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(71) Applicant: **Bergstein B.V.**
6466 NG Kerkrade (NL)

(72) Inventor: **The designation of the inventor has not yet been filed**

(74) Representative: **Renkema, Jaap**
IPecunia Patents B.V.
P.O. Box 593
6160 AN Geleen (NL)

(54) Process for decorating glazed ceramic tiles

(57) The present invention relates to a process for decorating a glazed ceramic tile, comprising the steps of: (a) applying a primer composition on the tile and optionally wiping off the excess primer composition from the tile; (b) applying an ink composition comprising a radiation curable component on the primer composition by inkjet technology and (c) curing the ink composition. The process may further comprise the step of (d) optionally providing a protective coating on top of the cured ink composition.

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Description

[0001] The present invention relates to a process for decorating a glazed ceramic tile. The invention further relates to a decorated glazed ceramic tile obtainable thereby.

[0002] Commercial ceramic and glassware is traditionally decorated by applying a design in colored ink onto the surface of the substrate, by means of screen printing, offset printing or any other direct application technique; and the thus decorated substrate is then fired, so as to burn off the organic components of the ink, and cause the ink design to "fuse" onto the surface of the glass. This traditional process however is time-consuming and energy-intensive, and at best results in heavy operational costs, and a requirement for significant floor space in factories. A further disadvantage of this long-established procedure is that the applied decoration until it has been fired is extremely prone to damage caused by the rubbing and scratching that occurs in normal handling operations, and this results in many rejects.

[0003] An alternative procedure is to use a radiation-curable Ink compositions. EP0668332 describes a method for applying a coloured decoration to a substrate The method comprises the steps of a) applying a radiation-curable, pigmented ink composition to the substrate In a predetermined design, said composition comprising a radiation-curable component capable when cured of bonding to the substrate, and a pigment component which is or includes one or more pyrrolopyrrol and/or isoindolinone pigment(s); and b) curing the radiation-curable Ink on the substrate by exposure to the radiation by which it Is curable, thereby bonding the ink to the substrate. The Ink composition may further comprise an adhesion promoter. The adhesion promoter may be acryloxy-functional silanes or glycidoxy-functional silanes.

[0004] Another example of the use of a curable ink is described in WO2005/095006. In this publication, a process for decorating ceramic tiles is disclosed comprising the steps of applying a curable ink and curing the Ink. Prior to applying the curable ink, the tile may be subjected to a blasting process or to a thermal process, or an adhesion promoter may be applied. The adhesion promoter may be a silane capable of creating Si-O-Si on the surface of the tile, such as gamma-aminopropyltrimethoxysilane.

[0005] While these processes may be satisfactory for decorating certain ceramic tiles, there is a need in the art for a process which results in a more precisely decorated ceramic tiles.

[0006] Accordingly, an object of the present invention is to provide a process In which above and/or other needs In the art is met.

[0007] The present invention provides a process for decorating a glazed ceramic tile, comprising the steps of:

(a) applying a primer composition on the tile and optionally wiping off the excess primer composition from the tile,
(b) applying an Ink composition comprising a radiation curable component on the primer composition by Inkjet technology and
(c) curing the ink composition.

[0008] The process may further comprise the step of (d) optionally providing a protective coating on top of the cured Ink composition.

[0009] The ink compositions defining the decoration pattern have improved bonding to the ceramic tiles, which gives a high wear resistance and a minimization of bleaching. This allows the tiles to be used outdoor for a long time.

[0010] The invention is based on the realization that the combination of the glazed ceramic tiles and inkjet technology further combined with the two step application of the primer and the ink compositions gives a decoration of a surprisingly high definition and durability.

[0011] The inventors have realized that the application of the inkjet technology for the ceramic tiles have significant advantages over other printing methods In that high definition is achievable. The width of the lines defining the printed pattern is restricted by the droplet size deposited by inkjet technology. Typically, size of the droplets deposited by inkjet technology ranges from 1 to 1000 μL, which allows making of a precisely-controlled microstructure. Furthermore, use of the inkjet technology allows for spatially addressable patterns on a surface without the need for masks which would be required by e.g. screen printing.

