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(54) Title: PROCESS OF MARKING A TEXTILE SUBSTRATE

(57) Abstract: The invention relates to the marking of textile products that have been dyed using a supercritical dyeing process. More particularly, the invention provides a process of marking a textile substrate with a tracer, said process comprising contacting the textile substrate with a supercritical or near-critical dyeing medium containing a dye and a tracer, said tracer being selected from a metal chelate and a chemiluminescent agent. The process of the present invention uses the supercritical or near-critical dyeing medium as a vehicle for depositing a tracer onto the textile substrate that is also dyed using this medium. The presence of the deposited tracer on the dyed textile can be detected using a simple and reliable authentication method. The invention also concerns a marked textile product obtained by the aforementioned process. Also provided are a dyeing composition that can be used in the aforementioned process as well as methods for authenticating textile products that have been marked using his process.

PROCESS OF MARKING A TEXTILE SUBSTRATE

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a process of marking a textile substrate with a tracer, said process comprising contacting the textile substrate with a supercritical or near-critical dyeing medium containing a dye and a tracer, said tracer being selected from a metal chelate and a chemiluminescent agent.

The invention also concerns a marked textile product obtained by the aforementioned process.

Also provided are a dyeing composition that can be used in the aforementioned process as well as methods for authenticating textile products that have been marked using his process.

BACKGROUND OF THE INVENTION

The textile industry is one of the largest polluters in the world. The World Bank estimates that almost 20% of global industrial water pollution comes from the treatment and dyeing of textiles. The textile industry is second only to agriculture as the biggest polluter of clean water globally. Dyeing, rinsing, and treatment of textiles all use large amounts of fresh water.

Cotton production accounts for 2.6% of annual global water usage. A single T-shirt made from conventional cotton requires 2700 litres of water, and a third of a pound of chemicals to produce.

Millions of gallons of wastewater discharged by mills each year contain chemicals such as formaldehyde, chlorine and heavy metals such as lead and mercury. These chemicals cause both environmental damage and human disease. Effluents released from mills are often at high temperatures and pH, which exacerbate the problem. Hence, there is a

compelling need to reduce the amount process-water used by the textile industry and also to reduce the amount of water pollution caused by this industry.

An important technical breakthrough that makes it possible to achieve this important goal is the use of supercritical carbon dioxide as a replacement for water in the dyeing of textiles. This supercritical dyeing process proceeds in a similar manner as the conventional dyeing method. However, instead of producing a large amount of polluted waste water, the supercritical dyeing process yields a spent dyeing mixture that can easily be recycled. The spent dyeing mixture is simply separated in clean carbon dioxide gas and spent dye by depressurization. In production systems both the dye and the carbon dioxide can be recycled, thus providing for a completely closed systems and an entirely environmentally friendly approach to textile dyeing.

There is a rapidly increasing interest in this new dyeing technology as many users of dyed textiles are keen to purchase dyed textiles that have been produced in a environmentally friendly way. A complicating factor, however, resides in the difficulty to distinguish a textile product that has been produced through supercritical dyeing from a textile product that has been produced in a conventional dyeing process.

Hence, there is a need for a method of authenticating textile products that have been dyed using an environmentally friendly supercritical dyeing process.

WO 99/14416 describes a method for authenticating a textile product, comprising the steps of:

- applying a colorless composition to at least one portion of at least one thread constituting a textile product, wherein the composition comprises at least one of a pair of a colorformer and an activator which react when mixed to produce a spectral response; and
- authenticating the textile product as genuine by mixing the other of the pair of the colorformer and activator at said at least one portion of the at least one thread to produce the spectral response ..

The colorless composition can be in a water base solution as well as a solvent base solution. The solvent base solution may contain alcohol, a hydrocarbon or mineral oil as a solvent.

US 6,524,859 describes a process for making a textile product, comprising the steps of:

- adding a toxicologically safe substance to a textile product for purposes of marking the textile product, without adversely affecting the quality of the textile product; and
- applying an absorbent probe to extract the substance from the textile product and to detect a presence or absence of the substance,

wherein the probe is rubbed on the textile product and subsequently dipped in a reaction liquid, with a discoloration of the probe indicating the presence of the substance.

The Example of the US patent illustrates the use of an indicator substance in the form of 5 g of sodium chloride dissolved in 100 g of a preparatory agent, e.g. an emulsion for coating or brightening. The added substance (sodium chloride) is invisible in the preparatory agent and can be detected later in the finished textile product through use of an approximately 1% solution of silver chromate in conjunction with e.g. a swab which is dipped into the red-brown silver chromate solution.

