

(19)



(11)

EP 4 143 378 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
07.08.2024 Bulletin 2024/32

(21) Application number: **20735032.3**

(22) Date of filing: **30.04.2020**

(51) International Patent Classification (IPC):
D06P 1/00 (2006.01) D06P 1/52 (2006.01)

(52) Cooperative Patent Classification (CPC):
D06P 1/5292; D06P 1/004

(86) International application number:
PCT/IT2020/000037

(87) International publication number:
WO 2021/220311 (04.11.2021 Gazette 2021/44)

(54) **TRACKING DYEING METHOD FOR FIBRES, YARNS, FABRICS AND GARMENTS.**

VERFAHREN ZUM NACHFÜHREN DER FÄRBUNG VON FASERN, GARNEN, GEWEBEN UND KLEIDUNGSSTÜCKEN

PROCÉDÉ DE SUIVI DE TEINTURE DE FIBRES, FILS, TISSUS ET VÊTEMENTS

(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

(43) Date of publication of application:
08.03.2023 Bulletin 2023/10

(73) Proprietor: **GRUPPO FLORENCE S.R.L.**
20121 Milan (IT)

(72) Inventors:
• **PEREZ AMARO, Lucia Gabriela**
51016 Montecatini Terme (PT) (IT)
• **GUAZZINI, Tommaso**
51016 Montecatini Terme (PT) (IT)

• **LANDINI, Luca**
51016 Montecatini Terme (PT) (IT)
• **SANDIAS, Francesco**
51016 Montecatini Terme (PT) (IT)
• **CHIELLINI, Emo**
51016 Montecatini Terme (PT) (IT)

(74) Representative: **Santi, Filippo et al**
Barzanò & Zanardo Roma S.p.A.
Via Piemonte 26
00187 Roma (IT)

(56) References cited:
EP-A1- 2 628 849 WO-A1-2014/133384
GB-A- 942 586

EP 4 143 378 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description**Technical field**

5 **[0001]** This invention relates to a tracking and imperceptible dyeing method for fibres, yarns, fabrics and garments. In particular, the invention relates to a cold dyeing method characterised by temperatures of below 70 °C with an overall treatment time of less than two hours and which does not use strong mineral acids. This method uses as trackers multi-responsive hybrid pigments, subsequently referred to as 'smart pigments', and uses organo-functionalised siloxanes previously hydrolysed as binding agents for dyeing said fibres, yarns, fabrics and garments, with the aim of producing
10 textile products with special characteristics of traceability and imperceptibility.

Background art

15 **[0002]** The prior art procedures for dyeing protein fibres, shown in Figures 1, 2 and 3, are mainly characterised by the presence of chemical substances, in the first steps of the dyeing, which define the treatment baths as strongly acidic, weakly acidic and neutral [Jose Cegarra, Publio Puente Jose Valdeperas - The dyeing of textile materials- Texilia - Paravia 1988]. These chemical agents are mainly sodium sulphate, sulphuric acid and/or ammonium acetate and their function is to make the protein-based fibre reactive to a particular type of dye belonging to groups I, II or III. The reactivity is guaranteed by a rapid diffusion of the acid substances, with a low molecular weight, towards the carboxylic groups of
20 the fibre which are protonated in this way. Once a high level of protonation has been reached, characterised by the presence of functional groups such as COOH, and taking advantage of the amphoteric nature of the protein fibres, several reactive points are obtained, characterised by the formation of NH_3^+ type groups. This cationic form interacts with the ionic dye (X^-), dissolved in the aqueous bath, thus forming an anionic complex with strong electrostatic interaction between the protein-based fibre and the colour. The times and temperatures of the various dyeing baths vary according
25 to the type of dye chosen. In general, all the procedures take longer than one hour, with gradual temperature ramps ranging from 45 minutes to one hour, reaching 100 °C as the optimum temperature and thus leading to the so-called boiling of the textile fibre. As shown in Figures 1, 2 and 3 the different methods are, currently, all hot methods and the overall time is more than 2 hours, using very strong chemicals such as sulphuric acid.

30 **[0003]** It is well known that the illegal production of textile products is a common problem and has been increasing over the years. The major and expensive textile brands are reproduced illegally and counterfeited accurately, making it difficult to distinguish them from the genuine products.

35 **[0004]** The consequences of these counterfeits are significant, mainly from an economic point of view, but also from an environmental and health point of view, due to the use of unsafe materials in the manufacture of replica textiles.

40 **[0005]** Moreover, the legal infringement is not only related to the quality and safety of counterfeit products, but also to the circumvention of entire production systems and supply chains, where the companies that are legally designated to produce yarns, fabrics, garments and clothing accessories are suffering a substantial reduction in sales due to the introduction of counterfeit products into their distribution channels. Some of these counterfeit products have high quality standards. The competition between two production systems, one legal and one illegal, which operate in parallel and in a synchronized way to produce objects of the same quality and design, pushes legal companies to adopt sophisticated security systems and tracing elements. These safety systems must be such as to guarantee and certify the originality
45 of the products and to be able to trace the textile elements and/or components at each production stage.

50 **[0006]** The need to protect textile brands has currently led to the development of methods for marking and authenticating products.

55 **[0007]** The state of the art highlights systems for marking and tracing yarns, for example with fluorescent, phosphorescent or photochromic compounds, or labels fitted with electronic chips.

60 **[0008]** However, in the known methods for tracking fabrics, the reactions to bind the marker are complex, or the preparation of the system containing the marker is not simple. In addition, in order to obtain a textile product which is able to show more than one characteristic, such as fluorescence when exposed to ultraviolet light or the photochromic property, it is necessary to use more than one tracer or complex yarn treatment systems.

65 **[0009]** In addition, the prior art methods for tracking fabrics are mostly represented by labels to be applied to the garments before they are sold in order to certify the originality of the finished product to the final consumer.

Disclosure of the invention

70 **[0010]** Therefore, the technical problem raised and resolved by the invention is that of providing a method for marking and tracking textile yarns which allows the above-mentioned drawbacks of the prior art to be overcome.

75 **[0011]** This problem is overcome by a method according to claim 1. Preferred features of the invention are present in the dependent claims.

[0012] The aim of the invention is to provide an innovative tracking dyeing method, consisting of an imperceptible tracking yarn made of natural coloured and/or raw fibre, dyed with a smart pigment. This pigment is a 2D nano-structuring pigment, capable of piezochromic, piezo-photochromic and optionally fluorescent activity.

[0013] The possible fluorescent activity of the pigment can be advantageously detected when the textile product is subjected to UV radiation at any stage of production, distribution and sales.

[0014] The application of the tracking dyeing method according to the invention avoids the counterfeiting of the textile product, as the tracking element, that is, the textile fibre marked with the smart pigment, has particular properties upstream and downstream of the dyeing treatment which can only be traced by the owner of the technology. Although the response of the smart 2D nano-structuring pigment, when fluorescent, is very similar to other systems with fluorescent activity already available on the market, it differs in that it can be multi-responsive, that is, it can also present piezochromic and photochromic activity and have a higher light fastness than current fluorescent-based security systems.

[0015] The dyeing method according to the invention, which uses the above mentioned pigment type, makes it possible to obtain a nano-coating or surface coating of pigment on the fibre in a single step and under bland conditions (below 60°C), through the formation of a covalent bond between the fibre and the pigment, regardless of the type of fibre or textile clothing product. This makes it advantageously possible to transfer the starter characteristics of the pigment, such as the fluorescence, to the natural fibre, making the pigment imperceptible when fixed to the textile structure and therefore not easy to detect and counterfeit.

[0016] The result of the dyeing method according to the invention is a clothing textile product preferably fluorescent with high fastness to light, photo-oxidative degradation, washing and all subsequent processes to which the fabric is subjected, such as over dyeing and bleaching.

