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J. GÖBEL

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UNDERGLAZE DECALCOMANIA AND METHOD OF MAKING SAME

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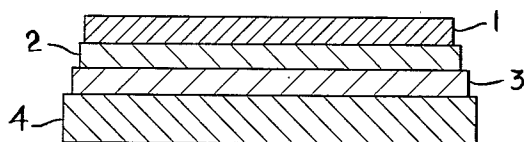


Fig 1

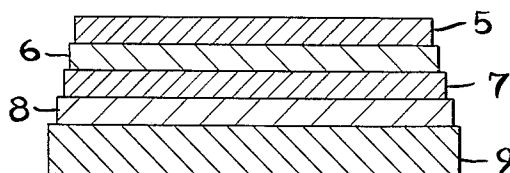


Fig 2

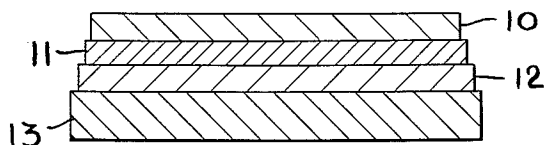


Fig 3

INVENTOR:
JOHANNES GÖBEL,
BY
Thomas G. Cinkler
ATTORNEY

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UNDERGLAZE DECALCOMANIA AND METHOD OF MAKING SAME

Johannes Göbel, Aschaffenburg (Main), Germany, assignor to Buntpapierfabrik A.G., Aschaffenburg (Main), Germany

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The present invention relates to decalcomania, or transfer pictures or designs, and more particularly to decalcomania for ceramic underglaze application and the like.

For purposes of ornamenting china, stoneware, clay tile and the like, the ceramic industry uses decalcomania which are printed with ceramic colors, assisted by suitable binders, on papers finished with special materials.

The decalcomania may be printed directly on a so-called metapaper finished with gum arabic, in which case a transfer lacquer is required for purposes of transfer to the ceramic body. Printing, however, may also be effected on skin paper. Skin paper is a transfer paper finished with a collodion film which on moistening of the carrier paper, can be withdrawn therefrom. Finally, the transfer pictures or designs may be printed on a paper finished with gum arabic, as in the first case mentioned above, and the print can then be coated with a special lacquer which then serves as carrier for the printed picture or design and which, on the carrier paper having been thoroughly moistened, can be withdrawn therefrom. Decalcomania of this kind can be used for underglaze as well as upperglaze applications. For upperglaze application, the lacquer film carrying the picture is withdrawn or pulled away from the carrier paper and applied to the ceramic body the glaze of which is completely finished, and then fired at suitable temperatures. For underglaze application, the film carrying the picture, applied to the porous ceramic body, must first be subjected to a baking process, i.e. the organic substances of the binder and the lacquer film must be burned before the glaze suspension is applied. This is necessary for the reason that the binder and the lacquer film, because of their hydrophobic characteristics, repel the aqueous glaze suspension so that in the places ornamented by pictures, the glaze dispersion would not adhere, but after drying, would chip off again.

It is the principal object of the present invention to provide decalcomania for underglaze application which require a single firing process only, and which permit dispensing with the previously necessary, additional baking step for burning the organic substances of the binder and the picture carrying lacquer film.

Other objects, and the manner in which the same are attained, will become apparent as the specification proceeds.

The present invention contemplates methods of producing decalcomania for ceramic underglaze application, by applying, in an optional sequence, on a carrier provided with a water soluble finish,

(a) The picture or design in ceramic colors, in a well-known manner, by means of binders on the basis of varnishes, drying oils, or lacquers, and

(b) A film of carboxy group containing polyvinyl compounds, whereupon if the ceramic picture constitutes the top layer, this may be coated, if desired, by an additional film of carboxy group containing polyvinyl compounds, to serve as a masking lacquer. Consequently, the layers may be arranged in any of the following sequences:

I. Carrier, polyvinyl film, ceramic picture, polyvinyl film (masking lacquer).

II. Carrier, polyvinyl film, ceramic picture.

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III. Carrier, ceramic picture, polyvinyl film.

