(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
04 November 2021 (04.11.2021)

WIPO | PCT

(10) **International Publication Number**
WO 2021/220310 A1

(51) **International Patent Classification:**
C09C 1/40 (2006.01) *C09K 9/00* (2006.01)
C09C 1/42 (2006.01)

(21) **International Application Number:**
PCT/IT2020/000036

(22) **International Filing Date:**
30 April 2020 (30.04.2020)

(25) **Filing Language:** Italian

(26) **Publication Language:** English

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) Title: PIGMENT FOR DYEING FIBRES, YARNS, FABRICS AND GARMENTS

(57) **Abstract:** The present invention concerns a multi-responsive piezochromic pigment for colouring or dyeing a textile support surface to be marked or identified, 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 layers are close together allowing a molecular aggregation of said organic filler, said molecular aggregation generating a change in the pigment coloration such that, in a configuration of use of the pigment applied on the support surface, when a compression is applied on 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 treated surface that has undergone compression with respect to the rest of the treated surface that has not undergone compression, allowing a marking or identification of the authenticity of the treated support surface, said molecular aggregation generating a change in pigment coloration such 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.

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PIGMENT FOR DYEING FIBRES, YARNS, FABRICS AND GARMENTS

Technical field

This invention relates to a pigment with optical activities for the dyeing of fibres, yarns, fabrics and garments. More specifically, the invention relates to a pigment comprising an organic component intercalated or adsorbed into an inorganic component, having piezochromic and, optionally, piezophotochromic and/or fluorescent activity.

Background art

As is well known, it is currently increasingly necessary to distinguish and identify fibres and/or yarns and/or fabrics and/or garments, also hereinafter meaning textile accessories for clothing. This in order to guarantee their originality and preserve the technique which allowed their production, as well as the quality parameters which characterise them and, finally, to combat the growing criminality linked to their counterfeiting.

There are currently pigments which change colour with temperature, light and pressure which are used for the imperceptible marking (to the naked eye) of different surfaces. Depending on what they react with, that is, the procedure or instrument which reads and reveals them, these pigments are divided into: ultraviolet, infrared, photo-chromatic, luminescent, fluorescent, OVI ("Optical Variable Ink"). These pigments highlight a variation in colour determined by the different angles at which they are observed. They are applied to the surface of the product or inserted directly into an element of the product, such as the labels. They are detected exclusively with the use of microscopes and other precision equipment. They can be supported by yarns, fabrics and garments (woven labels, security ties). As far as labels are concerned, their generation process is on average complicated as it requires specialized embroidery or weaving machines.

A disadvantage of the pigments used in the prior art is their poor resistance to washing and the rapid structural degradation after exposure to light.

Disclosure of the invention

The technical problem raised and resolved by the invention is to provide a pigment for the dyeing of fibres, yarns or fabrics to mark and/or identify said fibres, yarns or fabrics, which allows the above mentioned disadvantages of the prior art to be overcome.

This problem is overcome by a pigment according to claim 1.

Preferred features of the invention are present in the dependent claims.

The invention aims to provide a pigment, referred to below also as a smart pigment, with particular optical properties and consisting of an inorganic and organic component. The inorganic component is a lamellar solid commonly defined as a nano-filler or nanostructured material because the individual layers have thicknesses in the nanometre range and lengths which can easily reach a micron [AIM 2008 Pacini Editori's Polymeric Materials Technology Dictionary].

The pigment according to the invention therefore includes a nano-filler or hybrid nano-material, with piezochromic, piezophotochromic and optionally fluorescent activity, capable of being used as a tracer to uniquely mark and/or identify fibres, yarns, fabrics, and garments, also meaning textile accessories for clothing, for example in order to certify their originality. The invention therefore aims to add value to textile fabrics and accessories for clothing by means of a smart pigment suitably fixed to the textile product and capable of providing an optical response not originally present on the support. In this way the support is uniquely marked, thus attesting to its originality.

The main aim of the invention is therefore to guarantee the authentication of the textile accessories for clothing so as to limit the phenomenon of counterfeiting and to protect the textile trademarks by the use of the object of the patent. The textile products so marked at the various stages of processing will be compatible with any subsequent processing of the textile process.

The hybrid pigments according to the invention advantageously possess a mechanochromic response (Mechanochromism). More specifically, the mechanochromic response is given by the alteration of the optical response following a compression-type pressure stimulus. This behaviour is defined as piezochromism [Chromogenic Materials - Ullmann's Encyclopedia of Industrial Chemistry]. The energy derived from mechanical force can trigger chemical reactions which can also lead to the formation or breaking of covalent bonds, or it can induce variations in the geometry of molecules, such as, for example, conformational changes.

These variations are intramolecular, but when they occur on a large scale the molecules begin to interact with each other and the non-covalent forces lead to molecular aggregations, resulting in an alteration of the emission properties [Chromogenic Materials - Ullmann's Encyclopedia of Industrial Chemistry].

Usually, mechanochromism is accompanied by other chromogenic effects [Chromogenic Materials - Ullmann's Encyclopedia of Industrial Chemistry]. In this case, the effect in question is a photochromic response, which is reversible over time.

The innovative multi-sensory pigment according to the invention, which can be applied to coloured and/or raw fibres, advantageously has multiple optical properties, that is, piezochromism, photochromism and optionally fluorescence.

In particular, the smart pigment according to the invention is characterised by the fact of giving rise to a specific sequence of events, according to which the photochromic response can only be activated after the material has undergone an external stimulus, such as pressure, producing a piezochromic response. Advantageously, therefore, the piezophotochromic effect of the pigment according to the invention makes it possible to obtain multiple optical responses, which guarantee a higher safety factor than the prior art pigments.

Therefore, in the pigment according to the invention, a pressure stimulus produces a colour change, that is, a piezochromic effect, and at the same time an optical change, giving rise to a photochromic effect.

The smart pigment according to the invention is also advantageously characterised by a multiple reversible response, that is, the piezochromic response is partially reversible when the pigment is heated, whilst the photochromic response is reversible after a short period of time when the pigment is still piezochromic under normal ambient conditions. In this way, the textile clothing accessories can be marked with a smart pigment which is difficult to counterfeit and which permanently, uniquely and imperceptibly to the human eye modifies the reference textile support, thus attesting to the originality of textile clothing accessories.

Moreover, according to the invention, the textile support in question can also be distinguished by an optical fluorescent response coming from the organic component of the smart pigment, activated or not activated, which is easily detected by UV radiation. In fact, the use of an organic component with fluorescence characteristics, gives fluorescence to the pigment and allows a clearer and more easily detectable visualization with respect to the specific pigment coloration.

The fluorescent response to UV radiation of the smart pigment, although very similar to other systems with fluorescent activity already on the market, differs in terms of its piezochromic and photochromic response; the latter occurs only after an external pressure stimulus which activates the pigment, giving rise to a clear change in colour, which is reversible over time and visible to the human eye, when irradiated with LED light, UV and solar radiation. This pigment becomes imperceptible when fixed to the textile structure and is therefore not easy to detect and counterfeit.

Currently, therefore, a pigment such as the one proposed by the invention is not known, that is, a pigment consisting of an organic component intercalated or adsorbed in a nanostructured inorganic component which is able to respond to external stimuli such as pressure and radiation to LED, UV and solar light, producing a reversible response in a short time, consisting of a sharp change of colour.

The pigment according to the invention, if applied on a natural textile fibre such as wool, silk, linen, cotton, wool/silk, hemp or cashmere blends, previously coloured and/or raw, can advantageously give the fabric a unique fluorescent optical response to UV light, without altering the perception of colour for the fibres, yarns, fabrics or coloured garments and maintaining the feel of the product and constituting, according to the criteria indicated above, an imperceptible treatment, which is currently not available in products on the market.

Finally, the pigment according to the invention has a higher resistance to degradation due to light and washing than prior art pigments.

Brief description of the drawings

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 the evidence of the multisensory nature of the smart pigment LDH_FB351 shown in example 1. In particular, Figure 1a) is relative to the pigment as it is, Figure 1b) shows the pigment with evident piezochromic effect. Figure 1c) shows the pigment with evident photochromic effect and Figure 1d) shows the pigment with fluorescent effect;

- Figure 2 shows the XRD diffractogram of the LDH_FB351 pigment (continuous black line) shown in Example 1 and of the basic LDH_NO_3 (dashed black line);
- Figure 3 shows the thermogravimetric analysis of the LDH_FB351 pigment shown in Example 1;
- Figure 4 shows the LDH_FB351 pigment emission spectra of Example 1 after excitation at 405 nm, recorded in the range between 415 and 710 nm;
- Figure 5 shows the XRD diffractogram of the LDH_AIE pigment (continuous black line) shown in example 4 and of the basic LDH_NO_3 (dashed black line).
- Figure 6 shows the XRD diffractogram of the ZnAl_Yellow pigment shown in Example 9;
- Figure 7 shows the thermogravimetric analysis of the ZnAl_Yellow pigment shown in Example 9;
- Figure 8 shows the XRD diffractogram of the ZnAl_Magenta pigment shown in Example 10; and
- Figure 9 shows the thermogravimetric analysis of the ZnAl_Magenta pigment shown in Example 10.