US 4,655,788 describes a method for making security fibers and other materials luminescent by a dyeing process, comprising the steps of:

- immersing a dyeable material in a liquid bath comprising (i) at least one luminescent rare-earth chelate, (ii) at least one solvent in which the rare-earth chelate is soluble and in an amount sufficient to dissolve the chelate and (iii) at least one diluent in which the chelate is insoluble or poorly soluble, diluent being miscible with the solvent;
- removing at least a part of the solvent from the bath, the diluent being present in an amount sufficient to maintain the rare-earth chelate soluble in the bath;
- withdrawing the material from the liquid in the bath and drying it to obtain a material dyed with the luminescent chelate.

The Example 4 of the US patent illustrates the use of a dye, ERIO 1% Orange AS at 100% strength (Ciba-Geigy), and terbium chelate in methanol as a luminescent marker.

The luminescence of the rare-earth chelate is sensitive to the pH, being maximum at a neutral pH and diminishing gradually when the chelate environment departs from this neutral pH.

SUMMARY OF THE INVENTION

The inventors have developed a process of marking a textile product that has been dyed using a supercritical dyeing process. The process of the present invention uses the supercritical or near-critical dyeing medium as a vehicle for depositing a tracer onto the textile substrate that is also dyed using this medium. The presence of the deposited tracer on the dyed textile can be detected using a simple and reliable authentication method. The tracer that is used to mark the textile product is a metal chelate or a chemiluminescent agent.

Thus, one aspect of the invention relates to a process of marking a textile substrate with a tracer, said process comprising contacting a textile substrate with a supercritical or near-critical dyeing medium containing a dye and a tracer, said tracer being selected from a metal chelate and a chemiluminescent agent.

The present process offers the advantage that the marking of the textile substrate is achieved in the very same process step that the marking aims to certify, i.e. the super/near critical dyeing of a textile substrate. In addition, the process offers the advantage that the tracer is distributed throughout the fabric of the textile product. Thus, the tracer is effectively protected against, for instance, leaching and light-induced degradation. Only very small quantities of the tracer are required for marking the textile product as the authentication methods for detection of the tracer in dyed textile products are very sensitive.

The aforementioned authentication methods are based on the detection of chemiluminescence, triggered by the presence of the tracer substance in a marked textile product. The chemiluminescence reaction employed in the authentication process can be described in simplified form as follows:

In one embodiment of the invention the tracer substance is the chemiluminescent agent, and the authentication method employs one or more detection liquids to provide the activator as well as the metal ion that catalyses the chemiluminescence reaction.

In an alternative embodiment the tracer substance is a metal chelate providing the metal ion that catalyzes the chemiluminescent reaction, and the authentication method employs one or more detection liquids to provide the chemiluminescent agent and the activator. Because the metal is the catalyst and not a reactant, this embodiment offers the advantage that only a trace amount needs to be applied onto the textile. By employing metal in the form of a metal chelate it can be ensured that the metal tracer is distributed throughout the textile substrate. Furthermore, the metal chelate offers the advantage that it is embedded in the textile substrate and that it is very stable.

Another aspect of the invention relates to a marked textile product obtained by the aforementioned marking process.

A further aspect of the present invention concerns dyeing composition comprising at least 10 wt.% of dye and at least 1 mg of a tracer per kg of the dye, said tracer being selected from a metal chelate and a chemiluminescent agent.

Yet another aspect of the invention pertains to a method of authenticating a textile product, said method comprising treating the textile product by applying one or more detection liquids to produce a luminescence mixture containing at least 0.1 µg/l of a chemiluminescent agent, at least 0.1 µg/l of an oxidizing agent and at least 0.1 wt% of water-miscible organic solvent; and subjecting the treated textile product to chemiluminescent detection

A still further aspect of the invention relates to a method of authenticating a textile product, said method comprising treating the textile product by applying one or more detection liquids to produce a luminescence mixture containing at least 0.1 µg/l of dissolved metal cation, at least 0.1 µg/l of oxidizing agent and at least 0.1 wt% of

water-miscible solvent; and subjecting the treated textile product to chemiluminescent detection.

DETAILED DESCRIPTION OF THE INVENTION

Accordingly, a first aspect of the invention relates to a process of marking a textile substrate with a tracer, said process comprising contacting the textile substrate with a supercritical or near-critical dyeing medium containing a dye and a tracer, said tracer being selected from a metal chelate and a chemiluminescent agent.

The term "textile substrate" as used herein refers to an item comprising a flexible woven material consisting of a network of natural or artificial fibres (e.g. thread or yarn).

The term "dye" as used herein refers to a coloured substance that has an affinity to the substrate to which it is being applied and/or that is capable of reacting with such substrate under the formation of one or more covalent bonds..

The term "tracer" as used herein refers to a substance that can be detected in low concentrations as such, or following reaction or complexation with one or more other substances.

The term "supercritical" as used herein refers to a medium having a pressure and a temperature above its critical point.

The term "near-critical" as used herein refers to a medium having a pressure exceeding 80% of the critical pressure and a temperature exceeding 80% of the critical temperature (in °K).

