet pick up is 10-30 w%, preferably 20 w%, and the amount of active ingredients taken up by fibres is 1-5 w% for the lubricant and 0.1-1 w% for the biomarker. Thus the spraying treatment results in a biomarked sliver which will end up with a biomarked yarn when fed to a spinning machine.

[0034] EXAMPLE 2

[0035] Flax processing before spinning has specific features. Flax slivers undergo a series of doubling and drafting operations resulting in the production of a flax rove. The latter is scoured to eliminate non cellulosic substances and to help primary fibres to slide during spinning. Bleaching under oxidizing conditions at alkaline pH may also be performed.

[0036] In an embodiment of this invention, after scouring and bleaching, the flax rove is neutralized and the neutralizing solution discharged. Then, an aqueous solution containing a wetting agent and the biomarker is circulated from inside to outside of the perforated support onto which the rove is rolled. In a specific example a solution containing 1-5 g/L, preferably 2-3 g/L, of a non-ionic alkyl alcohol ethoxylate surfactant and 1-10 g/L, preferably 4-6 g/L, of protease biomarker (EC 3.4.21.62) is heated at 30-60°C, preferably 40-50°C, and circulated in the machine containing the rolls of flax rove for 10-30 min, preferably 15-20 min. The material-to-liquor ratio is typically from 1:10 to 1:30. The optimum absorption level for the biomarker is in the range 0.1-1 w%. Afterwards the biomarked rove is taken out, centrifuged, and dried. After spinning, the biomarked rove will result in a biomarked yarn.

[0037] EXAMPLE 3

[0038] Wet spinning is a specific flax spinning process leading to yarns of remarkable quality and fineness. The spinning machine is equipped with a trough full of water located on top of each spinning head upstream to the drafting frame. The flax rove passes through it before entering the drafting frame. In this illustrative embodiment, the water is substituted with an aqueous solution containing a wetting agent and the biomarker The rove passes through the aqueous solution contained in the basin thus picking up the solution containing the biomarker. Afterwards the rove enters the drafting frame where the yarn is formed and collected on spools. The biomarked yarn thus produced comprises flax fibres with a biomarker strongly adhering to their surface and physically entrapped into the fibrous network.

[0039] In a specific example, the impregnation trough is filled up with an aqueous solution containing catalase (EC 1.11.1.6) as biomarker (1-20 g/L, preferably 5-10 g/L), buffered at pH 7 with 50 mM phosphate buffer. The solution is maintained at room temperature. The level of the solution in the trough is controlled in order to ensure that the rove is always well immersed in the solution. Typical wet pick up values are 30-100 w%, preferably 50-80 w%. The optimum absorption level for the biomarker is in the range 0.1-1 w%. While passing through the drafting frame the biomarked rove is transformed into a biomarked yarn, which is collected on 100 g spools. Finally, the biomarked flax yarns coming from several spools are transferred onto packages of about 1 kg ready to be delivered to the knitter and/or weaver.

[0040] In another example of the same embodiment, a polyacrylic resin at 0.2-2 g/L, preferably 0.5-1 g/L, is added to the biomarker solution, together with a polyfunctional aziridine cross-linker at 0.5-4 w% of the resin weight, preferably 1.5-2.5 w%. The binding strength of the biomarker with fibres and its stability are enhanced under these application conditions.

[0041] *Biomarking textile materials in yarn or thread form*

[0042] EXAMPLE 4

[0043] Biomarking can be executed on the yarn already rolled onto cones just before delivery to the weaver. In an embodiment of this invention, a machine used to wrap up cones of flax yarn is equipped with humidifying units which are fed with an aqueous solution containing an antimould agent and the biomarker. The solution is forced to pass through the perforated cone from inside to outside at predetermined pressure and time. The process results in biomarked yarn which comprises fibres impregnated with the biomarker.

[0044] In a specific example, the biomarker is a catalase (EC 1.11.1.6) at 1-10 g/L, preferably 3-6 g/L, buffered at pH 7 with 50 mM phosphate buffer. It is mixed with benzo-isothiazolinone as antimould agent at 0.1-2 g/L, preferably 0.5-1 g/L. Then the solution is applied to the cone in such a way that the wet pick up is 1-20 w%, preferably 5-10 w%, and the amount of biomarker taken up by the yarn is 0.1-5 w%. This treatment results in a biomarked yarn.

