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(54) METHODS FOR DECORATING CERAMIC TILES

VERFAHREN ZUM DEKORIEREN VON KERAMIKFLIESEN

PROCÉDÉS DE DÉCORATION DE CARREAUX DE CÉRAMIQUE

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EP 2 877 346 B1

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method of decorating ceramic or glass materials, which method offers ease of production and in particular to such a method involving printing more than one color onto a ceramic substrate.

BACKGROUND OF THE INVENTION

[0002] The ability to manufacture decorated ceramic tiles, in a way that resembles printing, particularly digital printing, is of immense commercial and technological potential since printing is regarded as a very efficient, reliable and cost effective way to form decoration on surfaces.

[0003] UK patent application published GB 2 289 866 A discloses a method suitable for decorating a ceramic article. The method comprises the steps of (1) printing a liquid material by an ink jet printer on to the article to form the required pattern of an adhesive material, (2) supplying particulate decorative material on to the adhesive pattern, and (3) removing the excess of particulate material which has not adhered to the pattern.

[0004] The development of ceramic inks allowed the production of decoration by printing these inks on ceramic surfaces. This was demonstrated by using printing techniques such as screen printing, rotocolor, and even digital ink-jet and electro-photography printing.

[0005] Nevertheless, ceramic inks are limited by several major drawbacks:

1) Ceramic pigment particles are often characterized by high specific gravity. For example Fe-Cr-Ni-Co Black Spinel has specific gravity of 4.5 grams per cubic centimeter Zr-V Zircon Blue has specific gravity of 4.2 grams per cubic centimeter, Co-Cr Green Spinel has specific gravity of 4.3 grams per cubic centimeter. Due to their high density, the metal oxide suspensions thereof have a tendency for sedimentation. The sedimentation may cause serious problems, for example in ink-jet printing it may lead to clogging printing heads and ink supply system. Moreover, in some cases the sedimentation is not reversible; therefore the shelf life of such compositions is usually limited to several months.

2) Digital printing is a very important way of printing as it offers the ability to print without a master structure (stamp, mask etc). This allows the formation of varying structures without the costly need to change the master structure. Nevertheless, digital ink-jet printing is based on the spatially localized delivery of the ink using a print head. For ink-jet printing the print head must deliver the ink to the surface through narrow nozzles. For that purpose, the ink must be characterized by very restrictive properties, such as

low viscosity, in the range of few tens of cPs, sub-micrometer solid particles. On the other hand the ceramic pigments have very high hardness and therefore the process of reduction of particle size to sub-micrometer size is costly and characterized by high energy consumption and high depreciation of equipment. Moreover color properties of ceramic pigments may be sensitive to particle size and milling process. For example, Cadmium-Selenium Inclusion Red pigment has a very strong red color when the size of particles is above 5 micrometer (microns), however in the milling process the pigment may completely lose its color.

3) Ink jet inks may have only a limited percentage of the pigment (usually not more than 40% by weight). Because of low extinction coefficient of ceramic pigments, and their limited concentration in the ink, the tiles decorated by ink-jet technique are usually characterized by poor color strength and narrow color gamut.

[0006] The present invention relates to a method for applying at least a two-color decoration material having a particular shape or boundaries to a ceramic substrate, in accordance with appended independent claim 1 and appended dependent claims 2-9.

[0007] The present invention, in some embodiments thereof, relates to methods for printing or otherwise applying decoration materials having a particular shape(s) and/or boundary/boundaries, determined by forming an adhesive layer through a process having more than one stage, followed by applying the decoration material by means of dry silk screen, dry gravure or spray-gun. The decoration material remains only at the location(s) determined by the adhesive layer (or substantially only at these location(s)). By "remains" it is meant that the decoration layer may optionally be applied specifically to the adhesive layer or alternatively may optionally be applied to at least one location other than that determined by the adhesive layer, followed by removal of any decoration material not specifically adhered to the adhesive layer, for example and without limiting, by washing, brushing, tilting, air blowing or air suction.

[0008] Non-limiting examples of the decoration material include but are not limited to metal oxides, metals, precious metals, glass frits, lusters and special color effects pigments, organo-clay pigments, glazes, salts flux, mineralizers and pigment stains.

[0009] According to the present invention, the adhesive layer is formed through a process comprising a plurality of stages. Optionally, a plurality of adhesive layer components are applied during the plurality of stages, such that only when all such components have been applied, the adhesive layer becomes functionally adhesive to receive and adhere to the decoration layer. By "functionally adhesive" it is meant that the adhesive layer adheres to the decoration material.

[0010] Thus in the present invention, at least one ad-

hesive layer-forming component(s) are applied, followed by activation of the adhesive layer such that it becomes functionally adhesive.

[0011] According to the present invention, the adhesive layer is formed through a process comprising a plurality of stages. Optionally, a plurality of adhesive layer components are applied during the plurality of stages, such that only when all such components have been applied, the adhesive layer becomes functionally adhesive to receive and adhere to the decoration layer. By "functionally adhesive" it is meant that the adhesive layer adheres to the decoration material.

[0012] Thus in the present invention, at least one adhesive layer-forming component(s) are applied, followed by activation of the adhesive layer such that it becomes functionally adhesive.

[0013] According to some embodiments of the present invention, any suitable application process may optionally be used, referred to herein as "printing". In preferred embodiments of the present invention, a second, adhesive activator component is applied and establishes the pattern by creating the activated adhesive upon which the pigment is deposited. For example and without limitation, the adhesive layer may optionally be applied through digital patterning of the adhesive in any possible way (any of the above, ink-jet printing of the adhesive and alike).

[0014] As a non-limiting specific example, the adhesive layer may optionally be spread in a non-patterned manner atop the surface and only then is it patterned e.g., by reacting with another component and/or electromagnetic irradiation (photo curing) and/or thermally activated curing.

[0015] As another non-limiting specific example, at least one adhesive forming component is optionally reacted on the surface with at least one printable adhesive-activating component in a way to form the adhesive only at the desired locations.

[0016] According to the present invention there is now provided a method for applying at least a two color decoration material having a particular shape or boundaries on a substrate, comprising:

a: applying at least one adhesive-layer-forming component on said substrate, b: applying thereto an adhesive activator which renders said component functionally adhesive to form a first adhesive layer, said adhesive activator being selectively applied in accordance with pattern parameters of a chosen first color to appear in said decoration,

c: applying a ceramic pigment, in particulate form, as a decoration material, together with a further amount of at least one adhesive-layer-forming component,

d: removing excess of said ceramic pigment such that said pigment material remains only at the location

on the substrate determined by said first activated adhesive layer,

e: applying thereto further adhesive activator which renders said further amount of at least one adhesive-layer-forming component functionally adhesive, said further adhesive activator being applied in accordance with pattern parameters of a chosen further color to appear in said decoration

f: applying a different, further ceramic pigment, in particulate form, as a further decoration material, and

g: removing excess further pigment such that said further pigment material remains only at the location on the substrate determined by the further activated adhesive layer,

whereby a substrate, decorated with at least two colors, is formed.