The term "metal chelate" as used herein refers to a substance comprising at least one metal cation and one or more ligands, said substance comprising two or more separate coordinate bonds between the ligand and the metal cation.

The term "chemiluminescent agent" as used herein refers to a substance that is capable of emitting light (luminescence) as the result of a chemical reaction.

The present method may suitably be used to mark a variety of textile substrates. Preferably, the textile substrate comprises fibres containing one or more of the following fibrous materials: polyester, cotton, viscose rayon, nylon, spandex, linen, polyacrylate, silk, wool, polypropylene, polyethylene, aramid, regenerated cellulose (e.g. rayon). Even more preferably, the one or more fibrous materials are selected from polyester, cotton, viscose rayon, nylon, spandex, linen, polyacrylate, silk, wool, aramid and regenerated cellulose. The benefits of the present process are particularly appreciated if it is employed to mark a textile substrate comprising fibres that contain one or more fibrous materials selected from polyester, cotton, viscose rayon, nylon, linen, silk and wool. The aforementioned fibrous materials typically represent at least 20 wt.%, more preferably at least 50 wt.% and most preferably at least 70 wt.% of the textile substrate. Besides these fibrous materials the textile substrate may contain other materials such as, for instance, acetate or acrylic materials.

The supercritical or near-critical dyeing medium employed in the process preferably contains at least 80 wt.%, more preferably at least 90 wt. of one or more substances selected from carbon dioxide, propane, dimethylether, methane, C_{1-3} alcohols and combinations thereof. Even more preferably, the dyeing medium contains at least 60 wt.%, more preferably at least 80 wt.% and most preferably at least 90 wt.% of carbon dioxide.

The dyeing medium employed in the present process preferably is in a supercritical state when it is contacted with the textile substrate.

The dyeing medium employed in the present process typically contains at least 1 mg/kg of textile substrate, more preferably at least 10 mg/kg and most preferably at least 100 mg/kg of one or more dyes. The amount of dye contained in the dyeing medium usually does not exceed 50 wt.%. The aforementioned dyes are preferably selected from disperse dyes, reactive dyes and combinations thereof.

Reactive dyes employed in accordance with the present invention preferably are dyes which form a covalent chemical bond with textile substrate. Examples of reactive dyes are those listed under "Reactive Dyes" in the Colour Index Vol. 3 (3rd edition 1971) pages 2391-3560 and Vol. 6 (revised edition, 1975).

Disperse dyes employed in accordance with the present invention preferably are water insoluble dyes that are capable of dyeing polyester and acetate fibers (and optionally other fibres). Disperse dye molecules are generally based on an azobenzene or anthraquinone molecule with nitro, amine, hydroxyl, etc. groups attached to it.

The dye is preferably contained in the dyeing medium in dissolved and/or (finely) dispersed form.

The tracer is suitably contained in the dyeing medium in dissolved or (finely) dispersed form. Most preferably, the tracer contained in the dyeing medium is dissolved tracer. The tracer that is employed in accordance with the present invention preferably has a solubility in carbon dioxide at 250 bar and 120°C of at least 10^{-8}, more preferably at least 10^{-7} and most preferably 10^{-6} g tracer / g carbon dioxide.

According to a preferred embodiment the tracer used in the present process is a metal chelate. The use of a metal chelate as a tracer offers the advantage that only very small quantities of the metal chelate are required for marking the textile product because the metal ion acts as a catalyst in the chemiluminescence reaction that is used to authenticate the marked product.

The metal cation contained in the metal chelate is suitably selected from Fe^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Ca^{2+}, Ni^{3+}, Eu^{3+}, Zn^{2+} Sc^{3+}, Ti^{2+}, Ti^{3+}, Ti^{4+}, V^{2+}, V^{3+}, V^{5+}, Cr^{2+}, Cr^{3+}, Cr^{6+}, Co^{2+}, Co^{3+}, Zr^{3+}, Zr^{4+}, Nb^{3+}, Nb^{4+}, Nb^{5+}, Mo^{3+}, Mo^{4+}, Mo^{6+}, Tc^{4+}, Tc^{5+}, Tc^{7+}, Ru^{2+}, Ru^{3+}, Ru^{4+}, Rh^{+}, Rh^{2+}, Rh^{3+}, Pd^{2+}, Pd^{4+}, Ag^{+}, Ag^{2+}, Cd^{2+}, Hf^{4+}, Ta^{3+}, Ta^{4+}, Ta^{5+}, W^{6+}, Re^{4+}, Re^{6+}, Re^{7+}, Os^{3+}, Os^{4+}, Ir^{3+}, Ir^{4+}, Pt^{2+}, Pt^{4+}, Au^{3+}, Sr^{2+}, Ba^{2+} and combinations thereof. More preferably, the metal chelate is selected from Fe^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Ca^{2+}, Zn^{2+} and combinations thereof.

