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METHOD OF FORMING A CERAMIC IMAGE ON A CERAMIC SUBSTRATE

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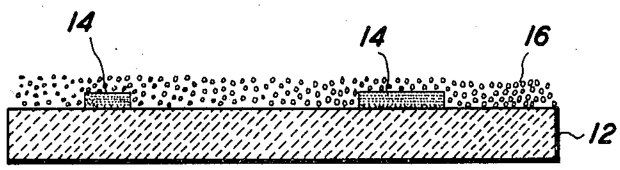

FIG. 1

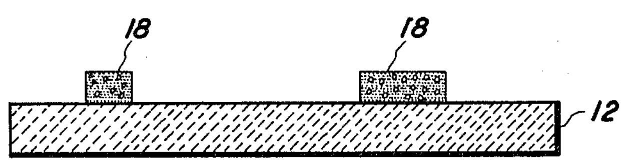

FIG. 2

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METHOD OF FORMING A CERAMIC IMAGE ON A CERAMIC SUBSTRATE

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ABSTRACT OF THE DISCLOSURE

A composite xerographic toner-ceramic powder image is formed on a ceramic article to be decorated and then fired, preferably after applying a glaze over desired portions of the article, to volatize and burn off the toner and leave behind a ceramic powder image on the glazed ceramic.

BACKGROUND OF THE INVENTION

This invention relates in general to an imaging system and more specifically to an improved system for forming a ceramic image on a ceramic substrate.

In order to impart an image or a design to a finished ceramic product, it is generally customary to take a ceramic article and transfer a decalcomania to the article, fire the article to burn away the temporary film carrying the design which becomes substantially permanently ceramed to the article. This decal step is then typically followed by a separate and distinct glazing step which takes place after the article has been cooled from the first firing. Glazing is generally accomplished by coating the article with a glazing material, which may be a clear glaze, and then firing the article a second time. This two step process is time consuming, often taking two days or more, and expensive because of the repeated steps.

Decalcomanias used in the art typically comprises a backing of a suitable grade of paper coated on one side with a film of a water soluble binder such as dextrin or glue and superimposed on this binder is a film of oxidized linseed oil, silicone based oil or the like with the design or image printed thereon in ceramic powder. Attempts to shorten this two step process to a one step, one firing process wherein the decal is transferred to the article and then the glaze is put on over the decal and the entire article fired once has produced inferior ceramics because it is found that upon firing, the film carrying the design of the ceramic powder decomposes in such a manner as to cause localized outgassing, a rather sudden disruption of gases which causes localized blowing of the glaze overcoating giving a crater or pocked marked effect and an undesirably rough and unsightly final product.

The same undesirable result may also be found in the method of imparting images to ceramics which entails combining ceramic powders in a liquid vehicle and painting on the article as described in Morgan Pat. 3,238,053 or the marking in image configuration on an article with an oil such as a vegetable oil, a litho-varnish, or a varnish or boiled linseed oil as described, respectively, in Hommel Pat. 1,531,613, Denk Pat. 1,473,903 and Schulze-Berge Pat. 296,226; then sprinkling ceramic powder over the oil design image on the article, the ceramic powder selectively adhering to the oiled portion of the article in image configuration. In addition, these concepts of liquid-ceramic powder imaging on an article are generally found to produce images of unsatisfactory resolution because of image spreading and possess the other inherent disadvantages of a liquid imaging process.

Thus, there is a continuing need for a better system for imaging and imparting ceramic designs to a ceramic article, especially in a single firing process.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a ceramic imaging system which overcomes the above-noted deficiencies and satisfies the above-noted wants.

It is a further object of this invention to provide a ceramic imaging method wherein the image or design and the glaze may be imparted to the article in a single firing process thereby providing for a simpler and faster ceramic imaging method.

It is a further object of this invention to provide a ceramic imaging method which reliably produces high resolution images and designs.

It is a still further object of this invention to provide a ceramic imaging system which does not employ conventional decal or liquid oil imaging methods.

It is a still further object of this invention to provide a single system to make high resolution conductive patterns or circuits on insulating ceramics.

The foregoing objects and others are accomplished in accordance with this invention by forming a composite xerographic toner-ceramic powder image on a ceramic article and preferably applying a glaze over desired portions of the article, including typically at least a portion of the composite toner and ceramic powder image and then firing the article to volatize and burn off the toner and render the image permanent and the article glazed.

BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention as well as other objects and further features thereof, reference is made to the following detailed disclosure of this invention taken in conjunction with the accompanying drawings wherein:

FIG. 1 is a partially schematic illustration of an unceramed article carrying a xerographic toner image and a dusting of ceramic powder during a process embodiment according to the invention.

FIG. 2 is a partially schematic illustration of a ceramic article carrying a composite xerographic toner-ceramic powder image during a process embodiment according to the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the process of xerography, for example, as disclosed in Carlson Pat. 2,297,691: a xerographic plate comprising a layer of photoconductive insulating material on a conductive backing is given a uniform electric charge over its surface and is then exposed to a light and shadow image pattern of the subject matter, the original, to be reproduced, usually by conventional projection techniques. This exposure discharges the plate areas in accordance with the radiation intensity that reaches them and thereby creates an electrostatic latent image on or in the photoconductive layer corresponding to the light and shadow image pattern. Development of the latent image is effected with an electrostatically charged, finely divided material, such as an electroscopic powder, called toner, that is brought into surface contact with the photoconductive layer and is held thereon electrostatically in a pattern corresponding to the electrostatic latent image. The developed, xerographic marking material image may be fixed or made permanent on the xerographic plate itself. Alternatively, if it is desired, to apply the developed xerographic powder image to paper, metal foil, plastic film, or other transfer material, the developed image may be transferred from the xerographic plate to such a support surface to which it may be affixed by any suitable means. Fixing of the developed image onto the xerographic plate itself becomes attractive for relatively inexpensive plates such as those comprising photoconductive material impregnated into paper. Illustratively, paper may be impregnated, by melting or from solution, with organic or inorganic photoconductive materials, such as anthracene or sulfur. Photoconductors comprising amorphous selenium are now found to be preferred as a reusable photoconductor in commercial xerographic imaging machines.

It was also well-known, early in the art, that materials such as zinc oxide in a binder may also be used as a photosensitive layer on paper. See Young, C. J. and Greig, H. G., RCA Review, 15, No. 4, 471 (1954), and Thomsen Pats. 2,727,807 and 2,727,808.

As described herein, the process of xerography is applied to the field of imaging on ceramics in a novel and most advantageous manner.

Ceramic as used herein, is intended to mean the product, or the manufacture of, any solid product such as pottery, earthenware, porcelain, tile, brick, glass, vitreous enamels, cement, plaster, refractories and so on made from essentialy inorganic, nonmetallic materials and which normally require or at least can withstand a firing step at least to a temperature high enough to volatilize the toner from the composite toner-ceramic powder images hereof and permanently fix the ceramic powder to the ceramic article.

Ceramic powder as used herein, is intended to encompass the above described materials or combinations thereof, in particularized form, for example, in the range of from about 50 microns to sub-micron size, suitable for forming fire permanentized images according to the invention and also including phosphors, fusible metallic colors such as are well known for painting on china or glass, powdered glass, i.e., glass frit, either alone or in combination with an inorganic heat resistant pigment such as are well known in the art and sold by numerous manufacturers thereof carrying a suitable pigment or coloring material embodied therein if desired.

Referring now to FIG. 1, there is illustrated as raised portions 14, a xerographic toner image which has been deposited on ceramic article **12**. The toner image is formed by any suitable xerographic technique and may be transferred from a xerographic plate or other surface by any suitable method as known to those skilled in the art.

However, a preferred method of transferring the toner image to article **12** is to form a releasable toner image by conventional xerographic techniques on a xerographic plate and then transfer this toner image to a toner offset preventing material, such as tetrafluoroethylene fluorocarbon substrate, which is found to be a preferred material, available under the trademark Teflon from Du Pont, for example in the form of about a 2 mil film of Teflon, with the toner image being at least partially fused to the Teflon, for example by temporarily tackifying the toner image. The Teflon film, image side down, is then placed on the ceramic article **12** which is heated preferably to a temperature sufficient to heat tackify the toner image such as between about 150° F. and 300° F. and a uniform pressure is applied to the back of the Teflon to ensure uniform contact of the image with the ceramic article, whereupon, the toner image tenaciously adheres to the surface of article **12** and at least partially melts into the tooth and small openings of article **12**. Alternatively, if article **12** during this process is not heated to a temperature in the above-mentioned toner melting range, a toner image may be tackified by applying heat or a solvent vapor for the toner or by other means to tackify it to allow the partial imbibing of the image into article **12**. The toner image is then allowed to harden and the Teflon sheet is stripped off, the 2 mil thickness allowing for easy stripping to leave at least a partially fixed toner image **14** on article **12**.

