

(19)



(11)

EP 3 146 860 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

27.01.2021 Bulletin 2021/04

(51) Int Cl.:

A41D 31/00 ^(2019.01) **D06N 3/00** ^(2006.01)
D06N 3/14 ^(2006.01) **D06P 1/00** ^(2006.01)
C09D 5/22 ^(2006.01) **C09K 11/77** ^(2006.01)

(21) Application number: **15716099.5**

(86) International application number:

PCT/ES2015/070198

(22) Date of filing: **20.03.2015**

(87) International publication number:

WO 2015/177386 (26.11.2015 Gazette 2015/47)

(54) **METHOD FOR MANUFACTURING LONG LASTING PHOSPHORESCENT FABRICS AND
FABRICS OBTAINED THEREOF**

VERFAHREN ZUR HERSTELLUNG LANGLEBIGER PHOSPHORESZIERENDER STOFFE UND IN
DIESEM VERFAHREN HERGESTELLTE STOFFE

PROCÉDÉ DE FABRICATION DE TISSUS PHOSPHORESCENTS DE DURÉE DE VIE ÉLEVÉE ET
TISSUS AINSI OBTENUS

(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**

• **SAIZ VEGA, José María**

E-39005 Santander (Cantabria) (ES)

• **ASPEEL, Bruno**

E-39500 Santander (Cantabria) (ES)

• **GONZÁLEZ, Roberto**

E-39500 Santander (Cantabria) (ES)

• **MARTÍNEZ, Vicente**

E-39500 Santander (Cantabria) (ES)

(30) Priority: **20.05.2014 ES 201430741**

(43) Date of publication of application:

29.03.2017 Bulletin 2017/13

(74) Representative: **Balder IP Law, S.L.**

Paseo de la Castellana 93

5ª planta

28046 Madrid (ES)

(73) Proprietors:

• **Universidad de Cantabria**

39005 Santander, Cantabria (ES)

• **Textil Santanderina S.A.**

39500 Santander (Cantabria) (ES)

(56) References cited:

NL-C2- 1 030 822 NL-C2- 1 030 822

US-A1- 2002 076 534 US-A1- 2004 126 615

(72) Inventors:

• **SANZ CASADO, Juan Marcos**

E-39500 Santander (Cantabria) (ES)

• **ALCARAZ DE LA OSA, Rodrigo**

E-39005 Santander (Cantabria) (ES)

• **MORENO GRACIA, Fernando**

E-39005 Santander (Cantabria) (ES)

• **GONZÁLEZ FERNÁNDEZ, Francisco**

E-39005 Santander (Cantabria) (ES)

• **ZOGU A: "IMPRESSION PIGMENTAIRE LES
EFFETS SPECIAUX", INDUSTRIE TEXTILE, STE
SIPPE SARL, METZ, FR, no. 1319, 1 April 2000
(2000-04-01), pages 45-49, XP000975767, ISSN:
0019-9176**

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).

EP 3 146 860 B1

Description**Field of the invention**

5 [0001] The present invention falls within the sector of phosphorescent fabrics for use in fields such as security, domestic, sports, health, professional, etc., and in particular it is related to a new method for manufacturing long lasting phosphorescent fabrics, and to the fabrics obtained for use in the above fields.

Background of the invention

10 [0002] The current process for manufacturing fabrics with phosphorescent properties for use in various fields is conventionally carried out by producing them with phosphorescent yarn or by adding phosphorescent patches to provide phosphorescence to the fabric. The components are applied in the fabric in the fiber itself (FR 2909096, KR20010016536, WO03002794, WO2006100175), by the application of heat adhesive or sewn photoluminescent patches made from
15 these fibers, or by a coating slurry (CN102154824, KR20120041887) to allow good phosphorescence properties. However, these manufacturing methods have some disadvantages such as loss of good feel of the fabric and adequate flexibility, thus the loss of fabric comfort, and breathability.