[0045] EXAMPLE 5

[0046] Yarns made of natural or man-made fibres or their blends usually undergo a processing cycle comprising scouring, dyeing and finishing. Treatments are carried out on yarns in hank or cone form. Typically, hanks of up to 1 kg each are processed into cabinets of up to 800 kg capacity, working with a material-to-liquor ratio up to 1:15. Cones up to about 1.2 kg each are processed into package dyeing machines of up to 600 kg capacity, working with a material-to-liquor ratio up to 1:10. In both processing equipments the yarn material is stationary while the fluid is flowing through the hank or cone at a controlled speed and for the number of cycles required by the treatment. Time-temperature processing diagrams are computer controlled and can be tailored to the properties of the material under processing.

[0047] Yarn finishing typically consists in a wet treatment able to impart softness and lubricity to the material thus improving handle and reducing friction during subsequent weaving, knitting, etc. Most softeners are cationic surfactants which bind by electrostatic attraction to the negatively charged groups at the fibre surface. They are based on quaternary ammonium salts with one or two long alkyl chains. Others can be derived from imidazolium, substituted amine salts, or

quaternary alkoxy ammonium salts. Silicone based compounds such as polydimethylsiloxane modified to contain amine or amide groups bind to the fibres and work by lubricating agents, thus imparting improved feel.

[0048] In an embodiment of this invention, after the dyeing and rinsing baths are discharged, a finishing bath is circulated in the cabinet or package dyeing machine. In a specific example, an aqueous solution containing a cationic softener at a concentration of 1-5 g/L, preferably 2-3 g/L, at pH 5 (adjusted with acetic acid), to which the biomarker (selected taking into account the incompatibilities listedabove) is added at a concentration of 1-5 g/L, preferably 2-3 g/L. Afterwards, the processing cycle is started. The temperature is raised from ambient to about 40°C and kept stationary for 20 min while the solution is circulated in the machine. Then the bath is discharged, the hanks or cones are removed from the cabinet or the package dyeing machine, respectively, squeezed or centrifuged to extract excess water, and dried in an oven with circulating warm air. The optimum absorption level for the biomarker is in the range 0.1-1 w%. The biomarked yarn thus produced comprises fibres with the biomarker intimately adhering to their surface.

[0049] EXAMPLE 6

[0050] Yarns are usually transferred from bobbins to other supports like cones of different sizes before the next processing stages like weaving or knitting. To this purpose winding machines are used. In an embodiment of this invention the yarn coming from the unwinding unit is guided to pass onto the surface of a roller partially immersed in an aqueous solution of the biomarker. The yarn picks up the solution while passing onto the roller surface thus becoming impregnated with the biomarker. The amount of solution picked up depends on the kind of yarn, on its construction, on the speed of the roller, etc. Afterwards the biomarked yarn reaches the take up unit and is wrapped on the destination cone.

[0051] In a specific example, the impregnating solution contains a non-ionic alkyl alcohol ethoxylate surfactant at 2-10 g/L, preferably 4-6 g/L, and peroxidase (EC 1.11.1.7) as the biomarker. The concentration of the biomarker is about 2-40 g/L, preferably 10-20 g/L. The yarns passing onto the roller picks up an amount of solution of about 30-80 w%, preferably 40-60 w% before reaching the winding head. The optimum absorption level for the biomarker is in the range 0.1-2 w%.

[0052] *Biomarking textile materials in woven or knitted fabric form*

[0053] EXAMPLE 7

[0054] Woven or knitted fabrics are usually finished to impart on them the visual, physical, and aesthetic properties demanded by end-users and consumers. A softening treatment represents a general approach for finishing many types of textile articles. However, more specific finishing treatments can be performed such as: antimicrobial, anti-pilling, crease resist, wash and wear, antistatic, hydrophilic or hydrophobic finish, etc., depending on the kind of textile and end-use destination. The finishing treatment usually takes place as a separate operation after dyeing/printing. Finishes can be applied on fabrics by continuous (typically: padding techniques) or discontinuous processes (typically: exhaust techniques).