[0017] Textile products dyed with the dyeing method according to the invention, in the presence of the smart pigment, are advantageously used as tracers to uniquely mark or identify fibres and/or yarns and/or fabrics and/or garments, also hereinafter meaning textile clothing accessories and to make a marked textile clothing accessory imperceptible to the naked eye, but visible when subjected to pressure and/or when irradiated under UV light and characterised by high light fastness. The textile products marked at the various processing stages by the method according to the invention are compatible with any subsequent processing of the textile process.

[0018] In addition, unlike the prior art tracing systems, the fabrics obtained with the method according to the invention not only attest to the originality of the product but are also able to trace the fabric itself, which is advantageous, for example, for haute couture fashion houses which commission the production lines of certain garments.

[0019] In particular, the tracking dyeing method according to the invention uses a smart piezochromic pigment which preferably also has a photochromic and fluorescent activity and which, when fixed to a textile product, transfers these activities to the textile substrate providing a traceable textile product. The method of dyeing the textile product according to the invention advantageously allows the substrate to be dyed in such a way as to fix the pigment without producing a significant change of colour in the starter product, but making it optically active under UV radiation. The smart pigment applied to the textile substrate is such that it remains imperceptible to mere observation and thus maintains the original colour, quality and coat of the substrate even after the finishing treatments usually carried out on the textile products into which the treated textile substrate has been woven, including dyeing or over-dyeing operations.

[0020] The dyeing method according to the invention is able to increase the compatibility between the textile product and the smart pigment, as it allows the formation of a thermally stable covalent bond between the fabric and the smart pigment. The fibre, yarn, fabric and/or garment obtained with this dyeing method are in fact covalently bound to the marker, that is, to the pigment, show piezochromic activity and, preferably, are also optically active under UV radiation. In this way the fibre, yarn, fabric, treated and/or marked garment is uniquely identified as genuine, that is, by simple observation under conventional UV sources if the pigment is fluorescent. The method according to the invention is advantageously applicable to all categories of protein fibres and does not use aggressive substances such as strong mineral acids.

[0021] In addition, the method according to the invention produces a fabric with excellent properties from the point of view of guaranteeing security and authenticity, thanks to the unique characteristics of the smart pigment. The multi-responsive, and in particular fluorescent, response of the smart pigment is, in fact, a guarantee of the originality of the textile products as well as the originality of the tracking system used.

[0022] The dyeing method according to the invention also makes it possible to preserve the noble characteristics of the natural fibres, such as softness and brilliance, as the dyeing operations are carried out at temperatures not exceeding 60 °C and in less than 2 hours.

[0023] There are no other additives/reagents such as sulphuric acid, acetic acid, equalising agent, formic acid, ammonium acetate, ammonium sulphate and there is a reduced number of operations, which are also fully compatible with current industrial procedures for dyeing skeins and/or spools.

[0024] Moreover, the temperature ramp is fast and fully compatible with the normal operations of adding the yarn to be treated, dispersing the pigment or dye and adding the siloxane bonding agent, all in a time not exceeding 15 - 25 mins. For example, as can be seen from Figure 11, which shows a diagram of the method according to the invention

wherein a wool yarn is used and a siloxane bonding agent Hydrosyl 2926 of between 5 and 10% by weight with respect to the weight of the fibre and a smart pigment of between 0.25 and 2% by weight with respect to the weight of the fibre, the maximum dyeing temperature applied in the method according to the invention represents the minimum temperature used in the traditional methods shown in Figures 1, 2, and 3.

[0025] A further advantage of the dyeing method according to the invention is that it does not discriminate the type of pigment, so the same procedure can be applied for the smart pigments based on lamellar solids type LDH and Zr phosphates.

[0026] For this reason, with respect to the methods currently used to guarantee the authenticity of a product or its traceability, this invention provides an imperceptible yarn, obtained with a multi-responsive pigment, covalently bound to the yarn or textile product by a bland dyeing method and in a single industrial production step, with UV activity and high light fastness.

[0027] Textiles dyed with smart pigments are disclosed in EP-A-2628849, a method for tracking dyeing textiles is disclosed in WO-A-2014/133384 and a method for fixing pigments on textiles with a siloxane is disclosed in GB-A-942586.

Brief description of the drawings

[0028] The invention will be now described, by an illustrative, but not limitative way, according to preferred embodiments thereof, with particular reference to the examples and the enclosed drawings, wherein:

Figure 1 shows a known dyeing process of wool in a strongly acidic bath;
 Figure 2 shows a known dyeing process of wool in a weakly acidic bath;
 Figure 3 shows a known dyeing process of wool in a neutral bath;
 Figure 4 shows a yarn of treated (a) and untreated (b) wool according to example 1, subjected to UV radiation;
 Figure 5 shows a yarn of treated (a) and untreated (b) wool according to example 1, seen with the naked eye;
 Figure 6 shows a white treated (a) and untreated (b) yarn according to example 1, subjected to UV radiation;
 Figure 7 shows the image obtained under the scanning electron microscope (SEM) of the white treated (a) and untreated (b) yarn of Figure 6;
 Figure 8 shows a graph obtained with EDX (Energy Dispersive X-ray Analysis) for the white treated (a) and untreated (b) yarn of Figure 6;
 Figure 9 shows a yarn of treated (a) and untreated (b) wool according to example 2, seen with the naked eye;
 Figure 10 shows a white treated (a) and untreated (b) yarn according to example 2, subjected to UV radiation.
 Figure 11 shows a schematic view of an application example of the tracking dyeing process according to the invention.
 A: immersion of the wool yarn in purified water and addition of the siloxane agent; B: addition of the smart pigment.

Detailed description of the invention and preferred embodiments

[0029] It is a specific object of the invention a tracking dyeing method for the colouring or dyeing of a natural fibre to be marked or identified, comprising the steps of:

- a) preparing a natural fibre in a dye tank;
- b) adding a siloxane agent in said tank; subsequently
- c) dispersing a liquid colouring solution comprising a pigment in said tank;
- d) heating the dye tank comprising the natural fibre, the siloxane agent and the colouring solution at a temperature comprised between 50°C and 70 °C, preferably at 60 °C;
- e) keeping the temperature constant for a time comprised between 1 and 3 hours;

wherein the pigment is a piezochromic pigment, comprising:

- an inorganic matrix having a lamellar conformation,
- an organic filler configured to be intercalated or absorbed between the lamellae of the inorganic matrix.

[0030] The pigment has a first configuration, at a first pressure value P1, wherein the inorganic matrix lamellae are spaced apart and at least one organic filling layer is positioned between two of the lamellae, and a second configuration, at a second pressure value P2, the value of the second pressure P2 being higher than the value of the first pressure P1, wherein the above-mentioned inorganic matrix lamellae are close together allowing a molecular aggregation of said organic filler.

[0031] Advantageously, the molecular aggregation generates a change in pigment coloration such that, in a configuration of use of the pigment applied to the support surface, when compression is applied to a portion of the treated

support surface, the pigment changes from the first to the second configuration, resulting in a change in coloration of the portion of the treated surface that has been subjected to compression with respect to the remaining treated surface not subjected to compression allowing a marking or identification of authenticity of the treated support surface.

[0032] Furthermore, advantageously, said molecular aggregation generates a change in pigment coloration so that, in a second configuration of use of the pigment once activated (piezochromic) and applied on the support surface, when UV irradiation is applied on a portion of the treated support surface, the pigment changes from a first coloration to a second coloration (photochromic), resulting in a change in colour and a fluorescent response of the portion of the treated surface which has undergone UV irradiation with respect to the remaining treated surface that has not undergone irradiation, allowing marking or identification of authenticity of the treated support surface.