[0003] Moreover, with these conventional manufacturing methods the typical times of phosphorescence decay in the fabric are not controlled, and its strength is not proven or is relatively low compared to the strength shown by a fabric to
20 which any other conventional textile dye has been applied (disperse, direct, acid, basic, reactive, vat...). In this sense, the resistance of these fabrics to washing is reduced (in some cases they do not resist the first wash) and phosphorescence typically disappears after a few washes making the fabric unusable for the initial purpose.

[0004] In view of the above there remains a need in the state of the art to provide phosphorescent fabrics with improved properties, in particular, long lasting phosphorescent fabrics, i.e. that maintain the phosphorescent properties for a long
25 time in a controlled manner, and that also maintain the mechanical, comfort and breathability features of the base fabric, and phosphorescence after repeated washes thereby extending the life of the fabric and the article of clothing made with it.

Description of the Figures

30 [0005] **Figure 1:** Depicts the attenuation of the luminance (mcd/m^2) as a function of the elapsed time (minutes) after the cessation of stimulation of a long lasting phosphorescent fabric according to Example 1 of the present invention. The line parallel to the X axis represents the threshold of the human eye adapted to darkness according to the standard UNE23035.

Description of the invention

35 [0006] In a first aspect the invention is related to a method for manufacturing a long lasting phosphorescent fabric with high strength.

[0007] The method of the invention can be implemented with any type of fabric, without there being any limitation in
40 this regard. The fabric may thus be a textile fabric or a nonwoven fabric, made from any "greige" (name used for raw fabrics without any process, such as when they leave the loom) and/or weave, made of any type of natural, artificial or synthetic fiber, or mixtures of fibers, by any conventional process.

[0008] In a particular embodiment the fabric is selected from polyester, cotton and cotton-polyester blend. In a particular
45 embodiment the fabric has previously been chemically bleached and/or mercerized. In a preferred embodiment the fabric has high visibility in accordance with the standard ISO 20471:2013. The high visibility of a fabric requires that it be steadily lit to emit visible light. In this regard, the inventors have surprisingly discovered that the method of the invention carried out on a high visibility fabric, and in particular when visibility is yellow, leads to no decrease in the brightness properties of the starting fabric. Therefore, it is possible to manufacture a high visibility fabric in accordance with the standard ISO 20471:2013, and preferably yellow, and at the same time with long lasting phosphorescence.

50 [0009] The method of the invention comprises the following stages:

- a) Preparing a composition for dyeing comprising a base paste, a fixing agent and 10% to 15% by weight of a pigment with respect to the total weight of base paste, fixing agent and pigment, in powder form which particles of a strontium aluminate pigment doped with europium and dysprosium, are encapsulated by coating them with a
55 translucent material in the visible-UV range,
- b) Coating the starting fabric with said composition by knife or rotary screen coating,
- c) Drying and
- d) Polymerizing by submitting the dried fabric obtained in c) to temperatures between 150 °C and 180 °C.

[0010] The pigment useful for implementing the invention is strontium aluminate doped with europium and dysprosium. The pigment for preparing the composition for dyeing must be in powder form, where the particles have a size between 1 and 100 microns. Preferably the particles have a d50 between 10 and 20 microns or d90 < 30 microns. The particle size is important in that it must be large enough to ensure that it produces phosphorescence and small enough to achieve its firm attachment to the fabric. Prior to its use, the pigment particles are preferably encapsulated to protect them from further contact, for example, with the components of the composition for dyeing or with external agents such as water, detergents, etc. Encapsulation can be done *a priori* by conventional methods, using starting compounds capable of generating a coating on the particles and that are transparent or translucent in the visible-UV, such as SiO₂, TiO₂, ZrO₂, Al₂O₃, among others, and mixtures thereof. The encapsulation leads to a fine coating of the particle which increases the particle size and decreases pigment phosphorescence. The inventors have observed that although the coating attenuates the passage of radiation there through, it is compensated by improved fixation of the pigment to the fabric. In a particular embodiment the coating of the particle is SiO₂. This may be obtained, for example, conventionally by contacting the particles with ethyl orthosilicate, in an alcoholic acidic solution, and then drying the resulting mixture.