A toner image may also be formed on a ceramic by coating the ceramic with a zinc oxide binder type photoconductor, charging the member, the ceramic material being dampened to render it electrically conductive, exposing by means of a projected light image and contacting toner to the latent electrostatic image.

After the above described transfer of the toner image to the ceramic aricle, the toner image is then tackified once again and dusted with ceramic powder, which adheres selectively to the tackified toner image portions of article **12**. Preferably the article is dusted with a ceramic powder to completely cover the toner areas followed by solvent vapor tackifying of the toner image which has been found to produce the highest quality, highest contrast images according to the invention. Techniques similar to those described in Walkup et al. Pat. 2,955,035 may be used to form this raised composite xerographic toner-ceramic powder image produced herein similar to that produced in said Walkup et al. patent. For the densest images, the solvent vapor is applied and ceramic powder dusting is continued until the toner image no longer sweats through to the surface of the dusted ceramic powder layer. At this point the tackified toner image is allowed to again harden and fix itself and unadhered ceramic powder is removed by shaking, blowing, brushing or otherwise removing ceramic powder from non-toner image portions of article **12**.

Referring now to FIG. 2, the article at this stage looks very much as illustrated in FIG. 2, with the image portions **18** now comprising ceramic powder **16** absorbed in a matrix of xerographic toner **14**.

Although a preferred method of forming a composite toner-ceramic powder image on a ceramic article has been described, any suitable method of forming such a composite image on a ceramic article may be used herein including transferring a toner image from a xerographic plate or other support surface to a toner offset preventing substrate, tackifying the toner image and dusting ceramic powder thereover, to form the composite image, removing loose ceramic powder, positioning the offset preventing substrate image side down against the ceramic article, tackifying the toner, for example, by a hot flat iron or other hot pressure surface to cause the toner with the ceramic powder to adhere to the ceramic base, and then stripping away the offset preventing substrate preferably after cooling the toner.

The composite image, as illustrated in FIG. 2, comprising the ceramic powder in a matrix of at least partially fused xerographic toner is stable enough so that unwanted background areas may be cleaned up by contacting the imaged ceramic article with a mild abrasive, for example, by scouring or brushing with any conventional, commercial detergent cleanser.

The article in this condition may then be fired to permanentize the ceramic powder image to the article but preferably a glazing compound is applied to the article before firing and generally over the entire atricle including over the image portions and the member is then fired typically to from about 700° C. to about 2000° C., and at even lower temperatures, for example, about 400° C. for luminescent screen work, depending on the ceramic article, ceramic powders and glaze used, to produce a smooth glazed, imaged, ceramic article without the gas exploded, outgas craters which were found in prior art, single firing processes. Conventional ceramic firing times and temperatures are found entirely sufficient to volatize off toners which may start to decompose at temperatures as low as 150° C.

Any suitable glaze material and method of application may be used including applying by brush, spray, dipping or other suitable means a water dispersion of clay with a frit, or premelted silicate glass, as is well known in the art or by dusting glaze powder on the article.

Clear or substantially transparent glazes are normally to be preferred to permit ready display of the ceramic design but glossy and mat glazes may also be used since depending on the thickness and opacity of the glaze overcoating, there may be sufficient "show through" of the ceramic design to present a commercially acceptable image.

It will be appreciated that the firing step of the invention may be preceded by other firings, without glaze, for the article for example to mature the body of the article to bisque form.

It is thought that the highly desirable, smooth, glazed surface of the final fired article results from the toner decomposing to gases in such a manner as to permit these gases to diffuse or otherwise escape through the glaze overcoat without disruptively exploding away the glaze overcoat to produce localized crater defects as was found to be produced in the prior art when, for example, linseed oil or silicone oil based decals were attempted to be fired off in a one step process with the glaze overcoating.

A preferred xerographic toner for use herein is found to have an average particle size of between about 5 and 15 microns comprising a styrene-butyl methacrylate copolymer, polyvinyl butyral and carbon black prepared as disclosed in Example I of Insalaco Pat. 3,079,342. This toner is preferred because of its capability of forming excellent xerographic images and transferring to ceramic articles according to the preferred method described herein, and because such toner decomposes at conventional ceramic firing temperatures in such a way as to permit diffusion of the gases produced by the toner decomposition through an overcoating of conventional ceramic glazing compound which is being fired simultaneously.