Detailed description of the invention and preferred embodiments

It is a specific object of the present invention a piezochromic pigment, for colouring or dyeing a supporting surface to be marked or identified, comprising an inorganic matrix having a lamellar conformation and an organic filler configured to be intercalated or adsorbed between the lamellae of said inorganic matrix.

The pigment according to the invention 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 above-mentioned lamellae, and a second configuration, at a second pressure value P2, wherein the value of the second pressure P2 is higher than the value of the first pressure P1, wherein the inorganic matrix lamellae are close together allowing a molecular aggregation of the organic filler.

Advantageously, the molecular aggregation generates a change in the pigment coloration such that, in a configuration of use of the pigment applied to the support surface, when a 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.

Furthermore, advantageously, the 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.

The piezochromic effect or piezochromic activity or piezochromic properties means, therefore, the change in optical response, that is, change in colour, following the application of a pressure stimulus, such as compression.

The inorganic matrix may include components belonging to the hydrotalcites group.

Preferably, said components belonging to the hydrotalcites group are layered double hydroxides (LDH), optionally MgAl and ZnAl, or lamellar solids such as zirconium phosphates.

Therefore, the piezochromic pigment according to the invention is an organic-inorganic hybrid material comprising two-dimensional (2D) nanostructured lamellar solids, preferably belonging to the natural and/or synthetic cationic clays family, such as layered double hydroxyde (LDH), also known as hydrotalcites (such as MgAl and ZnAl layered double hydroxides (LDH)), or lamellar solids of the zirconium phosphate (Zr phosphate) type, in whose inorganic layers the organic filler is intercalated or adsorbed.

Specifically, the lamellar solids, suitably intercalated, co-intercalated, adsorbed or chemically modified with an organic substance (such as optical brighteners or simply fluorescent molecules and/or acid dyes), produce an inorganic-organic multisensory hybrid system, that is, the pigment according to the invention, which is able to respond to external stimuli such as pressure and irradiation to LED, UV and solar light, producing a reversible response in a short time, accompanied by a clear colour change quantified by a DeltaE >2 in the CIELab chromatic space.

According to an embodiment of the invention, said organic filler may comprise aggregation-induced emission compounds (AIE).

More specifically, when said pigment comprises aggregation-induced emission compounds (AIE), the pigment preferably has a colour variation characterised by a DeltaE greater or equal to 2 in the CIELab chromatic space, when irradiated by LED, UV or solar light radiation.

According to the invention, the above-mentioned organic filler may comprise water-soluble and/or optical brightening agents, and/or fluorescent and/or azo dyes, and/or liquid crystals, and/or carboxylic acids, and/or anthroquinonic dyes, and/or acid dyes and/or optical brighteners. The category of organic molecules which can be used is vast (optical brighteners, fluorescent dyes, azo dyes, etc.).

The main feature of organic filler is that it comprises functional groups which are exchangeable and salifiable with a lamellar solid such as LDH.

The smart pigments according to the invention preferably also have fluorescent activity, in this case comprising an organic filler consisting of organic molecules having fluorescent activity in their non-intercalated state, such as fluorescent dyes.

Preferably, said fluorescent dyes comprises Fluorescent Brightener, more preferably Fluorescent Brightener 351, in particular Fluorescent Brightener 351 intercalated within an MgAl nitrate type LDH, as shown in Example 1 below.

Moreover, when said fluorescent dye is Fluorescent Brightener 351, said pigment is characterised by having a fastness to artificial light, when fixed on a textile substrate, 4/5 Xenon Lamp ISO 105-B01:2014 and a wet fastness 4/5 ISO 105- C06:2010.

Moreover, according to the invention, when said organic filler is a fluorescent dye, said pigment is preferably photochromic.

Photochromic effect or photochromic activity or photochromic properties means the change in optical response, that is, change in colour, as a result of radiation with LED light, sunlight, or UV light.

The pigment according to the invention can be both piezophotochromic and photochromic. Piezophotochromic effect means the achievement of a photochromic behaviour of the pigment, following the activation - for example by pressure - of a piezophotochromic effect.

More specifically, the properties of the assembly of the hybrid or host-guest system of the pigment according to the invention give rise to a piezochromic effect which in turn induces a photochromic effect, preferably, but not exclusively, observable after LED, UV and solar radiation and which maintains at the same time any fluorescent properties of the original water-soluble organic dyes, optical brighteners, organic fluorescent materials, fluorescent illuminants and/or aggregation induced emissions (AIE), which are intercalated or adsorbed in the cationic clay LDH or Zr phosphate.

Specifically, the intercalation gives greater stability to photodegradation thanks to the UV- protective effect of the LDH co-intercalated with carbonate ions (CO32-) [D.Yan, M. Wei, Photofunctional Layered Materials, Structure and Bonding 166 Springer International Publishing 2015]. In this way, the intermolecular interactions are altered, giving rise to a piezochromic effect, which in turn induces a subsequent aggregation effect of the organic component, thus also giving rise to a photochromic effect.

As mentioned above, the optical response of the pigment according to the invention, that is, piezochromic, photochromic and possibly fluorescent, is due to the combination of chemical and physical factors present in the smart pigment. More specifically, this response is based on the capacity of organic molecules to adopt particular molecular conformations within the interlayer region, also called tunnel, allowing the observation of the optical starting activities which belong to the organic substances, such as fluorescence, emissions after aggregation ("Aggregation Induced Emission"), colour, and to provide new optical responses, not previously visible, when these pigments are stimulated by external factors such as pressure and/or LED, sunlight and UV radiation.

The piezochromic activity is due to molecular arrangements and ways of packing molecules within the inorganic lamellar layers.

The compression due to the pressure action contracts the inter-lamellar space, inducing changes in host-guest interactions, arrangement and aggregation state of the host anions, influencing the optical properties.

The unique properties resulting from the particular assembly of the hybrid or host-guest system manifest themselves as a sequence of optical effects, in which the structural and chemical characteristics of the piezo/photochromic pigment play an important role, in order to ensure the originality of the products in which the pigment is contained.

A further object of the invention is a textile accessory comprising a piezochromic pigment as described above.

A further object of the invention is a method of synthesis of a piezochromic pigment as defined above, said method of synthesis being an ion exchange synthesis method, or a method of synthesis by intercalation and/or co-intercalation, or a method of synthesis by delamination from solvents with high solvation capacity or a method of synthesis by flocculation, or a method of synthesis by co-precipitation from a solution containing metal ions or sol-gel or a method of synthesis by hydrothermal growth or a method of synthesis by reconstruction of said inorganic LDH matrix from calcined hydrotalcite.

The technique of production and synthesis of the smart pigment according to the invention consists preferably, but not exclusively, of ion exchange techniques in aqueous solution from precursors of the same family of lamellar solids, such as, for example, MgAl carbonate and MgAl nitrate, MgAl chlorate, in the presence of organic molecules in solution, possibly fluorescent, belonging for example to the family of optical brighteners, optical whitening agents or simply fluorescent molecules and acid dyes

More specifically, the ion exchange synthesis method preferably includes the following steps:

(a) dissolving an organic component in aqueous solution;

(b) basifying said aqueous solution containing said organic component;

(c) adding an inorganic precursor component to the aqueous solution obtained in phase (b);

(d) separating a solid fraction from a liquid phase in the solution obtained in phase (c);

(e) drying said solid fraction obtained in phase (d), wherein, between phase (c) and phase (d) there is a phase of heating the solution obtained.

Therefore, advantageously, the invention relates to a smart hybrid organic-inorganic pigment composed of:

- an inorganic base consisting of lamellar solids such as zirconium phosphate and/or cationic clays such as layered double hydroxides (LDH, also known as hydrotalcite);

- one or more organic molecules intercalated or adsorbed belonging to the fluorescent molecules, azo dyes, liquid crystals, colorants, anthroquinone dyes, fluorescent dyes, carboxylic acids, dicharboxylic acids, aggregation induced emission molecules (AIEs) and/or combinations thereof, and having piezochromic, photochromic and optionally fluorescent properties.

More specifically, the inorganic base can be chosen from the hydrotalcites having formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][An^{-}]_{x/n}\cdot zH_2O$ (ratio Mg/Al 3:1, co-intercalated with counter-nitrate ion, carbonate and/or water molecules) or is chosen from lamellar solids such as alpha zirconium phosphate type B, functionalised or intercalated zirconium phosphate or co-intercalated with surfactants.

Preferably, the organic molecules to be intercalated or adsorbed possess some or all of the following characteristics: being planar and cumbersome molecules, containing functional groups capable of being adsorbed or intercalated between layers of LDH, being flexible, water-soluble, with the ability to make intramolecular bonds with a clear correlated colour change, ability to make tautomeric conversions, possessing hydroxy (-OH) and/or carboxyl (-COOH) groups capable of being converted to salified form, having liquid crystal properties, ability of charge transfer and aggregation-induced emission (AIE) complexes.