[0033] More specifically, the above-mentioned pigments, or smart pigments, consist of said organic filler comprising organic molecules, optionally fluorescent, intercalated and/or adsorbed in said inorganic matrix, or inorganic substrate, the latter consisting of a lamellar solid, preferably of the layered double hydroxide type - LDH. The pigments are characterised by a nano-structuring 2D structure, and can have multi-responsive activity, that is, piezochromic (colour change with pressure), piezophotochromic (colour change with pressure and further colour change after radiation with LED and/or UV light and/or solar radiation), and fluorescent.

[0034] Therefore, the tracking dyeing process according to the invention comprises the immersion of the fibres, yarns, fabrics and/or garments previously wetted in a solution containing the organo-functionalised siloxane agent and, subsequently, the smart tracer pigment, preferably fluorescent, is added to the dyeing bath.

[0035] The method according to the invention confers to the fabric the above-mentioned characteristics thanks to the mode and the stage of application of said siloxane agent, preferably made up of organo-functionalised siloxanes.

[0036] In particular, the siloxane agent, or binder agent, based on previously hydrolysed organo-functionalized siloxanes is used to create a coating to the support, meaning yarn, fibre, fabric or garment, and then the smart pigment without organic coating is added. Therefore, the fibre is firstly made reactive with respect to the smart pigments thanks to the appropriate chemical modification, or functionalization of the support, with the organo-functionalised siloxane agent, inserted at an earlier stage with respect to the smart pigment.

[0037] More specifically, the application of the method according to the invention leads to the formation of covalent bonds between the inorganic matrix of the smart pigment and the functional groups of the fibre or natural textile substrate, such as primary and secondary amine, hydroxyl and carboxylic groups.

[0038] The covalent bond is formed by the reaction between reactive organo-functional siloxane agents (adhesion promoters), the natural fibres, such as wool, silk, linen, cotton, hemp, cashmere and their mixtures and the pigments, in water and under mild thermal conditions.

[0039] The siloxane agent, reactive in an aqueous medium, is in fact preferably activated at a temperature below 60°C. The mild heat treatment promotes the formation of a rapid condensation reaction between the hydroxyl groups (-OH) of the inorganic matrix and the residual functional groups present in the natural fibres (hydroxyl, carboxyl and primary and secondary amines), mediated by the presence of the siloxane agent, which promotes the adhesion. More specifically, the various organic functions (amine, epoxy, alkoxide) contained in the adhesion promoter additive are able to react in the medium, producing by-products such as diols and alcohols, and covalently bind the textile fibres with the pigments used. The dyed product thus obtained is highly resistant to further hydrolysis, bleaching and washing reactions.

[0040] As mentioned above, the textile product dyed by the method according to the invention is characterised by imperceptibility of the tracking element, that is, of the pigment. The term imperceptibility means, on a visual level, the fact of not being able to perceive a substantial difference in colour that may originate in the textile product to be tracked according to the presence, within it, of the treated textile substrates, that is, a difference ΔE not greater than 0.5 when calculated according to the criteria of ISO 105 Part J03 "Calculation of colour differences" on the basis of the CMC formula (2:1).

[0041] According to the method of the invention, in order to obtain a textile product which can be tracked and is at the same time imperceptible, the treated textile substrates, that is, the tracker yarns, are preferably used in a very dispersed manner within the warp or weft yarns making up the textile product to be tracked. More specifically, it is preferable to use a percentage of tracker yarn not exceeding 1%, distributed randomly within an article on the basis of technical calculations, which gives rise to a "warp note" and/or "weaving note" and/or "weave".

[0042] Preferably, according to the invention, the liquid colouring solution can comprise a mixture of purified water and pigment wherein said pigment has a concentration by weight of between 0.85% and 5%. In addition, the liquid colouring solution can comprise a percentage by weight of pigment comprised between 0.1% and 5%, optionally 2%, with respect to the weight of the natural fibre.

[0043] According to a preferred embodiment, the siloxane agent is added in the tank in a percentage by weight of less than or equal to 20%, optionally comprised between 5% and 10%, with respect to the weight of the natural fibre.

[0044] The tracking dyeing method according to the invention may further comprise a step for homogenising a dye bath comprising the fibre and the siloxane agent or may comprise a step for homogenising a dye bath comprising the fibre, the siloxane agent and the colouring solution. More specifically, the homogenising step is preferably carried out

for a time comprised between 10 and 20 minutes.

[0045] During step a) of the dyeing method according to the invention, the natural fibre is placed in water and the ratio between the fibre and the water can be comprised between 1 mg/ml and 20 mg/ml.

[0046] According to a preferred embodiment of the method according to the invention, the pH is kept equal to the isoelectric point of the natural fibre. Even more preferably, the pH is kept in a range of values comprised between 4 and 7.

[0047] In the tracking dyeing method according to the invention, the fibre can be in a configuration wound on a spool, or reel, or skein.

[0048] According to the invention, the inorganic matrix of the piezochromic pigment may include components belonging to the hydrotalcites group. More specifically, components belonging to the hydrotalcites group are preferably layered double hydroxides (LDH), optionally MgAl and ZnAl, or lamellar solids being preferably zirconium phosphates, more preferably alpha zirconium phosphate type B plus zirconium phosphate.

[0049] In addition, according to the invention, the organic filling of the piezochromic pigment may include aggregation-induced emission compounds (AIEs), and/or water-soluble dyes, and/or optical brighteners, and/or fluorescent dyes, and/or azo dyes, and/or liquid crystals, and/or carboxylic acids, and/or anthroquinone dyes, and/or acid dyes. More specifically, the fluorescent dyes preferably comprise Fluorescent Brightener, optionally Fluorescent Brightener 351, or acid fluorescent dyes of group I.

[0050] According to the invention, the siloxane agent can be selected among amine / epoxy / octyl / methoxy / ethoxy functionalised hydrolysed siloxane agents, optionally Dynasylan Hydrosil 1153, Dynasylan Hydrosil 2627, Dynasylan Hydrosil 2926, Dynasylan Hydrosil 2776, Dynasylan Hydrosil 2909.

Examples

Example 1. Tracking dyeing method according to the invention for the application of a smart piezophotochromic pigment with fluorescent properties on wool yarns and characterisation of the yarn obtained.

Obtaining the tracking yarn

[0051] A spool of natural yarn such as wool, silk, cotton, linen and natural fibre blends was placed in the dyeing tank and distilled water was added at a ratio of 10/1 mg of fibre per ml of water.

[0052] The smart pigment named LDH_FB351 which has fluorescent piezophotochromic properties composed of an inorganic lamellar solid type component belonging to the family of layered double hydroxide (LDH) known as hydrotalcite, with the formula $[M2^{+}_{1-x}M3^{+}_x(OH)_2][An^-]_{x/n} \cdot zH_2O$ (3:1 Mg/Al ratio, co-intercalated with counterion nitrate and/or water and/or carbonate molecules - MgAl-LDH CAS 148884-57-5) intercalated with the organic molecule belonging to the family of optical brighteners or fluorescent brighteners named Fluorescent Brightener 351 (CAS 54351-85-8) was dispersed in water (10 mg/ml), considering the pigment at 2% with respect to the fibre weight.

[0053] A siloxane organic binder agent, Dynasylan® Hydrosil 2926 (Evonik), was added to the tank with the yarn (5 times the weight of the pigment), left in circulation for 10 mins. and then the pigment dispersion was added.

[0054] The mixture was heated at 60°C for 2 hours, preferably 1 hour. The bath water was then removed from the skein/spool by discharging the dyeing water and the resulting yarn was rinsed two to three times.

[0055] The treated yarn obtained in this way (Figures 4-5) did not show significant visual and tactile differences with the original yarn, but showed fluorescence when exposed to UV radiation (Figure 4), making its identification unequivocal but imperceptible to the naked eye (Figure 5).