[0012] The Invention is based on the realization that the high definition expected by inkjet printing is obtainable only under certain conditions.

[0013] As described above, inkjet printing allows a high definition printing. However, the definition of the pattern directly inkjet printed on a non-treated ceramic tile was surprisingly found to be less than expected. Surprisingly, the high definition expected from the inkjet printing was obtained only by the combination of the use of a glazed ceramic tile and the application of a primer composition on the surface before inkjet printing the ink composition. Although not wishing to be bound by theory, this is believed to be caused by smoothing of the surface by both the glazing and the primer composition which substantially reduces the amount of pores on the surface. The primer composition used without the glazing was found not to be enough for obtaining the high definition, but it assists the glazing in achieving the high definition. Furthermore, the primer composition improves the adhesion of the ink composition on the surface. It was further realized that the ink composition and the primer composition should not be mixed and inkjet printed, since the primer composition clogs the print head. Hence, any ink composition that further comprises an adhesion promoter is not suitable for the process according to the present invention.

[0014] The use of the curable Ink composition also of-

fers significant advantages over the traditional decorating method involving firing because radiation-curing is easy and inexpensive, requiring only lamps that emit the desired wavelength of light (or, in the case where no photopolymerization agent is included in the ink, an electron beam). Moreover the hazards and energy expenditures encountered in the use of firing ovens are totally eliminated. The use of the curable ink composition allows a very fast process.

[0015] Glaze is herein meant, as generally understood in the art, a layer or coating of a vitreous substance which has been fired to fuse to a ceramic object.

[0016] Inkjet technology is herein meant, as generally understood In the art, as any technology of depositing droplets to desired locations on the substrate irrespective of the type of force for discharging the droplets. It utilizes a controlled impulse to transfer fluid substances from miniature nozzles to solid surfaces. Using a piezoactuator, for example, an electric current through a piezoelectric crystal which expands to create an acoustic wave, which expels a droplet out of the nozzle, inkjet technologies include continuous and drop-on-demand devices. In addition to piezoelectric ink jets, heat may be used to form and propel drops of fluid using bubble-jet or thermal ink jet heads. Thus, the depositing of the droplets may be performed using several different inkjetting techniques, including both drop-on-demand techniques (e.g. thermo, piezoelectric-driven and electro-hydrodynamic jetting) as well as continuous jetting techniques (e.g. electrospraying and other methods based on Rayleigh jet breakup). Other techniques for creating microdroplets include technology such as pneumatic microvalve technology, double emulsion-solvent evaporation method or other emulsion methods.

[0017] Preferably, no heat treatment is performed between steps (a) and (b).

[0018] Heat treatment is herein meant a step where the tile is subjected to an elevated temperature to bind the primer composition to the tile, typically at a temperature of between 40 and 150 °C. This has an advantage that the process is fast and easy since the application of the ink composition can be performed directly after the application of the primer composition. Preferably, no drying step is performed between steps (a) and (b). Drying step is herein meant a step where the tile is subjected to an atmosphere with low moisture so that the primer composition solidifies. Thus, the surface onto which the Ink composition is applied may either be dry or molst. Wiping the excess primer composition off from the tile is herein not considered as a drying step. Furthermore, since it is preferred that the surface onto which the primer composition is applied and the surface onto which the ink composition is applied are smooth, surface roughening steps such as sand blasting for improving adhesion is preferably avoided. Accordingly, a preferred process according to the present invention consists of: (a) applying a primer composition on the tile and optionally wiping the excess primer composition off from the tile;

(b) applying an ink composition comprising a radiation curable component on the primer composition by inkjet technology,

(c) curing the ink composition and

(d) optionally providing a protective coating on top of the cured ink composition.