[0017] Preferably said substrate is selected from the group consisting of: unfired tiles ("green" tiles), fired tiles and unfired glaze (bisque), glazed and fired tiles (third fire), decal (ceramic transfer paper), glass and metal enamel.

[0018] More specifically, there is now provided, according to the present invention, a method for applying at least a two color decoration material having a particular shape or boundaries on a ceramic substrate, comprising:

a: applying at least one adhesive-layer-forming component on a ceramic substrate,

b: applying thereto an adhesive activator which renders said component functionally adhesive to form a first adhesive layer, said adhesive activator being selectively applied in accordance with pattern parameters of a chosen first color to appear in said decoration,

c: applying a ceramic pigment, in particulate form, as a decoration material, together with a further amount of at least one adhesive-layer-forming component,

d: removing excess ceramic pigment such that said pigment material remains only at the location on the substrate determined by said first activated adhesive layer,

e: applying thereto further adhesive activator which renders said further amount of at least one adhesive-layer-forming component functionally adhesive, said further adhesive activator being applied in accordance with pattern parameters of a chosen second color to appear in said decoration f: applying a different, further ceramic pigment, in particulate form, as a further decoration material, and

g: removing excess further pigment such that said further pigment material remains only at the location on the substrate determined by the further activated adhesive layer,

whereby a ceramic substrate, decorated with at least two colors, is formed.

[0019] In preferred embodiments of the present invention there is provided a method for applying at least a three color decoration material having a particular shape or boundaries on a ceramic substrate as defined above wherein in step f, said further ceramic pigment, in particulate form, is applied together with a yet further amount of at least one adhesive-layer-forming component, and steps d,e,f, and g are repeated with a third ceramic pigment whereby a ceramic substrate, decorated with at least three colors, is formed.

[0020] In especially preferred embodiments of the present invention there is provided a method for applying a multiple color decoration material having a particular shape or boundaries on a ceramic substrate as defined above wherein in step f, said further ceramic pigment, in particulate form, is applied together with a yet further amount of at least one adhesive-layer-forming component, and steps d,e,f, and g are repeatedly repeated with as many separate ceramic pigments respectively as determined for completing the multicolor decoration.

[0021] In US Patent No: 5,594,484, there is described and claimed a method of recording an image comprising the steps of a) providing a recording medium comprising a substrate and an adhesive layer made of a delayed-tack adhesive provided evenly or smoothly on a surface of the substrate; b) rendering the adhesive layer tacky in accordance with image information to form an imagewise tacky portion, and c) applying powder to the imagewise tacky portion.

[0022] As will be noted, said patent is directed to a method of providing a recording medium and all three of the examples in said patent teach the use of a recording paper which was provided with an adhesive to which was then applied a pigment and the printed surface of the recording paper was contacted with the surface of a white tile.

[0023] Thus, said patent does not teach or suggest a process for directly printing on "green" tiles and similar surfaces and does not teach or suggest the especially efficient process of the present invention for applying multi-color decorations to ceramic tiles. Said patent does mention in column 4 lines 1-7 that also, it is possible to use a one-pass type multicolor printing apparatus that does not involve plate making and comprises a plurality of units, each performing therein the steps of selectively giving tackiness to a substrate, developing with powder, and removing unnecessary powder so that development with different color powder can be carried out in a different unit.

[0024] Said description, however, is a teaching away from the present invention in that it clearly contemplates

a full process and thus an extra step for each color application in that it does not teach or suggest the unique and efficient method of the present invention wherein a further second, third, fourth, etc., ceramic pigment, in particulate form, is applied together with a yet further amount of at least one adhesive-layer-forming component on top of the previously deposited adhesive activator so that while said further ceramic pigment is being attached to the activated adhesive therebelow, the surface is already being primed to receive a further layer of adhesive activator and pigment.

[0025] In PCT publication WO95/15266 there is described a method of producing a decorative or functional transfer carrying a pattern, which method comprises printing the pattern in adhesive or a precursor thereof on transfer paper by an electronically controlled printing process so that the pattern corresponds to an electrically stored or generated digital image, in the case of precursor converting to the adhesive, and applying to the adhesive or precursor thereof decorative or functional material in finely divided form, such that the material is stuck by the adhesive and hence forms the pattern in the material. Said publication also mentions the possibility of carrying out said method wherein said steps are repeated with a different such decorative or functional material to build up a multicolor or complex effect transfer, however, the only description thereof in the specification appears on page 8 lines 1 1-12, wherein it is stated "the process may then be repeated for different colors and patterns to be combined with the original".

[0026] Thus also said publication is a teaching away from the present invention in that it clearly contemplates an extra step for each color application in that it also does not teach or suggest the unique and efficient method of the present invention wherein a further second, third, fourth, etc., ceramic pigment, in particulate form, is applied together with a yet further amount of at least one adhesive-layer-forming component on top of the previously deposited adhesive activator so that while said further ceramic pigment is being attached to the activated adhesive therebelow, the surface is already being primed to receive a further layer of adhesive activator and pigment.

SUMMARY OF THE INVENTION

[0027] In preferred embodiments of the present invention said adhesive activator is a solvent which causes the adhesive-layer-forming component to become functionally adhesive to the decoration layer.

[0028] In preferred embodiments of the present invention at least one component of said decoration material and said adhesive layer are applied through digital patterning. In preferred embodiments of the present invention said solvent is applied via an ink-jet printing print head.

[0029] Preferably said decoration material is applied in solid particulate form.

[0030] In some embodiments, the decoration material relates to metal oxides, metals, precious metals, glass frits, luster and color effects pigments, organo-clay pigments, glazes, salts flux, mineralizers, pigment stains and their combinations and their mixtures in combination with said first adhesive layer forming component.

[0031] In some embodiments of the invention, the method is based on forming the shape of a decoration material by producing and/or depositing and/or activating and/or deactivating an adhesive on a surface at the desired shape, following by depositing metal oxides particles and/or metals particles and/or precious metals particles and/or glass frits particles and/or luster particles and/or color effects pigments particles and/or organo-clay pigments particles and/or glazes particles and/or salts flux particles and/or mineralizers particles and/or pigment stains particles in combination with a further adhesive layer forming component, wherein said decoration material adheres to the activated adhesive which totally interacts with and adheres to said decoration material thus forming a decoration layer while said further deposited adhesive layer forming component is ready to receive further adhesive activator,.