The pigment according to the invention may comprise at least one of the organic molecules selected from the group which comprises: acid blue 25, acid blue 120, acid fuchsia, acid green 25, acid orange 7, acid orange 8, acid red 138, acid violet 7, acid yellow 17, acid yellow 25, red 48, methyl orange, amaranth, anhydride 4-amino-3,6-disolfo-1,8-potassium naphthalene, anhydride 1-phenyl-2,3- naphthalene carboxylic, fluorescent brightener 264, fluorescent brightener 5BM, fluorescent brightener 28, fluorescent brightener 353, fluorescent brightener VBL, fluorescent brighter 71, fluorescent brighter 9, fluorescent brightener 30, fluorescent brighter VBA, fluorescent brighter 134, fluorescent brightener 251, fluorescent brightener 113, fluorescent brightener 351, fluorescent brightener 357, fluorescent brightener 85, azofloxine, chlorazol black, sodium fluorescein, light green SF, brilliant blue R, xylenol orange tetrasodium salt, acid blue 129, 4-phenylcinnamic acid, merocyanine, (2,3-diidro-2-oxo-1H-imidazolo-4,5-diil)bis(benzene sulfonate) disodic, 1-(dimetilammino)-2,6-piridinebis(metilammina)-N,N,N',N',-tetraessigsauere, 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole], 1',3'-diidro-8-methoxy-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole], 1'-(2-hydroxyethyl)-3',3'-dimethyl-6-nitrospiro[1(2H)-benzopyran-2,2'-indoline], 1,3,3-trimethylindolinebenzopyrilospiran, benzyl viologen dichloride, 4'-hydroxy-4-biphenilcarbonitrile, 4-(dodecilossi)benzoic acid, 4-butossibenzoic acid, 4-cianobenzoic acid, 2-cianobenzoic acid, 4-esilbenzoic acid, Cholesteryl hemisuccinate, phenyl 1-hydroxy-2-naftoate, 7-hydroxycoumarin, 7-hydroxycoumarin-3-carboxylic acid, 2-osso-2H-acid 1-benzopyran-3-carboxylic, phenyl salicylate, resorcinol monobenzoate, 2-(2-hydroxyethyl)resorcinol, 4,4'-diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate, 4-methoxycinnamic acid, 4-(eptilossi)benzoic acid, 4-amino-1,1'-azobenzene-3,4'-disulfonic salt monosodic acid, azocarmine G, anhydride 1-phenil-2,3-naphtalendicarboxylic, sulfanilic acid azochromotrop, fluorescent brightener 220, brilliant blue R, Remazol brilliant blue , cholesteryl carbonate, cholesteryl chlorine, cholesteryl pelargonate, 2-(3-trifluorometilanilino)nicotinic acid, 1-sodium heptansulfonate, 4,4'-(1,2-Diphenylethene-1,2-diyl)dibenzoic acid, sodium 3,3'-{[(1,2-diphenylethene-1,2-diyl)bis(4,1-phenylene)]bis(oxy)}bis(propane-1-sulfonate, sulforhodamine B sodium salt, sulforhodamine G, violamine R, acid blue 80, N-[trans-4-(succinimidyloxycarbonyl)ciclohexylmethyl]-sulforhodamine B acid amide, merantine brilliant yellow 8G, Sodium 2-[7-(diethylamino)-2-oxo-2H-chromen-3-yl]-5-sulfamoyl-2,3-dihydro-1,3-benzoxazole-2-sulfonate and combinations of these, sodium 5-(aminosulphonyl)-2-[7-(diethylamino)-2-oxo-2H-1-benzopyran-3-yl]benzoxazolesulphonate, sulforhodamine B sodium salt, kiton red s, Acid Red 52, 2-(3-diethylamino-6-diethylazaniumylidene-xanthen-9-yl)-5-sulfo-benzenesulfonate.

According to a preferred embodiment, the hybrid pigment according to the invention has fluorescent properties when exposed to UV radiation.

Preferably, the hybrid pigment with fluorescent properties includes organic molecules, intercalated or adsorbed, chosen from those belonging to the Fluorescent Brightener classes, fluorescent acid dyes group I or AIE.

Advantageously, the hybrid pigment according to the invention has piezochromic properties, that is, it is able to undergo a colour change following an external pressure stimulus such as compression and/or grinding, for example in a range of between 3.5 and 200 bar, preferably less than 50 Bar.

More specifically, the piezochromic hybrid pigment according to the invention may comprise intercalated or adsorbed organic molecules chosen among those belonging to the classes of dyes, azo dyes, liquid crystals, carboxylic acids, anthroquinonic dyes, acid dyes and AIEs.

More specifically, the piezochromic colour variation preferably has a DeltaE >2 in the CIELab colour space.

Advantageously, once activated by pressure, the piezochromic pigment remains in this state of activation even after grinding.

Moreover, some embodiments according to the invention provide a piezochromic hybrid pigment with fluorescent properties when exposed to UV radiation.

Furthermore, after being subjected to pressure in the range of between 3.5 and 200 bar, the above-mentioned piezophotochromic hybrid pigment may show photochromic properties, thus adopting a piezophotochromic behaviour.

More specifically, the above-mentioned piezophotochromic-photochromic hybrid pigment provides a photochromic effect which generates a colour variation which has a DeltaE >2 in the CIELab chromatic space

Preferably, the above-mentioned photochromic effect is activated by an exposure to LED, UV or direct solar radiation and is a chromogenic effect, given by the confinement of the organic fluorescent molecules which, following a pressure stimulus, give rise to intermolecular interactions of the above-mentioned organic molecules mainly but not exclusively characterised by fluorescence, flatness and having at least one functional group exchangeable with the host inorganic system.

More specifically, according to the invention, the above-mentioned photochromic effect is reversible under ambient conditions in a time range of between 10 seconds and 5 minutes.

Moreover, the above-mentioned piezophotochromic hybrid pigment may exhibit fluorescent properties when exposed to UV radiation.

Advantageously, said piezophotochromic pigment with fluorescent properties may comprise organic molecules, intercalated or adsorbed, chosen from those belonging to the Fluorescent Brightener classes, fluorescent acid dyes group I and AIE.

Preferred embodiments of the invention comprise a method of obtaining the above-mentioned pigment by ion exchange or by intercalation and/or co-intercalation or by delamination from solvents with high solvation capacity, flocculation, co-precipitation from solutions containing metal ions, sol-gel, hydrothermal growth, LDH reconstruction.

Preferred embodiments of the fluorescent piezochromic pigment according to the invention comprise the pigments described below in examples 1-8, in particular a fluorescent piezochromic photochromic pigment wherein the organic filler comprises the organic molecule Fluorescent Brightener 351 (FB351) and the inorganic matrix is MgAl LDH-NO_3 (example 1); a piezochromic pigment wherein the organic filler comprises the organic molecule Acid Yellow 9 and the inorganic matrix is MgAl LDH-NO_3 (example 2); a piezochromic pigment wherein the organic filler comprises the organic molecule Remazol Brilliant Blue R and the inorganic matrix is MgAl LDH-NO_3 (example 3); a fluorescent piezochromic pigment wherein the organic filler comprises the organic filling 4,4′-(1,2-Diphenylethene-1,2-diyl)dibenzoic acid and the inorganic matrix is LDH-MgAl-NO_3 (example 4); a fluorescent piezochromic pigment wherein the organic comprises the organic molecules Sodium 2-[7-(diethylamino)-2-oxo-2H-chromen-3-yl]-5-sulfamoyl-2,3-dihydro-1,3-benzoxazole-2-sulfonate and sodium 1 heptanesulfonate and the inorganic matrix is LDH-NO_3 (example 5); a fluorescent piezochromic pigment wherein the organic matrix comprises the organic molecules Sulforhodamine B sodium salt and sodium 1 heptanesulfonate and the inorganic matrix is LDH MgAl-NO_3 (example 6); a fluorescent piezochromic pigment wherein the organic filler comprises the organic molecule Sulforhodamine B sodium salt and the inorganic molecule is LDH MgAl-NO_3 (example 7); a fluorescent piezochromic pigment wherein the organic filler comprises organic molecule Sodium 2-[7-(diethylamino)-2-oxo-2H-chromen-3-yl]-5-sulfamoyl-2,3-dihydro-1,3-benzoxazole-2-sulfonate and the inorganic matrix is LDH-NO_3.

Moreover, further embodiments of the pigment according to the invention are a fluorescent piezochromic pigment wherein the organic filler comprises the organic molecule Sodium 5-(aminosulphonyl)-2-[7-(diethylamino)-2-oxo-2H-1-benzopyran-3-yl]benzoxazolesulphonate (Yellow) and the inorganic matrix is ZnAl-LDH and a fluorescent piezochromic pigment wherein the organic filler comprises the organic molecule Sodium 2-(3-diethylamino-6-diethylazaniumylidene-xanthen-9-yl)-5-sulfo-benzenesulfonate (Magenta) and the inorganic matrix is ZnAl-LDH described in examples 9 and 10, respectively.

Examples

EXAMPLE 1. *Procedure for making and characterising a piezochromic photochromic fluorescent hybrid pigment according to the invention, wherein the organic molecule is Fluorescent Brightener 351 (FB351) (CAS 27344-41-8) and the inorganic base is MgAl LDH-NO3.*

A piezochromic photochromic fluorescent hybrid pigment according to the invention was made as follows.

The organic molecule Fluorescent Brightener 351 was dissolved in water free of CO_2 (1.28x10-2 mmol/mL) and the solution was basified with NaOH up to pH = 9.

