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Blanco

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[54] **METHOD FOR THE PREPARATION OF AN OVERGLAZE CERAMIC DECALCOMANIA**

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[58] **Field of Search** ..... 117/62, 13, 3.1–3.6, 117/70 A, 70 C, 70 S, 40, 45, 23, 25

[56] **References Cited**

UNITED STATES PATENTS

2,175,209	10/1939	Matthews	117/3.5
2,502,758	4/1950	Short	117/3.4 UX
2,734,840	2/1956	Kane	161/413 X
2,992,937	7/1961	Davis	117/13 X
1,651,470	12/1927	Sadtler	117/13 X
2,008,763	7/1935	Lawrence et al.	117/3.2 X

FOREIGN PATENTS OR APPLICATIONS

278,801	10/1927	Great Britain	117/25
6,548	5/1887	Great Britain	117/13
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[57] **ABSTRACT**

A method for the preparation of an overglaze ceramic decalcomania is provided wherein a wet ink formulation containing a liquid printing vehicle or medium and an oxide coloring agent, free of glass, is wet printed on a decalcomania backing sheet to form a wet design layer thereon free of glass, and a protective coating of prefused glass flux is separately deposited on the wet design layer, so that when the design layer and protective coating deposited thereon is positioned on a glazed piece of ware and fired, the protective coating of prefused glass flux fuses and tightly binds the design layer to the ware.

6 Claims, No Drawings

METHOD FOR THE PREPARATION OF AN OVERGLAZE CERAMIC DECALCOMANIA

BRIEF SUMMARY OF THE INVENTION

The present invention relates to a method of preparing an overglaze ceramic decalcomania or decal by wet printing a design layer, free of glass, on a backing sheet and separately depositing a protective coating of prefused glass flux on the wet design layer.

BACKGROUND OF THE INVENTION

A decal usually is comprised of a multi-layer structure including a backing, a design layer and a protective layer applied over the design layer. The colors in the design layer are formed from inorganic pigments or oxides. A layer facilitating release of the backing from the design may be interposed between the backing layer and the design layer.

A number of different types of decals are used at present in the pottery industry to apply patterns to ceramic ware. One of these is the so-called "underglaze" decal. This type of decal is applied to the ware after the ware has been formed but before it is glazed. Thereafter, a glaze is applied over the ware and decal. This glaze consists of a vitreous coating. The coating is formed directly from raw materials so that a very high temperature must be used in firing the ware to form the glass. The result of this process is a protective coating over the pigment such that the pigment will not be subject to chemical and mechanical attack such as produced by modern chemical detergents and mechanical washing devices. However, the use of such a high temperature as is necessary to form the glaze destroys the color value of many of the pigments that would be preferred to produce the desired colors. In addition, the glaze may be somewhat opaque so that the designs of the decal are obscured. It will be appreciated from the foregoing that this underglaze ceramic decal is limited in application.

As a result of these limitations, the so-called "overglaze" decals were developed. That is, decals which are applied to the ware after the high temperature glaze has been put on. These overglaze decals can generally be divided into two classes — silk screen decals and lithographic decals.

In the silk screen process a silk screen template or stencil is placed over the surface on which pigment is to be deposited and the pigment applied through the screen. If the decal were of the "water mount" or "slide off" type, the surface on which the pigment is applied would be the layer of water soluble gum which has been placed over a paper backing. In this process a relatively thick layer of pigment is deposited over the entire surface covered by the stencil. In order to increase the permanence of the design in the silk screen decal, a quantity of powdered low melting point glass may be mixed with the pigment so that when the pattern is set by the application of heat this powdered glass will fuse and become a part of the pattern itself. The silk screen decals, however, like the underglaze decals, are subject to a number of limitations. For example, the fine and clear cut designs and tonal variations available in the lithographic process cannot be obtained by the silk screen process. Also, the thicker pattern which results from this process is not always desirable. Because of these limitations lithographic decals are widely used in the industry.