[0019] The application of the primer composition may be performed by any known coating method, e.g. spin coating, dip coating, spray coating, screen printing, offset printing, flexography, pad printing, hand painting by brush and the like.

[0020] Preferably, the primer composition comprises an acryloxy-functional silane compound or an glycidoxy-functional silane compound. These silane compounds may be used may be used as a monomer, or its polymerized counterpart may also be used. Many acryloxy-functional silanes may be used, such as those described in U.S. Patent No 5,221,560, the disclosure of which is Incorporated herein by cross-reference. Preferably, the acryloxy-functional silane is selected from the group consisting of: 3-(2-aminoethylamino)propyltrimethoxysilane, 3-methacryloxypropyltrimethyoxysilane, 3-acryloxypropyltrlmethyoxysllane, 2-methacryloxyethyltrimethoxysilane, 2-acryloxyethyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltrimethoxysilane, 3-acryloxpropyltriethoxylsilane, 2-methacryloxyethyltriethoxysilane, 2-methacryloxyethyltriethoxysilane, and 2-acryloxyethyltriethoxysilane. Prefeably, the glycidoxy-functional silane is selected from the group consisting of: 3-glycidoxypropyltrimethoxysilane, 2-glycidoxyethyltrimeoxysilane, 3-glycidoxypropyltriethoxysilane, 2-glycidoxyethyltriethoxysilane and 3-glycidoxypropyltrimethyl silane. They were found to result In a very high adhesion of the ink composition to the tile.

[0021] Preferably, the primer composition is an aqueous dispersion of an acrylate polymer. Such aqueous dispersion was found to result in a very high adhesion of the ink composition to the tile.

[0022] The radiation-curable component In the Ink composition may be the ones described in EP0668332, which is incorporated herein by reference. The radiation-curable component in the ink composition may consist of monomers, oligomers and/or low molecular weight homopolymers, as well as copolymers, terpolymers, graft copolymers or block copolymers, so long as the component is curable (polymerized) by exposure to an electro beam or to actinic (including ultraviolet) radiation. After the curing of the Ink composition, the silane compound is bound both to the surface of the tile and the cured component.

[0023] The terms "actinic radiation" and "ultra-violet radiation" are here used in their normal sense. The term "actinic radiation" In general means light In the violet and ultra-violet regions which will bring about chemical changes, and may be regarded as corresponding to wavelengths of from 10 to 600nm. The term "ultra-violet (or UV) radiation" refers to the non-visible part of the ac-

tinic radiation, and may be regarded as corresponding to wavelengths of from 10 to 400nm., and preferably (for present purposes) 325-385nm.

[0024] In preferred embodiments of the invention, the radiation-curable component is curable by ultraviolet (UV) radiation having wavelengths of from 10 nm to 400nm, and preferably 325nm to 365nm.

[0025] In preferred embodiments of the invention, the UV radiation is radiated immediately after the application of the Ink composition. A preferred device used In the method of the present invention comprises an ink-jet printer and a UV lamp arranged next to it in such a way that the areas which have been ink-jet printed immediately receives a radiation from the UV lamp. The curing is preferably finished within 0.01-5 seconds.

[0026] The most convenient UV-light source is usually a so-called UV-conveyor, set up so that the substrate passes through for a period of time cumulatively sufficient to cure the ink composition completely and thus cause it to adhere to the substrate. If desired, the substrate may be moved through the conveyor in one or more passes, In order to achieve the required curing. The appropriate time varies depending on the nature of the substrate, but generally-speaking curing can be accomplished within an overall period of from 1 to 30 minutes, more preferably within 3-25 minutes.

[0027] Suitable radiation-curable component monomers In the ink composition include epoxides, cycloaliphatic epoxides, vinyl chloride, styrene, ethyl acrylate, vinyl acetate, bifunctional acrylic monomers such as hydroxy alkyl acrylates or hydroxy alkyl methacrylates, vinyl butyrate, vinyl methyl ether, methyl methacrylate, isobornyl acrylate and acrylonitrile, or mixtures thereof.