The inorganic starter base MgAl LDH-NO_3 (10 mg/mL) was added to the solution and the resulting dispersion was heated to between 40 and 70℃ for 24 hours.

Filtration was carried out with a cellulose acetate filter (pore diameter 5 µm) in a Büchner funnel and the solid was washed with water directly on the filter until a water with pH = 7 was obtained.

The recovered solid was dried at 60℃ for 48 hours to obtain the piezochromic, photochromic and fluorescent hybrid pigment.

The pigment thus obtained was a yellow powder, characterised by the CIELab colorimetric coordinates of L = 92.77, a' = -13.00 and b' = 29.60 (Figure 1a).

The pigment was fluorescent when exposed to UV radiation.

The pigment as such showed no photochromic effect at any radiation.

The pigment showed a piezochromic effect when pressed at 50 bar, turning to a green-yellow coloration, characterised by the CIELab colorimetric coordinates of L = 77.07; a' = 12.70 and b' = 29.60 and therefore had an ΔE of 17.62 with respect to the pigment as such (Figure 1b).

The piezochromic effect was not reversible under normal ambient conditions and remained in the pressure-activated colouring state without returning to the previous one.

The pigment activated by the pressure stimulus (piezochromic) maintained fluorescence when exposed to UV radiation (Figure 1d).

The pigment activated by the pressure stimulus showed photochromic effect if exposed for 5-10 seconds to LED and/or UV radiation between 395 nm and 415 nm and/or sunlight, turning to a green colour, characterised by CIELab colorimetric coordinates of L = 71.44, a' = -18.82 and b' = 26.83, and therefore had an ΔE of 8.30 with respect to the piezochromic pigment (Figure 1c).

The pigment activated by the LED and/or UV, and/or sunlight stimulus maintained fluorescence when exposed to UV radiation.

The pigment activated by the LED and/or UV and/or sunlight (photochromic) stimulus was reversible, and once the LED and/or UV and/or sunlight source was removed the pigment returned to the piezochromic activated state in a time interval of between 10 seconds and 5 minutes. Subsequently, the photochromic property could be activated again with LED and/or UV and/or sunlight radiation up to at least 20 times.

Figure 2 shows the different crystallographic structure of the pigment intercalated with FB351 (continuous black line) with respect to the starting LDH (dashed black line).

The pigment had a maximum organic component charge of 42 % by weight, equivalent to a chemical formula of the type: $Mg0.65Al0.35(OH)_2(NO_3)_{0.11}(C_{28}H_{20}O_6S_2)_{0.12}x\ H_2O$.

The pigment had a D90 in the range of 1-10 microns (wherein D90 means that 90% of the particles characterising the pigment have a size between 1-10 microns).

The pigment had a substantial loss in mass (approximately 40%) in the temperature range 400 - 600℃.

The fluorescent pigment response had a maximum intensity of between 450 and 500 nm, with a decay independent of the applied pressure.

The thermal stability characteristics of the pigment, shown in Figure 3, were also investigated

Lastly, Figure 4 shows the pigment emission spectra.

EXAMPLE 2. *Procedure for making and characterising a piezochromic hybrid pigment according to the invention, wherein the organic molecule is Acid Yellow 9 and the inorganic base is MgAl LDH-*NO_3.

A piezochromic hybrid pigment according to the invention was made as follows.

The organic molecule Acid Yellow 9 was dissolved in water free of CO2 (5.78x10-2 mmol/mL) at 70℃ and the solution was basified with NaOH up to pH = 6.

The inorganic precursor starter base MgAl LDH-NO3 (10 mg/mL) was added to the solution and the resulting dispersion was heated to 40 - 70℃, preferably to 70℃, for 24 hours.

Filtration was carried out with a cellulose acetate filter (pore diameter 5 μm) in a Büchner funnel and the solid was washed with water directly on the filter until a water with pH = 7 was obtained.

the recovered solid was dried at 60℃ for 48 hours to obtain the piezochromic hybrid pigment.

The pigment thus obtained was an orange powder, characterised by the CIELab colorimetric coordinates of L = 60.44, a' = 39.20 and b' = 65.20.

The pigment showed a piezochromic effect when pressed at 10 bar, turning to a red coloration, characterised by the CIELab colorimetric coordinates of L = 39.11; a' = 41.00 and b' = 32.00 and therefore had an ΔE of 39.50 with respect to the pigment as such.

The piezochromic effect was not reversible and remained in the pressure-activated colouring state without returning to the state prior to the pressure stimulus.

EXAMPLE 3. *Procedure for making and characterising a piezochromic hybrid pigment according to the invention, wherein the* *organic molecule is Remazol Brilliant Blue R and the inorganic base is MgAl LDH-NO_3.*

A piezochromic hybrid pigment according to the invention was made as follows.

The organic molecule Remazol Brilliant Blue R was dissolved in water free of CO_2 (3.85x10-2mmol/mL) and the solution was basified with NaOH up to pH = 9.

The inorganic precursor base MgAl LDH-NO3 (10 mg/mL) was added to the solution and the resulting dispersion was heated to 40 - 70°C, preferably to 70°C, for 24 hours.

The dispersion was centrifuged at 500 RPM for 10 minutes and the precipitated solid was washed 3 times with CO2-free water.

The recovered solid was dried at 60°C for 48 hours to obtain the piezochromic hybrid pigment.

The pigment thus obtained was a dark blue powder, characterised by CIELab colorimetric coordinates of L = 23.41, a' = 8.80 and b' = -19.30.

The pigment showed a piezochromic effect when pressed at 50 bar, turning to a dark green coloration, characterized by CIELab colorimetric coordinates of L = 22.53, a' = 3.90 and b' = -1.40, and therefore has an ΔE of 18.60 compared to the pigment as such.

The piezochromic effect was not reversible and remained in the pressure-activated colouring state without returning to the state prior to the pressure stimulus.

EXAMPLE 4. *Procedure for making and characterising a piezochromic fluorescent hybrid pigment according to the invention, wherein the organic molecule is 4,4'-(1,2-Diphenylethene-1,2-diyl)dibenzoic acid and the inorganic base is LDH-MgAl-NO_3.*

A piezochromic fluorescent hybrid pigment according to the invention was made as follows.

Maintaining an inert atmosphere throughout the preparation, the organic molecule 4,4'-(1,2-Diphenylethene-1,2-diyl) dibenzoic acid (CAS 1002339-79-8), belonging to the AIE family, was dissolved in water free of CO_2 (1.93×10^{-2} mmol/mL) at 45°C and the solution was basified with NaOH up to pH = 9-10.

The inorganic precursor starter base LDH-MgAl-NO_3 (10 mg/mL) was added to the solution and shaken at 500 rpm for 24 hours.

The pigment was recovered by centrifugation and filtration and was washed on the filter with water free of CO_2 until a water with pH = 7 was obtained.

The recovered solid was dried at 60°C to constant weight and in an inert atmosphere to obtain the piezochromic fluorescent hybrid pigment.

The pigment thus obtained was a light yellow powder, characterised by the CIELab colorimetric coordinates of L = 94.59, a' = -7.00 and b' = 9.60.

The pigment was fluorescent when exposed to UV radiation.

The pigment showed a piezochromic effect when pressed at 50 bar, turning to a light green coloration, characterized by CIELab colorimetric coordinates of L = 80.61; a' = -6.20 and b' = 25.50 and therefore had an ΔE of 21.19 compared to the pigment as it was.

The piezochromic effect was not reversible and remained in the pressure-activated colouring state without returning to the state prior to the pressure stimulus.

The pigment activated by the pressure stimulus maintained fluorescence when exposed to UV radiation.

The pigment obtained with the above-mentioned method had an XRD diffractogram as shown in Figure 5, where it can be seen that the crystallographic structure of the intercalated pigment (continuous black line) is different from the starting LDH (dashed black line).

EXAMPLE 5. *Procedure for making and characterising a piezochromic fluorescent hybrid pigment according to the invention, wherein the organic molecules are Sodium 2-[7-(diethylamino)-2-oxo-2H-chromen-3-yl]-5-sulfamoyl-2,3-dihydro-1,3-benzoxazole-2-sulfonate e sodium 1 heptanesulfonate and the inorganic base is LDH-NO_3.*

A piezochromic fluorescent hybrid pigment according to the invention was made as follows.

The organic molecule Sodium 2-[7-(diethylamino)-2-oxo-2H-chromen-3-yl]-5-sulfamoyl-2,3-dihydro-1,3-benzoxazole-2-sulfonate (CAS 93859-32-6) (**Yellow Fluo Cromacid 8GX**) belonging to the family of fluorescent azo dyes has been dissolved in water free f CO_2 at 45°C (5.41x10-2 mmol/mL) and the solution was basified with NaOH up to pH = 7.5-8.1.

The organic molecule sodium 1 heptanesulfonate (CAS 22767-50-6) was dissolved in water free of CO_2 at 45℃ (0.2332 g/50 mL) and the solution was basified with NaOH up to pH = 7.5-8.1.

The two solutions obtained have been combined and the inorganic precursor base LDH-NO_3 (10 mg/mL) has been added by shaking at 600 rpm for 24 hours.

The pigment was recovered by centrifugation and filtration and was washed on the filter with water free of CO_2 until a water with pH = 7 was obtained.