Examples of ligands that may suitably be employed in the metal chelates of the present invention include hexafluoro acetylacetonate, hexafluoro-diiminates, maltol, oxime, porphyrines, tetracycline, chlorotetracycline, oxytetracycline, cyclopentadienyl, carbonyl, anthocyanine and combinations thereof.

In another embodiment of the invention the tracer is a chemiluminescent agent, more particularly a chemiluminescent agent that exhibits chemiluminescence when mixed with an oxidizing agent. Examples of oxidizing agents that may incite the chemiluminescent agent to exhibit chemiluminescence include aliphatic epoxides, peroxides, ozone, chromate, chlorite hypochlorite and combinations thereof.

In accordance with an advantageous embodiment, the chemiluminescent agent employed in the present process gets intimately embedded in the fibres of the textile substrate. Thus, the chemiluminescent agent can be fixated effectively onto the textile substrate. Reactive moieties in the textile substrate can also form covalent bonds with a reactive chemiluminesent agent. These moieties typically selected from hydroxyl, amine, carboxyl, ether, ester, nitril, acetyl and combinations thereof. Most preferably, these reactive moieties in the textile substrate are selected from hydroxyl, amine, carboxyl, ether, ester, nitril, acetyl and combinations thereof. The covalent bonds are preferably formed during or immediately after the contacting of the textile substrate with the dyeing medium.

Examples of chemiluminescent agents that may advantageously be included in the dyeing medium include luminol, benzidine, phenolphtaleine, orthotolidine, leumalachite green, lucigenin, lophine, gallic acid, merbromine, fuchsin acid, diazofluorenone, 8-hydroxyquinoline and combinations thereof.

In the present process the dyeing medium when contacted with the textile substrate typically has a temperature of 20-180°C, more preferably of 38-150°C and most preferably of 40-140°C. The pressure of dyeing medium when contacted with the textile substrate preferably lies in the range of 5-100 MPa, more preferably of 8-70 MPa, most preferably in the range of 10-50 MPa.

According to a particularly preferred embodiment, the present process yields a dyed textile product. The textile product that is contacted with the dyeing medium in the present process preferably is a non-dyed textile product.

Another aspect of the invention concerns a marked textile product that is obtained by the method as defined herein, said product containing at least 0.1 ppb of the tracer.

In accordance with one embodiment, the marked textile product contains at least 0.02 ppb of metal chelate, more preferably 0.1-10 ppb of metal chelate and most preferably 0.1-15 ppb of metal chelate.

In accordance with another embodiment, the marked product contains at least 1 ppb of chemiluminiscent agent, more preferably 3-100 ppb of chemiluminiscent agent and most preferably 10-50 ppb of chemiluminescent agent.

Examples of marked textile products according to the present invention include yarn, thread, cellulose and hemicellulose fibers, fabric, clothing, footwear, upholstery fabric, curtains, window shades and technical textiles (such as textiles for automotive applications, medical textiles [e.g., implants], geotextiles [e.g. for reinforcing embankments], agrotextiles [e.g. textiles for crop protection], and protective clothing [e.g., heat and radiation protection for fire fighter clothing, molten metal protection for welders, stab protection and bulletproof vests]).

The textile products may take the form of loose fibres, slivers, yarns, threads, woven, knitted, braided, interlaced and unwoven materials,

A further aspect of the invention relates to a dyeing composition comprising at least 10 wt.% of dye and at least 1 mg of a tracer per kg of the dye, said tracer selected from a metal chelate and a chemiluminescent agent.

The dyeing composition may suitably contain further component besides the dye and the tracer. Examples of such further components include solvents, co-solvents, surfactants, matrix modifiers, softeners and combinations thereof. Preferably, dye

constitutes at least 50 wt.%, more preferably at least 80 wt.% and most preferably at least 90 wt.% of the dyeing composition.

The metal chelate is typically contained in the dyeing composition in a concentration of 0.1-100 mg per kg of dye, more preferably in a concentration of 0.5-50 mg per kg of dye and most preferably in a concentration of 1-20 mg per kg of dye.

The chemiluminescent agent is typically contained in the dyeing composition in a concentration of 0.1-100 mg per kg of dye, more preferably in a concentration of 0.5-50 mg per kg of dye and most preferably in a concentration of 1-20 mg per kg of dye.

The tracer employed in the dyeing composition preferably is a metal chelate or a chemiluminescent agent as defined herein before.

The dye in the dyeing composition is preferably selected from reactive dyes, disperse dyes and combinations thereof. Most preferably, the dye is disperse dye. Preferably, the disperse dye is an azobenzene dye or an anthraquinone dye.

The dyeing composition preferably is in the form of a liquid or a powder. Most preferably, the dyeing composition is in the form of a powder.