[0032] Depending on the specific application, the system may be further subjected to treatment steps aimed at one or a combination of the following: coating with different layers, pressing, air blowing, air suction, heating, drying, firing, polishing, trimming, cutting and the like.

[0033] In some embodiments of the invention, the method is based on forming the decoration layer by forming a patterned adhesive layer on a surface of the desired shape, using one or a combination of printing techniques such as, but not limited to ink-jet, flexography, rotogravure, offset and screen-print. In some embodiments of the invention, the patterned adhesive layer is formed by contacting two or more components. In some embodiments of the invention, the patterned adhesive layer is formed by contacting one or more printed components with another component that is pre-deposited atop the printing surface (hereinafter referred to as "substrate").

[0034] The present invention thus provides a method of decorating ceramic materials which offers ease of production using various decoration materials, and in particular to such a method, involving printing onto a substrate utilizing metal oxides, metals, precious metals, glass frits, luster and color effects pigments, organo-clay pigments, glazes, salts flux, mineralizers and pigment stains in combination with an adhesive layer forming component to produce a decoration layer characterized by high quality, high colour strength, wide colour gamut and conspicuous decoration effects even under harsh conditions.

[0035] The present invention, in some embodiments thereof, relates to methods for decorating ceramic materials, and, more particularly, but not exclusively, to methods for digitally decorating ceramic materials.

[0036] Thus, the basic principle of the new method of the present invention is patterning the desired structures

to be formed with adhesives, then contacting the adhesive pattern with one or more decoration materials such as, for example, pigment particles in combination with a further adhesive layer forming component, wherein the adhesive layer is formed through a process comprising a plurality of stages such that only when all the stages are complete does the adhesive layer becomes functionally adhesive to the decoration layer and further colored layers can be applied without repeating all the steps of the original one color process..

[0037] The decoration layer containing metal oxides, metals, precious metals, glass frits, luster and color effects pigments, organo-clay pigments, glazes, salts flux, mineralizers, pigment stains bound to the adhesive layer, may be further treated by one or more heating techniques, may be covered by a layer of glaze/frit, may serve as a base for further layer construction, and/or may be contacted with yet another one or more decoration materials, such as, for example, pigment particles and the like by the methods described above.

[0038] The method of the invention may be used, for example, for the production of glazed and non-glazed wall tiles, floor tiles, "green" tiles, decal, glass sheets, glass packaging, dinner ware, sanitary ware, ceramic products, clay slab, metal and metal enamel.

[0039] More specifically the methods of the present invention are adapted to be applied to: unfired tiles ("green" tiles), fired tiles and unfired glaze (bisque), glazed and fired tiles (third fire), decal (ceramic transfer paper), glass and metal enamel..

[0040] The methods of the present invention for applying multiple layers of multiple colors are especially adapted to be applied to unfired tiles ("green" tiles), which are not readily decorated by prior art processes,

[0041] In some embodiments of the invention, the formation of the patterned adhesive layer is achieved by pre-depositing one or more adhesive forming components on the substrate which are reactive to a particular material or solvent. Next one or more additional components are applied that contain such a material or solvent, thereby bringing these components into contact with each other and activating the adhesive. For example the pre-deposited component may optionally comprise one or more of water soluble and/or water swellable polymers, or one or more organic solvent soluble or swellable polymers, or one or more alkali soluble or swellable polymers; such that the additional adhesive-activating component(s) contain the relevant material or solvent (water, organic solvent and/or alkali, respectfully) and can be printed thereon.

[0042] In some embodiments of the invention, the component that is pre-deposited atop the substrate may contain one or more water soluble or water swellable polymers including, but not limited to, gelatin, arabic gum, polyvinyl alcohol and its derivatives, polyvinylpyrrolidone and its derivatives, carboxymethyl cellulose and alike. In some embodiments of the invention, the printed adhesive activator component may contain, optionally in addition

to other components, a mixture of water and/or one or more water soluble alcohols, and/or one or more water soluble mono- glycols, and/or one or more water soluble glycol oligomers, and/or one or more water soluble glycol polymers and/or one or more water soluble glycol esters and/or one or more water soluble polymers and/or one or more surfactants.

[0043] In some embodiments of the invention, the component that is pre-deposited atop the substrate may contain, optionally in addition to other components, one or more alkali soluble or alkali swellable polymers while the printed component may contain one or more alkali compounds and water. In some embodiments of the invention, the component that is pre-deposited atop the substrate may contain, optionally in addition to other components, one or more alkali soluble or alkali swellable polymers such as, but not limited to, polyacrylic acid, copolymers of acrylic acid with epoxy acrylates, alkyl acrylates, aryl acrylates, polyacrylic esters, polyacrylic amides, copolymers of the above. In some embodiments of the invention, the printed adhesive activator component may contain, optionally in addition to other components, a mixture of water and/or one or more alkali compound and/or one or more water soluble alcohols, and/or one or more water soluble mono- glycols, and/or one or more water soluble glycol oligomers, and/or one or more water soluble glycol polymers and/or one or more water soluble glycol esters and/or one or more alkali soluble polymers and/or one or more surfactants. In some embodiments of the invention, the printed adhesive activator component may contain, optionally in addition to other components, one or more alkali compound such as, but not limited to, ammonia, aminoalcohols, alkyl amines, aryl amines, hydroxides of alkaline metals and alike.

[0044] In some embodiments of the invention, the adhesive forming component that is pre-deposited atop the substrate may contain, optionally in addition to other components, one or more polymers that are soluble or swellable in organic solvents while the printed adhesive activator component may contain, optionally in addition to other components, one or more organic solvents that may dissolve or swell the pre-deposited component, thus forming the adhesive. In some embodiments of the invention, the adhesive forming component that is pre-deposited atop the substrate may contain one or more polymers such as, but not limited to, polyacrylates and their derivatives, polystyrenes and their derivatives, polyurethanes and their derivatives, polyesters and their derivatives, polyvinyl chloride and its derivative. In some embodiments of the invention, the printed adhesive activator component may contain, optionally in addition to other components, a mixture of one or more organic solvents, one or more solvent soluble polymers, one or more surfactants. In some embodiments of the invention, the printed adhesive activator component may contain, optionally in addition to other components, one or more organic solvents such as but not limited to alcohols, glycols, esters, amides, glycol esters and ketones.