[0056] Table 1 shows the colorimetric characteristics of the pigment used.

Table 1 - Colorimetric characteristics of piezo-photochromic pigment named LDH FB351

Colour - CIELAB coordinate of unpressed pigment	L = 92.77 a' = -13.00 b' = 29.60
Colour - CIELAB coordinate of the pigment pressed @ pressure <50 bar	L = 77.07 a' = -12.70 b' = 29.60 Turns to a yellow-green colour

Characterisation of the yarn treated with the multi-responsive or fluorescent piezophotochromic smart pigment.

[0057] The functionalisation of the textile fibres has been verified by experimental analyses.

[0058] As an example, images of UV radiation (Figure 6) and an SEM image (Figure 7) are shown with an EDX graph (Figure 8) on a white treated yarn and a white untreated yarn.

[0059] More specifically, the white treated yarn appears more expanded to the naked eye, with the fibres further apart, whilst the white untreated yarn appears more compact to the naked eye, with the fibres closer together.

[0060] Evidence of the fluorescent property is clear after UV lamp irradiation. The presence of the pigment, and therefore the fact that it has been functionalised by the method according to the invention, is attested by the SEM EDX analysis, where it is demonstrated that aluminium and magnesium, present in the pigment in question, can only be detected on the treated yarn.

[0061] The colour fastness to light, washing and over-dyeing on the treated wool yarn was verified, obtaining the fluorescent response degradation results shown below, visually evaluated in light boxes, based on the grayscale for degradation ISO 105 A02, using the light source of a Blacklight-Blue BLB-T8 fluorescent tube. The grayscale for degradation assigns values ranging from grade 5: no colour change to grade 1: maximum colour change, also comprising intermediate grades.

Test results

[0062]

ISO 105 B02: 2014 - Colour fastness to artificial light:

Test with xenon arc lamp

Degradation value: 4/5

ISO 105 C06: 2010 - Colour fastness to domestic and commercial washing

Degradation value: 4/5

ISO 105 X07: 1994 - Colour fastness with overdyeing: wool

Degradation value: 4/5

[0063] **Example 2.** *Method of tracking dyeing, according to the invention, natural yarns made of protein fibre - wool, with fluorescent piezochromic smart pigments named LDH_AIE, consisting of the organic molecule 4,4'-(1,2-Diphenylethene-1,2-diyl)dibenzoic acid* (cas n ° 1002339-79-8) *co-intercalated in a precursor hydrotalcite type Aluminium Magnesium Hydroxide Nitrate- LDH_NO3* (cas 148884-57-5).

Obtaining the tracking yarn

[0064] A spool of natural yarn such as wool, silk, cotton, linen and natural fibre blends was placed in the dyeing tank and distilled water was added at a ratio of 10/1 mg of fibre per ml of water.

[0065] The smart pigment named LDH_AIE, consisting of the organic molecule 4,4'-(1,2-Diphenylethene-1,2-diyl)dibenzoic acid co-intercalated in an inorganic component consisting of precursor hydrotalcite type Aluminium Magnesium Hydroxide Nitrate- LDH_NO3 (CAS 148884-57-5) was dispersed in water (10 mg/ml), considering the pigment at 2% with respect to the fibre weight.

[0066] An organosiloxane binder agent, Dynasylan® Hydrosil 2926, was added to the tank with the yarn (5 times the weight of the pigment), left in circulation for 10 mins. and then the pigment dispersion was added.

[0067] The mixture was heated at 60°C for 1 hour. The bath water was then removed from the skein/spool by discharging the dyeing water and the resulting yarn was rinsed two to three times.

Characterisation of yarn and smart pigment

[0068]

Table 2 shows the colorimetric characteristics of the pigment used.

Colorimetric characteristics of the piezochromic pigment named LDH_AIE	
Colour - CIELAB coordinate of unpressed pigment	L = 94.59; a' = -7.0; b' = 9.6.
Colour - CIELAB coordinate of the pigment pressed @ pressure <50 bar	L = 80.61 ; a' = -6.2; b' = 25.5. The colour of the pressed AIE shifts to yellow (coordinate b increases) and the brightness decreases (coordinate L decreases) with respect to the AIE as it is.

[0069] Figures 9 and 10 show the treated and untreated wool yarn, respectively observed with the naked eye and under UV radiation.

Test results

[0070]

ISO 105 B02: 2014 - Colour fastness to artificial light:

Test with xenon arc lamp
Degradation value: 2/3

ISO 105 C06: 2010 - Colour fastness to domestic and commercial washing
Degradation value: 3/4

Example 3. *Example of the tracking dyeing method according to the invention.*

[0071] The method for dyeing yarns by means of smart pigments according to the invention described below is a spool dyeing process compatible with an industrial process (Process A) and comprises the following steps:

1. Inserting the spool into the dyeing tank;
2. Cold rinsing;
3. Pre-setting "cold washing/dyeing cycle". Bath ratio 1:17 (The bath ratio specifies how much water must be present depending on the weight of the yarn). More specifically, a range of between 1:15 - 1:17 indicates narrow baths, while a value of 1:20 may indicate long baths);
4. Checking pH (value approx. 6.8). The best conditions for the dyeing are in the range of 4-12, preferably at pH 4.7;
5. Dispersing the smart pigment in purified water (30g in 3.5 litres of water), using 0.1-5%, preferably 2% by weight of the smart pigment with respect to the weight of the fibre;
6. Adding directly the organo-functionalised siloxane agent to the bath at 10% with respect to the weight of the fibre; preferably between 0.1 and 5% by weight. Leave in circulation for 10 min.
7. Next, dosing the dispersion/solution made previously (point 5) in the tank containing the yarn and the siloxane agent;
8. Homogenising the dye bath for 5-10 minutes;
9. Heating at 60 °C;
10. Leaving in treatment at 60°C for 1 hour;
11. Discharging;
12. Rinsing 3 times.

Example 4. *Example of the tracking dyeing method according to the invention.*

[0072] The method for dyeing yarns by means of smart pigments according to the invention described below is a skein functionalisation and dyeing process compatible with an industrial process (Process B-1) and comprises the following steps:

- (a) placing the yarn in water (1-20 mg/ 1 ml);
 (b) checking the pH of the water of step (a). The best conditions for dyeing are in the range of 4-12, preferably 4-7;
 (c) preparing the dispersion of the smart pigment in water (1-20 mg/ml), with a percentage of smart pigment in the range of 0.1-5% according to the fibre weight;
 5 (d) adding a siloxane agent to the water obtained in step (b) with a siloxane/fibre ratio by weight in the range of 1/4 to 1/10 (that is, between 0.1 and 0.25);
 (e) adding the dispersion of smart pigment in water obtained in step (c) to the water with the yarn and siloxane obtained in step (d);
 10 (f) heating to 60°C for 2 hours whilst shaking the system;
 (g) removing the treated yarn and washing it with water;
 (h) drying the treated yarn at room temperature.

Claims

1. A tracking dyeing method for colouring or dyeing a natural fibre to be marked or identified, comprising the following steps:

- f) preparing a natural fibre in a dye tank;
 g) adding a siloxane agent in said tank; subsequently
 h) dispersing a liquid colouring solution comprising a pigment in said tank;
 i) heating said dye tank comprising said natural fibre, said siloxane agent and said colouring solution at a temperature comprised between 50°C and 70 °C, preferably at 60 °C;
 j) keeping said temperature constant for a time comprised between 1 and 3 hours;
 25 wherein said pigment is a piezochromic pigment, comprising:

- an inorganic matrix having a lamellar conformation,
- an organic filler configured to be intercalated or absorbed between the lamellae of said inorganic matrix,

said pigment having a first configuration, at a first pressure value (P1), wherein said inorganic matrix lamellae are spaced apart and at least one organic filling layer is positioned between two of said lamellae, and a second configuration, at a second pressure value (P2), said second pressure (P2) being higher than said first pressure (P1), wherein said inorganic matrix lamellae are close together allowing a molecular aggregation of said organic filler,

said molecular aggregation generating a change in pigment coloration such that, in a configuration of use of the pigment applied to the support surface, when compression is applied to a portion of the treated support surface, the pigment changes from said first to said second configuration, resulting in a change in coloration of the portion of the treated surface that has been subjected to compression with respect to the remaining treated surface not subjected to compression allowing a marking or identification of authenticity of the treated support surface.

