Abstract:

VARDSEN, Antonio; AGRAMUNT Tornesa RICO, Partida s/n, 12191 La Pobla Tornesa (ES).

Inventors: VICENT PEÑA, Juan Bautista; Partida Rambleta s/n, 12191 La Pobla Tornesa (ES); ALBIOL RICO, Noelia; Partida Rambleta s/n, 12191 La Pobla Tornesa (ES); VALIENTE BORDANOVA, David; Partida Rambleta s/n, 12191 La Pobla Tornesa (ES); AGRAMUNT LERMA, Jose Vicente; Partida Rambleta s/n, 12191 La Pobla Tornesa (ES); BLASCO FUENTES, Antonio; Partida Rambleta s/n, 12191 La Pobla Tornesa (ES).

Agent: ZBM PATENTS - ZEA, BARLOCCI & MARK-VARDSEN; PL Catalunya, 1 2nd floor, 08002 Barcelona (ES).

It is provided an inkjet ink comprising an iron oxide based red pigment; a liquid vehicle comprising a solvent having a boiling point equal to or higher than 200°C selected from an ester, a glycol ester, a glycol ether ester, a fatty alcohol, and mixtures thereof, and at least one dispersant. It is also provided a process for the preparation of the inkjet ink, a process for the preparation of a constructive element by applying the inkjet ink, and the use of the inkjet ink for the decoration of constructive elements without being submitted to a firing process.
Red oil-based inkjet ink comprising iron oxide pigments.

The present invention relates to the field of inks. In particular, the invention relates to an inkjet ink, to a process for its preparation, and to its use for the decoration of constructive elements.

BACKGROUND ART

Decoration in precast elements whose surfaces are porous is achieved by several techniques, depending on the nature of the surface to be treated. For example, in the field of fibre cement organic pigment inks cured by ultraviolet (UV) or acrylic paints are typically used for this purpose. In the field of wood stains, varnishes and paints are commonly used.

The use of acrylic paints, suitable for outdoor use, restricts the decoration possibilities due to limitations on their application. On the other hand, organic pigment UV-curable inks can be applied by inkjet printing. However, they have a bad behaviour for outdoor use, and it is generally accepted that after two years they begin to lose their colouring characteristics.

In the decade 2000-2010, in the ceramic industry, inkjet printing technology using inorganic pigments applied on tiles was developed. This technique was a revolution in the industry, and in 2014 the degree of implementation was over 90% in Spain and Italy (leading European manufacturers) and 64% worldwide.

Inkjet technology allows great production flexibility, greater consistency in the decorating process, reducing the consumption of pigments, reducing the time required to change models, possibility of decorating to the edges of the piece, and reducing the time elapsed since the idea for a new product design to manufacturing.

In ceramic pieces, firing stage after the inkjet decoration allows to fix pigments, which became integrated into the vitreous structure of the material. This guarantees good adhesion and protection of the pigment.

Nevertheless, the application of inorganic pigment inks on porous support
materials that are not being to be subsequently subjected to a firing process presents several drawbacks such as incompatibility between the ink and the substrate, low opacity (which makes the substrate partially visible and produces chromatic variability when the properties of the substrate change), and solvent removal problems.

Therefore, there is still a need for an improved inkjet ink useful for the inkjet decoration of support materials, particularly porous support materials, which allows obtaining constructive elements with the high demanding quality properties and performance required by the market without the need of being submitted to a firing process.

SUMMARY OF THE INVENTION

Inventors have found an inkjet ink suitable for decorating constructive elements which will not be subjected to any thermal treatment after decoration, or that will be subsequently subjected to a thermal treatment at a maximum temperature of 300 °C. The ink of the invention provides good outdoors resistance compared to organic pigmented inks. The use of specific solvents in combination with dispersants and, optionally, rheological additives allows obtaining an ink comprising an iron oxide based red pigment which is stable and suitable for its inkjet application on a substrate, particularly on a porous substrate.

Thus, a first aspect of the invention is the provision of an inkjet ink comprising:

- an iron oxide based red pigment;
- a solvent or a mixture of solvents having a boiling point equal to or higher than 200 °C, particularly equal to or higher than 250 °C and equal to or lower than 400 °C, selected from, an ester, a glycol ester, a glycol ether ester, a fatty alcohol, and mixtures thereof,
- at least one dispersant.

The use of the specific solvents having a boiling point equal to or higher than 200 °C, particularly equal to or higher than 250 °C and equal to or lower than 400 °C, namely with relatively low vapour pressures, allows reducing the
evaporation of the solvent in the printheads, which prevents the clogging of inkjet nozzles, making the printing system more stable. Incidentally, the release of Volatile Organic Compounds (VOC) during the decoration process is also reduced. The solvents used in this invention are not curable by UV radiation, and therefore, this ink cannot be used in UV-curable printing systems.

In a second aspect the invention relates to a process for the preparation of an inkjet ink as defined above, the process comprising:

a) mixing the components of the ink as defined above;

b) adding at least one dispersant and submitting the mixture to a grinding process, a dispersion process, or a mixture thereof, until obtaining a homogeneous suspension having a viscosity from 10 to 200 cP at 40 °C;

c) diluting the suspension with a solvent or mixture of solvents; and

d) filtrating the suspension.

In another aspect the invention relates to the use of an inkjet ink as defined above for the decoration of a constructive element that will not be subsequently subjected to a firing process.

In still another aspect the invention relates to a constructive element comprising:

- a support material;

- a decorative coating formed by the inkjet ink as defined above; and

- at least one protective cured polymeric coating formed with a composition curing at a temperature of up to 300 °C.