[0011] The composition for dyeing comprises in addition to the pigment, a base paste and a fixing agent.

[0012] The composition for dyeing comprises between 10% and 15% by weight of a pigment with respect to the total weight of base paste, fixative and pigment.

[0013] The base paste in a particular embodiment comprises an aqueous suspension of polyurethane (PU). In a particular embodiment the fixing agent is a composition based on melamine-formaldehyde resin.

[0014] The composition for dyeing also comprises a thickener comprising polyacrylic acid in an amount between 1 g and 99 g per kg of base paste, fixing agent and pigment. The inventors of the present invention have observed that the presence of thickener gives the composition for dyeing a viscosity between 3 Pa·sec and 8 Pa·sec measured at 20 °C which is very suitable to make the fabrics provided by the present invention have a resistance to washing of at least 30 washes and attenuation times at or above 120 minutes. The pH value is also controlled to keep it above about 5.5 which is also important to achieve the desired results. Likewise, the base paste is inert to the pigment such that it does not alter it and enables the pigment particles to adhere to the fabric.

[0015] The coating of the fabric is carried out by printing techniques, by knife or rotary screen coating using a conventional apparatus for this purpose. In a preferred embodiment it is carried out by knife-on-air coating. Then, it is proceeded to the drying of the composition for dyeing at temperatures comprised between 120 °C and 150 °C. The drying time is variable; typically of between 20 sec and 120 sec but it depends on other parameters of the process: such as the composition for dyeing, the type of fabric, etc. Then the polymerization takes place, where the previously dried fabric is subjected to temperatures of between 150 °C and 180 °C. The polymerization time is also variable; typically from 30 sec to 180 sec. In a particular embodiment the drying and the polymerization occur simultaneously. In a particular embodiment the polymerization is performed by applying consecutive thermal cycles at temperatures between 150 °C and 180 °C. Generally, each of the cycles has a duration between 5 sec and 30 sec. In a particular embodiment the drying and polymerizing are carried out in 6 cycles at successive temperatures of 120 °C, 140 °C, 170 °C, 170 °C, 170 °C and 170 °C.

[0016] The resulting fabric has a pigment density, that is, an amount of pigment per fabric surface unit, that is variable depending on the amount of thickener used, the height of the blade, the inclination of the blade, the starting fabric, the conditions of the method, etc. In a particular embodiment the amount is comprised between 0.1 g/m² and 1000 g/m², preferably between 1 and 100 g/m², and more preferably between 1 and 40 g/m². In a particular embodiment for a pigment concentration of 15% by weight with respect to the total weight of base paste, fixing agent and pigment, the resulting density of pigment is 30 g/m².

[0017] The method of the invention may also comprise one or more additional stages of finishing treatment. These stages are generally referred to any conventional process of finishing treatment to which the fabrics are usually subjected. Examples of said finishing treatments are knife coating with acrylates to provide strength and rigidity to the fabric; treatment with a softener applied by padding bath to confer the fabric a soft, elastic, and hydrophilizing touch, for example, by applying a quaternized silicone polymer nanoemulsion modified with nonionic emulsifiers; Teflon-type waterproofing treatment with polytetrafluoroethylene (PTFE); anti-stain treatment; antacid treatment; the application of permanent press finishing by padding bath; sanforizing, a treatment comprising washing and pressing to prevent the fabric from shrinking subsequently or calendering, applying temperatures and pressures, for example in cold temperature at 30 kg.

[0018] In another aspect the invention relates to the long lasting phosphorescent fabric obtained by the method of the invention.