The recovered solid was dried at 60℃ to constant weight and in an inert atmosphere to obtain the piezochromic fluorescent hybrid pigment.

The pigment thus obtained was an opaque orange-yellow powder, characterised by the CIELab colorimetric coordinates of L = 70,37, a' = 25.40 and b' = 95.90.

The pigment was fluorescent when exposed to UV radiation.

The pigment showed a piezochromic effect when pressed at 50 bar, turning to a red coloration, characterised by the CIELab colorimetric coordinates of L = 39.72; a' = 21.60 and b' = 34.60 and therefore had an ΔE of 68.67 with respect to the pigment as such.

The piezochromic effect was not reversible and remained in the pressure-activated colouring state without returning to the state prior to the pressure stimulus.

EXAMPLE 6. *Procedure for making and characterising a piezochromic fluorescent hybrid pigment according to the invention, wherein the organic molecules are Sulforhodamine B sodium salt e sodium 1 heptanesulfonate and the inorganic base is LDH MgAl-NO_3.*

A piezochromic fluorescent hybrid pigment according to the invention was made as follows.

The organic molecule Sulforhodamine B sodium salt (CAS 3520-42-1) (Red Fluo Cromacid B) belonging to the aminoxanthene family was dissolved in water free of CO_2 at 45℃ (2.69x10-2 mmol/mL) and the solution was basified with NaOH up to pH = 7.5-8.1.

The organic molecule sodium 1 heptanesulfonate (CAS 22767-50-6) was dissolved in water free of CO_2 at 45 ℃ (0.2332 g/50 mL) and the solution was basified with NaOH up to pH = 7.5-8.1.

The two solutions obtained have been combined and the inorganic precursor starter base LDH MgAl-NO_3 (10 mg/mL) has been added and shaken at 600 rpm for 24 hours.

The pigment was recovered by centrifugation and filtration and was washed on the filter with water free of CO_2 until a water with pH = 7 was obtained.

The recovered solid was dried at 60°C to constant weight and in an inert atmosphere to obtain the piezochromic fluorescent hybrid pigment.

The pigment thus obtained was a violet powder, characterised by the CIELab colorimetric coordinates of L = 28.59, a' = 49.60 and b' = -25.70.

The pigment was fluorescent when exposed to UV radiation.

The pigment showed a piezochromic effect when pressed at 50 bar, turning to a dark yellow coloration, characterised by the CIELab colorimetric coordinates of L = 20.41; a' = 9.30 and b' = 0.50 and therefore had an ΔE of 48.76 with respect to the pigment as such.

The piezochromic effect was not reversible and remained in the pressure-activated colouring state without returning to the state prior to the pressure stimulus.

EXAMPLE 7. *Procedure for making and characterising a piezochromic fluorescent hybrid pigment according to the invention, wherein the organic molecule is Sulforhodamine B sodium salt and the inorganic base is* LDH MgAl-NO_3.

A piezochromic fluorescent hybrid pigment according to the invention was made as follows.

The organic molecule Sulforhodamine B sodium salt (CAS 3520-42-1) (Red Fluo Cromacid B) belonging to the aminoxanthene family was dissolved in water free of CO_2 at 45°C (1.925×10^{-2} mmol/mL) and the solution was basified with NaOH up to pH = 7.5-8.1.

The inorganic precursor starter base LDH MgAl-NO_3 (10 mg/mL) was added to the previous solution and shaken at 600 rpm for 24 hours.

The pigment was recovered by centrifugation and filtration and was washed on the filter with water free of CO_2 until a water with pH = 7 was obtained.

The recovered solid was dried at 60°C to constant weight and in an inert atmosphere to obtain the piezochromic fluorescent hybrid pigment.

The pigment thus obtained was a violet powder, characterised by the CIELab colorimetric coordinates of L = 20.90, a' = 38.30 and b' = -3.50.

The pigment was fluorescent when exposed to UV radiation.

The pigment showed a piezochromic effect when pressed at 50 bar, turning to a dark yellow violet colour, characterized by the CIELab colorimetric coordinates of L = 28.12; a' = 14.30 and b' = 10.20 and therefore has an ΔE of 28.56 compared to the pigment as it was.

The piezochromic effect was not reversible and remained in the pressure-activated colouring state without returning to the state prior to the pressure stimulus.

EXAMPLE 8: *Procedure for making and characterising a piezochromic fluorescent hybrid pigment according to the invention, wherein the organic molecule is Sodium 2-[7-(diethylamino)-2-oxo-2H-chromen-3-yl]-5-sulfamoyl-2,3-dihydro-1,3-benzoxazole-2-sulfonate and the inorganic base is LDH-*NO_3.

A piezochromic fluorescent hybrid pigment according to the invention was made as follows.

The organic molecule Sodium 2-[7-(diethylamino)-2-oxo-2H-chromen-3-yl]-5-sulfamoyl-2,3-dihydro-1,3-benzoxazole-2-sulfonate (CAS 93859-32-6) (Yellow Fluo Cromacid 8GX) belonging to the family of fluorescent azo dyes has been dissolved in water free f CO_2 at 45°C ($3.85x10^{-2}$ mmol/mL) and the solution was basified with NaOH up to pH = 7.5-8.1.

The inorganic precursor starter base LDH-NO_3 (10 mg/mL) was added to the previous solution and shaken at 600 rpm for 24 hours.

The pigment was recovered by centrifugation and filtration and was washed on the filter with water free of CO_2 until a water with pH = 7 was obtained.

The recovered solid was dried at 60°C to constant weight and in an inert atmosphere to obtain the piezochromic fluorescent hybrid pigment.

The pigment thus obtained was a powder of opaque orange-yellow colour, characterised by CIELab colorimetric coordinates of L = 56.42, a' = 14.50 and b' = 64.30.

The pigment was fluorescent when exposed to UV radiation.

The pigment showed a piezochromic effect when pressed at 50 bar, turning to a red coloration, characterised by the CIELab colorimetric coordinates of L = 67.95; a' = 1.70 and b' = 3.60 and therefore had an ΔE of 63.10 with respect to the pigment as such.

The piezochromic effect was not reversible and remained in the pressure-activated colouring state without returning to the state prior to the pressure stimulus.

EXAMPLE 9. *Characterisation of a piezochromic fluorescent hybrid pigment according to the invention, wherein the organic molecule is Sodium 5-(aminosulphonyl)-2-[7-(diethylamino)-2-oxo-2H-1-benzopyran-3-yl]benzoxazolesulphonate and the inorganic base is LDH ZnAl,* for example LDH ZnAl-NO_3.

A piezochromic fluorescent pigment according to the invention (ZnAl_Yellow), wherein the organic molecule is Sodium 5-(aminosulphonyl)-2-[7-(diethylamino)-2-oxo-2H-1-benzopyran-3-yl]benzoxazolesulphonate and the inorganic base is LDH ZnAl, has been prepared as shown in the above examples.

An X-ray diffraction analysis (XRD) was performed, the results of which are shown in Figure 6.

A thermogravimetric analysis (TGA/DSC) was performed, shown in Figure 7, showing a total weight loss of approximately 43.55% and a water loss of approximately 8.82%, indicating a percentage loading of the organic molecules in hydrotalcite of about 23%.

A chemical-physical analysis was also carried out, the results of which are shown in the following table:

Appearance	Dark yellow solid
Interlayer distance	11.2 Å
Humidity	8.82%

The product, when stored in closed containers in a cool, dry place, kept its properties intact for a period of not less than 36 months from the date of manufacture.

The pigment showed a piezochromic response after application of 50 Bar pressure for approximately 15 seconds.

EXAMPLE 10. Characterization of a piezochromic fluorescent hybrid pigment according to the invention (ZnAl_Magenta), wherein the organic molecule is 2-(3-diethylamino-6-diethylazaniumylidene-xanthen-9-yl)-5-sulfo-benzenesulfonate and the inorganic base is LDH ZnAl, for example LDH ZnAl -NO_3.

A piezochromic fluorescent pigment according to the invention, wherein the organic molecule is 2-(3-diethylamino-6-diethylazaniumylidene-xanthen-9-yl)-5-sulfo-benzenesulfonate and the inorganic base is LDH ZnAl, has been prepared as shown in the above examples.

An X-ray diffraction analysis (XRD) was performed, the results of which are shown in Figure 8.

A thermogravimetric analysis (TGA/DSC) was performed, shown in Figure 9, showing a total weight loss of approximately 41.81% and a water loss of approximately 10.01%, indicating a percentage loading of the organic molecules in hydrotalcite of about 19.3%.

A chemical-physical analysis was also carried out, the results of which are shown in the following table:

Appearance	Purple solid
Interlayer distance	11.2 Å
Humidity	10.01%

The product, when stored in closed containers in a cool, dry place, kept its properties intact for a period of not less than 36 months from the date of manufacture. The pigment showed a piezochromic response after application of 50 Bar pressure for approximately 15 seconds.

The invention is described by way of example only, without limiting the scope of application, according to its preferred embodiments, but it shall be understood that the invention may be modified and/or adapted by experts in the field without thereby departing from the scope of the inventive concept, as defined in the claims herein.