DETAILED DESCRIPTION OF THE INVENTION

All terms as used herein in this application, unless otherwise stated, shall be understood in their ordinary meaning as known in the art. Other more specific definitions terms as used in the present application are as set forth below and are intended to apply uniformly throughout the specification and claims unless an otherwise expressly set out definition provides a broader definition.
The term "naphthenic hydrocarbon" refers to an organic compound of carbon and hydrogen which general formula is \( \text{C}_n\text{H}_{2n} \) that contains one or more saturated cyclic structures.

The term "fatty acid" refers to a linear, unbranched, saturated or unsaturated carboxylic acid containing from 6 to 24 carbon atoms, particularly from 10 to 18 carbon.

The terms "particle size" and "particle size distribution", as used herein, are in terms of diameter irrespective of the actual particle shape. The term "diameter", as used herein, means the equivalent sphere diameter, namely the diameter of a sphere having the same diffraction pattern, when measured by laser diffraction, as the particle.

As used herein, the term "primer" is an undercoat put on support materials before printing. Priming ensures better adhesion of subsequent coating layers to the surface and provides additional protection for the material being decorated or painted. As used herein, the term "decorative coating" relates to a coating having merely an aesthetic effect, an informative effect or a functional effect. Examples of aesthetic effects include decorative elements mimicking the appearance of natural materials such as stone, wood, marble or synthetic materials such as concrete, cement, weaving or pottery. Examples of information elements include graphical elements as symbols, images, marks, logotypes, and signposting. Examples of functional elements include light conductor elements, fluorescent elements, electrically conductive elements or, in general, any other element capable of providing additional functionality to the construction element.

As used herein, the term "protective coating" relates to a coating having merely a protective effect and which is cured by UV radiation, thermal treatment or other different techniques. The protective coating is applied after the decorative coating, so it is the final layer.

As used herein, the term "curing" refers to the hardening of non-solid polymers, which results from polymerization and/or crosslinking. By the appropriate choice of free radical initiators, curing can be initiated by UV light or by the action of heat or moisture.
As used herein, the term "weight percent", "percentage by weight" or "wt.%" refers to the percentage by weight of the ingredient per weight of the overall composition.

Inkjet ink

As mentioned above, the inkjet ink of the invention comprises iron oxide \( \text{Fe}_2\text{O}_3 \) red pigment; a solvent having a boiling point equal to or higher than 200 °C, particularly equal to or higher than 250 °C and equal to or lower than 400 °C, selected from a hydrocarbon, an ester, an ether, a glycol ester, a glycol ether ester, a fatty alcohol, and mixtures thereof; and a dispersant.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the inkjet ink has a viscosity from 4 to 40 cP at 40 °C, and a solid content from 10 to 60 wt.% with respect to the weight of the overall composition.

The inorganic colour pigment of the inkjet ink of the invention is iron oxide red pigment (herein and hereinafter iron oxide indicates \( \text{Fe}_2\text{O}_3 \), also known as CI Pigment Red 101, CI Pigment Red 102, CI (1975) No. 77491, INS No. 172(ii), or inorganic red pigments containing at least 10 wt.% in \( \text{Fe}_2\text{O}_3 \) as hematite.

Iron oxide red pigment has advantages over organic red pigments. It can be produced by cost-effective preparation processes, it is environmentally friendly, stable to light, and readily dispersible, and is not altered by UV radiation.

Advantageously, the use of the iron oxide red pigment provides to the ink a higher stability against the action of solar radiation than the one of inks formulated with organic pigments.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the iron oxide red pigment is in an amount from 10 to 60 wt.%, particularly from 10 to 50 wt.%, more particularly from 15 to 30 wt.% based on the total weight of the inkjet ink.
In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the solvent is selected from the group consisting of; an ester derived from a fatty acid, a benzoic acid, a polycarboxylic acid, or a hydroxyl containing acid; a glycol ester, a glycol ether ester, a fatty alcohol, and mixtures thereof.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the ester is selected from the group consisting of fatty acid, benzoic acid, polycarboxylic acid, and hydroxyl containing acid esters. Examples of suitable fatty acids include hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic (lauric) acid, tridecanoic acid, tetradecanoic (myristic) acid, pentadecanoic acid, hexadecanoic (palmitic) acid, heptadecanoic acid, octadecanoic (stearic) acid, nonadecanoic acid, eicosanoic acid, oleic acid, linoleic acid, linolenic acid, and erucic acid. Examples of suitable polycarboxylic acids include succinic acid, glutaric acid, maleic acid, phthalic acid. Examples of suitable hydroxyl-containing acids include tartaric acid, tartronic acid, lactic acid, citric acid, mucic acid, malic acid, hydroxy-butryric acid and glycolic acid.

Examples of the alcohol forming the ester include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, 2-ethylhexyl, caprylyl, nonyl, capryl, undecyl, lauryl, tridecyl, isodecyl, myristyl, cetyl-alcohol, stearyl, oleil (unsaturated), and arachidyl alcohols, and a C12-Guerbet alcohol, a C14-Guerbet alcohol, a C16-Guerbet alcohol, a C18-Guerbet alcohol, and a C20-Guerbet alcohol.

Examples of polyalcohols forming the ester include ethylene glycol, propylene glycol, glycerol, neopentyl glycol (NP), trimethylolpropane (TMP), pentaeritritol (PE), sorbitol, xylitol, erythitol, galactitol, and mannitol.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the glycol ester is selected from the group including, without being limited to, propylene glycol diacetate, propylene glycol octoate, and mixtures thereof.