Yet another aspect of the invention relates to a method of authenticating a textile product, said method comprising treating the textile product by applying one or more detection liquids onto the textile product to produce a luminescence mixture containing at least 0.1 µg/l of a chemiluminescent agent, at least 0.1 µg/l of an oxidizing agent and at least 0.1 wt% of a water-miscible solvent; and subjecting the treated textile product to chemiluminescent detection. This particular authentication method is designed to authenticate textile products that have been marked with a tracer in the form of a metal chelate.

The chemiluminescent agent employed in this method preferably is a chemiluminescent agent as defined herein before.

A still further aspect of the invention relates to a method of authenticating a textile product, said method comprising applying one or more detection liquids onto the textile product to produce a luminescence mixture containing at least 0.1 µg/l of dissolved metal cation, at least 0.1 µg/l of oxidizing agent and at least 0.1 wt% of a water-miscible solvent; and subjecting the treated textile product to chemiluminescent detection. This authentication method is designed to authenticate textile products that have been marked with a tracer in the form of a chemiluminescent agent.

The oxidizing agent employed in the aforementioned authentication methods is preferably selected from aliphatic epoxides, peroxides, ozone, chromate, chlorite hypochlorite and combinations thereof. Most preferably, the oxidizing agent is selected from aliphatic epoxides, peroxides, chromate, chlorite hypochlorite and combinations thereof.

The dissolved metal cation is preferably selected from Fe^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Ca^{2+}, Ni^{3+}, Eu^{3+}, Zn^{2+}, Sc^{3+}, Ti^{2+}, Ti^{3+}, Ti^{4+}, V^{2+}, V^{3+}, V^{5+}, Cr^{2+}, Cr^{3+}, Cr^{6+}, Co^{2+}, Co^{3+}, Zr^{3+}, Zr^{4+}, Nb^{3+}, Nb^{4+}, Nb^{5+}, Mo^{3+}, Mo^{4+}, Mo^{6+}, Tc^{4+}, Tc^{5+}, Tc^{7+}, Ru^{2+}, Ru^{3+}, Ru^{4+}, Rh^{+}, Rh^{2+}, Rh^{3+}, Pd^{2+}, Pd^{4+}, Ag^{+}, Ag^{2+}, Cd^{2+}, Hf^{4+}, Ta^{3+}, Ta^{4+}, Ta^{5+}, W^{6+}, Re^{4+}, Re^{6+}, Re^{7+}, Os^{3+}, Os^{4+}, Ir^{3+}, Ir^{4+}, Pt^{2+}, Pt^{4+}, Au^{3+}, Sr^{2+}, Ba^{2+} and combinations thereof. Even more preferably, the dissolved metal cation is selected from Fe^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Ca^{2+}, Ni^{3+}, Eu^{3+}, Zn^{2+} and combinations thereof.

The water-miscible solvent that is employed in the aforementioned authentication methods provides at least a part of the luminescence mixture that is designed to produce the chemiluminescence that is used to detect the tracer. The use of water-miscible organic solvent ensures a high reaction rate between the reactants participating in the chemiluminescence reaction, for instance because it increases solubility of one or more reactants (e.g. the chemiluminescent agent) in the luminescence mixture. A high reaction rate is desirable as it enables detection of very low levels of tracer.

In case the water-miscible solvent is used in the authentication method that is designed to detect a metal chelate tracer, said solvent preferably facilitates the chemiluminescence reaction by dechelating the metal chelate. By liberating the metal

cation from the metal chelate, said metal cation can act as a catalyst in the oxidation reaction that causes the chemiluminescent agent to produce chemiluminescence.

According to a particularly preferred embodiment, the luminescence mixture that is produced by the application of one or more detection liquids contains water as well as water-miscible organic solvent. The mixture of water and water-miscible organic solvent provides a good reaction medium for the chemiluminescence reaction as the main reactants (chemiluminescent agent, oxidizing agent, metal ions) usually are highly soluble is such a medium.

The water in the luminescence mixture may suitably be provided by the one or more reaction liquids that are applied onto the textile product. It is also feasible to employ a wet textile product and to apply essentially water-free reaction liquid(s).

Typically, the luminescence mixture that is produced in the authentication methods contains 0.1-95 wt.% of the water-miscible organic solvent. Even more preferably, the luminescence mixture contains 1-90 wt.% of the water-miscible organic solvent Most preferably, the luminescence mixture contains 10-80 wt.% of the water-miscible organic solvent

The water content of the luminescence mixture typically lies in the range of 0.1-99 wt.%, more preferably of 1-90 wt.% and most preferably of 10-80 wt.%.