CLAIMS

1. A piezochromic pigment, for colouring or dyeing a support surface to be marked or identified, 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 the pigment coloration such that, in a configuration of use of the pigment applied to the support surface, when a 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 piezochromic pigment according to the previous claim, wherein said inorganic matrix comprises components belonging to the hydrotalcites group.

3. The piezochromic pigment 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 such as zirconium phosphates.

4. The piezochromic pigment according to any one of the preceding claims, where said organic filler comprises aggregation-induced emission (AIE) compounds.

5. The piezochromic pigment according to the previous claim, having a colour variation characterised by a DeltaE greater than or equal to 2 in

the CIELab chromatic space, when irradiated by LED, UV or solar light radiation.

6. The piezochromic pigment according to any one of the preceding claims, wherein said organic filler comprises 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.

7. The piezochromic pigment according to the preceding claim, wherein said fluorescent dyes comprise Fluorescent Brightener, optionally Fluorescent Brightener 351.

8. The piezochromic pigment according to the preceding claim, wherein said fluorescent dye is Fluorescent Brightener 351 and wherein said pigment is characterised by having a fastness to artificial light 4/5 Xenon Lamp ISO 105-B01:2014 and a wet fastness 4/5 ISO 105-C06:2010 when fixed on a textile support.

9. The piezochromic pigment according to any one of claims 6-8, wherein, when said organic filler is a fluorescent dye, said pigment is photochromic.

10. A textile clothing accessory comprising a piezochromic pigment according to any one of claims 1 to 9.

11. A method of synthesis of a piezochromic pigment as defined in any one of claims 1 to 9, said method of synthesis being an ion exchange synthesis method, or a method of synthesis by intercalation and/or co-intercalation, or a method of synthesis by delamination from solvents with high solvation capacity or a method of synthesis by flocculation, or a method of synthesis by co-precipitation from a solution containing metal ions or sol-gel or a method of synthesis by hydrothermal growth or a method of synthesis by reconstruction of said inorganic LDH matrix from calcined hydrotalcite.

12. The ion exchange synthesis method according to the preceding claim, said method including the following steps:

(a) dissolving an organic component in aqueous solution;

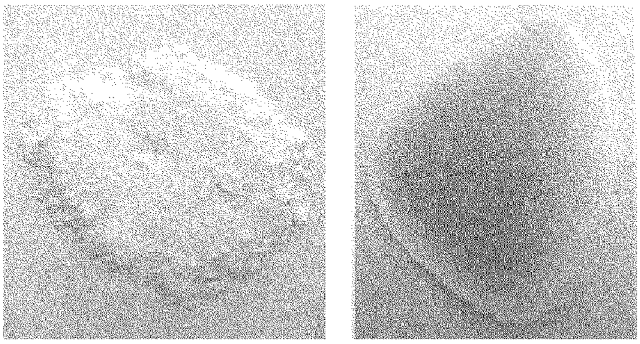
(b) basifying said aqueous solution containing said organic component;

(c) adding an inorganic precursor component to the aqueous solution obtained in phase (b);

(d) separating a solid fraction from a liquid phase in the solution obtained in phase (c);

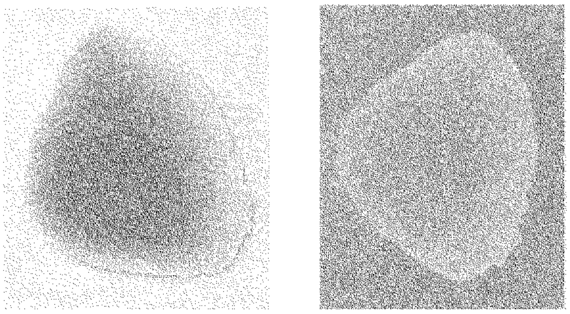
(e) drying said solid fraction obtained in phase (d),

wherein, between said phase (c) and said phase (d) there is a phase of heating the solution obtained.



a) LDH_FB351
as such

b) LDH_FB351
50 bar
(piezochromic)



c) LDH_FB351
50 bar_LED
(photochromic)

d) LDH_FB351
50 bar
(fluorescent)

Fig. 1

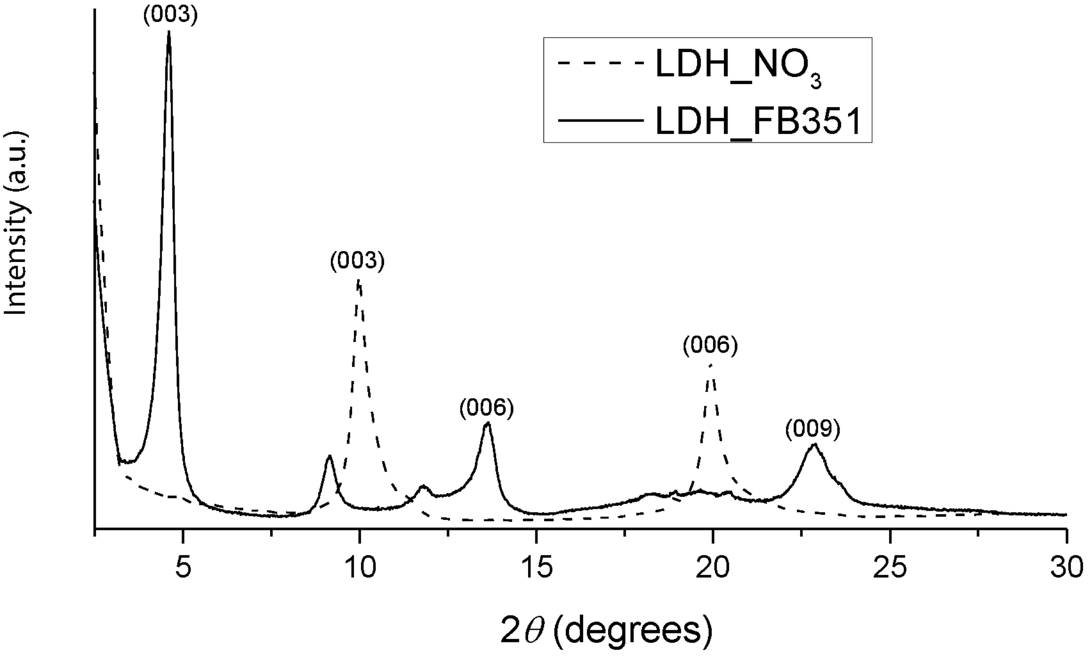


Fig. 2

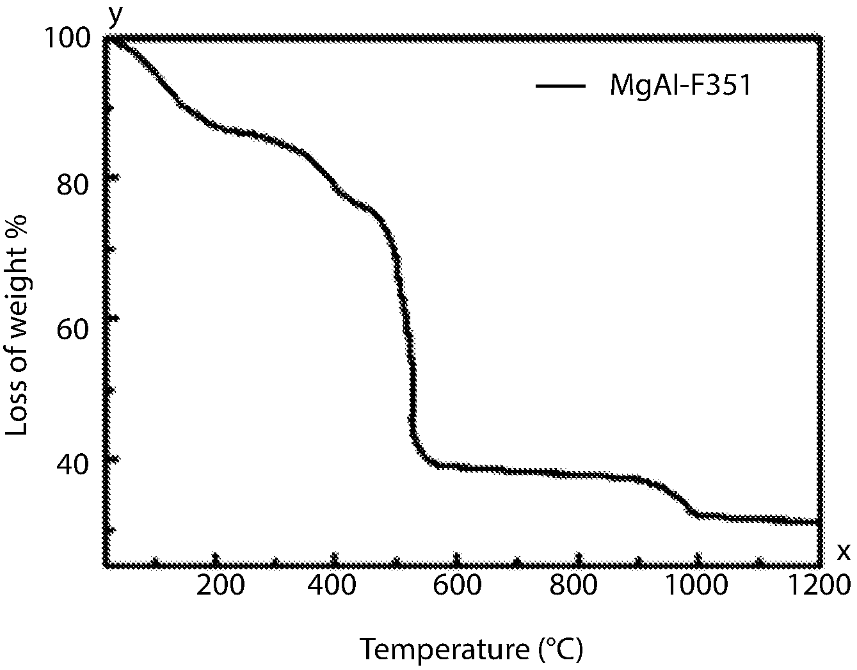

y
100
80
60
40
Loss of weight %
MgAl-F351
x
200
400
600
800
1000
1200
Temperature (°C)