[0019] The fabric has many advantages, notable here being the long lasting phosphorescence which in the context of the present invention refers to the fact that the attenuation time after the fabric is subjected to the action of a light source in the UV range is equal to or greater than 120 minutes, preferably equal to or greater than 130 min, more preferably equal to or greater than 140 min and even more preferably equal to or greater than 150 min. Attenuation time means the time during which the fabric, due to the light emission of its excited particles, is visible to the human eye adapted to the darkness after the cessation of the light stimulus impinging on the fabric. The long lasting phosphorescence

can therefore occur in the fabric when desired, within said period of attenuation, once the fabric has been stimulated with UV light.

[0020] In a preferred embodiment the fabric of the invention is a high visibility and long lasting phosphorescence fabric. The inventors have found in this sense that the properties of high visibility in accordance with the standard ISO 20471:2013 remain in the resulting fabric; also, the starting color is not modified after subjecting the fabric to the method of the invention, and the long lasting phosphorescence property is further achieved. Therefore, the resulting fabric has the ability to emit light when it is subjected to constant light stimulus, that is, at times of very short duration, and the ability to emit long lasting phosphorescence in the absence of light stimulus.

[0021] A further advantage of the fabric of the invention is that it can be subjected to various finishing treatments, for modifying or adding certain properties to the fabric, and it does not lose its long lasting phosphorescence properties.

[0022] Additionally, the starting fabrics keep their mechanical properties of good hand, flexibility, comfort and breathability and keep their thermal features after implementing the method of the invention. Regarding the strength to light of the starting fabric, it is even possible to expect an improvement since the pigments which are incorporated absorb the UV radiation, preventing at least part of said radiation to deteriorate the fabric.

[0023] As for the strength against washes, attenuation times equal to or greater than 120 min are achieved after 30 washes, following the protocol described below. These times are obtained after at least 30 washes of the article of clothing, following the protocol that is described below; typically these are equal or greater, the smaller the number of washes.

[0024] Finally, the possibility of applying phosphorescent properties to a fabric by the process object of the invention has additional economic advantages, since the same base fabric can be used as in any other dyeing process.

[0025] The fabric of the invention finds application in various fields such as security, domestic, sports, health, or others. It can therefore be used for the manufacture of any type of article without limitation. In particular, it is used to make articles of clothing for use in these areas, for example, so in another aspect the present invention provides an article of clothing comprising a fabric according to the present invention. Examples of said articles of clothing are jackets, overalls, aprons, gowns, sportswear, etc., and they have the same mechanical and thermal properties mentioned above for the fabric.

Examples

Example 1: Method for manufacturing a cotton fabric with long lasting phosphorescence

[0026] It was carried out with a chemically bleached and mercerized cotton fabric (standard treatment of the cotton fibers with sodium hydroxide to alter the chemical structure of the fiber, converting the initial cellulose-alpha in a polymorphic structure of cellulose-beta, increasing the total surface of the fiber and its reflectance, providing it with more shine and a softer feel). The composition for dyeing was prepared using as base paste 87% of a polyurethane based aqueous suspension (Tubicoat FBWW, CHT Bezema); 3% of a melamine-formaldehyde resin as fixing agent (Tubicoat Fixierer HT, CHT Bezema); and 10% of strontium aluminate doped with europium and dysprosium, coated with a SiO₂ protective layer (grain sizes 1-100 µm - in the present example d₉₅ < 30 µm) (MHG-6EW, ZHEJIANG MINHUI LUMINOUS TECHNOLOGY CO., LTD). The composition for dyeing also comprised 12 g per kg of the total of the above components, of a polyacrylic acid based thickener (aqueous solution of ammonium acrylate dispersed in isoparaffin with surfactants, petroleum distillates - hydrotreated light fraction - 10-25%, anhydrous ammonia <0.5%, residual monomers MAK<1%), (Tubicoat Verdicker LP, CHT Bezema). The composition for dyeing for the application had an approximate viscosity of 6 Pas (relative humidity between 70% and 80% and room temperature 20 °C; Viscometer HAAKE VT-02).