[0045] In some embodiments of the invention, the printed adhesive activator component may be deposited by ink-jet printing, using commercially available and/or especially designed ink-jet printers. In some embodiments of the invention, the printers may be based on thermal (bubble) jet principle. In some embodiments of the invention, the printers may be based on piezzo jet principle. In some embodiments of the invention, the printers may be based on continuous ink jet principle.

[0046] In some embodiments of the invention, the first adhesive layer forming component is dispersed and/or formed homogeneously on the printing surface and said desired shape is achieved by photo-irradiation of the surface through a mask, rendering the exposed parts of the adhesive non adhesive by means of a photo-curing process. In some embodiments of the invention, said first adhesive layer forming component, dispersed homogeneously on the printing surface, may contain, optionally, in addition to other components, one or more free-radical and/or cationic UV-curable resins and/or one or more photo-initiators and/or one or more surfactants. In some embodiments of the invention, said first adhesive layer forming component may contain, optionally in addition to other components, one or more UV-curable resins such as, but not limited to, urethane acrylates, epoxyacrylates, aminoacrylates, poly ester acrylates, oligo ester acrylates, poly amide acrylates, oligo amide acrylates, epoxy derivatives, oxetane derivatives and the like

[0047] In some embodiments of the invention, said first adhesive layer forming component that is dispersed homogeneously on the printing surface may contain, optionally in addition to other components, one or more photo-initiators such as, but not limited to, alfa-hydroxyketones, alfa-animoketons, Bis-Acyl-Phosphine Oxide (BAPO), Mono-Acyl-Phosphine Oxide (MAPO), 2-Iso-propylthioxanthone (ITX), Ethyl-4-Dimethyl amino benzoate (EDB), sulphonium derivatives, iodonium derivatives and alike.

[0048] In some embodiments of the invention, said first adhesive layer forming component, in its desired shape, is achieved by photo-irradiation of a coated surface through a mask, rendering the exposed parts of the coated surface adhesive by means of a photo-reaction process.

[0049] In some embodiments of the invention, said first adhesive layer forming component is patterned on a non-planar object such as a rugged surface, a surface that contains steps, surfaces at a different height, rectangles, cubes, curved objects, bent surfaces and the like.

[0050] In some embodiments of the invention, after forming the patterned adhesive activator adhesive layer, the substrate is exposed to a decoration material in combination with components of a further adhesive layer forming component.. In some embodiments of the invention, the decoration materials may consist of metal oxides, metals, precious metals, glass frits, luster and special color effects pigments, organo-clay pigments, glazes, salts flux, mineralizers and pigment stains material

in combination with components of an adhesive layer forming component.. In some embodiments of the invention, the decoration materials may be organic materials. In some embodiments of the invention, the decoration materials may be inorganic materials. Examples of such materials are, but not limited to, metals, metal oxides, metal salts, silicon oxides, silicates, aluminate metal oxides, metals, precious metals, glass frits, luster and special color effects pigments, organo-clay pigments, glazes, salts flux, mineralizers and pigment stains material in combination with components an adhesive layer forming component. In some embodiments of the invention, the decoration materials may exist in the form of small particles, preferably, but not limited to, having a mean size of between 10 nanometers and hundreds of micrometers. In some embodiments of the invention, the decoration materials may exist as a powder of dry small particles without any liquid medium. In some embodiments of the invention, the decoration materials may exist as small particles dispersed in a carrier liquid medium. In some embodiments of the invention, the liquid carrier medium may contain, optionally in addition to other components, water, organic solvents, resins, surfactants, acids, bases, ions.

[0051] The decoration materials comprise metal oxides, metals, precious metals, glass frits, luster and special color effects pigments, organo-clay pigments, glazes, salts flux, mineralizers and pigment stains in combination with components of said first adhesive layer forming component when a further decorative layer is to be applied, otherwise the decoration materials simply comprise metal oxides, metals, precious metals, glass frits, luster and special color effects pigments, organo-clay pigments, glazes, salts flux, mineralizers and pigment stains .

[0052] In some embodiments of the invention the decoration material may contain one or more water soluble or water swellable polymers including, but not limited to, gelatin, arabic gum, polyvinyl alcohol and its derivatives, polyvinylpyrrolidone and its derivatives, carboxymethyl cellulose and alike.

[0053] In some embodiments of the invention the decoration material may contain in addition to other components, one or more alkali soluble or alkali swellable polymers such as, but not limited to, polyacrylic acid, copolymers of acrylic acid with epoxy acrylates, alkyl acrylates, aryl acrylates, polyacrylic esters, polyacrylic amides, copolymers of the above. In some embodiments of the invention the decoration material may contain in addition to other components one or more polymers such as, but not limited to, polyacrylates and their derivatives, polystyrenes and their derivatives, polyurethanes and their derivatives, polyesters and their derivatives, polyvinyl chloride and its derivative.

[0054] In some embodiments of the invention, the decoration materials may be deposited on the substrate using screens, brushes, rollers, spray techniques.

[0055] In some embodiments of the invention, after the

decoration materials are deposited, optionally after one or more additional steps, the excess of the particles that were not adhered to the adhesive layer may be removed from the substrate. In some embodiments of the invention, the excess of the decoration material particles may be removed by the use of one or any combination of the following techniques: gravitation, air flow (air gun), brushes, vacuum cleaning, electrostatic cleaning, ultrasound cleaning, washing, evaporation, exposure to heat, exposure to ultrasonic waves, exposure to electromagnetic irradiation such as infrared and/or microwaves. In some embodiments of the invention, the excess of the decoration materials particles that were removed may be used again in the deposition process.

[0056] In some embodiments of the invention, the substrate may be glazed- and non-glazed, fired- and not fired-, wall tiles, floor tiles, decal, glass sheets, glass packaging, dinnerware, sanitary ware, ceramic products, clay slab, metal and metal enamel.

[0057] In some embodiments of the invention at least one of said decoration material and said adhesive layer are applied through digital patterning.

[0058] In some embodiments of the invention said ceramic substrates comprise "green" ceramic tiles.

[0059] In other embodiments of the invention said ceramic substrates comprise burned ceramic tiles.

[0060] In yet other embodiments of the invention said ceramic substrates comprise glass sheets.

[0061] In yet other embodiments of the invention said ceramic substrates comprise decal sheets.

[0062] Optionally the present invention further comprises treating the substrate, after application of the adhesive layer and the decoration material, with heat.