[0055] In a specific example a wool knitted fabric is subjected to a softening treatment in an overflow machine. An aqueous solution containing a cationic softener at a concentration of 1-5 g/L, preferably 2-3 g/L, at pH 5 (adjusted with acetic acid), to which a catalase biomarker (EC 1.11.1.6) is added at a concentration of 1-5 g/L, preferably 2-3 g/L, is circulated into the overflow. The material-to-liquor ratio is from 1:10 to 1:30. The temperature is raised from ambient to about 40°C and kept stationary for 20 min while the solution is circulated in the machine. Then the bath is discharged, the fabric is removed and dried. The optimum absorption level for the biomarker is in the range 0.1-1 w%. The biomarked fabric thus produced comprises fibres with the biomarker intimately adhering to their surface.

[0056] In another example a flax woven fabric is subjected to a softening treatment in a jigger machine, which operates on open width by transferring the fabric back and forth from roller to roller via the medium of a softening solution located at the base of the machine. The softening bath solution contains a cationic softener at a concentration of 1-5 g/L, preferably 2-3 g/L, at pH 5 (adjusted with acetic acid), to which a protease biomarker (EC 3.4.21.62) is added at a concentration of 1-5 g/L, preferably 2-3 g/L. The material-to-liquor ratio is from 1:2 to 1:4. The number of passages can be two or more. The temperature is raised from ambient to about 40°C and kept stationary until completion of the selected number of passages. Then the bath is discharged, the fabric is removed and dried. The optimum absorption level for the biomarker is in the range 0.1-1 w%. The biomarked fabric thus produced comprises fibres with the biomarker intimately adhering to their surface.

[0057] As a specific example of a continuous finishing process, a cotton woven fabric is impregnated in a foulard with a solution containing a cationic softener at a concentration of 1-10 g/L, preferably 3-6 g/L, at pH 5 (adjusted with acetic acid), to which a protease biomarker (EC 3.4.21.62) is added at a concentration of 1-20 g/L, preferably 5-10 g/L. Typical wet pick up values are 30-100 w%, preferably 50-80 w%. Afterwards, the fabric passes through the drying unit operated under the conditions definedabove. The optimum absorption level for the biomarker is in the range 0.1-1 w%. The biomarked fabric thus produced comprises fibres with the biomarker intimately adhering to their surface.

[0058] *Detection of biomarker activity on the textile material*

[0059] EXAMPLE 8

[0060] The following protocol refers to the detection of the bioactivity of any form of textile material biomarked with catalase biocatalyst (EC 1.11.1.6). As a specific example, a flax yarn biomarked with catalase is sampled in form of a

small hank of about 1 g. An aqueous solution of hydrogen peroxide (H_2O_2) in 50 mM phosphate buffer pH 7 is prepared by diluting the 30 w% stock solution from 30 to 200 times, preferably from 80 to 120 times, in order to have a H_2O_2 concentration in the range of 0.2-1 w%. The test is carried out at room temperature. The biomarked flax hank is immersed into the H_2O_2 solution. The catalase reaction follows the scheme:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

The oxygen gas formed by the reaction is released in form of bubbles as soon as the yarn is immersed in the H_2O_2 solution. As a control, a non-biomarked yarn is immersed into the H_2O_2 solution. No bubbles formation is observed under these circumstances.

[0061] EXAMPLE 9

[0062] The protocol of this example refers to the detection of the bioactivity of any form of textile material biomarked with peroxidase biocatalyst (EC 1.11.1.7). As a specific example, a small hank of about 1 g of cotton yarn biomarked with peroxidase is prepared. A 1 w% solution of pyrogallol (1,2,3-trihydroxybenzene) in 0.1 M phosphate buffer pH 6 is prepared (Reagent A). A fixed volume of 30 w% H_2O_2 solution (Reagent B) is diluted 100 times with water. The test is carried out at room temperature. The 1 g hank of biomarked yarn is immersed in 100 ml of Reagent A. Then, 10 ml of Reagent B are slowly added under agitation. The peroxidase reaction follows the scheme:

$$\text{Pyrogallol} + H_2O_2 \rightarrow \text{Purporogallin}$$

The purporogallin compound formed by peroxidase-catalyzed oxidation of pyrogallol has a brown colour which becomes visible at naked eye as soon as the reaction starts and then deepens with further progressing of the reaction. As a control, a non-biomarked yarn is immersed into Reagent A. When Reagent B is added, no colour change (browning) is observed under these circumstances.