2. The tracking dyeing method according to the previous claim, wherein said liquid colouring solution comprises a mixture of purified water and pigment wherein said pigment has a concentration by weight of between 0.85% and 5%.
3. The tracking dyeing method according to any one of the preceding claims, wherein said liquid colouring solution comprises a percentage by weight of pigment comprised between 0.1% and 5%, optionally 2%, with respect to the weight of the natural fibre.
4. The tracking dyeing method according to any one of the preceding claims, wherein said siloxane agent is added in said tank in a percentage by weight of less than or equal to 20%, optionally comprised between 5% and 10%, with respect to the weight of the natural fibre.
5. The tracking dyeing method according to any one of the preceding claims, further comprising a step for homogenising a dye bath comprising said fibre, said siloxane agent, or a step for homogenising a dye bath comprising said fibre, said siloxane agent and said colouring solution.
6. The tracking dyeing method according to the previous claim, wherein said homogenising step is carried out for a time comprised between 10 and 20 minutes.

7. The tracking dyeing method according to any one of the preceding claims, wherein in said step (a) said natural fibre is placed in water, wherein the ratio between said fibre and said water is comprised between 1 mg/ml and 20 mg/ml.
8. The tracking dyeing method according to any one of the preceding claims, wherein the pH is kept equal to the isoelectric point of the natural fibre.
9. The tracking dyeing method according to any one of the preceding claims, wherein the pH is kept in a range of values comprised between 4 and 7.
10. The tracking dyeing method according to any one of the preceding claims, wherein said fibre is in a configuration wound on a spool, or reel, or skein.
11. The tracking dyeing method according to any one of the preceding claims, wherein said inorganic matrix of said piezochromic pigment comprises components belonging to the hydrotalcites group.
12. The tracking dyeing method according to the previous claim, wherein said components belonging to the hydrotalcites group are layered double hydroxides (LDH), optionally MgAl and ZnAl, or lamellar solids being preferably zirconium phosphates, more preferably zirconium phosphate plus alpha zirconium phosphate type B.
13. The tracking dyeing method according to any one of the preceding claims, wherein said organic filling of said piezochromic pigment comprises aggregation-induced emission compounds (AIEs), and/or water-soluble dyes, and/or optical brighteners, and/or fluorescent dyes, and/or azo dyes, and/or liquid crystals, and/or carboxylic acids, and/or anthroquinone dyes, and/or acid dyes.
14. The tracking dyeing method according to the previous claim, wherein said fluorescent dyes comprise Fluorescent Brightener, optionally Fluorescent Brightener 351, or acid fluorescent dyes of group I.
15. The dyeing method according to claim 13 or 14, wherein said siloxane agent is selected from amine / epoxy / octyl / methoxy / ethoxy functionalised hydrolysed siloxane agents.

Patentansprüche

1. Tracking-Färbeverfahren zum Färben oder Färben einer zu markierenden oder zu identifizierenden Naturfaser, umfassend die folgenden Schritte:
 - f) Vorbereiten einer Naturfaser in einem Färbetank;
 - g) Zugabe eines Siloxanmittels in den Tank; anschließend
 - h) Dispergieren einer flüssigen Färbelösung, die ein Pigment enthält, in dem Tank;
 - i) Erhitzen des Färbetanks, der die Naturfaser, das Siloxan und die Färbelösung enthält, auf eine Temperatur zwischen 50°C und 70°C, vorzugsweise auf 60°C;
 - j) Konstanthalten der Temperatur über einen Zeitraum von 1 bis 3 Stunden;wobei das Pigment ein piezochromes Pigment ist, das Folgendes umfasst:
 - eine anorganische Matrix mit einer lamellaren Konformation,
 - einen organischen Füllstoff, der so konfiguriert ist, dass er zwischen den Lamellen der anorganischen Matrix interkaliert oder absorbiert wird,wobei das Pigment bei einem ersten Druckwert (P1) eine erste Konfiguration aufweist, bei der die Lamellen der anorganischen Matrix voneinander beabstandet sind und mindestens eine organische Füllschicht zwischen zwei der Lamellen angeordnet ist, und bei einem zweiten Druckwert (P2) eine zweite Konfiguration aufweist, wobei der zweite Druck (P2) höher als der erste Druck (P1) ist, wobei die Lamellen der anorganischen Matrix nahe beieinander liegen und eine molekulare Aggregation des organischen Füllstoffs ermöglichen, wobei die molekulare Aggregation eine Änderung der Pigmentfärbung erzeugt, so dass in einer Gebrauchskonfiguration des auf die Trägeroberfläche aufgetragenen Pigments, wenn Druck auf einen Teil der behandelten Trägeroberfläche ausgeübt wird, das Pigment von der ersten in die zweite Konfiguration wechselt, was zu einer Änderung der Färbung des Teils der behandelten Oberfläche, der Druck ausgesetzt war, in Bezug auf die verbleibende behandelte Oberfläche, die keinem Druck ausgesetzt war, führt, was eine Markierung oder Iden-

tifizierung der Echtheit der behandelten Trägeroberfläche ermöglicht.

2. Tracking-Färbeverfahren nach dem vorhergehenden Anspruch, wobei die flüssige Färbelösung eine Mischung aus gereinigtem Wasser und Pigment umfasst, wobei das Pigment eine Gewichtskonzentration zwischen 0,85% und 5% aufweist.
3. Tracking-Färbeverfahren nach einem der vorhergehenden Ansprüche, wobei die flüssige Färbelösung einen Gewichtsprozentatz des Pigments zwischen 0,1% und 5%, gegebenenfalls 2%, bezogen auf das Gewicht der Naturfaser, aufweist.
4. Tracking-Färbeverfahren nach einem der vorhergehenden Ansprüche, wobei das Siloxan in dem Tank in einem Gewichtsprozentanteil von weniger als oder gleich 20%, gegebenenfalls zwischen 5% und 10%, bezogen auf das Gewicht der Naturfaser, zugesetzt wird.
5. Tracking-Färbeverfahren nach einem der vorhergehenden Ansprüche, das ferner einen Schritt zum Homogenisieren eines Färbekades, das die Faser und das Siloxanmittel enthält, oder einen Schritt zum Homogenisieren eines Färbekades, das die Faser, das Siloxanmittel und die Färbelösung enthält, umfasst.
6. Tracking-Färbeverfahren nach dem vorhergehenden Anspruch, wobei der Homogenisierungsschritt während einer Zeit zwischen 10 und 20 Minuten durchgeführt wird.
7. Tracking-Färbeverfahren nach einem der vorhergehenden Ansprüche, wobei in Schritt (a) die Naturfaser in Wasser gegeben wird, wobei das Verhältnis zwischen der Faser und dem Wasser zwischen 1 mg/ml und 20 mg/ml liegt.
8. Tracking-Färbeverfahren nach einem der vorangehenden Ansprüche, wobei der pH-Wert gleich dem isoelektrischen Punkt der Naturfaser gehalten wird.
9. Tracking-Färbeverfahren nach einem der vorhergehenden Ansprüche, bei dem der pH-Wert in einem Wertebereich zwischen 4 und 7 gehalten wird.
10. Tracking-Färbeverfahren nach einem der vorhergehenden Ansprüche, wobei die Faser in einer auf eine Spule, eine Rolle oder einen Strang gewickelten Konfiguration vorliegt.
11. Tracking-Färbeverfahren nach einem der vorhergehenden Ansprüche, wobei die anorganische Matrix des piezochromen Pigments Komponenten umfasst, die zur Gruppe der Hydrotalcite gehören.
12. Tracking-Färbeverfahren nach dem vorhergehenden Anspruch, wobei es sich bei den Komponenten, die zur Gruppe der Hydrotalcite gehören, um geschichtete Doppelhydroxide (LDH), gegebenenfalls MgAl und ZnAl, oder um lamellare Feststoffe handelt, bei denen es sich vorzugsweise um Zirkonphosphate, besonders bevorzugt um Zirkonphosphat, sowie um Alpha-Zirkonphosphat Typ B handelt.
13. Tracking-Färbeverfahren nach einem der vorhergehenden Ansprüche, wobei die organische Füllung des piezochromen Pigments aggregationsinduzierte Emissionsverbindungen (AIE) und/oder wasserlösliche Farbstoffe und/oder optische Aufheller und/oder Fluoreszenzfarbstoffe und/oder Azofarbstoffe und/oder Flüssigkristalle und/oder Carbonsäuren und/oder Anthrochinonfarbstoffe und/oder Säurefarbstoffe umfasst.
14. Tracking-Färbeverfahren nach dem vorhergehenden Anspruch, **dadurch gekennzeichnet, dass** die Fluoreszenzfarbstoffe Fluoreszenzaufheller, gegebenenfalls Fluoreszenzaufheller 351, oder saure Fluoreszenzfarbstoffe der Gruppe I umfassen.
15. Färbeverfahren nach Anspruch 13 oder 14, wobei das Siloxanmittel ausgewählt ist aus amin / epoxy / octyl / methoxy / ethoxyfunktionalisierten hydrolysierten Siloxanmitteln.