[0028] Examples of the radiation-curable components include the cationically-UV-curable cycloaliphatic epoxides sold under the tradename CYRACURE by Union Carbide Chemicals and Plastics Company, Danbury, Connecticut. U.S.A., such as CYRACURE UVR 6110, 6100, 6379, 6351 and 6200.

[0029] Generally the radiation-curable component constitutes about from 10% to 95% by weight of the total ink composition, preferably from 15% to 70%, and usually most advantageously from 35% to 85%.

[0030] The ink composition may comprise any known pigment component for imparting desired colors. Examples of the pigment component include pyrrolopyrrol and/or isoindolinone pigment as described In EP0668332.

[0031] When the radiation-curable component is to be cured by UV or other actinic radiation (rather than by an electron beam) it is then very desirable that the composition should Include a photoinitiator, which will catalyze polymerization of the component upon exposure to the radiation to which the component Is sensitive, If an electron beam Is used to cure the composition it may be possible to dispense with a photoinitiator. The proportion of photoinitiator is not critical, but typically Is from about 1 to 20%, preferably 3 to 15%, by weight with respect to the ink composition.

[0032] Carbonyl compounds such as ketones and derivatives thereof are especially suitable for this purpose. Thus for example methyl ethyl ketone, benzophenone, benzyl dimethyl ketal, 1-hydroxycycylohexylphenylketone, 2,2-dimethoxy-2-phenylacetophenone, diethoxyacetophenone and 2-methyl-1-(methylethiophenyl)-2-(4-morpholinyl)-1-propanone are all excellent photoinitiators. Other photosensitive onium salts are also particularly good UV-activated photoinitiators. The use of photosensitive onium salts to promote the curing of epoxides when exposed to UV radiation is described in U.S. Patents Nos. 4,058,401, 4,138,255 and 4,161,478, the disclosure of all of which is Incorporated herein by cross-reference. The photosensitive onium salts mentioned in these Patents are good UV-light photoinitiators, Triaryl sulphonium salts are preferred, in particular a triaryl sulphonium salt sold by Union Carbide under the tradename CYRACURE UVI 6974.

[0033] Other ingredients may be added to the radiation-curable composition, including stabilizers, inert fillers, wetting agents, leveling agents and so on. If present, these ingredients will normally constitute about from 1% to 95% by weight of the total composition.

[0034] The pigment component of the ink composition of this invention may constitute from about 1% up to 50% by weight of the total composition, and preferably from about 15% to 35%.

[0035] The Ink compositions of this invention will preferably contain from about 15% to 40% of the pigment and from 55% to 85% of the radiation-curable component.

[0036] The process according to the present invention may further comprise the step of providing a protective coating on top of the cured ink composition. This further improves the resistance of the decorated tile to mechanical and/or chemical damage. The material of a protective coating and its application method are known to the skilled person. The protective coating is preferably transparent. An example of the protective coating includes polyurethane. Examples of the application method Include spin coating, dip coating, spray coating, screen printing, offset printing, flexography, pad printing, hand painting by brush and the like.

[0037] A further aspect of the present invention relates to a decorated glazed ceramic tile obtainable by the process according to the present invention.

[0038] A further aspect of the present invention relates to a floor or a wall provided with the decorated glazed ceramic tiles according to the present invention.

[0039] A further aspect of the present invention relates to use of inkjet technology for decorating glazed ceramic tiles provided with a layer of a primer composition. Preferably, the primer composition comprises a silane compound as described above or an aqueous dispersion of an acrylate polymer.

[0040] It is noted that the Invention relates to all possible combination of features recited herein, especially

the claims.

[0041] The Invention is hereinafter illustrated by means of the following nonlimiting examples:

Figure 1 shows a decorated non-glazed ceramic tile obtained according to a comparative experiment and Figure 2 shows a decorated glazed ceramic tile obtained according to the present invention.

