(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 562 144 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
27.02.2013 Bulletin 2013/09

(51) Int Cl.:
C03C 3/097 *(2006.01)* ***C03C 8/08*** *(2006.01)*
C04B 41/52 *(2006.01)* ***C04B 41/89*** *(2006.01)*

(21) Application number: **12005662.7**

(22) Date of filing: **03.08.2012**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **22.08.2011 ES 201131405**

(71) Applicant: **Sociedad Anónima Minera Catalano-Aragonesa**
50001 Zaragoza (ES)

(72) Inventors:
- **Caballero López, Miguel Angel**
  50001 Zaragoza
  (ES)
- **Pérez Aparicio, Joaquin Javier**
  50001 Zaragoza
  (ES)
- **Navarrp Soriano, Elena**
  50001 Zaragoza
  (ES)

(74) Representative: **Schäfer, Matthias W.**
Schwanseestraße 43
81549 München (DE)

(54) Procedure for obtaining a metallic effect on ceramic bases by ink injection

(57) Procedure for obtaining a metallic effect on ceramic bases by injection, in which the known ceramic glaze formulation to obtain metallised finishes is broken down into two separate compounds: on the one hand, a glaze with part of the oxides needed to obtain the metallic effect, which is applied in the conventional manner on the ceramic base and, on the other hand, a metallic ink with the other necessary part of the oxides, which is applied by ink injection over the previous layer, finishing off with a firing process.

This procedure affords the advantage of enabling ink injection machines to be used to create the metallised effect, with the consequent savings on process time, improvement in productivity and reduction in the economic cost of its manufacture.

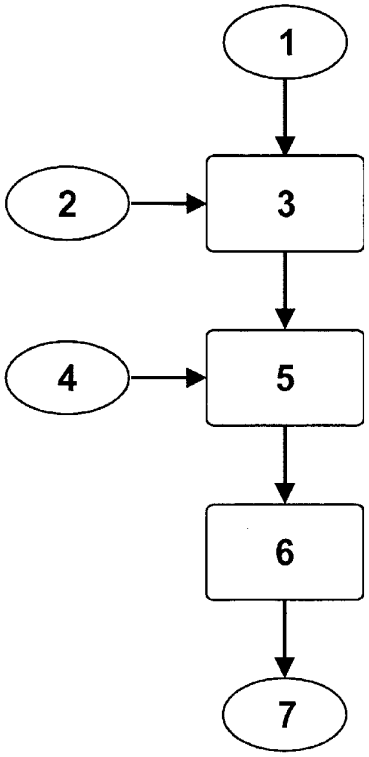

Fig. 1

EP 2 562 144 A2

Description

[0001] The present description relates, as its title indicates, to a procedure for obtaining a metallic effect on ceramic bases by injection, in which the known ceramic glaze formulation to obtain metallised finishes is broken down into two separate components: on the one hand, a glaze with part of the oxides needed to obtain the metallic effect, applying it in the conventional manner on the ceramic base, and on the other, a metallic ink with the other necessary part of the oxides, applying it by ink injection over the previous layer, finishing off with a firing process. As a result a decorated ceramic tile with a metallic effect is obtained.

[0002] The technique for the digital printing of tiles using ink injection machines is increasingly widespread, this being a cost-effective system offering great flexibility of the process. It is commonly used to decorate ceramic tiles by applying ceramic pigments that give the tiles their colour once they have been fired.

[0003] There are descriptions of several related procedures, such as, for example, that of Patent ES 2131466 *"Automatic procedure for decorating ceramic substrates",* describing, in general terms, the use of an ink injection system in ceramics, that of Patent ES 2289916 *"Colloidal dispersion of ceramic pigments",* which presents, in a very general manner, the manufacture of inks to be applied by injection. These procedures and inks only produce different coloured finishes by injection, it not being possible to achieve a metallic finish.

[0004] Some advances have be made in the incorporation of metallic particles in inks for injection on ceramic materials, as described, for example, in Patent P201031196 *"Procedure for the production of a metallic suspension for printing ceramic elements",* that provides a technique for adding noble metals to inks to obtain a chromatic range with more intense colours, but it does not allow metallic finishes to be obtained.