Revendications

1. Procédé de teinture de suivi pour la coloration ou la teinture d'une fibre naturelle à marquer ou à identifier, comprenant les étapes suivantes:

f) préparation d'une fibre naturelle dans une cuve de teinture ;
 g) ajout d'un agent siloxanique dans ladite cuve; puis
 h) dispersion d'une solution colorante liquide comprenant un pigment dans ladite cuve;
 i) chauffer ladite cuve de teinture comprenant ladite fibre naturelle, ledit agent siloxanique et ladite solution colorante à une température comprise entre 50°C et 70°C, de préférence à 60°C;
 j) maintenir ladite température constante pendant une durée comprise entre 1 et 3 heures;
 dans lequel ledit pigment est un pigment piézo-chromique, comprenant:

- une matrice inorganique ayant une conformation lamellaire,
- une charge organique configurée pour être intercalée ou absorbée entre les lamelles de ladite matrice inorganique,

ledit pigment présente une première configuration, à une première valeur de pression (P1), dans laquelle lesdites lamelles de la matrice inorganique sont espacées et au moins une couche de charge organique est positionnée entre deux desdites lamelles, et une seconde configuration, à une seconde valeur de pression (P2), ladite seconde pression (P2) étant supérieure à ladite première pression (P1), dans laquelle lesdites lamelles de la matrice inorganique sont proches les unes des autres, ce qui permet une agrégation moléculaire de ladite charge organique,

Cette agrégation moléculaire génère un changement de coloration du pigment de sorte que, dans une configuration d'utilisation du pigment appliqué à la surface de support, lorsqu'une compression est appliquée à une partie de la surface de support traitée, le pigment passe de ladite première à ladite seconde configuration, ce qui entraîne un changement de coloration de la partie de la surface traitée qui a été soumise à une compression par rapport au reste de la surface traitée qui n'a pas été soumise à une compression, ce qui permet de marquer ou d'identifier l'authenticité de la surface de support traitée.

2. Procédé de teinture par traçage selon la revendication précédente, dans lequel ladite solution liquide de coloration comprend un mélange d'eau purifiée et de pigment dans lequel ledit pigment a une concentration en poids comprise entre 0,85% et 5%.
3. Procédé de teinture par traçage selon l'une quelconque des revendications précédentes, dans lequel ladite solution colorante liquide comprend un pourcentage en poids de pigment compris entre 0,1% et 5%, éventuellement 2%, par rapport au poids de la fibre naturelle.
4. Procédé de teinture par traçage selon l'une quelconque des revendications précédentes, dans lequel ledit agent siloxane est ajouté dans ladite cuve dans un pourcentage en poids inférieur ou égal à 20%, éventuellement compris entre 5% et 10%, par rapport au poids de la fibre naturelle.
5. Procédé de teinture par traçage selon l'une quelconque des revendications précédentes, comprenant en outre une étape d'homogénéisation d'un bain de teinture comprenant ladite fibre, ledit agent siloxane, ou une étape d'homogénéisation d'un bain de teinture comprenant ladite fibre, ledit agent siloxane et ladite solution colorante.
6. Procédé de teinture par traçage selon la revendication précédente, dans lequel ladite étape d'homogénéisation est réalisée pendant un temps compris entre 10 et 20 minutes.
7. Procédé de teinture par traçage selon l'une quelconque des revendications précédentes, dans lequel, lors de ladite étape (a), ladite fibre naturelle est placée dans de l'eau, le rapport entre ladite fibre et ladite eau étant compris entre 1 mg/ml et 20 mg/ml.
8. Procédé de teinture par traçage selon l'une quelconque des revendications précédentes, dans lequel le pH est maintenu égal au point isoélectrique de la fibre naturelle.
9. Procédé de teinture par traçage selon l'une quelconque des revendications précédentes, dans lequel le pH est maintenu dans une gamme de valeurs comprises entre 4 et 7.
10. Procédé de teinture par repérage selon l'une quelconque des revendications précédentes, dans lequel ladite fibre est dans une configuration enroulée sur une bobine, ou un dévidoir, ou un écheveau.
11. Procédé de teinture par traçage selon l'une quelconque des revendications précédentes, dans lequel ladite matrice

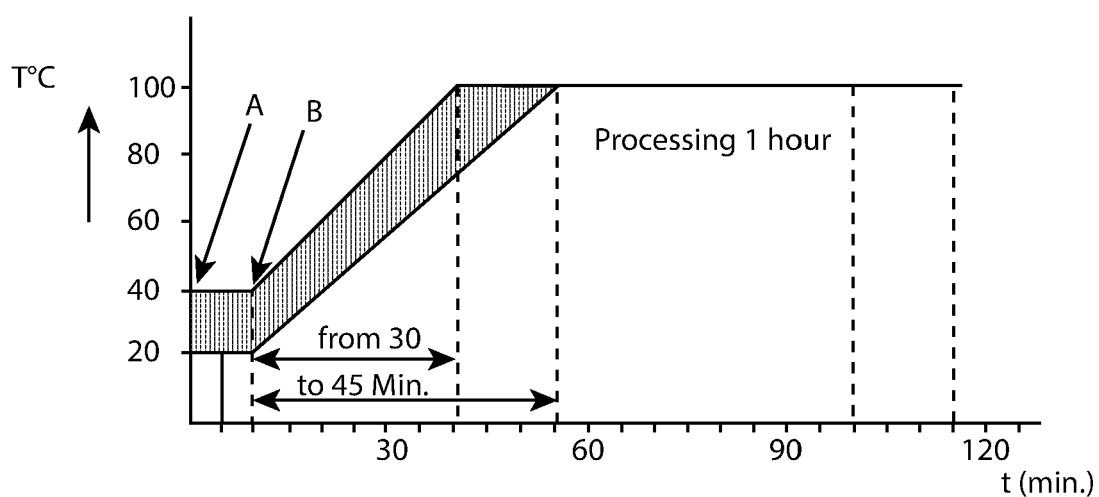
inorganique dudit pigment piézochromique comprend des composants appartenant au groupe des hydrotalcites.