Fig. 3

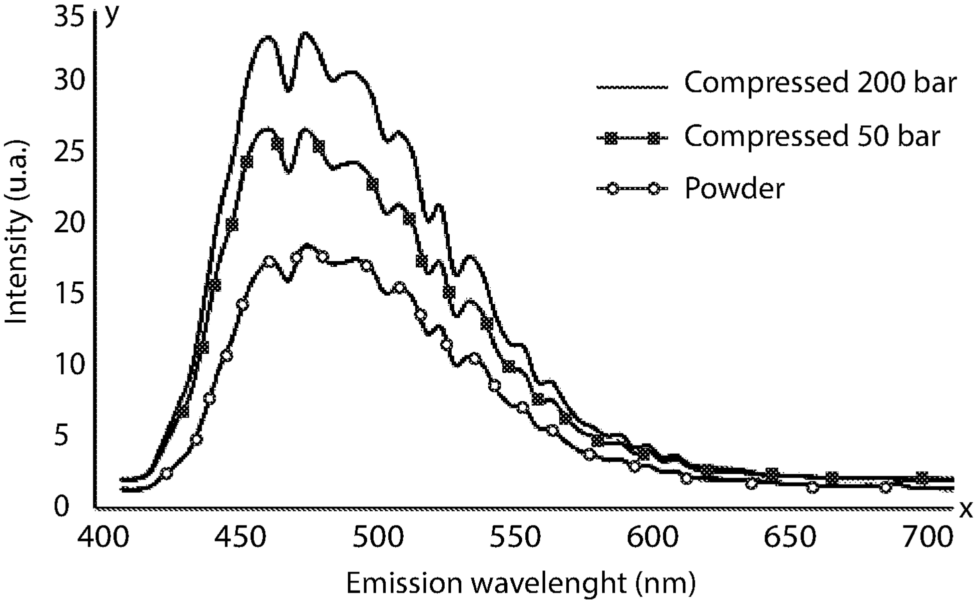

35
30
25
20
15
10
5
0
y
Intensity (u.a.)
Compressed 200 bar
Compressed 50 bar
Powder
x
400
450
500
550
600
650
700
Emission wavelenght (nm)

Fig. 4

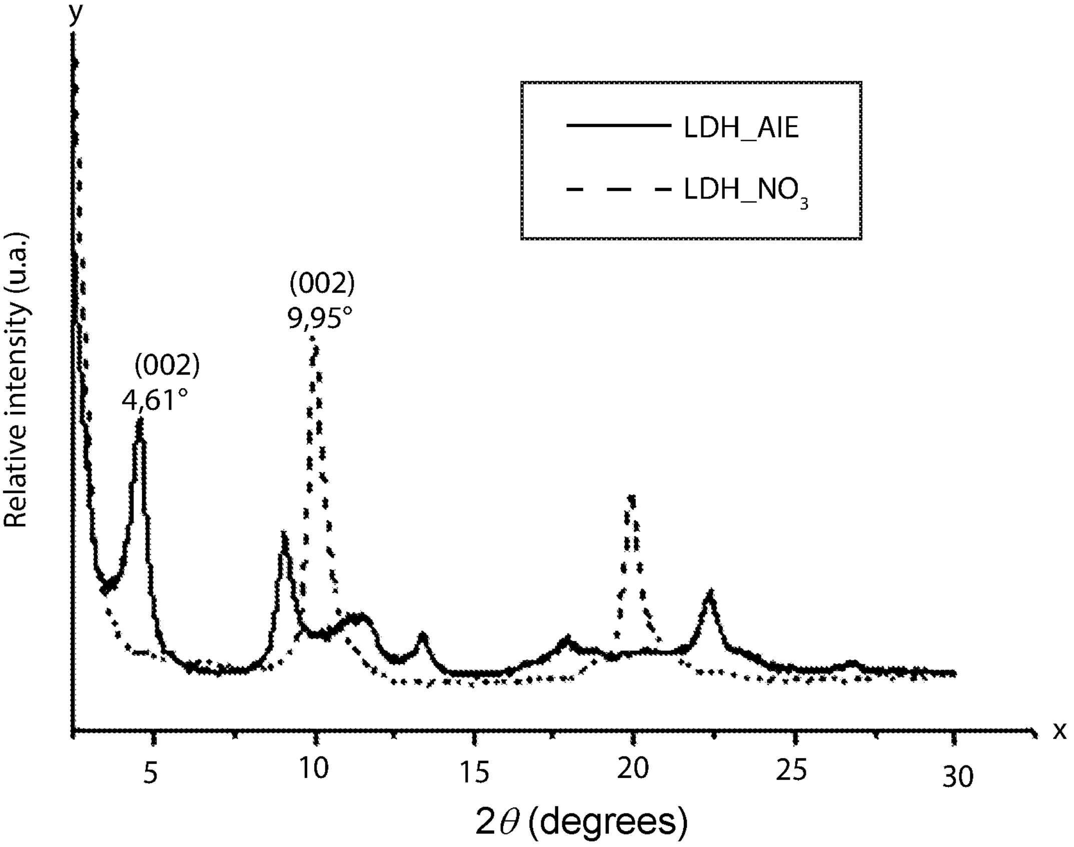

y
LDH_AIE
LDH_NO_3
Relative intensity (u.a.)
(002)
9,95°
(002)
4,61°
x
5
10
15
20
25
30
2θ (degrees)

Fig. 5

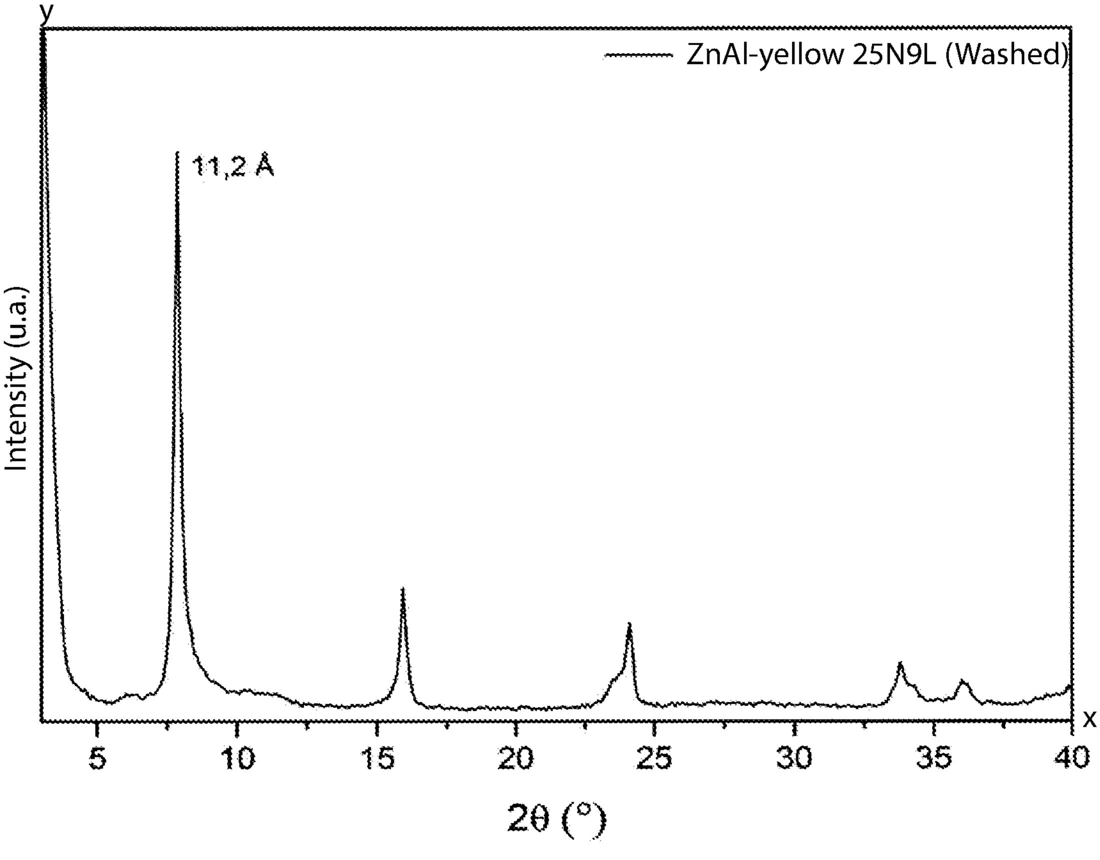

y
ZnAl-yellow 25N9L (Washed)
11,2 Å
Intensity (u.a.)
x
5
10
15
20
25
30
35
40
2θ (°)

Fig. 6

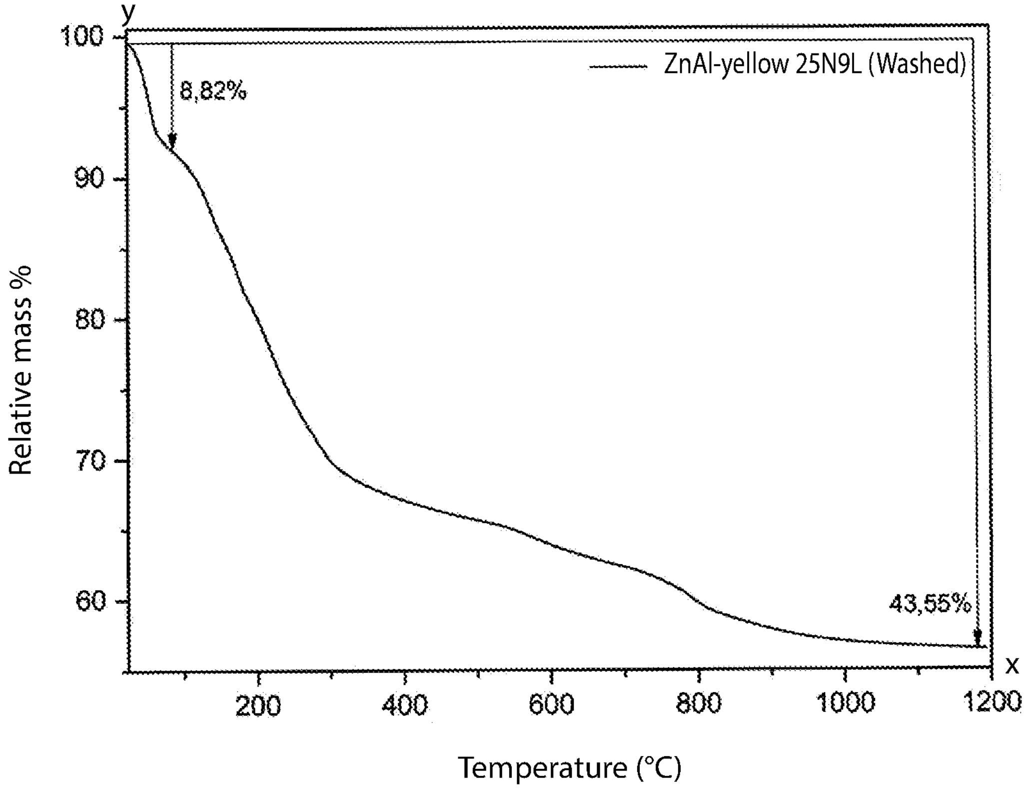

y
x
100
90
80
70
60
200
400
600
800
1000
1200
Relative mass %
Temperature (°C)
ZnAl-yellow 25N9L (Washed)
8,82%
43,55%