Comparative experiment 1

[0042] A non-glazed ceramic tile was provided. The surface of the tile was cleaned with water. A primer composition comprising 3-acryloxypropyltrimethoxysilane sold under product name SPC-0541available from Mimaki Europe B.V. was applied as the primer composition to the cleaned surface by brush coating, resulting In a layer having a thickness of 1.2 mm. The excess of the primer composition was wiped off by a cloth. The tile was decorated according to the desired pattern using an inkjet printer using UV curable ink compositions sold under product names SPC-0371W5 (white), SPC-0404HY (yellow), SPC-0371M (magenta), SPC-0371LM (magenta), SPC-0371C (cyan), SPC-0371 K-2 (black) and SPC-0371LC-2 (cyan), all available from Mimaki Europe B.V.. SPC-0371LC-2 comprises isooctyl acrilate, phenyl bis (2,4,6-trimethylbenzoyl)-phosphine oxide and dlpropylene glycol diacrylate. The other ink compositions comprise monoalkyl esters of acrylic acid and isooctyl acrilate and depending on the color, they further comprise phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide, 2-methyl-1-(4- methylthiophenyl)- 2- morpholinopropan- 1- one and/or 2-benzyl-2-dimethylamino-4-morpholinobutylrophenone.

[0043] The ink composition was immediately cured by UV radiation.

[0044] The decorated tile was visibly analyzed and was found to have undesired white spots, as can be seen in Figure 1.

Example 1

[0045] A ceramic tile of comparative experiment 1 was provided, but in this example the ceramic tile was a glazed ceramic tile. The surface of the tile was cleaned with water. A primer composition comprising 3-(2-aminoethylamino)propyltrimethoxysilane sold under product name glas-primer available from A.M.Ramp & Co GmbH RUCO Druckfarben was applied as the primer composition to the cleaned surface by brush coating, resulting in a layer having a thickness of 1.2 mm. The excess of the primer composition was wiped by a cloth. The ink composition used In the comparative example 1 was applied in the same way as the comparative example 1.

[0046] The decorated tile was visibly analyzed and was found to have a very high definition.

[0047] Three types of adhesion tests were conducted: scratch test, tape test and Schnitt test. The results are shown in Table 1.

[0048] The scratch test was performed by scratching the decorated tile by scratching its surface by a fingernail When no coating was removed, the result is indicated as +/+.

[0049] The tape test was performed by applying an adhesive tape commercially available from 3M to the surface of the decorated tile and pressing onto the tape. When no decoration was removed with the tape, the result is indicated as +/+. A slight removal of the coating is indicated as +/-.

[0050] The Schnitt test was performed in accordance with ISO10545-7, i.e. lines were drawn on the surface of the decorated tile by a sharp knife to form squares. An adhesive tape was applied to the surface as in the tape test. The adhesion strength of the coating is indicated by the number of the squares removed with the adhesion tape.

Example 2

[0051] Example 1 was repeated, except that the primer composition was a product sold under product name SPC-0541 from Mimaki comprising 3-acryloxypropyltrimethoxysilane.

[0052] The decorated tile was visibly analyzed and was found to have a very high definition. The results of adhesion tests are shown in Table 1.

Example 3

[0053] Example 1 was repeated, except that an aqueous dispersion of an acrylate polymer sold under product name RD-Multiprim from RD Coatings was used as the primer composition.

[0054] The decorated tile was visibly analyzed and was found to have a very high definition. Figure 2 shows the decorated tile according to this example. The results of adhesion tests are shown in Table 1.

Table 1

	Scratch test	Tape test	Schnitt test
Ex. 1	+/+	+/-	-/-
Ex. 2	+/+	+/+	+/-
Ex. 3	+/+	+/+	+/+

Claims

1. A process for decorating a glazed ceramic tile, comprising the steps of:

   (a) applying a primer composition on the tile and optionally wiping off the excess primer composition from the tile;
   (b) applying an Ink composition comprising a ra-

diation curable component on the primer composition by inkjet technology,
(c) curing the ink composition and
(d) optionally providing a protective coating on top of the cured ink composition.