12. Procédé de teinture par traçage selon la revendication précédente, dans lequel lesdits composants appartenant au groupe des hydrotalcites sont des hydroxydes doubles stratifiés (LDH), éventuellement du MgAl et du ZnAl, ou des solides lamellaires étant de préférence des phosphates de zirconium, plus préférentiellement du phosphate de zirconium, plus du phosphate de zirconium alpha de type B.

13. Procédé de teinture par traçage selon l'une quelconque des revendications précédentes, dans lequel ladite charge organique dudit pigment piézochromique comprend des composés d'émission induite par agrégation (AIE), et/ou des colorants hydrosolubles, et/ou des azurants optiques, et/ou des colorants fluorescents, et/ou des colorants azoïques, et/ou des cristaux liquides, et/ou des acides carboxyliques, et/ou des colorants anthroquinoniques, et/ou des colorants acides.

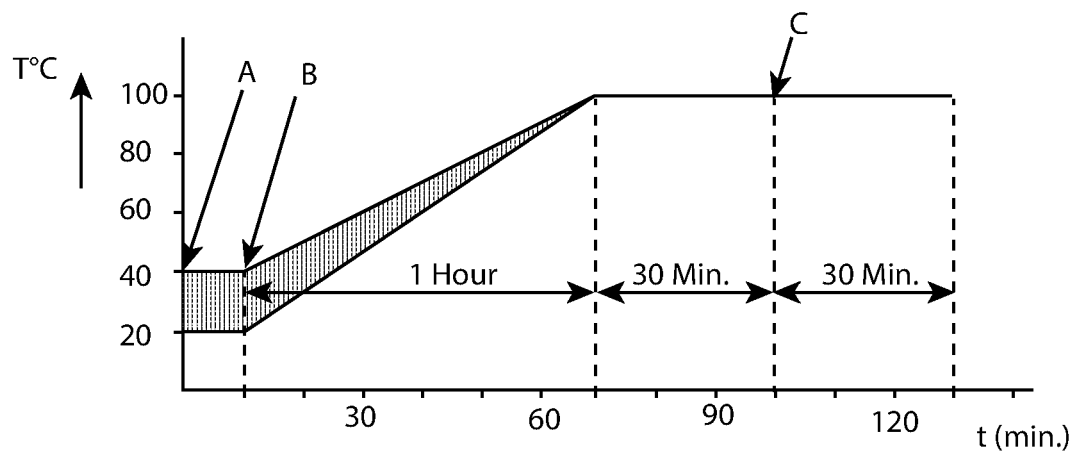
14. Procédé de teinture par traçage selon la revendication précédente, dans lequel lesdits colorants fluorescents comprennent l'azurant fluorescent, éventuellement l'azurant fluorescent 351, ou des colorants fluorescents acides du groupe I.

15. Procédé de teinture selon la revendication 13 ou 14, dans lequel ledit agent siloxanique est choisi parmi les agents siloxaniques hydrolysés fonctionnalisés à l'amine / à l'époxyde / à l'octyle / au méthoxy et / à l'éthoxy.



A: Sodium sulfate 20% s.p.f. Sulfuric acid 66° Bé 4% s.p.f. pH 2-3
 B: Dye X% s.p.f.

Fig. 1



A: Sodium sulfate 10-20% s.p.f.
 Acetic acid 4% s.p.f. (pH 4-5)
 Leveling agent 1% s.p.f.
 B: Dye X% s.p.f.
 C: Sulfuric or formic acid 1-2% s.p.f. or acetic acid 1-2% s.p.f.