Lithographic decals are formed by printing a layer of the desired pattern for one pigment in a clear varnish and then dusting the pigment over the entire sheet in a lithographic process. The sheet is then cleaned leaving pigment only where the varnish is. The sheet is then permitted to dry. If other colors are desired, the foregoing process must be repeated for each color. It will be appreciated that a large proportion of pigment is wasted in this process because it is dusted over the entire sheet and a great deal is not recovered in the cleaning process. A great deal less is required in the method of the present invention because pigment is only printed on these areas where it is desired.

Kane, U. S. Pat. No. 2,734,840, discloses a lithographic decal which is strongly resistant to chemical and mechanical attack and which is made by dusting a mixture of powdered glass and solid pigment powder or solid pigment globules on a backing sheet containing an adhesive such as a gum or varnish to form a dry design layer thereon and thereafter covering the pigment-glass design layer with a layer of powdered low melting point glass. Conventional wet printing techniques such as offset printing cannot be employed to form the dry design layer disclosed by Kane. If the pigment-glass mixtures of Kane are employed in a wet printing medium, the presence of the glass with the pigment dilutes the color value of the pigment. Excessively large amounts of pigment would be required to compensate for color dilution, the result of which would be the formation of excessively thick design layers, which serve no useful purpose. In addition, spreading of the color by means of printing rollers, employed in wet printing techniques, is difficult because of the present of relatively large glass particles.

British Pat. No. 1,094,104 to Johnson, Matthey & Co. discloses a ceramic pigment transfer and method for making the same wherein an ink comprising a printing medium or varnish incorporating a ceramic pigment is applied to a backing sheet and a covering layer of an adhesion-promoting flux of glass-forming constituents is applied over the pigment layer. The covering layer is adapted to fuse to form an outer protective layer when fired. The flux of glass-forming constituents is said to include constituents adapted to form a lead-borosilicate glass, such as lead oxide, boric acid and silica.

It has been found that where glass-forming constituents, such as lead oxide, boric acid and silica, are coated on the pigment layer and fired, these glass-forming constituents each have a different melting point and therefore melt at different times on the pigment layer, causing the pigment layer to become spotty. It is only after all of these glass-forming constituents melt and chemically react that glass is, in fact, formed. However, by this time it is too late and the design is already discolored. The problem of discoloration of the design or pigment layer is inherent in the process of this British patent.

Lawrence, U. S. Pat. No. 2,008,763, discloses a transfer or decal substitute wherein a design is applied to a base by means of a marking composition comprised in gum dammar (70 parts), castor oil (20 parts), kerosene (40 parts) and boiled linseed oil (20 parts) and which can contain a metallic pigment. After the marking is applied to the base, the marking may be dusted with a non-fusible bronze powder which clings to the moist design. The marking is then allowed to dry

at room temperature by evaporation of the kerosene. The transfer thereby produced has the inherent limitation that the non-fusible bronze powder layer could mask or interfere with the marking if a metallic pigment other than bronze is employed in the marking. These decals are not ceramic decals.

OBJECTS

It is, accordingly, an object of the present invention to provide an improved method for printing a decal. Another object is to provide a method for forming an improved overglaze decal which requires less pigment. Still another object is to provide a faster, more economical method for preparing a decal. A further object is to provide an improved method for applying a flux layer to the design layer of a decal. These and other objects of the present invention will be apparent from the following description.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, there is provided a method for the preparation of an overglaze ceramic decalcomania, which comprises forming a wet ink formulation free of glass and comprising an oxide coloring agent and a liquid printing medium or vehicle such as a drying oil, varnish or resin, wet printing the wet ink formulation on a decalcomania backing sheet to form a wet design layer thereon free of glass, and separately depositing on the wet design layer a protective coating in the form of a prefused glass flux. If desired, the prefused glass flux layer may be initially deposited on the backing sheet and the wet design layer wet printed on the glass layer. When the backing sheet containing the wet design layer and protective coating is positioned on a glazed piece of ware and fired, the protective coating of prefused glass flux fuses and tightly binds the design layer to the ware.