In a particular embodiment, optionally in combination with one or more
features of the particular embodiments defined above or below, the glycol ether ester is selected from the group including, without being limited to, diethylene glycol n-butyl ether acetate, dipropylene glycol methyl ether acetate, and mixtures thereof.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the fatty alcohol is selected from the group consisting of $C_8$-$C_{24}$, particularly $C_{10}$-$C_{22}$, fatty alcohols, such as decanol, dodecanol, tetradecanol, pentadecanol, hexadecanol, octadecanol, lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, oleyl alcohol, and mixtures thereof.

The solvent exhibits a low polarity. Particularly, the solvent has a solubility in water equal or lower than 10 g/100 ml H$_2$O at room temperature. The term "room temperature" refers to about 20°-25° C.

By the use of a low polarity solvent an improved behaviour in the print head is achieved. Thus, solvent based inkjet inks of the invention are water free. Particularly, problems derived from the incorporation of water in the printheads are avoided, thus the operation of the printheads is more reliable as they provide a higher printing quality and have a longer life.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the solvent is in an amount from 25 to 90 wt.%, particularly from 40 to 75 wt.%, based on the total weight of the inkjet ink.

The ink of the invention can further comprise other solid components such as an additional inorganic pigment, an inorganic filler, and mixtures thereof.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the ink of the invention comprises a further inorganic pigment in order to modify the chromaticity coordinates of the ink.

Examples of additional inorganic pigments include yttrium oxide and alumina (n° EINECS 234-443-8); cobalt orthophosphate (n° EINECS 236-655-6);
manganese oxide-alumina (n° EINECS 269-061-0); chrome tin pink sphene (n° EINECS 269-073-6); chrome alumina pink corundum (n° EINECS 269-083-0); chrome alumina pink spinel (n° EINECS 269-230-9); zirconium iron pink zircon (n° EINECS 270-210-7); chrome tin orchid cassiterite (n° EINECS 269-104-3), antimony nickel-titanium oxide yellow (n° EINECS 232-353-3); pyrochlore, antimony lead yellow (n° EINECS 232-382-1); chromium antimony titanate (n° EINECS 269-052-1); chromium tungsten titanate (n° EINECS 269-054-2); tin-vanadium yellow cassiterite (n° EINECS 269-055-8); vanadium zirconium yellow baddeleyite (n° EINECS 269-063-1); zirconium praseodymium silicate (n° EINECS 269-075-7); manganese-antimony titanate (n° EINECS 270-185-2); chromium-niobium titanate (n° EINECS 271-891-3); nickel-niobium titanate (n° EINECS 271-892-9); zirconium-cadmium silicate (n° EINECS 277-135-9); antimonium titanate (n° EINECS 305-908-3); silicic acid zirconium salt cadmium pigment-encapsulated (n° EINECS 310-077-5); iron hydroxide oxide yellow (n° EINECS 257-098-5), and mixtures thereof. Particularly, the amount of the further inorganic pigment is from 0.5 to 25 wt.%, more particularly from 1 to 15 wt.%, based on the total weight of the ink.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the inkjet ink further comprises an inorganic filler. Particularly, the inorganic filler is selected from the group consisting of titanium dioxide, zirconium silicate, zirconium oxide, tin oxide, cerium oxide, zinc oxide, aluminum oxide, silica, kaolin, calcium carbonate, magnesium carbonate, calcium magnesium carbonate, barium carbonate, sodium feldspar, potassium feldspar, nepheline, calcium silicate, mullite, wollastonite, and talc. Particularly, the amount of the inorganic filler is from 0.5 to 25 wt.%, more particularly from 1 to 20 wt.%, based on the total weight of the ink.

Advantageously, by the use of the filler the opacity of the ink is increased and thus the performance of the decorative colour coating is improved, while allowing reducing the percentage of organic components, such as the solvents.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the inkjet ink further comprises a rheological modifier. Particularly, the rheological modifier
is selected from high molecular weight polyamides such as Crayvallac Extra (Total), polyesters such as Thixatrol UV 1104 (Elementis Especialities), poly(ester-amides) such as Sylvaclear C75V (Arizona Chemicals), hydrocarbon based polymers such as Oppanol B200 (Basf), trihydroxystearin, organo-clays such as steralkonium hectorite, organo-silicas such as treated fumed silica with polysiloxanes, organically modified montmorillonite, organically modified aluminium-magnesium silicate, natural polysaccharides or derivatives thereof such as carboxymethyl cellulose, and stearate salts. In a more particular embodiment, the rheological modifier is a stearate salt selected from the group consisting of lithium, aluminium, calcium, ammonium, magnesium, potassium, sodium, and zinc stearate. Particularly, the amount of the rheological modifier is from 0.1 to 5 wt.%, more particularly from 0.2 to 2.5 wt.%, based on the total weight of the ink.

Other examples of natural polysaccharides or derivatives thereof are alginic acid, pectin, xanthan gum, hyaluronic acid, chondroitin sulfate, a natural gum or a derivative thereof such as arabic gum, guar gum, cationic guar gum, and karaya gum, chitosan or a derivative thereof such as carboxymethylchitosan, and N-hydroxy-dicarboxyethyl-chitosan, cellulose or a derivative thereof such as cellulose gum, cationic hydroxyethylcellulose, a cellulose ether, and cetyl hydroxyethylcellulose, starch, modified potato starch, dextrins and cyclodextrins.