Although, the above described toner is preferred for use herein, any suitable xerographic toner or other marking material used to develop latent electrostatic images in xerography may be used herein, and is intended to be included in the term xerographic toner as used herein. Typical xerographic toners are described in Insalaco Pat. 3,079,342, as well as Carlson Resissue Pat. 25,136, Copely Pat. 2,659,670, Landrigin Pat. 2,753,308, Insalaco Pat. 2,891,011, Walkup Pat. 2,618,551, Walkup et al. Pat. 2,638,416 and others.

Also, in the preferred solvent vapor tackifying of the toner image during the ceramic powder dusting step hereof, the vapor of any suitable solvent for the toner may be used. A preferred solvent is trichloroethane. However, the vapor of any suitable solvent for xerographic toner may be used.

The following examples further specifically define the present ceramic imaging invention. The parts and percentages are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of the xerographic toner-ceramic powder imaging method of this invention.

EXAMPLE I

A high quality xerographic toner image including line copy is formed on the flat, amorphous selenium photoconductor, xerographic plate on the Model D Processor xerographic imaging machine available from Xerox Corp. Exposure is on the #4 camera companion to the Model D. The toner is the styrene-butyl methacrylate copolymer polyvinyl butyral and carbon black toner described in Example I of Insalaco Pat. 3,079,342. Development is by the cascade technique.

This releasable toner image on the xerographic plate is transferred to about a 2 mil thick Teflon film by the conventional corona charging transfer provided for in the Model D Processor.

This toner image is then at least partially fused by subjecting it to the vapors of trichloroethane for about five seconds to tackify the toner image. This partial fixing step permits the toner bearing Teflon film to be positioned on the ceramic article without undesired transfer of toner to the article.

The Teflon film, image side down, is then placed on the ceramic article which is an unglazed, unfired ceramic saucer in bisque form which is preheated to about 200° F. The back of the Teflon film is lightly pressed with cotton to ensure uniform contact of the toner image to the ceramic. The toner image tackified by the heated ceramic melts into the tooth of the ceramic.

The ceramic is cooled to about room temperature, such as between about 10° C. and about 30° C. and the Teflon film is stripped from the ceramic.

The ceramic, bearing the toner image is then dusted with a uniform layer of ceramic powder comprising a conventional fritted color pigment to a thickness of about four mils over all toner image areas desired to be converted to a ceramic image.

The dusted side of the ceramic is then subjected to the vapors of trichloroethane. In a matter of minutes, the toner image is seen to bleed or sweat through to the surface of the dusted ceramic powder layer. Additional ceramic powder is dusted until no more bleeding occurs.

The solvent vapor is removed, the loose ceramic powder is removed to leave on the ceramic a composite toner-ceramic powder image. The ceramic is lightly scrubbed with detergent cleanser to clean up background, and English Porcelain glaze comprising particles with a mean diameter of between about 7–10 microns of

	Percent
Na_2O	2.3
K_2O	5.2
CaO	10.8
Al_2O_3	14.3
SiO_2	67.4
	100.0

in a water base is sprayed onto the entire surface of the ceramic including over the composite toner-ceramic powder image.

The ceramic is then fired at cone 9 to sublime off the toner without disrupting the glaze overcoating, to form a clear glazed ceramic with a ceramic image of high density and contrast, resolution exceeding 3 lp/mm. in line copy areas and otherwise of high quality.

EXAMPLE II

Example I is followed except the glaze is about 96% of the particles in the English Porcelain glaze described in Example I, about ¼% cobalt oxide, about 2¾% clay and about 1% of a conventional electrolyte, the particles mixed dry to form a bluish powder, the powder then being added to water and sprayed, to form a clear blue glaze over the ceramic image.

Although specific components and proportions have been stated in the above description of preferred embodiments of the ceramic imaging method hereof, other suitable materials, as listed herein, may be used with similar results. In addition, other materials may be added to the materials used herein or variations may be made in the various processing steps to synergize, enhance, or otherwise modify the system. For example, stearates may be added to toners as described in copending application Ser. No. 511,242, filed Dec. 2, 1965, to enhance flowability. Chemical powder may be added to toners to react with the ceramic to form visible images.

Also, the ceramic powder of this invention may comprise a powdered phosphor and the process hereof may be used to form multicolor, i.e. tricolor, luminescent screens as used in color television tubes, and as more particularly described in Donahue Pat. 2,796,374. Illustratively, one set of dots may be formed on a glass substrate each dot comprising a composite xerographic toner-blue-emitting phosphor; and then the second and third sets of dots may be deposited by the method hereof, each set of dots comprising a phosphor having a different emission color, i.e. the second set of dots may comprise a green-emitting phosphor and the third set a red-emitting phosphor. Firing or baking temperatures and suitable glazes therefore, which may differ somewhat from those used in more conventional ceramics are known to those skilled in luminescent screen work.