[0063] EXAMPLE 10

[0064] The protocol of this example refers to the detection of the bioactivity of any form of textile material biomarked with protease biocatalyst (EC 3.4.21.62). As a specific example, a small piece of cotton fabric biomarked with protease, having a size of 1 to 4 cm^2, corresponding from about 10 to 100 mg of material, is cut and used for the test. A 100 mM HEPES NaOH buffer pH 7.5 is prepared (Reagent A). A 20 mM solution of N-Succinyl-Ala-Ala-Pro-Phe p-Nitroanilide solution is prepared in Dimethyl sulfoxide (Reagent B). The test is carried out at 37°C. 4 parts of Reagent A are mixed with 1 part of Reagent B and equilibrated at 37°C under gentle stirring. Then the piece of fabric is immersed in 5 to 50 ml of the Reagent A+B mixture. The protease reaction follows the scheme:

$$\text{N-Succinyl-Ala-Ala-Pro-Phe p-Nitroanilide} + H_2O \rightarrow \text{N-}$$

Succinyl-Ala-Ala-Pro-Phe + p-nitroaniline The p-nitroaniline compound formed by protease-catalyzed oxidation of N-Succinyl-Ala-Ala-Pro-Phe p-Nitroanilide has a yellow colour which becomes visible at naked eye as soon as the reaction starts and then deepens with further progressing of the reaction. As a control, a non-biomarked fabric is immersed into Reagent A+B mixture. No colour change is observed under these circumstances.

Claims

1. A method for biomarking a textile material, comprising the step of putting the said textile material into contact with an aqueous solution containing a biomarker substance for a time and in conditions sufficient to allow the said biomarker substance to be retained by the said textile material in a detectable amount, wherein the said biomarker substance is a protein.

2. The method of claim 1, wherein the said protein is able to interact with a substrate that can undergo a detectable reaction upon contact with such a protein.

3. The method according to claim 2, wherein the said detectable reaction comprises specific activity tests resulting in colour changes of a solution containing a compound acting as substrate of the biocatalyst, and wherein the said detection is by visual inspection or by means of a UV/Vis spectrophotometer.

4. The method of any claim 1 to 3, wherein the biomarker is included in a carrier media comprising aqueous solutions of polymers, adhesives, binders, cross-linking agents, textile auxiliaries, softeners, lubricants, textile finishes, anti-static, water-proof, softening, antimicrobial agents.

5. The method of any claim 1 to 4, wherein the application of the biomarker is made at any processing stage where a treatment under wet conditions can be carried out, preferably in the finishing step.

6. The method of any claim 1 to 5, wherein the said textile material is selected from any kind of textile materials in form of loose fibres, tops, tow, sliver, yarn, woven, knitted, nonwoven or braided fabric, garment, natural or artificial or synthetic fibres or their blends.

7. The method of any claim 1 to 6, wherein the said biomarker substance is an enzyme and it is preferably selected from the group consisting of oxidoreductases, transferases, hydrolases, lyases, isomerases and ligases.

8. The method of any claim 1 to 7, wherein the biomarker substance is applied to the textile material under the following conditions:

- temperature ≤100°C, preferably ≤80°C in pad-drying conditions, or ≤70°C, preferably ≤50°C in exhaust conditions;
- pH 4 to 10, preferably 6 to 8;
- application time ≤5 min, preferably ≤ 2.5 min in pad-drying conditions, or ≤40 min, preferably ≤20 min in exhaust conditions.

9. The method of any claim 1 to 8, wherein the said biomarker substance is selected in order to be inert against the textile material, stable in the application conditions and compatible with textile auxiliaries and finishing products.