Advantageously, the rheological modifier allows reducing sedimentation and easies the redispersion by shaking or stirring. Particularly, in case of sedimentation, the redispersed ink is able to pass through a sieve of 1.5 μm without leaving any residue, this indicating that the dispersion is suitable to be used in inkjet printers fitted with 30 μm nozzle printheads.

Particles in inkjet inks must be small enough to permit free flow of the ink through the inkjet-printing device, to get maximum colour strength, and to reduce sedimentation.

In a particular embodiment of the ink of the invention, particles of solid components comprised in the ink, namely the iron oxide red pigment and, optionally, the additional inorganic pigment, the inorganic filler, or a combination thereof, have a particle size distribution wherein D₉₀ is equal to
or lower than 0.9 µm, particularly from 0.25 to 0.60 µm, more particularly, from 0.25 to 0.45. Particularly, the ink of the invention is able to pass through a sieve with a 1 µm mesh without leaving any residue.

For particle size distributions, using a volume base calculation, \( D_{50} \) is the median value, namely the particle size diameter that splits the distribution with half above and half below this diameter. \( D_{90} \) describes the diameter where ninety percent of the distribution has a smaller particle size and ten percent has a larger particle size.

Particle size can be determined, for example, by laser light scattering using a particle size analyser, such as the Mastersizer™ apparatus available from Malvern Instruments Ltd. In the case of the ink composition of the present invention, particle size was determined introducing 3 drops of dispersion in 100 ml of isopropyl laurate. Afterwards the sample was manually homogeneized and measured.

The ink of the invention can further comprise other additives usually used in the preparation of inks such as dispersants, surfactants, anti-foaming, buffer for pH control, bactericides, fungicides, and preservatives. The appropriate additives and their amounts can readily be determined by those skilled in the art. Usually, the amount of these other additives in the ink is from 0.05 to 20 wt.%, particularly from 2 to 15 wt.%, based on the total weight of the inkjet ink.

Apart from providing optimum rheological behaviour of the ink, the rheological modifier, optionally together with at least one of the additional additives mentioned above, allows reaching a high solid content with low viscosities, as well as preventing degradation of the ink over time.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the at least one additive is a dispersant.

Suitable dispersants include propilen oxide (PO) homo-polymer, ethylene oxyde (EO)/PO random co-polymer, EO/PO block co-polymer, phosphate ester, alkyl ammonium salt of copolymer with acidic groups, alkanol ammonium salt of polycarboxylic acid, polyamine amide and acidic polyester
The obtained dispersions have a physicochemical stability suitable to be used in an inkjet printer. Thus, there is no significant variation in viscosity or in density over time. The variation in density and viscosity over a period of 1 month must be lower than 8% and 4 cP respectively. Additionally, sedimentation is negligible not affecting the later use of the inks.

Process for the preparation of an inkjet ink

As commented above, the invention also relates to a process for the preparation of the inkjet ink as defined above, the process comprising a) mixing the components of the ink; b) adding at least one dispersant and submitting the mixture to a grinding process, a dispersion process, or a mixture thereof, until obtaining a homogeneous suspension with a viscosity
from 10 to 200 cP at 40 °C; c) diluting the suspension with a solvent or mixture of solvents; and d) filtrating the suspension.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, in step b) of the process above the mixture is submitted to a grinding process until obtaining a homogeneous suspension having particles with a maximum particle diameter of less than 0.9 µm.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the inkjet ink has a viscosity from 4 to 40 cP at 40 °C, and a solid content from 10 to 60 wt.% with respect to the weight of the overall composition.

The colour inkjet ink can be prepared as follows. First, the different components are mixed using a suitable dispersing system, such as a ball mill, basket mill, or a stirrer, until obtaining a homogeneous mixture. Then, the mixture is submitted to a grinding and/or dispersion process, in order to achieve a homogeneous suspension, particularly having a viscosity from 10 to 200 cP (at 40 °C) and, more particularly, having particles with the specified particle sizes. The grinding and/or dispersion process can be carried out with a microball mill, such as a Netzsch mill, LabStar type, with yttrium or cerium doped ZrO₂ microspheres from 0.2 to 5 mm in diameter and with a load from 50% to 98% of the volume of the grinding chamber. During the grinding and/or dispersion process viscosity controls, for instance with a rotational viscometer such as Brookfield LVDV, and particle size distribution measures, for instance particle analysis by laser diffraction with a Malvern Mastersizer 2000, can be performed. Subsequently, filtration of the concentrate through filter media such as fiberglass or polypropylene of different pore sizes, and dilution with one or more solvents is carried out to obtain the final ink with the required rheological behaviour. Particularly, the obtained colour inkjet ink has a viscosity from 4 to 40 cP (at 40 °C) and a solid content from 10 to 60 wt.%.

Preparation of a constructive element

As commented above, the inkjet ink of the invention can be used for the decoration of constructive elements without being submitted to a firing
process.

Advantageously, the use of the inkjet ink of the invention comprising iron oxide red pigment provides to the constructive element a decorative coating with a durability, when used outdoors, which is higher than that of constructive elements decorated with decorative coatings made of inks containing organic pigments.

The inkjet ink of the invention can be applied on a support material by digital printing, particularly by inkjet printing. Then, a protective polymeric coating comprising a polymer curable at a temperature up to 300 °C and, optionally, a solvent, can be applied on the printed support material in order to fix the ink to the support at the same time that providing protection to both the support and the ink.

Support material

There is no limitation on the type of support material. The support material may be a porous support material such as wood, fibre cement, concrete, ceramic, gypsum, and gypsum board (such as Pladur®).