[0063] In especially preferred embodiments of the present invention there is provided a method for applying a decoration material having a particular shape or boundaries on a ceramic substrate, comprising applying at least one adhesive-layer-forming component on a ceramic substrate, followed by applying thereto an adhesive activating component which renders said component functionally adhesive, said adhesive activating component being applied in accordance with pattern parameters of a chosen first color to appear in said decoration, applying a ceramic pigment in particulate form, as a first decoration material, in combination with components of a further adhesive layer forming component, such that said first pigment material remains at the location on the substrate determined by the activated adhesive layer, subsequently applying thereto a further adhesive activating component which once again renders said component functionally adhesive, said further adhesive activating component being applied in accordance with pattern parameters of a chosen second color to appear in said decoration, and applying a different ceramic pigment, in particulate form, as a second decoration material in combination with components of yet a further adhesive layer forming component, such that said second pigment material remains at the location on the substrate determined by

the further activated adhesive layer, whereby a ceramic substrate, decorated with at least two colors, is formed and subsequently applying thereto a further adhesive activating component which renders said further adhesive layer forming component functionally adhesive, said further adhesive activating component being applied in accordance with pattern parameters of a chosen third color to appear in said decoration, and applying a different ceramic pigment, in particulate form, as a third decoration material wherein the final pigment to be applied is applied without the addition of a further adhesive layer forming component.

[0064] In some embodiments of the invention, the decoration image may be produced on an intermediate substrate such as decals and then transferred to the substrate by conventional methods usable in ceramic or glass industry.

[0065] Depending on the specific embodiment of any of the embodiments of the invention, the coated shapes may be further subjected to one or more and/or combinations of additional processes aimed at:

a. Patterning additional adhesive layer and deposition additional layer of the decorative material

b. Coating the powder layer with different layers such as glaze, frit, glass flakes, special effect pigments, a protective layer, an anti slip layer and an anti bacterial layer

c. Removing undesired powder and/or adhesive using one or more of the following processes: exposure to heat, exposure to ultrasonic waves, exposure to electromagnetic irradiation such as infrared and/or microwaves, gravitation, air flow (air gun), brushes, vacuum cleaning, electrostatic cleaning,

d. Firing the shape to achieve its final physical, chemical, functional and aesthetic properties.

[0066] These complex chemical and physical reactions of the specimen components in the firing process will make up and determine the characteristics of the specimen including the decoration motif.

[0067] While the invention will now be further described in connection with certain particular embodiments in the following examples and with reference to the accompanying drawings so that aspects thereof may be more fully understood and appreciated, it is not intended to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus, the following examples will serve to illustrate the practice of this invention, it is to be understood that the particulars shown are by way of example and for purposes of illustrative discussion of particular embodiments of the present invention only and are presented in the cause of

providing what is believed to be the most useful and readily understood description of formulation procedures as well as of the principles and conceptual aspects of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0068]

FIG. 1 shows some non-limiting examples of a ceramic tile coated with a polymer film;

FIG. 2 shows an example of a ceramic tile coated with a polymer film. Some areas of the film is activated by contact with an adhesive activating liquid printed on top of the film;

FIG. 3 shows a ceramic tile with particles of cyan pigment particles connected to the activated areas of the polymer film; and

FIG. 4 shows a ceramic tile with particles of cyan and yellow pigment particles connected to the activated areas of the polymer film.

DETAILED DESCRIPTION OF THE INVENTION

[0069] Example 1: Decoration of a ceramic tile suitable for "Third fire", decoration on the surface of a previously glazed and fired tile.

1) A four color (CMYK) job was selected for printing. The job contained 10 partially overlapping patches of each color ranging from 10% to 100% coverage.

2) A "third fire" glossy-white ceramic tile (manufactured by Kaleseramik, Turkey) 15x15 cm, A, was covered with a polymer, P which contained a 4% water solution of polyvinyl alcohol (Celvol E523S, by Sekisui) using a knife coater, forming, after drying, a ceramic surface bearing polymer (20 micrometers thick), AP, Figure 1.

3) A solvent mixture, SM, consisting of 50% v/v water and 50% v/v ethylene-glycol was jetted on the surface of the tile bearing polymer, AP, using a commercially available ink-jet flatbed printer (Lexmark, T640A) in a pattern of cyan separation. By contacting polymer P with the solvent mixture SM, an adhesive, SMP was formed, having the shape of the cyan separation of the image depicted in Figure 2.

4) Ceramic decoration materials: Colorobbia Cyan POG-500; red POG-501; yellow POG-502; black POG-504, (size 5-10 micrometer) each in combination with 15%-35% (by weight) polyvinyl alcohol (Celvol E523S, by Sekisui), were prepared.

5) The patterned adhesive side of the patterned sheet, APP, was contacted with a mixture of polymer P and cyan ceramic decoration material in powder form, in a way that caused the adhesive SMP to be covered with the pigment particles and fully utilized as an adhesive thereby, forming a cyan powder patterned image, CyAPM, on top of the tile. Figure 3. The excess of the pigment powder was removed from the substrate using a fine brush.

6) Then the tile was again introduced into the ink-jet printer and another pattern (yellow separation) was printed with the same solvent mixture SM. By contacting polymer P with the solvent mixture SM, a further activated adhesive is again formed. Additionally, contact of the solvent mixture, SM, with areas covered cyan pigment (CyAPM) produces an adhesive. The newly patterned adhesive side of the patterned sheet was contacted with a powder of yellow ceramic decoration material in a way that caused the adhesive to be covered with the pigment particles, forming a yellow pigment powder patterned image, YeAPM, and mixtures of cyan and yellow pigments (resulting in green shades), CyYeAPM on top of the tile. Figure 4. The excess of the pigment powder was removed from the substrate using a fine brush.

7) The magenta followed by the black separations were printed in the same manner described in 5 using magenta and black ceramic decoration material.

8) After applying four separations the tile was placed in a ceramic kiln for a firing cycle of 60 min. heated to temperature of 900°C. All organic materials such as polymer and solvent were burned in the kiln. The firing cycle started at room temperature. Along the elevation of the temperature chemical and physical reactions take place. At a temperature of a few hundred degrees the organic materials go through reactions of evaporation and/or thermolysis. At a temperature of around 500°C, some of the inorganic materials start softening and/or melting. Solid state reactions of fusing and sintering take place. When maximum temperature has been reached, the decoration layer and the substrate basis are fused into one block. On cooling becomes part of the finished article.

9) Lab color values of the finished article were measured. The following values correspond to the 100% patch: cyan: 52.84, -17.07, -40.45; magenta: 61.72, 41.29, 1.69; yellow: 89.68, -8, 67.03; black: 11.61, -0.97, -2.43. Same image printed using silk screen obtained similar results were $\Delta E > 3$.