10. The method of any claim 1 to 9, for manufacturing a biomarked sliver, comprising:

- feeding spraying heads mounted on a drawing frame of a combing machine with an aqueous solution containing 10-50 g/L, preferably 20-30 g/L, of a non-ionic fatty acid polyglycol ester with softening/lubricating/antistatic activity and an aqueous solution of a peroxidase biomarker in an amount of 1-10 g/L, preferably 3-6 g/L;
- buffering the solution at pH 6;
- spraying the running sliver at room temperature in such a way that the wet pick up is 10-30 w%, preferably 20 w%, and the amount of active ingredients taken up by the fibres is 1-5 w% for the lubricant and 0.1-1 w% for the biomarker.

11. The method of any claim 1 to 9, for manufacturing a biomarked rove, comprising:

- scouring, bleaching and neutralising a flax rove;
- circulating an aqueous solution containing 1-5 g/L, preferably 2-3 g/L, of a non-ionic alkyl alcohol ethoxylate surfactant and 1-10 g/L, preferably 4-6 g/L, of protease biomarker from inside to outside of the perforated support onto which the rove is rolled;
- heating at 30-60°C, preferably 40-50°C, and circulating in the machine containing the rolls of flax rove for 10-30 min, preferably 15-20 min, wherein the material-to-liquor ratio is from 1:10 to 1:30 and the optimum absorption level for the biomarker is in the range 0.1-1 w%.

12. The method of any claim 1 to 9, for manufacturing a biomarked rove, comprising:

- providing a wet spinning apparatus comprising an impregnation trough which a flax rove is made to pass through;
- filling the said impregnation trough with an aqueous solution containing 1-20 g/L, preferably 5-10 g/L of catalase as biomarker, buffered at pH 7, wherein the wet pick up values are 30-100 w%, preferably 50-80 w% and the optimum absorption level for the biomarker is in the range 0.1-1 w%.

13. The method of claim 12, wherein the said biomarker solution is added with a polyacrylic resin at 0.2-2 g/L, preferably 0.5-1 g/L, together with a polyfunctional aziridine cross-linker at 0.5-4 w% of the resin weight, preferably 1.5-2.5 w%.

14. The method of any claim 1 to 9, for manufacturing a biomarked yarn, comprising:

- equipping a machine used to wrap up cones of flax yarn with humidifying units which are fed with an aqueous solution containing a catalase at 1-10 g/L, preferably 3-6 g/L, buffered at pH 7, and benzo-isothiazolinone as antimould agent at 0.1-2 g/L, preferably 0.5-1 g/L;
- applying the said solution to the cone from inside to outside in such a way that the wet pick up is 1-20 w%,

preferably 5-10 w%, and the amount of biomarker taken up by the yarn is 0.1-5 w%.

15. The method of any claim 1 to 9, for manufacturing a biomarked yarn, comprising:

- subjecting yarns in hank or cone form to dying and rinsing;
- circulating a finishing bath in the cabinet or package dyeing machine, wherein the finishing bath comprises an aqueous solution containing a cationic softener at a concentration of 1-5 g/L, preferably 2-3 g/L, at pH 5, to which the biomarker is added at a concentration of 1-5 g/L, preferably 2-3 g/L;
- raising the temperature from ambient to about 40°C and keeping stationary until the optimum absorption level for the biomarker in the range 0.1-1 w% is reached.

16. The method of any claim 1 to 9, for manufacturing a biomarked yarn, comprising:

- guiding a yarn coming from the unwinding unit to pass onto the surface of a roller partially immersed in an aqueous solution comprising a non-ionic alkyl alcohol ethoxylate surfactant at 2-10 g/L, preferably 4-6 g/L, and peroxidase at a concentration of about 2-40 g/L, preferably 10-20 g/L, wherein the yarn passing onto the roller picks up an amount of solution of about 30-80 w%, preferably 40-60 w% before reaching the winding head and has an optimum absorption level in the range 0.1-2 w%.

17. The method of any claim 1 to 9, for manufacturing a biomarked fabric, comprising:

- subjecting a wool knitted fabric to a softening treatment in an overflow machine, wherein an aqueous solution containing a cationic softener at a concentration of 1-5 g/L, preferably 2-3 g/L, at pH 5, to which a catalase biomarker is added at a concentration of 1-5 g/L, preferably 2-3 g/L, is circulated into the overflow with a material-to-liquor ratio from 1:10 to 1:30;
- raising the temperature from ambient to about 40°C and keeping stationary until an optimum absorption level for the biomarker in the range 0.1-1 w% is reached.