When wet printing the wet ink formulation on the decalcomania backing sheet, a relatively thin design layer is formed which may be of any color of any desired intensity. The design layer should have a thickness within the range of from about 2 to about 8 microns and preferably from about 2 to about 6 microns.

The wet design layer can be formed in accordance with the invention employing only a fraction (for example from one-twentieth to one-fifth) of the pigment as would be required in prior art processes wherein dry or solid pigments plus glass is employed to obtain the same intensity of color as obtained in such processes. Accordingly, the use of wet printing results in a process which is far and away more efficient than prior art processes as exemplified by the Kane patent mentioned heretofore.

The prefused glass flux protective layer is colorless so that it does not interfere with or mask the colors of the design layer. The prefused glass flux may include a metallic oxide. The metallic oxide would be present in an amount within the range of from about 1 to about 8 percent by weight.

An amount of the prefused glass flux should be deposited on the wet design layer so that the protective glass coating thereafter formed will have a thickness within the range of from about 6 to about 28 microns and preferably from about 9 to about 20 microns. Thus, the ratio of thickness of the glass protective coating to the design layer should be within the range of from about 2:1 to about 3.5:1 and preferably from about 2:1 to about 2.5:1.

The decal of the present invention may be provided with any suitable backing, such as a dry strippable backing or a solvent mount or a water mount slide-off decal. The backing may be of paper or other suitable material such as, for example, plastic or fabric.

The wet design layer may be applied to the backing as one or more layers of an ink comprising an oxide colorant and a printing medium or vehicle without a glass flux or binder. The ink should contain from about 30 to about 60 percent by weight and preferably from about 35 to about 45 percent by weight oxide colorant. The printing medium or vehicle may be formed, for example, from one or more of such materials as drying oils, varnishes, or resins. Some examples of suitable resins are alkyds, phenolics, urea-formaldehydes, melamine-formaldehydes, polyesters, melamine alkyds, vinyls, and acrylics. Various additives may be incorporated into the vehicles, for example, dryers, promotors, and/or accelerators.

The coloring agents of the design layer comprise ceramic pigments, having an average particle size within the range of from about 0.5 to about 2 microns which are incorporated into the binder or vehicle. Preferably, the pigments are metallic oxides of fine particle size, such as of an average particle of less than about 1 micron. The pigments which may be used and the manner of their use are known to those skilled in the art. The oxides of the following elements are mentioned merely by way of example of some suitable ceramic pigments and the colors obtainable therefrom:

Oxide of	Color
Fe, Cr, Zn	Brown
Co, Al	Blue
Cr	Green
PB, Sb, Cd	Yellow
Cd, Se, S	Red

As known to those skilled in the art, the composition of the vehicle or binder of the design layer is varied depending upon the oxide or oxides used as coloring agent. No glass is present in the design layer. While the ink formulation must be varied depending upon the oxides employed, as is known to those skilled in the art, some typical ink formulations wherein the parts are expressed as parts by weight are as follows:

Ingredient	1	2	3
Gel #100 (linseed-alkyd resin varnish gelled by aluminum octoate, supplied by Zobel Co.)	10	12	15
Linseed #4 (linseed oil of 62.1 stokes viscosity)	10	.....	.....
Linseed #1 (linseed oil of 14.4 stokes viscosity)	15	.....	.....
Lead drier	2	4	4
Manganese drier	2	4	4
Oxide (pigment)	60	120	120
Aroplaz 2506 (alkyd resin supplied by Archer-Daniels)	.....	30	25
Aroplaz 1274 (alkyd resin supplied by Archer-Daniels)	.....	30	25
Puffo #2 (thixotropic control agent supplied by Mooney)	.....	3	3
Petroleum jelly	.....		5

The coating or layer of powdered glass may be a low melting point glass or a high melting point glass having an average particle size within the range of from about 4 to about 12 microns. The essential requirement is that the glass would fuse at the firing temperature employed to bond the design to the ware. A low melting point glass may be composed essentially of powdered

pre-fused lead boro-silicate glass which may also contain increments of one or more of the oxides of lithium, sodium, potassium, magnesium, calcium, aluminum, cadmium, zirconium or titanium.