2. The process according to claim 1, wherein no heat treatment is performed between steps (a) and (b).

3. The process according to claim 1, wherein step (b) is performed directly after wiping off the excess primer composition on the tile.

4. The process according to claim 1 consisting of steps (a)-(d).

5. The process according to any one of claims 1-4, wherein the primer composition comprises an acryloxy-functional or glycidoxy-functional silane compound or a polymer of said silane compound.

6. The process according to any one of claims 1-5, wherein the primer composition comprises a silane compound selected from the group consisting of: 3-(2-aminoethylamino)propyltrimethoxysilane, 3-methacryloxypropyltrimethyoxysilane, 3-acryloxypropyltrimethyoxysilane, 2-methacryloxyethyltrimethoxysilane, 2-acryloxyethyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltrimethoxysilane, 3-acryloxpropyltriethoxylsilane, 2-methacryloxyethyltriethoxysilane, 2-methacryloxyethyltriethoxysilane, 2-acryloxyethyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 2-glycidoxyethyltrimeoxysilane, 3-glycidoxypropyltriethoxysilane, 2-glycidoxyethyltriethoxysilane 3-glycidoxypropyltrimethyl silane, 3-glycidoxypropyltrimethoxysilane, 2-glycidoxyethyltrimeoxysilane, 3-glycidoxypropyltriethoxysilane, 2-glycidoxyethyltriethoxysilane and 3-glycidoxypropyltrlmethyl silane.

7. The process according to any one of claims 1-4, wherein the primer composition is an aqueous dispersion of an acrylate polymer.

8. The process according to any one of claims 1-7, wherein step (c) involves an application of ultraviolet radiation.

9. The process according to any one of claims 1-8, wherein the ink composition further comprises a photoinitiator.

10. A decorated glazed ceramic tile obtainable by the process according to any one of claims 1-9.

11. A floor provided with the decorated glazed ceramic tiles according to claim 10.

12. A wall provided with the decorated glazed ceramic tiles according to claim 10.

13. Use of inkjet technology for decorating glazed ceramic tiles provided with a layer of a primer composition.

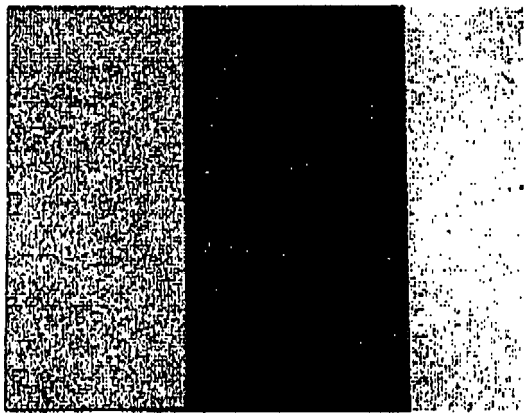

Figure 1

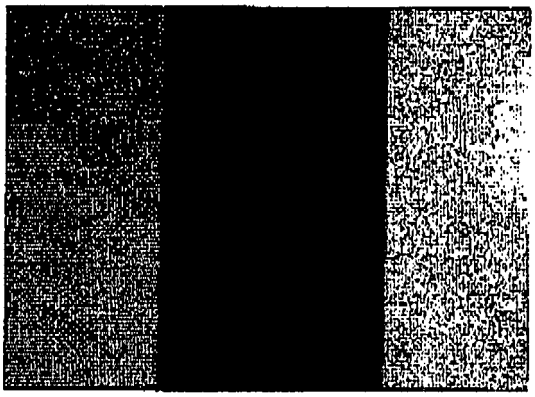

Figure 2

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EUROPEAN SEARCH REPORT

Application Number
EP 11 00 1214

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	2 September 2011	Vogel, Thomas

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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