Fig. 7

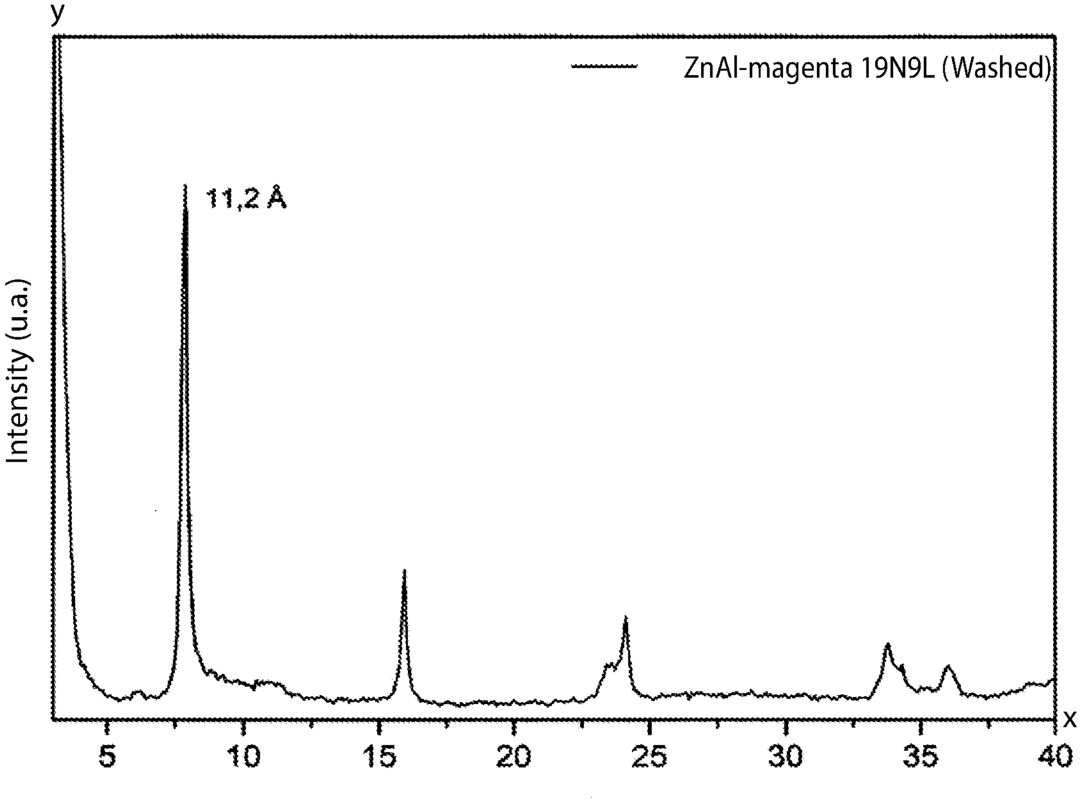

y
x
Intensity (u.a.)
2θ (°)
5
10
15
20
25
30
35
40
ZnAl-magenta 19N9L (Washed)
11,2 Å

Fig. 8

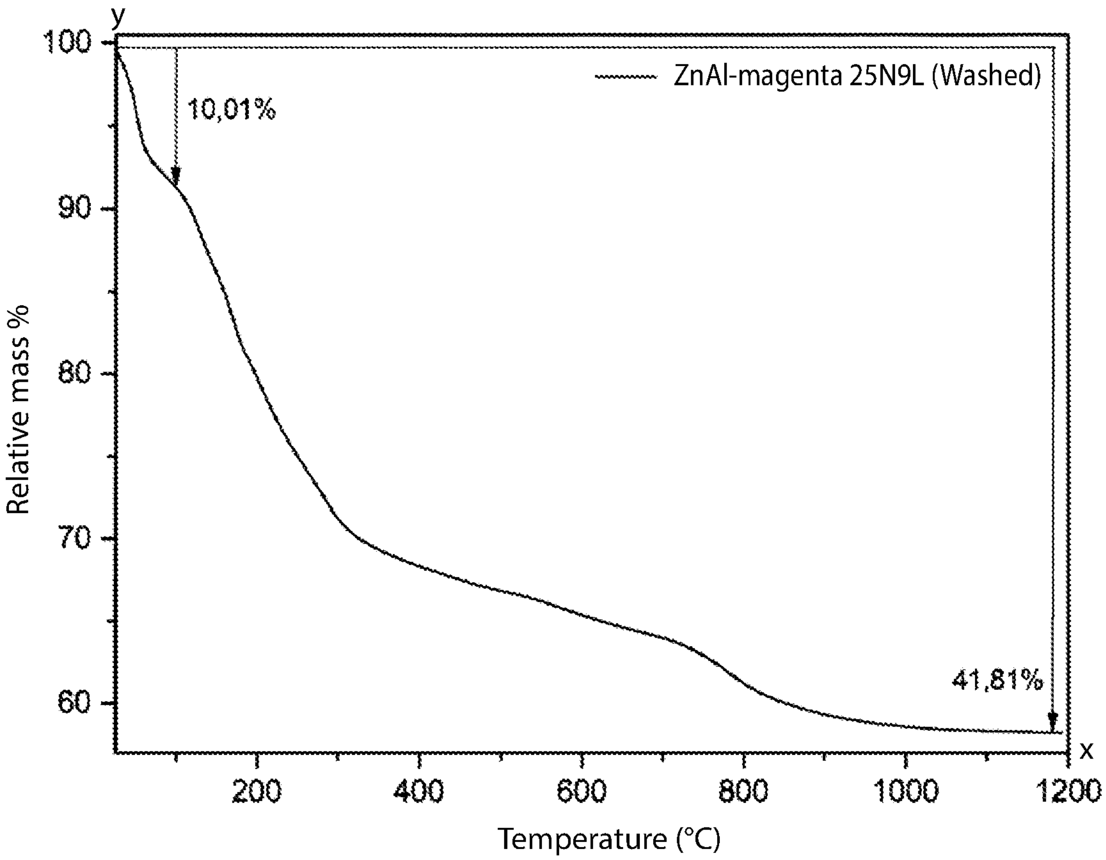

y
100
90
80
70
60
Relative mass %
ZnAl-magenta 25N9L (Washed)
10,01%
41,81%
x
200
400
600
800
1000
1200
Temperature (°C)

Fig. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2020/000036

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09C1/40 C09C1/42 C09K9/00
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)
C09C H05B C09K

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	DONGPENG YAN ET AL: "Layered Host-Guest Materials with Reversible Piezochromic Luminescence", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 50, no. 31, 17 June 2011 (2011-06-17), pages 7037-7040, XP055771395, ISSN: 1433-7851, DOI: 10.1002/anie.201102232 abstract page 7037 - page 7038 figure 2 -----	1-5,11

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search 4 February 2021	Date of mailing of the international search report 16/02/2021
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Mertins, Frédéric

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2020/000036

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	EP 2 628 531 A2 (FERRINI SOCIETA A RESPONSABILITA LIMITATA [IT] ET AL.) 21 August 2013 (2013-08-21) abstract examples 1-3 figure 3 paragraphs [0003], [0047], [0051] -----	1-11
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X	FENG J ET AL: "New photo-thermally stable acid yellow 17 intercalation pigment having supra-molecular structure", WPI / THOMSON,, vol. 2011, no. 45, 2 March 2011 (2011-03-02), XP002742171, abstract -----	1-9,11
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 628 849 A1 (FERRINI SOCIETA A RESPONSABILITA LIMITATA [IT]) 21 August 2013 (2013-08-21) abstract claims 1-15 paragraph [0034] example 1 -----	1-11
X	CN 101 982 509 A (UNIV BEIJING CHEMICAL) 2 March 2011 (2011-03-02) abstract claims 1-5 examples 1-4 -----	1-12

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KR 20050049784	A	27-05-2005	NONE	
EP 2628849	A1	21-08-2013	NONE	
CN 101982509	A	02-03-2011	NONE	