In a particular embodiment of the constructive element of the invention, optionally in combination with one or more features of the particular embodiments defined above or below, the support material is porous.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the support material is a modular element in the form of a plate or a board. In another particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the support material is selected from the group consisting of a wood strip, a strip of fibre cement, a brick, a concrete slab, and a concrete paver.

In another particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the support material has a porosity greater than 1 vol.% measured by mercury porosimetry (cf. Giesche, H. "Mercury porosimetry: a general (practical)
In another particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the constructive element of the invention further comprises a primer undercoating between the support material and the decorative coating.

Primer composition

The aim of the primer is to obtain a better colour gamut development, facilitate adhesion of the decorative layer and of the protective layer, hide the substrate colour, improve the smoothness of the surface (reducing variability), enhance porosity, and/or increase the wettability of the ink so that the solvent in the ink drains correctly (avoiding the defect known as "lack of drying").

For the purpose or the invention, any primer composition known in the art can be used. As an example, the primer can comprise a polyurethane as a primary binder resin, a neutralizing agent such as an amine and, optionally, a third component such as an epoxy or an acrylic resin. Primer compositions are commercially available, such as the polyester/acyrylic primer composition from BASF Corporation as Smoke U28AW031. The primer composition can further comprise a crosslinking agent, opacifying agents (fillers), and a solvent system.

In a particular embodiment, the amount of crosslinking agent is from 0.1 to 10 wt.%, particularly from 3 to 7 wt.%, more particularly of a 5 wt.%. The crosslinking agent interacts with the protective polymeric coating improving the adhesiveness of the coating.

Examples of crosslinking agents include, without being limited to, poly(hexamethylene-diisocyanate), m-tolylidene diisocyanate, hexamethylene diisocyanate, ethylene diisocyanate, 1,2-diisocyanatopropane, 1,3-diisocyanatopropane, 1,4-butylene diisocyanate, lysine diisocyanate, 2,4-toluene diisocyanate diphenylmethane, 2,6-toluene diisocyanate diphenylmethane, 4,4'-diisocyanate; 1,6-hexamethylene diisocyanate, p-phenylene diisocyanate; tetramethyl xylene diisocyanate, and m-xylene
diisocyanate.

The primer affords good adhesion to the surface to be decorated and/or coated, particularly to the protective coating and/or to the inkjet ink.

The primer composition can be applied by conventional methods such as by spraying or roller coating.

In a particular embodiment of the constructive element of the invention, optionally in combination with one or more features of the particular embodiments defined above or below, the primer undercoating comprises at least one opacifying agent. The presence of the opacifying agent has the advantage that whiteness is increased and thus the performance of the decorative colour coating is improved.

In another particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the opacifying agent is selected from calcium carbonate (CaCO$_3$), aluminium oxide (Al$_2$O$_3$) and titanium dioxide (TiO$_2$). Particularly, the opacifying agent is TiO$_2$.

**Inkjet Printing Method**

The colour inkjet ink of the invention can be applied on a support material by digital printing such as inkjet printing. Digital printing refers to methods of printing from a digital-based image directly to a variety of media. The inkjet printing method includes the steps of: a) feeding an inkjet printhead with a colour inkjet ink comprising an inorganic pigment and at least one solvent; and b) jetting the colour inkjet ink with the inkjet printhead on a support material, optionally undercoated with a primer.

The invention also relates to a process for the preparation of the constructive element of the invention by applying the colour inkjet ink as defined above by digital printing onto a support, and subsequently applying a topcoating comprising a curable polymer and, optionally, a solvent, to form a protective polymeric coating that cures at a temperature of up to 300 °C.

In a particular embodiment, optionally in combination with one or more
features of the particular embodiments defined above or below, the digital printing is made by inkjet printing. Particularly, inkjet printing is performed with a single-pass printer. Advantageously, the use of the single-pass inkjet printers allows reducing the cost of the process compared to current cost for the decoration of certain substrates such as fibre cement.

In a particular embodiment, the process of the invention further comprises an additional step of applying a primer composition on the substrate previously to the application of the colour inkjet ink.

Protective polymeric coating

The protective polymeric coating is formed with a composition comprising a curable polymer and, optionally, a solvent. Curing of the protective polymeric coating takes place in the absence of any firing process, namely at a temperature of up to 300 °C. The solvent of the coating composition can be removed by volatilization during the curing process.

The protective polymeric coating allows fixing the inorganic ink to the porous support material. Additionally, it provides protection of the ink and of the constructive element as a whole by providing wear resistance and hardness. Thus, depending on the specific components, the polymeric coating can provide protection against several factors such as surface abrasion, scratch, and chemical attack. Additionally, it can provide the sought final appearance of the product, including for example a matte, bright or satin finish. Properties of the protective coating can be adjusted depending on the final application of the constructive element (indoor or outdoor siding or flooring, level of pedestrian traffic).

The protective polymeric coating has an appropriate adhesiveness with all of the substrate and/or the primer if present. In a particular embodiment, the protective polymeric coating exhibits adhesiveness from 0 to 3, particularly from 0 to 2, according to the adhesion measurement test defined in UNE-EN ISO 2409. This standard classifies the level of adhesion on five categories, being category 0 the best result.

In a particular embodiment of the constructive element of the invention,
optionally in combination with one or more features of the particular embodiments defined above or below, the polymeric coating is UV curable. Thus, once applied, the coating composition can be cured by UV radiation as is known to those skilled in the art. In this regard, the irradiation is applied until complete curing of the coating.

Example of a suitable curable protective coating compositions are such as the ones disclosed in US4393187 (Example, line 55, column 9, to line 9, column 11) and US5571570 (line 64, column 2, to line 28, column 5).