The water-miscible solvent employed in the present authentication method preferably is a liquid at 20°C and atmospheric pressure that can be mixed with water at this temperature and pressure in all proportions, forming a homogeneous solution.
The water-miscible organic solvent is preferably selected from aliphatic C_{1-6} alcohols, aromatic C_{4-12} alcohols, C_{3-6} ketones, C_{2-6} esters, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and combinations thereof. More preferably, the water-miscible organic solvent is selected from aliphatic C_{1-6} alcohols, C_{3-6} ketones and combinations thereof. Even more preferably, the water-miscible organic solvent is selected from methanol, ethanol, ethylene glycol, propanol (e.g. 1-propanol and 2-propanol), propanediol (e.g. 1,2 propanediol and 1,3-propanediol), glycerol, butanol, butanediol

(e.g. 1,2-butanediol, 1,3-butanediol and 1,4 butanediol), pentanediol (e.g. 1,5-pentanediol), triethylene glycol, THF, 1,2-dimethoxyethane, 2-butoxyethanol, acetone and combinations thereof. Most preferably, the water-miscible organic solvent is acetone.

It should be understood that in the aforementioned authentication methods the textile product may be treated by successively applying different liquids that together form the detection liquid. Thus, the invention encompasses, for instance, a method in which successively a liquid containing a chemiluminescent agent, a liquid containing an oxidising agent and a water-miscible organic solvent are applied. Likewise, the invention encompasses a method in which successively a liquid containing an oxidizing agent, a liquid containing dissolved metal cation and a water-miscible organic solvent are applied.

According to a particularly preferred embodiment the authentication method employs at least two detection liquids. In accordance with a preferred embodiment of the present authentication methods an aqueous detection liquid containing the oxidizing agent is applied to the textile product before application of a detection liquid containing at least 0.1 wt%, more preferably at least 1wt.% and most preferably at least 10 wt.% of the water-miscible organic solvent. The aqueous detection liquid may suitably contain dissolved metal cation in case the authentication method is used to detect a chemiluminescent agent.

The one or more detection liquids employed in the aforementioned authentication methods may suitably be applied onto the textile product by, for instance, spraying, dripping, pouring, impregnating or soaking.

The luminescence mixture that is produced in the authentication methods of the present invention preferably remains in direct contact with the textile product up till the moment the treated textile product is subjected to chemiluminescent detection. The authentication methods advantageously detect the chemiluminescence that is produced by reactions occurring within said luminescence mixture.

The chemiluminescent detection in the aforementioned authentication methods typically comprises the use of a sensor that is capable of detecting radiation having a wavelength of 400-750 nm, especially of 420-735 nm. According to a particularly preferred embodiment, the authentication method employs a handheld device that comprises the aforementioned sensor. According to a particularly preferred embodiment the handheld device is arranged in such a way that it can be held against a textile product to prevent external light (i.e. day light and/or from artificial light sources) from reaching the sensor. Thus, the radiation recorded by the sensor can be restricted to radiation originating from the chemiluminescence reaction.

Typically, in the authentication method the treated textile product is subjected to chemiluminescent detection within 60 seconds, more preferably within 10 seconds and most preferably within 2 seconds after the textile product has been contacted with the detection liquid.

According to a particularly preferred embodiment, the textile product that is authenticated in the present method is a marked textile product as defined herein before.

- The invention also provides a kit for authenticating a textile product, said kit comprising:one or more detection liquids as defined herein before; and
- a light detector for detecting light emitted during chemiluminescence.

According to a particularly preferred embodiment, the kit comprises at least two, separately packaged, detections liquids. More particularly, the kit comprises an aqueous detection liquid containing an oxidizing agent as defined herein before and a detection liquid containing at least 0.1 wt.% of the water-miscible organic solvent as defined herein before. According to a particularly preferred embodiment, the aforementioned aqueous detection liquid additionally contains a chemiluminescent agent as defined herein before or, alternatively, the kit comprises a second separately packaged aqueous detection liquid containing such a chemiluminescent agent.

The light detector preferably is a portable electronic device that comprises a light sensor for detecting incoming light, said light sensor being arranged to generate a signal representative of the intensity of the incoming light.

According to a preferred embodiment, the light detector is arranged to detect light having a wavelength within the range of 400-750 nm, especially of 420-735 nm.

The light detector contained in the present kit preferably is arranged to selectively detect light having a wavelength within a narrow bandwidth, e.g. a bandwidth of not more than 40 nm, more preferably of not more than 20 nm. Such selective detection may suitably be achieved by employing a colour filter that only transmits to the light sensor light having a wavelength within a narrow bandwidth. Accordingly the light detector advantageously comprises a colour filter that is located in the optical pathway between incoming light and the sensor.

The light detector preferably comprises a photo multiplier tube to enable detection of low intensity chemiluminescence.

According to another preferred embodiment the light detector comprises a indicator device that is arranged to produce a sign indicating whether or not the signal generated by the light sensor exceeds a pre-set threshold value. The indicating device preferably is a light emitting device or an acoustic device.

The invention is further illustrated by the following non-limiting examples.