[0005] Obtaining metallic finishes in ceramics is conventionally linked to the use of special, quite thick glazes, such as that described in patent P200401851 *"Metallic glaze composition",* which creates a metallised base of sufficient thickness, on to which the desired colour decoration can be subsequently applied. This procedure has the drawback that it is first necessary to cover the whole of the tile with the metallic glaze, and then cover it by decorating it with the desired colours, with the consequent waste of materials and resultant higher economic cost. Furthermore, these types of compositions require a great thickness in the metallised areas which makes these compositions unsuitable for injection. Indeed, the fact that a high minimum thickness is needed to obtain the metallic effect is incompatible with injection technology which can only achieve a very thin ink layer, with a maximum of 42 to 80 pL, which is insufficient to obtain a metallic effect.

[0006] Metallic effects are chiefly achieved by applying layers of glaze with a weight per area unit of between 0.3 and 0.5 Kg/m^2, either by waterfall application, airbrush or disc. An injection head enables the supply of a weight of approximately 0.022 Kg/m2 of applied solid, which is much less than that required, hence, a priori, it is not considered technically possible to obtain metallic effects on ceramic tiles by ink injection.

[0007] To solve the problems that currently exist in creating a metallic effect on tiles and other ceramic elements, improving the current state of the art by overcoming the technical problem of the ink thickness required, and in order to provide certain elements that facilitate and improve economic performance and efficacy, a procedure has been developed to obtain a metallic effect on ceramic bases by injection in which the known ceramic glaze formulation to obtain metallised finishes is broken down into two separate compounds:

- on the one hand, a glaze with part of the oxides needed to obtain the metallic effect, applying it in the conventional manner over the ceramic base, and on the other hand, a metallic ink with the other necessary part of the oxides, applying it by ink injection over the previous layer and finishing off with a firing process. As a result a decorated ceramic tile with a metallic effect is obtained.

[0008] This procedure affords multiple advantages over those currently available, the most important being that it permits the use of ink injection machines to create the metallic effect, with the consequent saving of process time, improvement in productivity and reduction in the economic cost of its manufacture.

[0009] Another important advantage of this procedure is that it enables considerable savings of the materials used in the manufacture given that, conventionally, the whole of the base was metallised and then covered with the decoration in the areas required, whilst with this procedure the metallised finish can be applied selectively, in a local manner, only to the areas in which it is necessary, thanks to the fact the same injection head that is used for the decoration is employed.

[0010] To gain a better understanding of the object of the present invention figure -1- of the attached drawing shows a simplified block diagram of the process of obtaining the metallic effect on ceramic bases by injection.

[0011] The procedure for obtaining the metallic effect on ceramic bases by injection, which is the object of the present invention, basically comprises, as can be observed in the drawing attached, the separate use of a glaze (2) with part of the oxides needed to obtain the metallic effect, including Si and Al, and a metallic ink (4) with the necessary part of the oxides, including Fe as the majority element.

[0012] This separate use is carried out by means of a first phase of application (3) of the glaze (2) on a ceramic base

(1), followed by a second phase of injection (5) of the metallic ink (4) on the layer previously deposited on the ceramic base (1), completed by a third phase of firing (6).

[0013] The application phase (3) of the glaze (2) on a ceramic base (1) is carried out by means of a process chosen from amongst the group of: bell, airbrush, rotary, disc or waterfall.

[0014] The injection phase (5) of the metallic ink (4) is preferably carried out using an injection head capable of providing a thickness of between 6 and 200 pL per drop.

[0015] The firing phase (6) is carried out by means of a normal ceramic cycle, from the traditional double firing at 900°C to high-temperature porcelain stoneware firing at 1300°C, with firing cycles of preferably between 0.5 and 24 h.

[0016] The metallic ink (4) is formulated by selecting only some of the oxides needed to obtain the metallic effect, since the technique of injection printing only allows a very light weight to be applied. Depending on the type of metallic ink (4) chosen, glaze formulations will be used that provide the rest of the oxides.