[0027] The composition was applied by means of knife-on-air coating and then the fabric was subjected to drying and polymerizing in a RAME machine (machine used in the finishing of the fabrics, to widen them and correct the distortions of the weave). For this purpose, the following thermal cycle was applied: 12 sec at 130 °C, 12 sec at 155 °C, 12 sec at 170 °C, 12 sec at 170 °C, and 12 sec at 170 °C.

[0028] Then the long lasting phosphorescence characteristics of the fabric obtained were determined, and are shown in Figure 1.

[0029] In order to determine the strength of the fabric of the invention against washes the following experimental protocol was followed (based on the standards DIN 67510, UNE 23035 and ISO 16069, designed for emergency signs with no direct equivalent in the textile industry):

- Lighting: Xenon arc lamp 150 W.
- Sample position: at such a distance that the illuminance at the center of the sample and at four points equidistant from the center of the same (3 cm) is 1000 + 30 lux.
- Lighting time: 5 min.
- Luminance measurements L (mcd/m²) every minute after the cessation of the illumination, for a total of 30 min.

- Used detector 'LMT B520 L' with the measuring head of 5 cm diameter in contact with the sample.
- Calculation of the attenuation time: a quadratic regression is performed between minute 10 and minute 30 according to the following equation (luminance in mcd/m² and time in minutes):

$$\text{Log}(L) = a \cdot \log(t)^2 + b \cdot \log(t) + c$$

where t is the time elapsed since the cessation of the illumination. After obtaining the values of a , b and c the value of the attenuation time is obtained, t_{atten} , by extrapolating the equation obtained to the luminance threshold value for the human eye adapted to darkness ($L_{\text{threshold}} = 0.3 \text{ mcd/m}^2$).

[0030] The washes were performed according to the program 6A in accordance with the standard UNE-EN ISO 6330:2012: 15 minutes wash at 40 °C without detergent and with a load of more than 3 kg, followed by three rinses with a duration of 3 minutes, 2 minutes and 2 minutes, and air drying.

[0031] The Table 1 below shows the results of a test of the attenuation time and the luminance 10 minutes after cessation of stimulation of a fabric according to the invention (example of embodiment 1) after a number of washes of zero and one:

	Number of washes	
	0	1
Attenuation time with the fabric of the invention (real time)	138 min	132 min
Luminances (10 min after cessation of stimulation) with the fabric of the invention	Number of washes	
	0	1
	5.5 mcd/m ²	5.5 mcd/m ²

[0032] Additionally, the strength against washes is demonstrated by the tests shown in the following table, in which the luminances and times to reach the luminance value of 0.3 mcd/m² have been measured in accordance with the standard UNE23035 and the like - DIN 67510 or ISO 16069 - (threshold value of the human eye adapted to darkness; the attenuation time in this case is real following the cessation of the stimulation - 5 min Xe lamp, 1000 Lux - that is, the one measured without estimation until the luminance of the sample reaches the threshold value). Table 2 below shows the results:

Results	Number of washes			
	0	1	10	30
Long Lasting Photoluminescent Fabric of the invention	$t_{\text{atten}} = 138 \text{ min}$	$t_{\text{atten}} = 132 \text{ min}$	$t_{\text{atten}} = 129 \text{ min}$	$t_{\text{atten}} = 125 \text{ min}$
	$L(10 \text{ min}) = 5.5 \text{ mcd/m}^2$	$L(10 \text{ min}) = 5.5 \text{ mcd/m}^2$	$L(10 \text{ min}) = 5.2 \text{ mcd/m}^2$	$L(10 \text{ min}) = 4.7 \text{ mcd/m}^2$

[0033] The invention is not limited to the specific embodiments that have been described but it also covers, for example, the variants that can be performed by the person having ordinary skill in the art within what can be derived from the claims.

[0034] The invention is not limited to the specific embodiments that have been described but it also covers, for example, the variants that can be performed by the person having ordinary skill in the art within what can be derived from the claims.