EXAMPLES

Example 1

A supercritical dyeing medium containing CO_2 (120°C, 250 bar), 1-2% of disperse dye (20 mg per kg textile) and approximately 1% Fe(II)-maltol by weight of the disperse dye was used to dye a polyester fabric (polyethyleneterephtalate).

After dyeing, a piece of the dyed fabric was sprayed with an alkaline solution that had previously been prepared by mixing 1.2 g luminol, 6 g NaOH and 150 g water. Next, 3-4 droplets of aqueous H_2O_2 solution (3%) were dropped onto the parts that had been spayed with the alkaline solution.

A chemiluminescent reaction occurred as soon as acetone was added to the area of the textile product that had been treated with the alkaline solution and the oxidizing agent. The chemiluminescence reaction produced a blue light for several seconds.

Example 2

Example 1 was repeated, except that this time iron pentacarbonyl ($Fe(CO)_5$) was used instead of Fe(II)-maltol.

Again, blue chemiluminescent light was observed when the acetone was added.

Example 3

A supercritical dyeing medium containing CO_2 (120°C, 250 bar), 1-2% of disperse dye (20 mg per kg textile) and approximately 1% 8-hydroxyquinoline by weight of the disperse dye was used to dye a polyester fabric (polyethyleneterephtalate).

After dyeing, a piece of the dyed fabric was sprayed with a detection solution having the composition specified in Table 1.

Table 1

	Wt.%
Mn(II)	1
NaOH	4
H_2O_2	2-5
Water	92-95

A chemiluminescence reaction was observed as soon as acetone was added to the area of the textile product that had been sprayed with the detection liquid. The chemiluminescence reaction produced a blue intense light that lasted for several seconds.

CLAIMS

1. A process of marking a textile substrate with a tracer, said process comprising contacting the textile substrate with a supercritical or near-critical dyeing medium containing a dye and a tracer, said tracer being selected from a metal chelate and a chemiluminescent agent.

2. Process according to claim 1, wherein the textile substrate comprises fibres containing one or more of the following fibrous materials polyester, cotton, viscose rayon, nylon, spandex, linen, polyacrylate, silk, wool, polypropylene, polyethylene, aramid and regenerated cellulose.

3. Process according to claim 2, wherein the tracer is a metal chelate.

4. Process according to claim 1 or 2, wherein the tracer is a chemiluminescent agent that exhibits chemiluminescence when mixed with an oxidizing agent.

5. A marked textile product obtained by the method according to any one of the preceding claims, said product containing at least 0.1 ppb of the tracer, said tracer being either a chelate of a metal cation selected from Fe^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Ca^{2+}, Ni^{3+}, Eu^{3+}, Zn^{2+}, Sc^{3+}, Ti^{2+}, Ti^{3+}, Ti^{4+}, V^{2+}, V^{3+}, V^{5+}, Cr^{2+}, Cr^{3+}, Cr^{6+}, Co^{2+}, Co^{3+}, Zr^{3+}, Zr^{4+}, Nb^{3+}, Nb^{4+}, Nb^{5+}, Mo^{3+}, Mo^{4+}, Mo^{6+}, Tc^{4+}, Tc^{5+}, Tc^{7+}, Ru^{2+}, Ru^{3+}, Ru^{4+}, Rh^{+}, Rh^{2+}, Rh^{3+}, Pd^{2+}, Pd^{4+}, Ag^{+}, Ag^{2+}, Cd^{2+}, Hf^{4+}, Ta^{3+}, Ta^{4+}, Ta^{5+}, W^{6+}, Re^{4+}, Re^{6+}, Re^{7+}, Os^{3+}, Os^{4+}, Ir^{3+}, Ir^{4+}, Pt^{2+}, Pt^{4+}, Au^{3+}, Sr^{2+}, Ba^{2+} and combinations thereof or a chemilumiscent agent that exhibits chemilumiscence when mixed with an oxidizing agent

6. A dyeing composition in the form of a powder comprising at least 10 wt.% of dye and at least 1 mg of a tracer per kg of the dye, said tracer being selected from a metal chelate and a chemiluminescent agent.

7. Dyeing composition according to claim 6, wherein the tracer is a metal chelate.

8. Dyeing composition according to claim 6, wherein the tracer is a chemiluminescent agent that exhibits chemiluminescence when mixed with an oxidizing agent.

9. A method of authenticating a textile product, said method comprising treating the textile product by applying one or more detection liquids onto the textile product to produce a luminescence mixture containing at least 0.1 µg/l of chemiluminescent agent, at least 0.1 µg/l of an oxidizing agent and at least 0.1 wt% of a water-miscible organic solvent; and subjecting the treated textile product to chemiluminescent detection.

10. Method according to claim 9, wherein the chemiluminescent agent exhibits chemiluminescence when mixed with an oxidizing agent in the presence of a metal catalyst selected from Fe^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Ca^{2+}, Ni^{3+}, Eu^{3+}, Zn^{2+} and combinations thereof.