A - In a preferred embodiment of the invention, the metallic ink (4) is formed mainly by iron Fe inks in which an iron oxide raw material is used to provide the Fe in the metallic ink (4). This iron oxide raw material can be chosen from amongst iron salts or oxides, preferably haematite Fe_2O_3, black iron oxide FeO or magnetite Fe_3O_4. A particularly interesting use occurs when a ferrofluid is used as an ink, which is a suspension of nanoparticles of iron oxides of an average size of around 10 nm. The corresponding glaze (2) is formulated using, as essential elements, Si, Al, P and Li oxides to which other optional oxides of Na, K, Mg, Ca can be incorporated, according to the composition:

SiO_2	40 - 60%
Al_2O_3	10 - 30%
P_2O_5	10 - 30%
R_2O + RO	5 - 15%
ZrO_2 + TiO_2	0 - 10%
B_2O_3	0 - 10%

Where:

R_2O: Li_2O + Na_2O + K_2O
RO: MgO + CaO + SrO + BaO

B - In an alternative embodiment of the invention, the metallic ink (4) is formed mainly by Fe and P oxide pigment inks, as the main oxides, said oxides being within the ranges of:

P_2O_5	40 - 70%
Fe_2O_3	10 - 50%

Furthermore, the glaze is formulated using, as essential elements, Si, Al, and Li oxides to which other optional oxides of Na, K, Mg, Ca can be incorporated, according to the composition:

SiO_2	40 - 60%
Al_2O_3	10 - 30%
R_2O + RO	5 - 20%
ZrO_2 + TiO_2	0 - 10%
B_2O_3	0 - 10%

Where:

R_2O: Li_2O + Na_2O + K_2O
RO: MgO + CaO + SrO + BaO

C - In a second alternative embodiment of the invention, the metallic ink (4) is formed mainly by Fe, P and Li oxide pigment inks, as essential elements, according to the composition:

P_2O_5	40 - 70%
Fe_2O_3	10 - 50%

(continued)

Li_2O	0 - 30%

The glaze, for its part, is formulated using Si and Al oxides as essential elements, to which other optional oxides of Li, Na, K, Mg, Ca, can be incorporated, according to the composition

SiO_2	40 - 60%
Al_2O_3	10 - 30%
R_2O + RO	5 - 30%
ZrO_2 + TiO_2	0 - 10%
B_2O_3	0 - 10%

Where:

R_2O: Li_2O + Na_2O + K_2O
RO: MgO + CaO + SrO + BaO

[0017] These possible combinations of metallic ink (4) and glaze (2) can be summarised in the following table:

OPTION	METALLIC INK (4)	GLAZE (2)
A	Fe compounds (oxides or salts)	Glazing of essential P - Si - Al - Li oxides
B	Fe- P oxide pigment	Glazing of essential Si -
		Al - Li oxides
C	Fe - P - Li oxide pigment	Glazing of essential Si - Al oxides

[0018] As a result a ceramic tile is obtained with a metallic effect decoration that can be measured using colorimetric techniques such as goniospectrophotometry.

[0019] Given that the special ceramic glaze (2), due to its composition and in itself, is white and can have a matt or gloss finish, other decorating techniques can be incorporated to improve the final finish of the piece, such as pigmented inks or by colouring the glaze (2) with ceramic pigments, without interfering in the reaction that occurs between the glaze (2) and the overlaid metallic ink (4) that produces the metallic effect. Furthermore, depending on the type of metallic ink (4) and glaze (2) used, the metallic effect finishes can be matt or gloss.

[0020] As an example of the application of this procedure, by way of an experiment, a water suspension of a glaze was prepared, in line with the following composition:

SiO_2	54.4%
ZrO_2	3.3%
P_2O_5	16.1%
Al_2O_3	19.1%
Li_2O	1.6%
Na_2O	2.7%
K_2O	0.9%
MgO	1.2%
CaO	0.2%

[0021] This suspension was used to glaze ceramic porcelain stoneware body tiles with a coating thickness of 300 g/m^2.