Claims

1. Method for obtaining a long lasting phosphorescent fabric comprising the following stages:

- Preparing a composition for dyeing comprising a base paste, a fixing agent and 10% to 15% by weight of a pigment with respect to the total weight of base paste, fixing agent and pigment, in powder form which particles of a strontium aluminate pigment doped with europium and dysprosium, are encapsulated by coating them with a translucent material in the visible-UV range,
- Coating the starting fabric with said composition by knife or rotary screen coating,

c) Drying and

d) Polymerizing by submitting the dried fabric obtained in c) to temperatures between 150 °C and 180 °C.

2. Method according to claim 1, wherein the pigment particles have a size comprised between 1 and 100 microns.
3. Method according to claim 1 or 2, wherein the particles have a d50 of between 10 and 20 microns and a d90 < 30 microns.
4. Method according to claim 3, where the translucent or transparent material is SiO₂.
5. Method according to claim 1 wherein the composition for dyeing also comprises a thickener comprising polyacrylic acid in an amount comprised between 1 g and 99 g per kg of base paste, fixing agent and pigment.
6. Method according to any one of the previous claims wherein the drying of the composition is carried out at temperatures comprised between 120 °C and 150 °C.
7. - Method according to any one of the previous claims wherein step d) is performed by applying consecutive thermal cycles, at temperatures between 150 °C and 180 °C.
8. Method according to any one of claims 6 or wherein steps c) and d) are carried out in 6 cycles at successive temperatures of 120 °C, 140 °C, 170 °C, 170 °C, 170 °C and 170 °C.
9. Method according to any one of the previous claims also comprising one or more stages of finishing treatment wherein the finishing treatment is a by knife-on-air coating with acrylates; treatment with softener applied by padding bath; a waterproofing treatment; an anti-stain treatment; an antacid treatment; the application of permanent press finishing by padding bath; sanforizing; or calendering.
10. Method according to any one of the previous claims wherein the fabric is selected from cotton, polyester and cotton-polyester blend.
11. Method according to any one of the previous claims wherein the fabric is high visibility fabric in accordance with the standard ISO 20471:2013
12. Long lasting phosphorescent fabric obtained by the method according to any one of the previous claims.
13. Fabric according to claim 12, which has a pigment density of 30 g/m² at a pigment concentration of 15% by weight with respect to the total weight of base paste, fixing agent and pigment.
14. of clothing comprising the fabric according to any one of claims 12 to 13 .

Patentansprüche

1. Verfahren zum Erhalten eines langlebigen phosphoreszierenden Stoffes, umfassend die folgenden Schritte:
 - a) Herstellen einer Zusammensetzung zum Färben, umfassend eine Basispaste, ein Fixiermittel und 10 Gew.-% bis 15 Gew.-% eines Pigments, in Bezug auf das Gesamtgewicht von Basispaste, Fixiermittel und Pigment, in Pulverform, wobei die Partikel eines mit Europium und Dysprosium dotierten Strontiumaluminat-Pigments durch Beschichten dieser mit einem im sichtbaren Bereich und im UV-Bereich lichtdurchlässigen Material eingekapselt sind,
 - b) Beschichten des Ausgangsstoffes mit der Zusammensetzung durch Messer- oder Rotationssiebbeschichtung,
 - c) Trocknen und
 - d) Polymerisieren, indem der in c) erhaltene getrocknete Stoff Temperaturen zwischen 150 °C und 180 °C ausgesetzt wird.
2. Verfahren nach Anspruch 1, wobei die Pigmentpartikel eine zwischen 1 und 100 µm umfasste Größe aufweisen.