18. The method of any claim 1 to 9, for manufacturing a biomarked fabric, comprising:

- subjecting a flax woven fabric to a softening treatment in a jigger machine, which operates on open width by transferring the fabric back and forth from roller to roller via the medium of a softening solution located at the base of the machine, wherein the softening bath solution contains a cationic softener at a concentration of 1-5 g/L, preferably 2-3 g/L, at pH 5, to which a protease biomarker is added at a concentration of 1-5 g/L, preferably 2-3 g/L, with a material-to-liquor ratio from 1:2 to 1:4 and with two or more passages;
- raising the temperature from ambient to about 40°C and keeping stationary until completion of the selected number of passages and an optimum absorption level for the biomarker in the range 0.1-1 w% is reached.

19. The method of any claim 1 to 9, for manufacturing a biomarked fabric, comprising:

- in a continuous finishing process, impregnating a cotton woven fabric in a foulard with a solution containing a cationic softener at a concentration of 1-10 g/L, preferably 3-6 g/L, at pH 5, to which a protease biomarker is added at a concentration of 1-20 g/L, preferably 5-10 g/L, with wet pick up values of 30-100 w%, preferably 50-80 w% and an optimum absorption level for the biomarker in the range 0.1-1 w%.

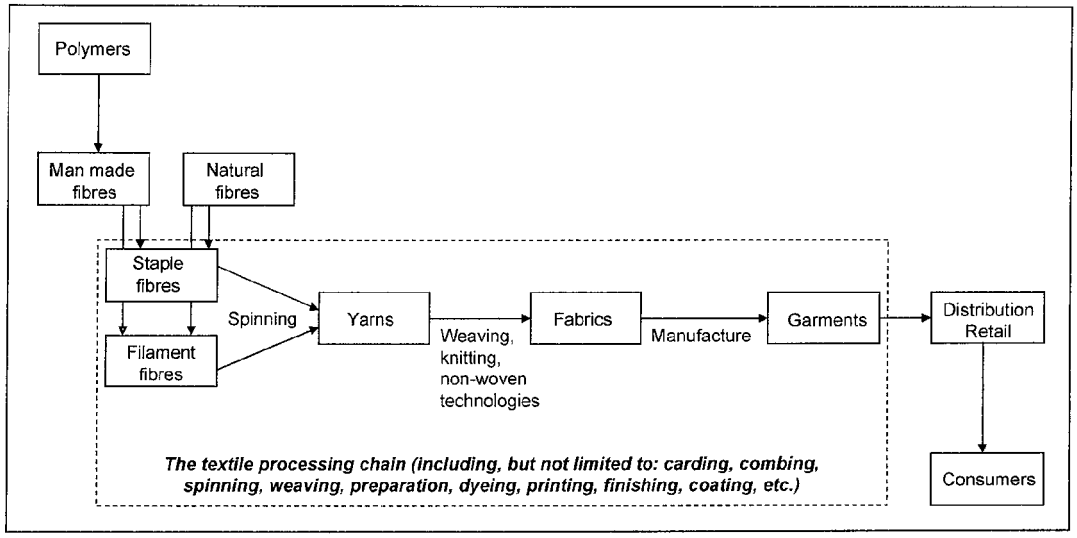
Polymers
Man made fibres
Natural fibres
Staple fibres
Filament fibres
Spinning
Yarns
Weaving, knitting, non-woven technologies
Fabrics
Manufacture
Garments
Distribution Retail
Consumers
The textile processing chain (including, but not limited to: carding, combing, spinning, weaving, preparation, dyeing, printing, finishing, coating, etc.)