[0070] Example 2: Decoration of a "first fire" (non fired "green") ceramic floor tile. A "green" tile is manufactured by pressing ceramic powder in a mold.

[0071] A "green" ceramic tile (by Negev Ceramics, Israel) was decorated according to the procedure described in Example 1 with some modifications:

1) A four color (CMYK) job was selected for printing. The job contained 10 patches of each color ranging from 10% to 100% coverage.

2) A water dispersible acryl-styrene copolymer (BASF, Joncryl 617) was used as polymer P to create a 20 micrometer (micron) film.

3) Dipropylene glycol methyl ether was used as the adhesive activator.

4) Pigments suitable for first fire decoration such as Colorobbia PGE-5110 Blue, Colorobbia PGE-5316 Red, Colorobbia PGE-5204 Yellow and Colorobbia PGE-5407 Black were used. Each of the pigments was prepared in combination with 15%-35 (by weight) acryl-styrene copolymer (BASF, Joncryl 617).

5) After completing printing all separations the tile was fired at 1230 C.

6) Lab color values of the finished article were measured. The following values correspond to the 100% patch: cyan: 78.74, -9.47, -6.78; magenta: 48.1, 41.99, 8.96; yellow: 90.24, -6.3, 60.25; black: 14.5, 3.0, 5.51. Same image printed by a digital ceramic obtained the following values: cyan: 64.47, -0.16, -19.54; magenta: 58.11, 32.20, -2.63; yellow: 82.14, -6.56, 26.88; black: 33.63, -5.44, 7.52

[0072] Example 3: Decoration of a ceramic tile suitable for "third fire" using special effect pigments. "Third fire" is decoration on the surface of a previously glazed and fired tile.

1. A file containing two patches each a 100% coverage were printed. One bronze color and the other glossy-transparent.

2. A "third fire" glossy-white ceramic tile (Kaleseramik, Turkey) 15x15 cm, was decorated according to the procedure described in Example 1. Special effect pigments: Keramicon CSS-6205, Merck Iriodin 100 were used instead of regular CMYK pigments.

3. Amount of pigment on tile was measured. 65 gr/sq. meter of Keramicon CSS-6205 (glossy transparent) was deposited on the finished article; 60 gr/sq. meter Merck Iriodin 100 (bronze) was deposited on the finished article.

[0073] Example 4: Decoration of a "third fire" ceramic

tile by printing on a decal and transfer to the tile.

1. The process was similar to example 1. A decal paper sheet which contained paper coated with silicone release and arabic gum layer on top of the silicone was purchased from Tullis-Russell UK and was used as a substrate instead of the ceramic tile. After printing all separations on the decal, the image was transferred from the decal to the tile using a standard procedure described in (<http://home.comcast.net/~frankgaydos/Decal-1.html>). The tile was placed in a kiln, for a firing cycle of 60 min. heated to temperature of 900° C. All organic materials such as polymer and solvent were burned in the oven. Firing cycle started at room temperature. Along the elevation of the temperature chemical and physical reactions take place. At a temperature of a few hundred degrees organic materials go through reactions of evaporation and/or thermolysis. Around 500° C, some of the inorganic materials start softening and/or melting and solid state reactions of fusing and sintering take place. When maximum temperature is reached the decoration layer and the base substrate are it fused into one block that on cooling becomes part of the article.

2. Decal #70063 manufactured by Calcodecor S.A. was purchased from Kramicon. It was applied to a pre-glazed and pre-fired glossy-white tile. The decal was applied following the procedure described in <http://home.comcast.net/~frankgaydos/Decal-1.html>. The tile was placed in a kiln together with the tile described above in the previous section.

3. The two tiles, one described in the step 1) and the one prepared the traditional way as described above (section 2) had the same appearance in terms of color values.

[0074] Example 5: Decoration of a ceramic tile suitable for "third fire" using standard CMYK and bronze pigments. "Third fire" is a decoration of the surface of a previously glazed and fired tile.

1. A five color (CMYK and bronze) file was selected for printing. The file contained 10 patches for each color ranging from 10% to 100% coverage. In addition, the file contained a set of 10 patches for all five colors to be printed one on top of the other.

2. A water dispersible acryl copolymer (BASF, Joncryl 617) was used as polymer P to create a 20 micrometer (micron) thick layer on the tile surface.

3. Dipropylene glycol methyl ether was used as the adhesive activator.

4. Equal amounts (weight) of water emulsion of acryl-based polymer (BASF, Joncryl 660) was mixed with the each pigment. (Colorobbia Cyan POG-500, Colorobbia yellow POG-502, Colorobbia, magenta POG-501, Colorobbia, black POG-503 and Keramicon CSS-6205). The mixture was dried at 120° C

and ground to fine powder using a lab ball-mill. A "third firing" glossy-white ceramic tile (Kaleseramik, Turkey) 15x15 cm, was decorated.

5. The tile was printed as described in Example 1, stages 5-7.

6. The amount of pigment deposited directly on polymer P (acryl-based polymer BASF, Joncryl 617), and the amount of pigment deposited on the previously pigmented layer were equal.

[0075] It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

Claims

1. A method for applying at least a two-color decoration material having a particular shape or boundaries to a ceramic substrate, comprising:

- applying at least one adhesive-layer-forming component to a ceramic substrate,
- selectively applying an adhesive activator which renders said adhesive-layer-forming component adhesive to form an adhesive layer, according to a chosen color pattern of said decoration,
- applying a ceramic pigment, in particulate form, as a decoration material, together with a further amount of at least one adhesive-layer-forming component,
- removing excess of said ceramic pigment such that said pigment material remains only at the location on the substrate determined by said activated adhesive layer,
- selectively applying a further adhesive activator which renders said further amount of at least one adhesive-layer-forming component adhesive to form a further activated adhesive layer, according to a chosen color pattern of said decoration
- applying a different, further ceramic pigment, in particulate form, as a further decoration material, and
- removing excess further pigment such that said further pigment material remains only at the location on the substrate determined by the further activated adhesive layer,

whereby a ceramic substrate, decorated with at least two colors, is formed.