[0022] Two metallic inks were also prepared:

INK 1

Glycol-based carrier for inks:	60%
Micronized magnetite (Fe_3O_4):	40%

Once the magnetite had been dispersed in the glycol-based carrier, it was milled in a horizontal microball mill to obtain an ink suspension with a grain size with D_{99} heat of less than 700 nm.

INK 2

Ferrofluid with a concentration of 30% magnetite, with an average size of 10 nm dispersed in octane.

[0023] Finally these inks were used to decorate the glazed tiles, using a ceramic printer equipped with an XAAR1001 head, capable of printing drop sizes of between 6 y 42 pl.

[0024] Once the ceramic tiles had been decorated, they were fired at a temperature of 1200°C in a conventional ceramic roller kiln with a firing cycle of 60'.

[0025] As a result, in both cases, ceramic tiles were obtained in which a clear metallic effect could be observed with a drop size of 30 pl onwards.

Claims

1. Procedure for obtaining a metallic effect on ceramic bases by injection, of the type used in the manufacture of tiles and other ceramic items, **characterized in that** it uses, separately, a glaze (2) with part of the oxides needed to obtain the metallic effect, including Si and Al, and a metallic ink (4) with the other part of the oxides required, including Fe as the major element, carrying out a first phase of application (3) of the glaze (2) on a ceramic base (1), continuing with a second phase of injection (5) of the metallic ink (4) on the coat previously deposited on the ceramic base (1), finishing off with a third phase of firing (6).

2. Procedure for obtaining a metallic effect on ceramic bases by injection, according to claim 1, wherein the metallic ink (4) is formed mainly by Fe iron inks, in which a raw material of iron oxide is used, and the glaze (2) is formed mainly by Si, Al, P and Li, according to the range of compositions:

Composition of glaze (2)	
SiO_2	40 - 60%
Al_2O_3	10 - 30%
P_2O_5	10 - 30%
R_2O + RO	5 - 15%
$ZrO_2 + TiO_2$	0 - 10%
B_2O_3	0 - 10%

Where:

R_2O: $Li_2O + Na_2O + K_2O$
RO: MgO + CaO + SrO + BaO

3. Procedure for obtaining a metallic effect on ceramic bases by injection, according to claim 2, wherein the raw material of iron oxide, which is used mainly to provide the Fe in the metallic ink (4), is selected from the group: haematite Fe_2O_3, black iron oxide FeO, magnetite Fe_3O_4.

4. Procedure for obtaining a metallic effect on ceramic bases by injection, according to claim 3, wherein the raw material of iron oxide that is used mainly to provide the Fe in the metallic ink (4) is in the form of a suspension of nanoparticles of iron oxides or ferrofluid.

5. Procedure for obtaining a metallic effect on ceramic bases by injection, according to claim 1, wherein the metallic ink (4) is formed mainly by Fe and P pigment inks, as major elements, and the glaze (2) is formed mainly by Si, Al, and Li, according to the range of compositions:

Composition of the metallic ink (4)	
P_2O_5	40 - 70%
Fe_2O_3	10 - 50%

Composition of the glaze (2)	
SiO_2	40 - 60%
Al_2O_3	10 - 30%
R_2O + RO	5 - 20%
ZrO_2 + TiO_2	0 - 10%
B_2O_3	0 - 10%

Where:

R_2O: Li_2O + Na_2O + K_2O
RO: MgO + CaO + SrO + BaO

6. Procedure for obtaining a metallic effect on ceramic bases by injection, according to claim 1, wherein the metallic ink (4) is formed mainly by Fe, P and Li pigment inks, as the chief elements, and the glaze (2) is formed mainly by Si and Al, according to the range of compositions:

Composition of the metallic ink (4)	
P_2O_5	40 - 70%
Fe_2O_3	10 - 50%
Li_2O	0 - 30%

Composition of the glaze (2)	
SiO_2	40 - 60%
Al_2O_3	10 - 30%
R_2O + RO	5 - 30%
ZrO_2 + TiO_2	0 - 10%
B_2O_3	0 - 10%

Where:

R_2O: Li_2O + Na_2O + K_2O
RO: MgO + CaO + SrO + BaO

7. Procedure for obtaining a metallic effect on ceramic bases by injection, according to any of the preceding claims, wherein the glaze (2) incorporates, in the form of oxides, elements selected from the group formed by Na, K, Mg, Ca.