A pre-fused flux may, for example, be formed according to the following formulation:

INGREDIENT	% BY WEIGHT
lead oxide	50
boric acid	30
silica	19
alumina	1
zirconia	trace
titania	trace

According to the present invention new and improved printing procedures are obtainable. It is possible to wet print the design according to conventional printing techniques such as by screen printing or offset lithography and then to apply over the wet design a prefused glass flux to permit fusion of the design to a ceramic surface. The flux may be applied over the design by various methods, such as, silk screening, offset printing, or by printing a clear film over the design and then dusting a prefused flux over the film. If desired, the dusting operation may be eliminated by incorporating the flux into film such as a printing varnish, oil or resin.

It is also possible to print the design as above and to dust a prefused flux over each color as each color is printed. In this way a separate step of applying flux over the entire design is eliminated. The flux that is picked up by the tacky varnish will enable the ceramic-calcined pigment to fuse to the ceramic surface. This procedure also prevents offsetting of the ink when the printed designs are stacked or piled on top of one another.

It is also possible to print a prefused flux (either as a dust or as a moist coating) on an adhesive-coated paper, such as paper coated with gum arabic and dextrin. The flux coated paper is then overprinted with the pigmented vehicle or design. It is then possible, if desired to overprint the design with another flux whereby the design is sandwiched between two flux prints.

It is also possible to silk screen a white color on an adhesive-coated paper and then to print the design, for example by offset printing, on top of the white color by use of a wet print. (It is not possible to dust the design in the form of a dry powder as the dust would cling to the white leaving a stain on the non-design portion of the decal after firing.) Such a design can be fired on a transparent glass. The white background is necessary since offset printing does not deposit sufficient color to provide opaqueness on transparent glass. In place of the white color, it is also possible to employ a silk screen flux.

A further advantage of the method invention is that the decal thereby produced can include dark colors printed on lighter colors, which is not now possible.

It will be appreciated that the present description has been by way of example only and is not intended as a limitation to the scope of the invention.

I claim:

1. A method for the preparation of an overglaze ceramic decalcomania, which comprises forming a wet ink formulation free of glass and consisting essentially of a liquid printing medium or vehicle and an oxide coloring agent, wet printing said wet ink formulation on a decalcomania backing sheet to form a wet design layer thereon free of glass, and separately depositing on said wet design layer a colorless protective coating consisting essentially of a prefused glass flux, so that when the backing sheet, having deposited thereon the wet design layer and protective coating, is positioned on a glazed piece of ware and fired, the protective coating of prefused glass flux fuses and tightly binds the design layer to the ware and does not mask the color of the design layer.

2. The method in accordance with claim **1**, which comprises forming the wet ink formulation by mixing the coloring agent in a wet printing medium of drying oils, varnishes or resins.

3. The method in accordance with claim **1**, wherein the protective coating consists essentially of prefused glass and pigment, prefused glass in printing varnish or prefused glass and pigment in printing varnish.

4. The method in accordance with claim **1**, wherein the prefused glass flux is applied over the wet design by silk screening or offset printing.

5. The method in accordance with claim **1**, wherein the design layer formed has a thickness within the range of from about 2 to about 8 microns.

6. The method in accordance with claim **1**, wherein the ratio of thickness of the glass-protective coating to the design layer is within the range of from about 2:1 to about 3.5:1.

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