11. Method according to claim 9 or 10, wherein the chemiluminescent agent is selected from luminol, benzidine, phenolphtaleine, orthotolidine, leumalachite green, lucigenin, lophine, gallic acid, merbromine, fuchsin acid, diazofluorenone, 8-hydroxyquinoline and combinations thereof.

12. A method of authenticating a textile product, said method comprising treating the textile product by applying one or more detection liquids to produce a luminescence mixture containing at least 0.1 µg/l of dissolved metal cation, at least 0.1 µg/l of oxidizing agent and at least 0.1 wt% of a water-miscible organic solvent; and subjecting the treated textile product to chemiluminescent detection.

13. Method according to claim 12, wherein the dissolved metal cation is selected from Fe^{2+}, Fe^{3+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Ca^{2+}, Ni^{3+}, Eu^{3+}, Zn^{2+}, Sc^{3+}, Ti^{2+}, Ti^{3+}, Ti^{4+}, V^{2+}, V^{3+}, V^{5+}, Cr^{2+}, Cr^{3+}, Cr^{6+}, Co^{2+}, Co^{3+}, Zr^{3+}, Zr^{4+}, Nb^{3+}, Nb^{4+}, Nb^{5+}, Mo^{3+}, Mo^{4+}, Mo^{6+}, Tc^{4+}, Tc^{5+}, Tc^{7+}, Ru^{2+}, Ru^{3+}, Ru^{4+}, Rh^{+}, Rh^{2+}, Rh^{3+}, Pd^{2+}, Pd^{4+}, Ag^{+}, Ag^{2+}, Cd^{2+}, Hf^{4+}, Ta^{3+}, Ta^{4+}, Ta^{5+}, W^{6+}, Re^{4+}, Re^{6+}, Re^{7+}, Os^{3+}, Os^{4+}, Ir^{3+}, Ir^{4+}, Pt^{2+}, Pt^{4+}, Au^{3+}, Sr^{2+}, Ba^{2+} and combinations thereof.

14. Method according to any one of claims 9-12, wherein the oxidizing agent is selected from aliphatic epoxides, peroxides, ozone, chromate, chlorite hypochlorite and combinations thereof.

15. Method according to any one of claims 9-14, wherein the textile product is a marked textile product according to claim 5.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2014/050113

A. CLASSIFICATION OF SUBJECT MATTER
INV. D06P1/00 D06P1/94 D06P1/81 B41M3/14 G01N33/36
B41M3/00 D06H1/00
ADD.
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)
D06P B41M G01N D06H

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 897 694 A (WOOLF JEROME A [US]) 27 April 1999 (1999-04-27) column 1, lines 8-16 column 2, line 60 - column 3, line 25 column 8 - column 9; example 1 formula 5	6,7
X A	US 2009/186155 A1 (AOYAMA MICHIKO [JP]) 23 July 2009 (2009-07-23) paragraphs [0006], [0021], [0026], [0045]; examples 1-7	6,8 1-5, 12-15
Y A	US 4 655 788 A (JALON MICHEL [FR]) 7 April 1987 (1987-04-07) column 1, line 8 - line 11 column 2, line 49 - column 3, line 50; examples 1,4	1-3,5 4

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[X] Further documents are listed in the continuation of Box C.

[X] 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
19 May 2014	26/05/2014

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2014/050113

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2003 085613 A (RAILWAY TECHNICAL RES INST) 20 March 2003 (2003-03-20) abstract paragraphs [0005] - [0007], [0009] - [0010]; figure 4	5 1-4,6-11
Y	SAUS W ET AL: "DYEING OF TEXTILES IN SUPERCRITICAL CARBON DIOXIDE", TEXTILE RESEARCH JOURNAL, SAGE PUBLICATIONS, LONDON, GB, vol. 63, no. 3, 1 March 1993 (1993-03-01), pages 135-142, XP000360491, ISSN: 0040-5175 the whole document	1-3
X	GB 878 806 A (IBM) 4 October 1961 (1961-10-04) page 1, line 37 - line 47 page 2, line 92 - line 111	6,7

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NL2014/050113

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-15

   marked textile

1.1. claims: 1-4

   directed to a supercritical or near critical dyeing medium

1.2. claim: 5

   directed to the specific list of metal cations of the chelates or chemiluminescent agent of claim 5

1.3. claims: 6-8

   directed to the powder form of the dye composition and the amount of dye in it (at least 10wt%)

1.4. claims: 9-11

   directed to the first composition of the luminescence mixture (at least 0.1ug/l of chemiluminescent agent and at least 0.1 ug/l of an oxidizing agent)

1.5. claims: 12-15

   directed to the second composition of the luminescence mixture (at least 0.1ug/l of dissolved metal cation and 2) at least 0.1 ug/l of an oxidizing agent)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/NL2014/050113

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