2. The method of claim 1, wherein said decoration material comprises one or more of, metal oxides, metals, precious metals, glass frits, luster and special color effects pigments, organo-clay pigments, glazes, salts flux, mineralizers, pigment stains pigments, metal oxides, silicates, glazes, stains or combinations thereof. 5
3. The method of claim 1, wherein said adhesive activator is a solvent which causes the adhesive-layer-forming component to become functionally adhesive to the applied decoration layer. 10
4. The method of claim 1, wherein said adhesive activator is deposited by ink-jet printing. 15
5. The method of claim 1, wherein said ceramic substrate comprises "green" ceramic tiles. 20
6. The method of claim 1, wherein said ceramic substrate comprises fired ceramic tiles. 25
7. The method of claim 1, wherein said ceramic substrate comprises glass sheets.
8. The method of claim 1, wherein said ceramic substrate comprises decal sheets. 30
9. The method of claim 1, further comprising treating the substrate, after application of the adhesive layer and the decoration material, with heat. 35

Patentansprüche

1. Verfahren zum Anbringen mindestens eines zweifarbigen Dekorationsmaterials mit einer bestimmten Form oder Abgrenzung auf einem Keramiksubstrat, umfassend:
 - a. Anbringen mindestens einer klebstoffschichtbildenden Komponente auf einem Keramiksubstrat, 45
 - b. selektiv Anbringen eines Klebstoffaktivators, der die klebstoffschichtbildende Komponente klebend macht, um eine Klebstoffschicht zu bilden, gemäß einem ausgewählten Farbmuster der Dekoration, 50
 - c. Anbringen eines Keramikpigments, in Partikelform, als Dekorationsmaterial, zusammen mit einer weiteren Menge mindestens einer klebstoffschichtbildenden Komponente, 55
 - d. Entfernen von Überschuss des Keramikpigments, sodass das Pigmentmaterial nur an der durch die aktivierte Klebstoffschicht bestimmten

Stelle auf dem Substrat verbleibt,
 e. selektiv Anbringen eines weiteren Klebstoffaktivators, der die weitere Menge mindestens einer klebstoffschichtbildenden Komponente klebend macht, um eine weitere aktivierte Klebstoffschicht zu bilden, gemäß einem ausgewählten Farbmuster der Dekoration,
 f. Anbringen eines verschiedenen, weiteren Keramikpigments, in Partikelform, als weiteres Dekorationsmaterial, und
 g. Entfernen überschüssigen weiteren Pigments, sodass das weitere Pigmentmaterial nur an der durch die weitere aktivierte Klebstoffschicht bestimmten Stelle auf dem Substrat verbleibt,

wodurch ein mit mindestens zwei Farben dekoriertes Keramiksubstrat gebildet wird.

2. Verfahren nach Anspruch 1, wobei das Dekorationsmaterial eines oder mehr von Metalloxiden, Metallen, Edelmetallen, Glasfritten, Glanz- und speziellen Farbeffektpigmenten, Organo-Ton-Pigmenten, Glasuren, Salz-Flussmittel, Mineralisatoren, Pigmentfärbemitteln, Pigmenten, Metalloxiden, Silikaten, Glasuren, Färbemitteln oder Kombinationen davon umfasst.
3. Verfahren nach Anspruch 1, wobei der Klebstoffaktivator ein Lösungsmittel ist, das die klebstoffbildende Komponente veranlasst, an der angebrachten Dekorationsschicht funktionell haftend zu werden.
4. Verfahren nach Anspruch 1, wobei der Klebstoffaktivator durch Tintenstrahldruck aufgebracht wird.
5. Verfahren nach Anspruch 1, wobei das Keramiksubstrat "grüne" Keramikfliesen umfasst.
6. Verfahren nach Anspruch 1, wobei das Keramiksubstrat gebrannte Keramikfliesen umfasst.
7. Verfahren nach Anspruch 1, wobei das Keramiksubstrat Glasplatten umfasst.
8. Verfahren nach Anspruch 1, wobei das Keramiksubstrat Dekorbögen umfasst.
9. Verfahren nach Anspruch 1, weiter das Behandeln des Substrats, nach dem Anbringen der Klebstoffschicht und des Dekorationsmaterials, mit Hitze umfassend.

Revendications

1. Procédé pour l'application d'au moins un matériau de décoration bicolore possédant une configuration

particulière ou des limites particulières sur un substrat en céramique, comprenant le fait de :

- a. appliquer au moins un composant de formation d'une couche adhésive sur un substrat en céramique ; 5
- b. appliquer de manière sélective un activateur de l'adhésif qui rend adhésif ledit composant de formation d'une couche adhésive pour former une couche adhésive, en fonction d'un motif de couleur sélectionné de ladite décoration ; 10
- c. appliquer un pigment céramique, sous forme particulière, à titre de matériau de décoration conjointement avec une quantité supplémentaire d'au moins un composant de formation d'une couche adhésive ; 15
- d. éliminer l'excès dudit pigment céramique d'une manière telle que ladite matière pigmentaire subsiste uniquement à l'endroit sur le substrat déterminé par ladite couche adhésive activée ; 20
- e. appliquer de manière sélective un activateur supplémentaire de l'adhésif qui rend adhésive ladite quantité supplémentaire d'au moins un composant de formation d'une couche adhésive, pour former une couche adhésive davantage activée, en fonction d'un motif de couleur sélectionné de ladite décoration ; 25
- f. appliquer un pigment céramique supplémentaire différent, sous forme particulière, à titre de matériau de décoration supplémentaire ; et 30
- g. éliminer l'excès du pigment supplémentaire d'une manière telle que ladite matière pigmentaire supplémentaire subsiste uniquement à l'endroit sur le substrat déterminé par la couche adhésive davantage activée ; 35

par lequel on obtient la formation d'un substrat en céramique décoré avec au moins deux couleurs. 40

- 2. Procédé selon la revendication 1, dans lequel ledit matériau de décoration comprend un ou plusieurs matériaux choisis parmi des oxydes métalliques, des métaux, des métaux précieux, des frites de verre, des pigments possédant des effets spéciaux de brillant et de couleurs, des pigments d'organoargile, des émaux, des flux salins, des minéralisateurs, des pigments de teintures pigmentées, des oxydes métalliques, des silicates, des émaux, des teintures ou leurs combinaisons. 45 50
- 3. Procédé selon la revendication 1, dans lequel ledit activateur de l'adhésif est un solvant qui fait en sorte que le composant de formation d'une couche adhésive dispose d'une fonctionnalité adhésive par rapport à la couche de décoration appliquée. 55
- 4. Procédé selon la revendication 1, dans lequel ledit

activateur de l'adhésif est déposé via une impression par jet d'encre.