As an instance the coating composition comprises: (a) 35% to 65% by weight of a first acrylate aliphatic urethane having a molecular weight of 500 to 2000 and formed by the reaction of (i) a first multifunctional acrylate with a molecular weight of 190 to 500 and containing at least three polymerizable unsaturated groups per molecule, with (ii) an aliphatic urethane based on a polymer of allyl carbomonocycle diisocyanate with alkanepolyol polyacrylates; (b) 5% to 25% by weight of a second acrylated aliphatic urethane having a molecular weight of 1200 to 2600 and formed by the reaction of a second multifunctional acrylate with a molecular weight of 110 to 500 with an aliphatic urethane based on a polyether and having a molecular weight of 800 to 2200; (c) 10% to 55% by weight of a third multifunctional acrylate having a molecular weight of between 170 and 1000 and containing at least two polymerizable unsaturated groups per molecule; and (d) a photopolymerization initiator or sensitizer.

As stated above, the coating composition can also comprise a suitable solvent. Examples of such solvents include, without being limited to, ester solvents, such as ethyl acetate and butyl acetate, ketone solvents such as acetone, methylisobutylketone, and methylethyl ketone; alcohols such as butyl alcohol; and aromatic solvents such as toluene and xylene. The amount of solvent included will vary in accordance with the particular application at hand. Particularly, the amount of solvent is from 0% to 95%, more particularly from 40% to 60%, by weight of the entire coating composition.

In a particular embodiment, optionally in combination with one or more features of the particular embodiments defined above or below, the constructive element of the invention comprises additional coating layers
each one conferring a specific property such as hardness, gloss, wear resistance, self-cleaning, or bactericidal.

The coating composition can be applied by any conventional coating method known in the art such as curtain coating, roller coating, and spraying.

Throughout the description and claims the word "comprise" and variations of the word, are not intended to exclude other technical features, additives, components, or steps. Furthermore, the word "comprise" encompasses the case of "consisting of.

The following examples are provided by way of illustration, and they are not intended to be limiting of the present invention. Furthermore, the present invention covers all possible combinations of particular and preferred embodiments described herein.

EXAMPLES

Example 1 - Preparation of an iron oxide red pigment ink

A red ink with the following composition was prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>wt.%</th>
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</thead>
<tbody>
<tr>
<td>Iron oxide (C.I. Red pigment 101)</td>
<td>15</td>
</tr>
<tr>
<td>DISPERPLAST 1150 (BYK)</td>
<td>5</td>
</tr>
<tr>
<td>MASSOCARE PHS (MASSÓ)</td>
<td>10</td>
</tr>
<tr>
<td>2-ethylhexyl stearate</td>
<td>70</td>
</tr>
</tbody>
</table>

First, all components except half of the 2-ethylhexyl stearate used in the final composition were mixed, dispersed and ground, in order to achieve a homogeneous suspension having a particle size distribution with a D90 less than 0.9 µm in diameter. The grinding process was carried out with a microball mill (Netzsch LabStar) containing 1 mm yttrium doped ZrO2 beads. During the grinding process particle size distribution was monitored using the laser diffraction technique (Malvern Mastersizer 2000). To carry out the measurement 3 drops of dispersion were added to 100 ml of isopropyl laurate).
Subsequently, the suspension was diluted using the remaining 2-ethylhexyl stearate to obtain the final ink with the required rheological behaviour, particularly viscosity was 15 cP (Brookfiled LVDV) and content solid was 15 wt.%. The ink was finally filtered through a polypropylene 1.5 μm filter media.

Example 2 - Preparation of an iron oxide red pigment ink

A red ink with the following composition was prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide (C.I. Red pigment 101)</td>
<td>15</td>
</tr>
<tr>
<td>DISPERPLAST 1150 (BYK)</td>
<td>5</td>
</tr>
<tr>
<td>Isopropyl laurate</td>
<td>21.5</td>
</tr>
<tr>
<td>2-ethylhexyl palmitate</td>
<td>21.5</td>
</tr>
<tr>
<td>2-ethylhexyl stearate</td>
<td>12</td>
</tr>
<tr>
<td>Exxsol D140</td>
<td>9</td>
</tr>
<tr>
<td>2-Hexyldodecan-1-ol</td>
<td>10</td>
</tr>
</tbody>
</table>

First, all components except isopropyl laurate were mixed, dispersed and ground, in order to achieve a homogeneous suspension having viscosity of 150 cP and a particle size distribution with a D₉₀ less than 0.9 μm in diameter. The grinding process was carried out with a microball mill (Netzsch LabStar) containing 1 mm yttrium doped ZrO₂ beads. During the grinding process particle size distribution was monitored using the laser diffraction technique (Malvern Mastersizer 2000). To carry out the measurement 3 drops of dispersion were added to 100 ml of isopropyl laurate.

Subsequently, the suspension was diluted using isopropyl laurate to obtain the final ink with the required rheological behaviour, particularly viscosity was 25 cP (Brookfiled LVDV) and content solid was 15 wt.%. The ink was finally filtered through a polypropylene 1.5 μm filter media.

Example 3 - Preparation of an iron oxide red pigment ink

A red ink with the following composition was prepared:
First, all components except isopropyl laurate were mixed, dispersed and ground, in order to achieve a homogeneous suspension having a particle size distribution with a D_{90} less than 0.9 µm in diameter. The grinding process was carried out with a microball mill (Netzsch LabStar) containing 1 mm yttrium doped ZrO₂ beads. During the grinding process particle size distribution was monitored using the laser diffraction technique (Malvern Mastersizer 2000).