Also, by the method hereof conductive patterns made up of an electrically conductive ceramic powder may be placed on electrically insulating ceramics for use in integrated circuits and miscellaneous micro-electronic components.

Also, although conventional xerographic process steps may be followed to give a xerographic toner image for use herein, xerographic toner images may be formed by a multitude of other techniques such as depositing toner through a stencil, for example, as described in Pat. No. 3,487,775, or as taught in Childress et al. Pat. No. 3,081,698.

It will be understood that various other changes in the details, materials, steps and arrangements of parts, which have been herein described and illustrated in order to explain the nature of the invention will occur to and may be made by those skilled in the art upon a reading of this disclosure, and such changes are intended to be included within the principle and scope of this invention.

What is claimed is:

1. A method of forming a ceramic powder imaged ceramic article comprising the steps of:

(a) forming a composite xerographic toner-ceramic powder image on the ceramic article; and,

(b) firing the ceramic article sufficiently to sublime off the xerographic toner and fuse the ceramic powder to the ceramic article.

2. A method according to claim **1** wherein between steps (a) and (b) a glaze is applied to the ceramic article and over at least part of the composite toner-ceramic powder image and wherein the firing is sufficient to sublime the toner and fuse the ceramic powder and the glaze to the ceramic article.

3. A method according to claim **1** wherein the composite xerographic toner-ceramic powder image is formed on the ceramic article by:

(a) forming a xerographic toner image on the ceramic article;

(b) covering at least part of the toner image portion of the ceramic article with a layer of ceramic powder;

(c) tackifying the toner image to cause ceramic powder to become embodied therein; and,

(d) removing all loose ceramic powder from the ceramic.

4. A method according to claim **3** wherein the xerographic toner image is formed on the ceramic article by:

(a) forming a releasable xerographic toner image on a substrate;

(b) transferring at least part of the toner image to a toner offset preventing substrate;

(c) placing the toner offset preventing substrate, image side down, against the ceramic article;

(d) tackifying the toner image;

(e) applying a uniform pressure to the back of the toner offset preventing substrate to ensure uniform contact of tackified toner image with the ceramic article;

(f) resolidifying the toner image; and,

(g) stripping the toner offset preventing substrate from the ceramic article to substantially completely leave the toner image behind on the ceramic article.

5. A method according to claim **4** wherein the releasable xerographic toner image is formed on a substrate by xerographically forming the toner image on a xerographic plate and then transferring at least part of the toner image to the substrate.

6. A method according to claim **4** wherein the toner offset preventing substrate is a tetrafluoroethylene fluorocarbon.

7. A method according to claim **3** wherein after forming the composite xerographic toner-ceramic powder image and before firing, a glaze is applied to the ceramic article and over at least part of the composite toner-ceramic powder image and wherein the firing is sufficient to sublime the toner and fuse the ceramic powder and the glaze to the ceramic article.

8. A method according to claim **4** wherein after forming the composite xerographic toner-ceramic powder image and before firing, a glaze is applied to the ceramic article and over at least part of the composite toner-ceramic powder image and wherein the firing is sufficient to sublime the toner and fuse the ceramic powder and the glaze to the ceramic article.

9. A method according to claim **4** wherein the toner image is tackified when it is on the toner offset preventing substrate by bringing it into contact with the ceramic article heated to between about 150° F. and about 300° F., and wherein the toner image on the ceramic article is tackified by exposing it to the vapors of a solvent liquid for the toner.

10. A method according to claim **2** wherein the xerographic toner comprises particles of an average particle size of between about 5 and 15 microns comprising a styrenebutyl methacrylate copolymer, polyvinyl butyral and carbon black.

11. The method according to claim **3** wherein the ceramic powder is electrically conductive.

12. The method of claim **3** wherein the forming of a xerographic toner image on the ceramic article includes

rendering the article electrically conductive;

providing the article with a photoconductive layer;

charging the article;

forming an electrostatic latent image, and

contacting the electrostatic latent image with toner.

13. The method of claim **12** wherein the electrostatic latent image is formed by exposing the charged article to an image pattern of electromagnetic radiation in image formation.

14. The method of claim **12** wherein the photoconductor includes zinc oxide binder.

15. The method of claim **12** wherein said article is rendered electrically conductive by coating it with an electrically conductive liquid.

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