- 5. Procédé selon la revendication 1, dans lequel ledit substrat en céramique comprend des carreaux de céramique « à l'état vert ». 5
- 6. Procédé selon la revendication 1, dans lequel ledit substrat en céramique comprend des carreaux de céramique à l'état cuit. 10
- 7. Procédé selon la revendication 1, dans lequel ledit substrat en céramique comprend des plaques de verre. 15
- 8. Procédé selon la revendication 1, dans lequel ledit substrat en céramique comprend des feuilles de décalcomanie. 20
- 9. Procédé selon la revendication 1, comprenant en outre le fait de soumettre le substrat, après l'application de la couche adhésive et du matériau de décoration, à un traitement thermique. 25 30 35

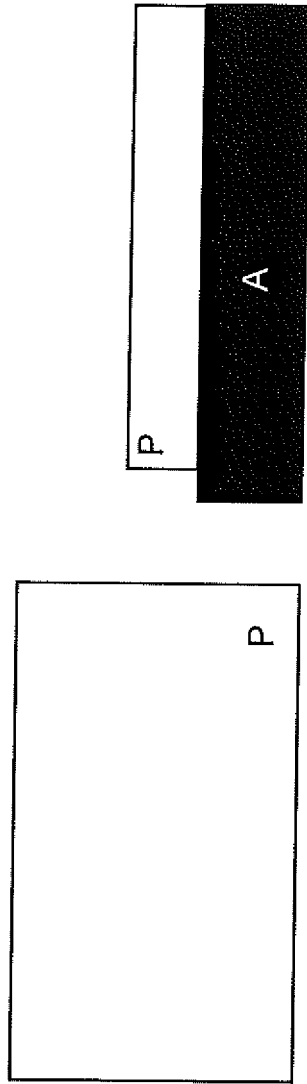


Figure 1

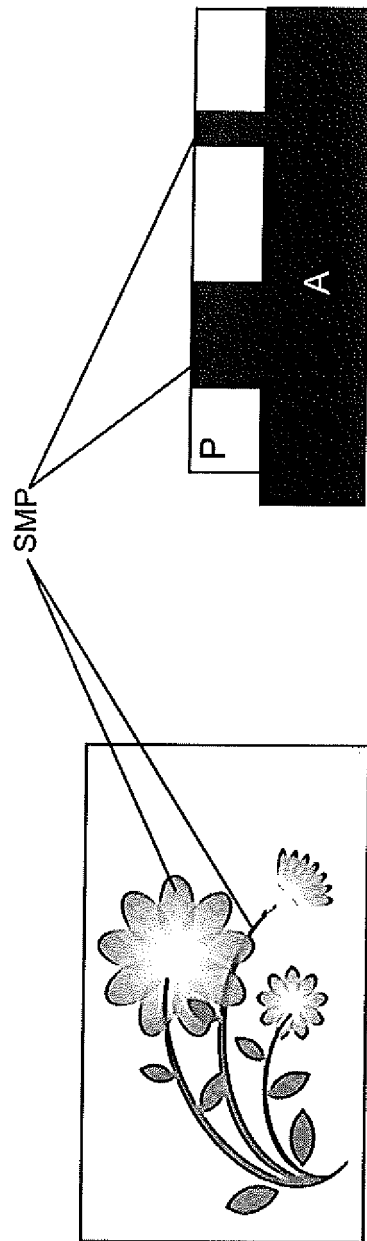


Figure 2

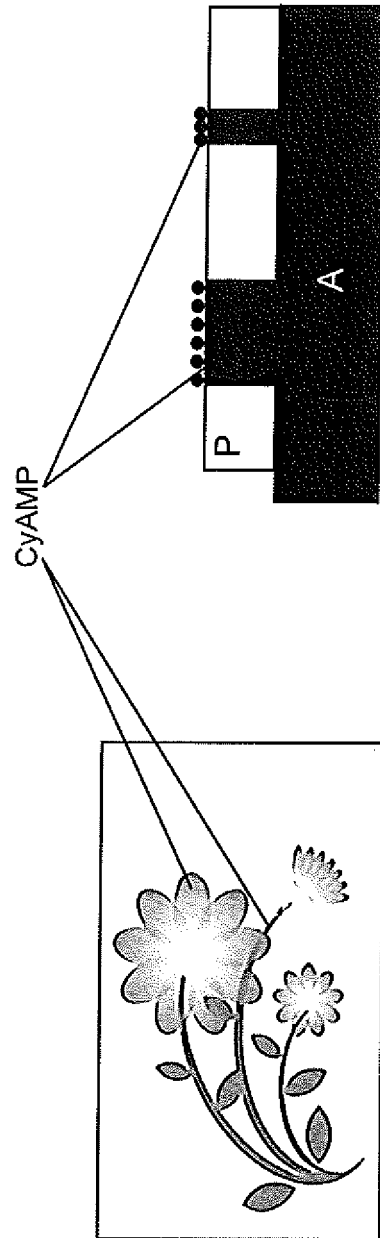


Figure 3

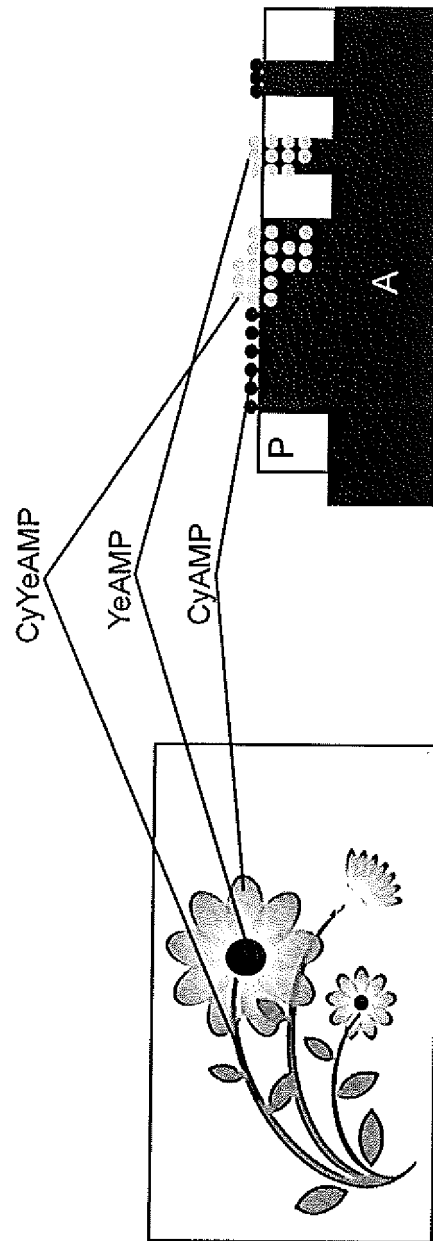


Figure 4

REFERENCES CITED IN THE DESCRIPTION

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