To carry out the measurement 3 drops of dispersion were added to 100 ml of isopropyl laurate).

Subsequently, the suspension was diluted using isopropyl laurate to obtain the final ink with the required rheological behaviour, particularly viscosity was 27 cP (Brookfield LVDV) and content solid was 20 wt.%. The ink was finally filtered through a polypropylene 1.5 µm filter media.

Example 4 - Preparation of an iron oxide red pigment ink with additional pigment

A red ink with the following composition was prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide (C.I. Red pigment 101)</td>
<td>20</td>
</tr>
<tr>
<td>MASSOCARE PHS (MASS0)</td>
<td>10</td>
</tr>
<tr>
<td>TEGO DISPERS 656 (EVONIK)</td>
<td>5</td>
</tr>
<tr>
<td>Isopropyl laurate</td>
<td>24.7</td>
</tr>
<tr>
<td>Gliceryl tricaprate/tricaprylate</td>
<td>23</td>
</tr>
<tr>
<td>Exxsol D140</td>
<td>9</td>
</tr>
<tr>
<td>2-Hexyldecan-1 -ol</td>
<td>5.3</td>
</tr>
</tbody>
</table>
First, all components except isopropyl laurate were mixed, dispersed and ground, in order to achieve a homogeneous suspension having a particle size distribution with a $D_{90}$ less than 0.9 $\mu\text{m}$ in diameter. The grinding process was carried out with a microball mill (Netzsch LabStar) containing 1 mm yttrium doped ZrO$_2$ beads. During the grinding process particle size distribution was monitored using the laser diffraction technique (Malvern Mastersizer 2000). To carry out the measurement 3 drops of dispersion were added to 100 ml of isopropyl laurate.

Subsequently, the suspension was diluted using isopropyl laurate to obtain the final ink with the required rheological behaviour, particularly viscosity was 24 cP (Brookfiled LVDV) and content solid was 30 wt.%. The ink was finally filtered through a polypropylene 1.5 $\mu\text{m}$ filter media.

**Example 5 - Preparation of an iron oxide red pigment ink with filler**

A red ink with the following composition was prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide (C.I. Red pigment 101)</td>
<td>20</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>10</td>
</tr>
<tr>
<td>MASSOCARE PHS (MASSÓ)</td>
<td>9.5</td>
</tr>
<tr>
<td>SOLDOC PG-280 (IQL)</td>
<td>5</td>
</tr>
<tr>
<td>Pentaerythrityl tetraisostearate</td>
<td>10</td>
</tr>
<tr>
<td>Triethylene glycol-di-(2-ethylhexanoate)</td>
<td>7.5</td>
</tr>
<tr>
<td>Nytex 8120</td>
<td>27.5</td>
</tr>
<tr>
<td>2-Octyldodecan-1-ol</td>
<td>10.5</td>
</tr>
</tbody>
</table>

First, all components except Nytex 8120 were mixed, dispersed and ground, in order to achieve a homogeneous suspension having a particle size distribution with a $D_{90}$ less than 0.9 $\mu\text{m}$ in diameter. The grinding process was carried out with a microball mill (Netzsch LabStar) containing 1 mm yttrium doped ZrO$_2$ beads. During the grinding process particle size distribution was monitored using the laser diffraction technique (Malvern Mastersizer 2000). To carry out the measurement 3 drops of dispersion were added to 100 ml of
isopropyl laurate).

Subsequently, the suspension was diluted using Nytex 8120 to obtain the final ink with the required rheological behaviour, particularly viscosity was 26 cP (Brookfiled LVDV) and content solid was 30 wt.%. The ink was finally filtered through a polypropylene 1.5 μm filter media.

Example 6 - Preparation of an iron oxide red pigment ink

A red ink with the following composition was prepared:

<table>
<thead>
<tr>
<th>Component</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron oxide (C.I. Red pigment 101)</td>
<td>20</td>
</tr>
<tr>
<td>Pyrogenic (Fumed) Amorphous Silica</td>
<td>1</td>
</tr>
<tr>
<td>DISPERPLAST 1150 (BYK)</td>
<td>12.5</td>
</tr>
<tr>
<td>Isopropyl laurate</td>
<td>49.5</td>
</tr>
<tr>
<td>Gliceryl tricaprate/tricaprylate</td>
<td>5</td>
</tr>
<tr>
<td>Triethylenglycol-di-(2-ethylhexanoate)</td>
<td>3</td>
</tr>
<tr>
<td>Exxsol D140</td>
<td>9</td>
</tr>
</tbody>
</table>

First, all components except half of the isopropyl laurate used in the final composition were mixed, dispersed and ground, in order to achieve a homogeneous suspension having a particle size distribution with a D₉₀ less than 0.9 μm in diameter. The grinding process was carried out with a microball mill (Netzsch LabStar) containing 1 mm yttrium doped ZrO₂ beads. During the grinding process particle size distribution was monitored using the laser diffraction technique (Malvern Mastersizer 2000). To carry out the measurement 3 drops of dispersion were added to 100 ml of isopropyl laurate).

Subsequently, the suspension was diluted using the remaining isopropyl laurate to obtain the final ink with the required rheological behaviour, particularly viscosity was 25 cP (Brookfiled LVDV) and content solid was 21 wt.%. The ink was finally filtered through a polypropylene 1.5 μm filter media.

Example 7 - Preparation of a decorated fibre cement constructive element
A low density fibre cement plate (1200-1500 kg/m$^3$) of 1.2 m wide, 2.4 m long and 6 mm thick, manufactured by the Hatschek process, was decorated in the following way.