3. Verfahren nach Anspruch 1 oder 2, wobei die Partikel einen d_{50} von zwischen 10 und 20 μm und einen $d_{90} < 30 \mu\text{m}$ aufweisen.
4. Verfahren nach Anspruch 3, wobei das lichtdurchlässige oder transparente Material SiO_2 ist.
5. Verfahren nach Anspruch 1, wobei die Zusammensetzung zum Färben außerdem ein Polyacrylsäure umfassendes Verdickungsmittel in einer zwischen 1 g und 99 g pro kg Basispaste, Fixiermittel und Pigment umfassten Menge, umfasst.
6. Verfahren nach einem der vorangehenden Ansprüche, wobei das Trocknen der Zusammensetzung bei zwischen 120 °C und 150 °C umfassten Temperaturen durchgeführt wird.
7. Verfahren nach einem der vorangehenden Ansprüche, wobei Schritt d) durch Anwenden von aufeinanderfolgenden thermischen Zyklen, bei Temperaturen zwischen 150 °C und 180 °C, durchgeführt wird.
8. Verfahren nach einem der Ansprüche 6 oder 7, wobei die Schritte c) und d) in 6 Zyklen bei aufeinanderfolgenden Temperaturen von 120 °C, 140 °C, 170 °C, 170 °C, 170 °C und 170 °C durchgeführt werden.
9. Verfahren nach einem der vorangehenden Ansprüche, außerdem umfassend einen oder mehrere Schritte einer Veredelungsbehandlung, wobei die Veredelungsbehandlung eine durch Lufrakelbeschichtung mit Acrylaten; eine Behandlung mit einem mittels Klotzflotte aufgetragenen Weichmacher; eine Imprägnierungsbehandlung; eine Antifleckenbehandlung; eine säurebindende Behandlung; die Aufbringung einer Permanent-Press-Ausrüstung mittels Klotzflotte; Sanforisieren; oder Kalandrieren ist.
10. Verfahren nach einem der vorangehenden Ansprüche, wobei der Stoff ausgewählt ist aus Baumwolle, Polyester und Baumwolle-Polyester-Mischung.
11. Verfahren nach einem der vorangehenden Ansprüche, wobei der Stoff ein Stoff mit hoher Sichtbarkeit gemäß der Norm ISO 20471:2013 ist.
12. Langlebiger phosphoreszierender Stoff, erhalten durch das Verfahren nach einem der vorangehenden Ansprüche.
13. Stoff nach Anspruch 12, der eine Pigmentdichte von 30 g/m^2 bei einer Pigmentkonzentration von 15 Gew.-%, in Bezug auf das Gesamtgewicht von Basispaste, Fixiermittel und Pigment, aufweist.
14. Artikel oder Kleidung, umfassend den Stoff nach einem der Ansprüche 12 bis 13.