FIGURE 1

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 10 18 8180

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X A	EP 1 500 741 A1 (BARTHOLDY CONSULTADORIA E SERV [PT]) 26 January 2005 (2005-01-26) * paragraph [0008] - paragraph [0012] * * examples 2, 25 * -----	1-6,8,9 10-19	INV. D06M15/15 D06M16/00 D06M23/06 D06H1/00
X	CORTEZ ET AL: "Transglutaminase mediated grafting of silk proteins onto wool fabrics leading to improved physical and mechanical properties", ENZYME AND MICROBIAL TECHNOLOGY, STONEHAM, MA, US, vol. 40, no. 7, 27 April 2007 (2007-04-27), pages 1698-1704, XP022059246, ISSN: 0141-0229, DOI: DOI:10.1016/J.ENZMICTEC.2006.10.013 * paragraph [2.2.4] * -----	1-7,9	ADD. G01N33/36
X	WO 98/33162 A1 (BIOCODE INC [US]) 30 July 1998 (1998-07-30) * page 3, line 7 - line 20 * * page 8, line 2 - line 18 * * page 8, line 25 - line 29 * * page 10, line 24 - line 25 * -----	1-6	TECHNICAL FIELDS SEARCHED (IPC) D06M D06H G01N
X	WO 87/06383 A1 (BIOTECHNICA LTD [GB]) 22 October 1987 (1987-10-22) * page 3, line 16 - page 5, line 4 * * page 5, line 26 - page 6, line 1 * * page 16, line 24 - page 17, line 9 * -----	1-6	
X	US 2009/286250 A1 (HAYWARD JAMES ARTHUR [US] ET AL) 19 November 2009 (2009-11-19) * claims 1,10,14,16 * * paragraph [0050] * -----	1-6	
	-/--		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	1 April 2011	Fiocco, Marco

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
.....
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 10 18 8180

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2005/060332 A2 (VALTION TEKNILLINEN [FI]; GROENQVIST STINA [FI]; HURME EERO [FI]; SMOL) 7 July 2005 (2005-07-07) * page 2, line 23 - page 3, line 25 * * page 4, line 11 - line 15 * * page 6, line 25 - line 29 * * examples * -----	1-7	
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	1 April 2011	Fiocco, Marco

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
.....
& : member of the same patent family, corresponding document

2

EPO FORM 1503 03.82 (P04C01)

Europäisches Patentamt
European Patent Office
Office européen des brevets

Application Number
EP 10 18 8180

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☒ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

Europäisches Patentamt
European Patent Office
Office européen des brevets

LACK OF UNITY OF INVENTION
SHEET B

Application Number
EP 10 18 8180

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 10(completely); 1-9(partially)

   Method for manufacturing a biomarked sliver
   ---

2. claims: 11-13(completely); 1-9(partially)

   Method for manufacturing a biomarked rove
   ---

3. claims: 14-16(completely); 1-9(partially)

   Method for manufacturing a biomarked yarn
   ---

4. claims: 17(completely); 1-9(partially)

   Method for manufacturing a biomarked wool fabric
   ---

5. claims: 18(completely); 1-9(partially)

   Method for manufacturing a biomarked flax fabric
   ---

6. claims: 19(completely); 1-9(partially)

   Method for manufacturing a biomarked cotton fabric.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 10 18 8180

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

01-04-2011

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1500741 A1	26-01-2005	NONE	
WO 9833162 A1	30-07-1998	AU 6245098 A	18-08-1998
		EP 0954838 A1	10-11-1999
		US 5942444 A	24-08-1999
WO 8706383 A1	22-10-1987	EP 0303610 A1	22-02-1989
		JP 2726877 B2	11-03-1998
		JP 63503242 T	24-11-1988
US 2009286250 A1	19-11-2009	NONE	
WO 2005060332 A2	07-07-2005	BR PI0418046 A	17-04-2007
		BR PI0418145 A	17-04-2007
		CA 2549471 A1	07-07-2005
		CA 2549519 A1	07-07-2005
		EP 1704281 A1	27-09-2006
		EP 1702107 A2	20-09-2006
		FI 20031903 A	24-06-2005
		WO 2005061790 A1	07-07-2005
		US 2007151679 A1	05-07-2007
		US 2007131362 A1	14-06-2007

EPO FORM P0459

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

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1847831 A1 **[0009]**
- WO 2004094713 A2 **[0010]**
- WO 2007035581 A2 **[0010]**
- US 20080299559 A **[0010]**