First, a primer (Bona Prime Classic, a waterborne one-component acrylate dispersion commercialized by Bona) was sprayed onto the fibre cement plate by airless spraying in order to form a uniform layer providing whiteness to the surface and with the aim of promoting adhesion of the subsequent layers.

Then, the decorative layer was applied by inkjet printing. Digital printing was performed with a single-pass printer with DOD (Drop on Demand) piezoelectric printheads. Four different inks were used to obtain a decorative layer which imitates wood, particularly blue ink (CIS-BU4301 from Esmalglass-itaca group), red ink (Example 2), yellow ink (CIS-YE5308 from Esmalglass-itaca group), and black ink (CIS-BK6304 from Esmalglass-itaca group).

Subsequently, 30 g/m$^2$ of a protective coating consisting of a 100% solids UV curable resin (Uvinol 850, a solvent-free, UV-curing, clear epoxy acrylate sealer and topcoat commercialized by Tikkurila Coatings) was applied by roller coating over the decorative layer. An applicator roller having a roll 238 mm in diameter coated with 40 shores hardness ethylene propylene diene monomer (EPDM) was used. Once applied onto the decorative layer, the protective coating was cured by action of ultraviolet light with two mercury lamps 120 W each.
CLAIMS

1. An inkjet ink comprising:
   - an iron oxide based red pigment;
   - a solvent having a boiling point equal to or higher than 200 °C selected from the group consisting of an ester, a glycol ester, a glycol ether ester, a fatty alcohol, and mixtures thereof,
   - at least one dispersant.

2. The ink according to claim 1, wherein the ester is selected from the group consisting of fatty acid, benzoic acid, polycarboxylic acid, and hydroxyl containing acid esters.

3. The ink according to any one of claims 1 or 2, wherein the solvent has a solubility in water equal or lower than 10 g/1 00 ml H₂O at room temperature.

4. The ink according to any one of claims 1 to 3, wherein the iron oxide red pigment is in an amount from 10 to 60 wt.%, particularly from 10 to 50 wt.%, more particularly from 15 to 30 wt.% based on the total weight of the inkjet ink.

5. The ink according to any one of claims 1 to 4, wherein the solvent is in an amount from 25 to 90 wt.%, particularly from 40 to 75 wt.%, based on the total weight of the inkjet ink.

6. The ink according to any one of claims 1 to 5, further comprising another inorganic pigment in an amount from 0.5 to 25 wt.%, more particularly from 1 to 15 wt.%, based on the total weight of the ink.

7. The ink according to any one of claims 1 to 6, further comprising an inorganic filler in an amount from 0.5 to 25 wt.%, more particularly from 1 to 20 wt.%, based on the total weight of the ink.

8. The ink according to claim 7, wherein the inorganic filler is selected from the group consisting of titanium dioxide, zirconium silicate, zirconium oxide, tin oxide, cerium oxide, zinc oxide, aluminium oxide, silica, kaolin, calcium
carbonate, magnesium carbonate, calcium magnesium carbonate, barium carbonate, sodium feldspar, potassium feldspar, nepheline, calcium silicate, and talc.

9. The ink according to any one of claims 1 to 8, further comprising a rheological modifier in an amount from 0.1 to 5 wt.%, more particularly from 0.2 to 2.5 wt.%, based on the total weight of the ink.

10. The ink according to claim 9, wherein the rheological modifier is selected from:
   - a high molecular weight polyamide, a polyester, a poly(ester-amide), and a hydrocarbon based polymer,
   - trihydroxystearin,
   - an organo-clay, an organo-silica, organically modified montmorillonite, organically modified aluminium-magnesium silicate,
   - a natural polysaccharide or a derivative thereof; and
   - a stearate salt.

11. The ink according to claim 10, wherein the rheological modifier is a stearate salt selected from the group consisting of lithium, aluminium, calcium, ammonium, magnesium, potassium, sodium, and zinc stearate.

12. The ink according to any one of claims 1 to 11, wherein particles of solid components comprised in the ink, such as the iron oxide red pigment and, optionally, the inorganic filler, and the additional inorganic pigment, have a particle size distribution wherein \( D_{90} \) is lower than 0.9 \( \mu \text{m} \), particularly from 0.25 \( \mu \text{m} \) to 0.60 \( \mu \text{m} \), more particularly, from 0.25 to 0.45.

13. A process for the preparation of an inkjet ink as defined in any one of claims 1 to 12, the process comprising:
   a) mixing the components of the ink as defined in any one of claims 1 to 12;
   b) adding at least one dispersant and submitting the mixture to a grinding process or a dispersion process, or a mixture thereof, until obtaining a homogeneous suspension having a viscosity from 10 to 200 cP at 40 °C;
c) diluting the suspension with a solvent or mixture of solvents; and
d) filtering the suspension.

14. Use of an inkjet ink as defined in any one of claims 1 to 12, for the
decoration of a constructive element that will not be subsequently subjected
to a firing process.

15. A constructive element comprising:
   - a support material;
   - a decorative coating formed by the inkjet ink as defined in any one of
     claims 1 to 12; and
   - at least one protective cured polymeric coating formed with a
     composition curing at a temperature of up to 300 °C.
# INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

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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)

C09D

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

<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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* Further documents are listed in the continuation of Box C.

**Date of the actual completion of the international search**

21 December 2016

**Date of mailing of the international search report**

05/01/2017

**Name and mailing address of the ISA/Authorized officer**

European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Feldmann, Gabriele
<table>
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