8. Procedure for obtaining a metallic effect on ceramic bases by injection, according to any of the preceding claims, wherein the glaze (2) incorporates complementary ceramic pigments to obtain a specific colouring other than white.

9. Procedure for obtaining a metallic effect on ceramic bases by injection, according to claim 1, wherein the phase of application (3) of the glaze (2) on a ceramic base (1) is carried out by means of a process chosen from amongst the group formed by : bell, airbrush, rotary, disc or waterfall.

10. Procedure for obtaining a metallic effect on ceramic bases by injection, according to claim 1, wherein the phase of injection (5) of the metallic ink (4) is performed using an injection head capable of providing a thickness of between 6 and 200 pL per drop.

11. Procedure for obtaining a metallic effect on ceramic bases by injection, according to claim 1, wherein the firing phase (6) is carried out at temperatures of between 900 and 1300°C, in firing cycles of between 0.5 and 24 h.

12. Tile (7) with metallic effect obtained according to the procedure described in claims 1 to 11.

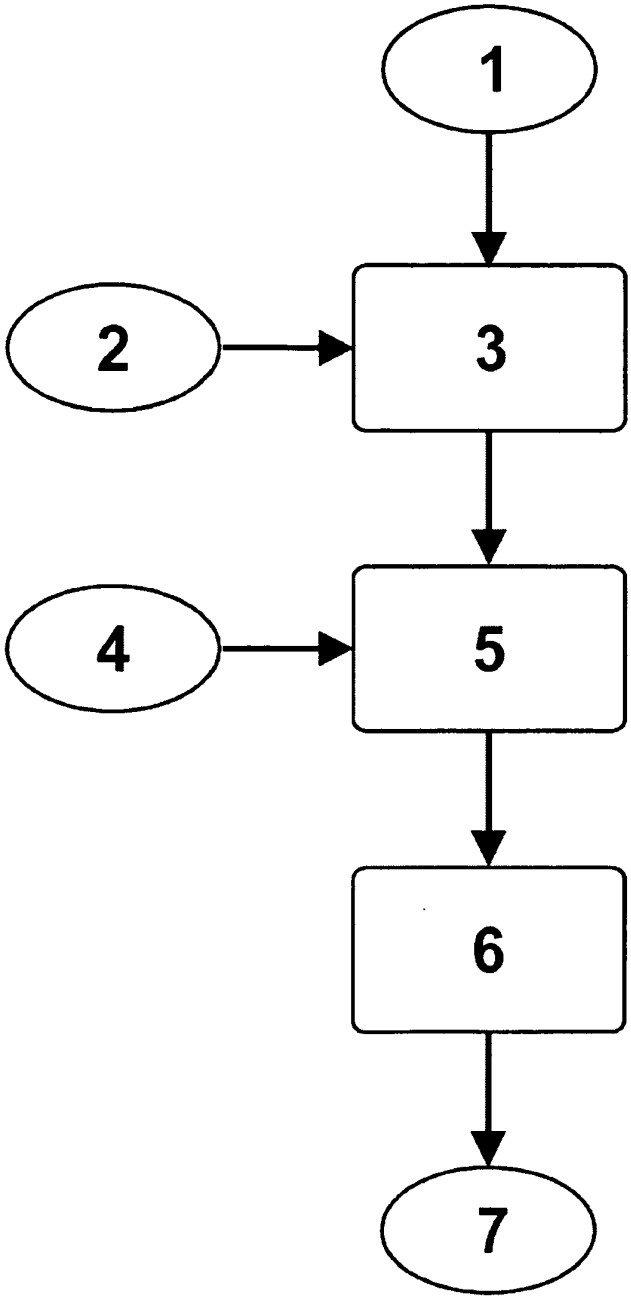

Fig. 1

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- ES 2131466 **[0003]**
- ES 2289916 **[0003]**
- ES P201031196 **[0004]**