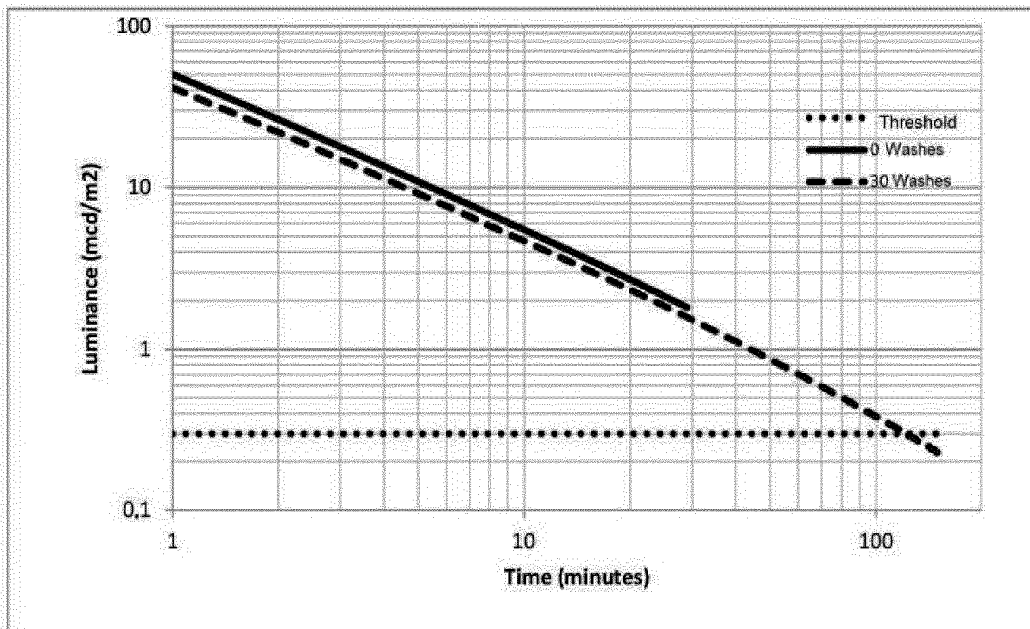
Revendications

1. Procédé d'obtention d'un tissu phosphorescent de durée de vie élevée comprenant les étapes consistant à :
 - a) préparer une composition pour teinture comprenant une pâte de base, un agent fixateur et 10 à 15 % en poids d'un pigment, par rapport au poids total de la pâte de base, de l'agent fixateur et du pigment, sous forme de poudre dont les particules d'un pigment d'aluminate de strontium enrichi en europium et en dysprosium sont encapsulées en les enrobant d'un matériau translucide dans la gamme visible-UV,
 - b) enduire le tissu de départ avec la composition par enduction à la racle ou enduction au cadre rotatif,
 - c) sécher et
 - d) polymériser en soumettant le tissu séché obtenu en c) à des températures comprises entre 150 °C et 180 °C.
2. Procédé selon la revendication 1, dans lequel les particules de pigment ont une taille comprise entre 1 et 100 microns.
3. Procédé selon la revendication 1 ou 2, dans lequel les particules ont un d_{50} compris entre 10 et 20 microns et un $d_{90} < 30$ microns.
4. Procédé selon la revendication 3, dans lequel le matériau translucide ou transparent est du SiO_2 .
5. Procédé selon la revendication 1, dans lequel la composition pour teinture comprend également un épaississant

EP 3 146 860 B1

comprenant de l'acide polyacrylique en une quantité comprise entre 1 g et 99 g par kg de pâte de base, d'agent de fixation et de pigment.

- 5 6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le séchage de la composition est effectué à des températures comprises entre 120 °C et 150 °C.
7. Procédé selon l'une quelconque des revendications précédentes dans lequel l'étape d) est réalisée en appliquant des cycles thermiques consécutifs, à des températures comprises entre 150 °C et 180 °C.
- 10 8. Procédé selon l'une quelconque des revendications 6 ou 7, dans lequel les étapes c) et d) sont effectuées en 6 cycles à des températures successives de 120 °C, 140 °C, 170 °C, 170 °C, 170 °C et 170 °C.
- 15 9. Procédé selon l'une quelconque des revendications précédentes, comprenant également une ou plusieurs étapes de traitement de finition, dans lequel le traitement de finition est une enduction d'acrylates au couteau d'air ; un traitement avec un adoucissant appliqué par bain de foulardage ; un traitement d'imperméabilisation ; un traitement antitache ; un traitement antiacide ; l'application d'un apprêt d'infroissabilité par bain de foulardage ; un sanforisage ; ou un calandrage.
- 20 10. Procédé selon l'une quelconque des revendications précédentes dans lequel le tissu est choisi parmi le coton, le polyester et le mélange coton-polyester.
11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le tissu est un tissu à haute visibilité conformément à la norme ISO 20471:2013.
- 25 12. Tissu phosphorescent à durée de vie élevée obtenu par le procédé selon l'une quelconque des revendications précédentes.
13. Tissu selon la revendication 12, qui a une densité de pigment de 30 g/m² à une concentration de pigment de 15 % en poids par rapport au poids total de la pâte de base, de l'agent fixateur et du pigment.
- 30 14. Article d'habillement comprenant le tissu selon l'une quelconque des revendications 12 à 13.



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

- FR 2909096 [0002]
- KR 20010016536 [0002]
- WO 03002794 A [0002]
- WO 2006100175 A [0002]
- CN 102154824 [0002]
- KR 20120041887 [0002]