Fig. 2

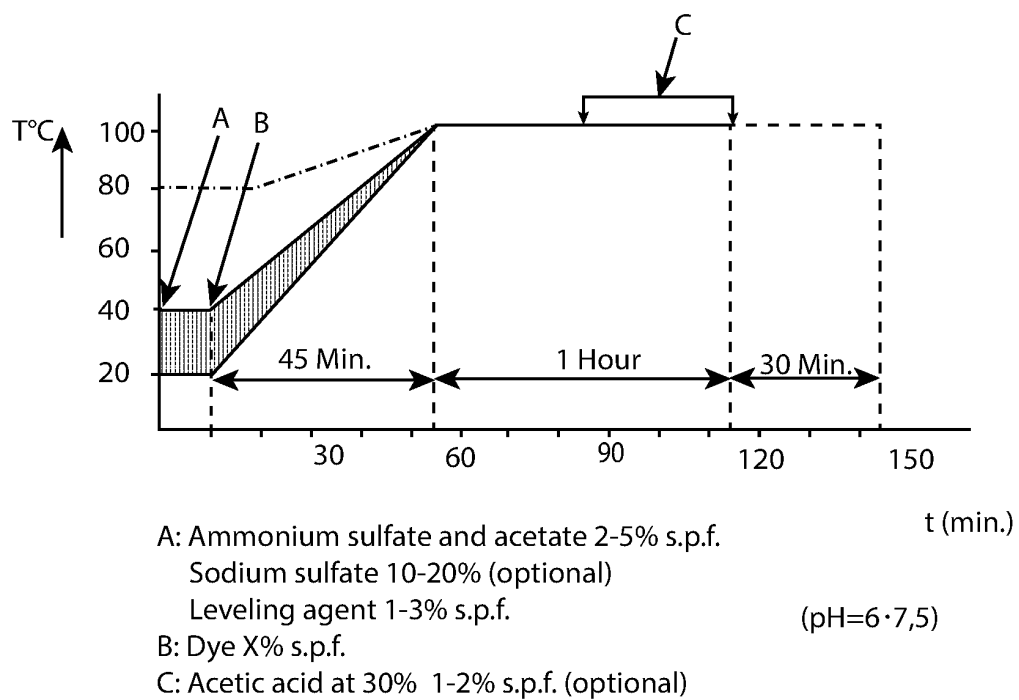


Fig. 3

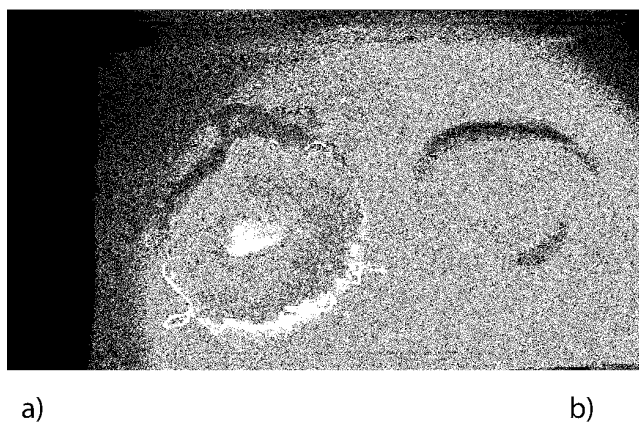


Fig. 4

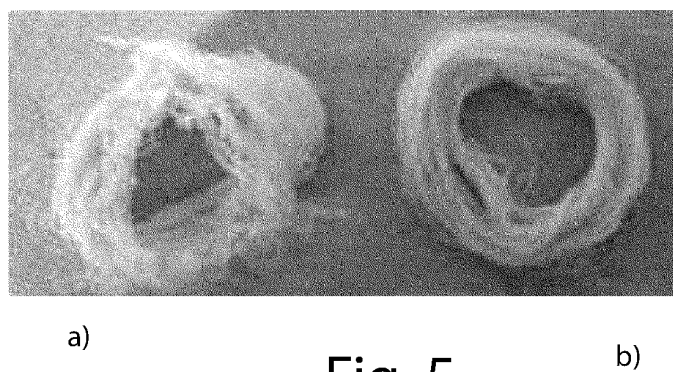


Fig. 5

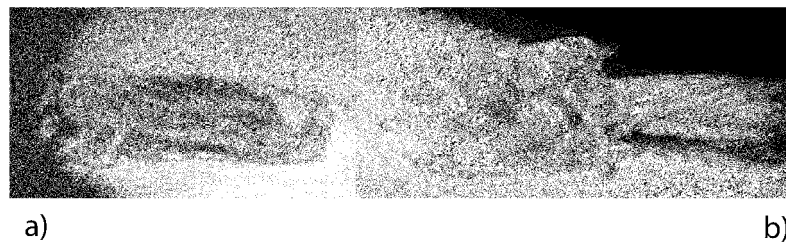


Fig. 6

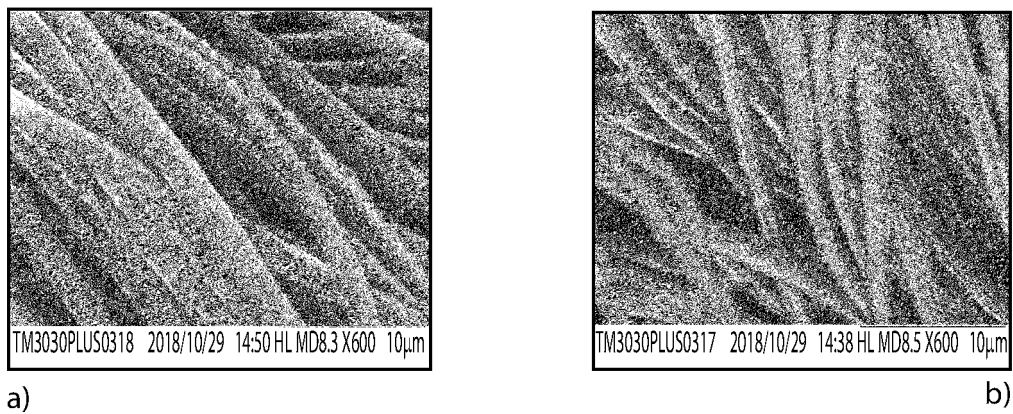


Fig. 7

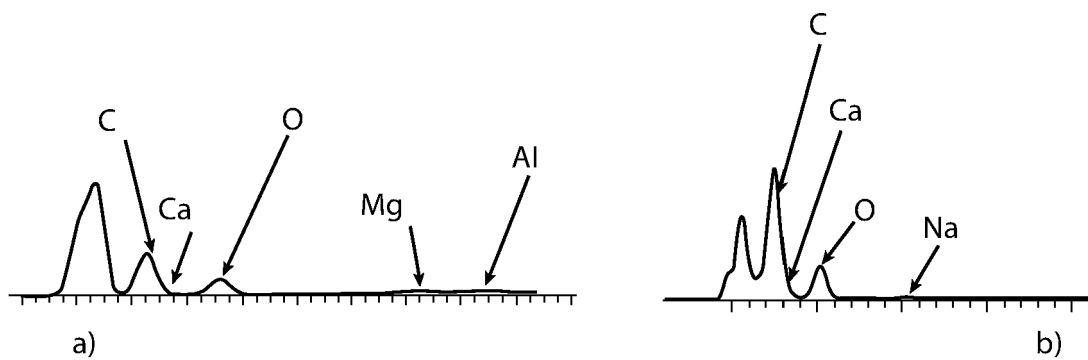


Fig. 8

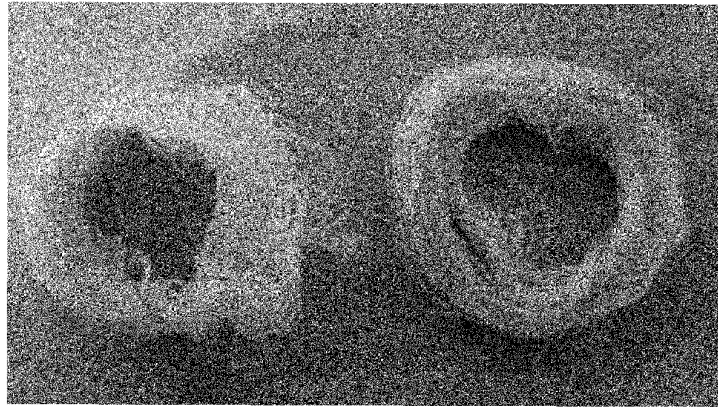


Fig. 9

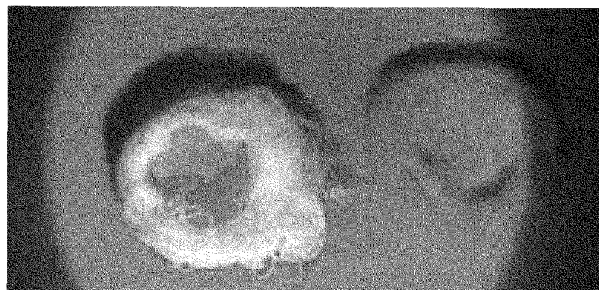


Fig. 10

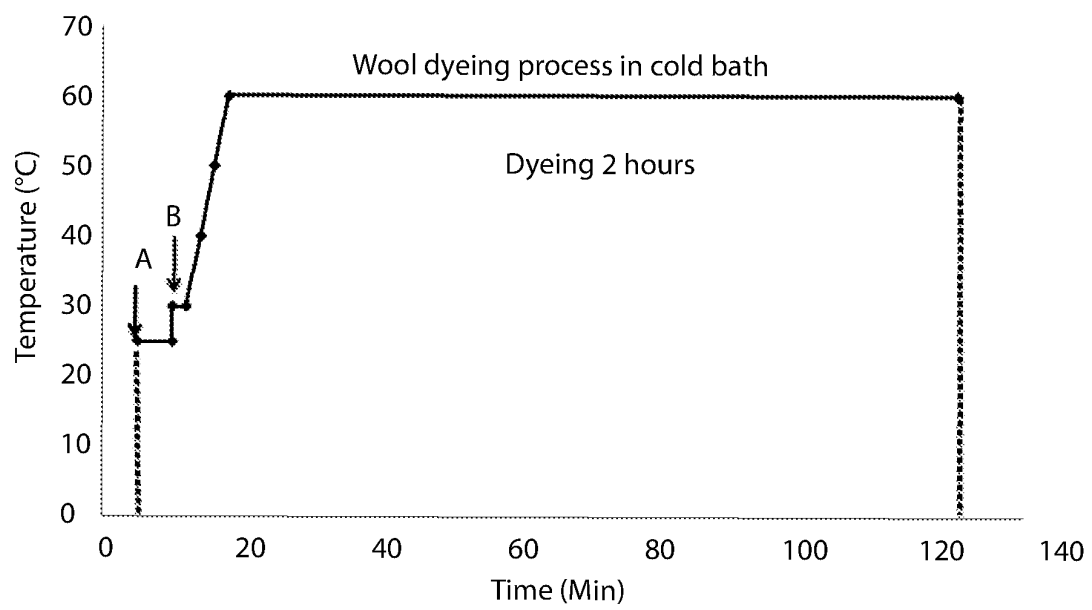


Fig. 11

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 2628849 A [0027]
- WO 2014133384 A [0027]
- GB 942586 A [0027]

Non-patent literature cited in the description

- JOSE CEGARRA ; PUBLICO PUENTE JOSE VAL-DEPERAS. *The dyeing of textile materials- Textilia - Paravia*, 1988 [0002]
- CHEMICAL ABSTRACTS, 148884-57-5 [0052] [0063] [0065]
- CHEMICAL ABSTRACTS, 54351-85-8 [0052]
- CHEMICAL ABSTRACTS, 1002339-79-8 [0063]