As the carrier, the invention may employ the well known papers which, for example, have been coated with gum arabic ("meta-papers"), or textile materials coated with a water soluble layer. Foils of synthetic materials such as vinyl polymers, e.g. polyvinyl chloride, or cellulose derivatives, such as cellophane, or foils of polyesters or epoxy resins may be used. In this case, a water soluble separating layer is unsuitable, a separating coat melting at elevated temperature on the basis of hydrophilic waxes, such as polyethylene glycol being preferred. The water soluble coating may be dextrin, gum arabic or polyvinyl alcohol, to mention a few examples.

As the vinyl polymers for the polyvinyl film, homopolymers, copolymers and polymeric mixtures of carboxy group containing vinyl compounds are contemplated. Such carboxy group containing vinyl compounds include, for example, acrylic acid, methacrylic acid, maleic acid etc. The copolymers or polymeric mixtures may contain other compounds compatible or susceptible of being copolymerised with, the carboxy group containing vinyl compounds, such as polyacrylic acid ester, polymethacrylic acid ester, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl alkyl ether, polyvinyl acetals, styrene etc. The only condition to be fulfilled is that the copolymer or polymeric mixture is soluble, or swells, in water, or at least that it commences to swell in dilute alkaline solutions. The uppermost film serving as a masking lacquer, may consist of a homopolymer, copolymer or polymeric mixture of the same composition. The films may be applied, in the form of solutions or dispersions, by silk screen printing, or doctoring etc. As the solvents or dispersing agents, e.g. alcohols, glycols, hydrocarbons, ketones, ethers, esters and water may be employed.

The ceramic picture is applied, in a manner known by itself, by silk screen printing, lithography, or any other kind of printing; as the binders, printing varnish, printing oils or other binders having a lacquer base, may be used. For the ceramic colors and binders, all materials traditionally used for this kind of decalcomania may be employed; for the colors, e.g. oxides and silicates, and for the binders, e.g. those having a base of unsaturated oils, cellulose ethers, cellulose esters, higher hydrocarbons; carboxy group containing polyvinyl compounds are also suitable as binders.

The finished picture can be withdrawn from the carrier paper once this has been moistened, and transferred onto the porous, non-glazed ceramic body.

In order to ensure a perfect adhesion on the porous, non-glazed ceramic mass, the polyvinyl film, prior to application on the ceramic body, is preferably "activated" by swelling in a mildly alkaline solution, such as a 1% solution of soda, whereby the sodium salts of the acids are formed causing the film to become sticky, with the result that it firmly adheres to the ceramic body and on drying, does not scale off again. This activation of the film may be effected quite generally by means of aqueous solutions of alkali hydroxides, alkali carbonates, ammonia, organic amines such as triethanol amine, and other alkaline substances.

A swelling of the film can also be effected by immersion in suitable solvents, such as alcohols, e.g. methanol, ethanol etc., ketones such as acetone, ethers, e.g. diethyl ether, dibutyl ether etc. The activation may be dispersed with and still, a perfect adhesion of the film on the ceramic body obtained if the film is applied to the body under pressure.

The picture bearing film is withdrawn from the carrier and dried on the ceramic body, whereupon in the usual manner, a glaze suspension is applied by immersion or spraying. Once the water has evaporated, the ceramic

body is fired as usual, in a muffle oven, at temperatures from about 1000 to 1200° C. The organic material of the polyvinyl film depolymerises when heated to about 400° C., and evaporates when further heated to about 500° C., i.e. at temperatures below the sintering point of the glaze material, with the result that the vapor can still escape through the pores of the glaze material without damaging the material, i.e. without causing the glaze material to become detached from the ceramic body, or to crack.

The invention is illustrated by the following examples which are to be understood as having an explanatory and illustrative, rather than limitative character.

Example 1

5 kg. polymethacrylic acid (a low viscosity grade) are suspended in 95 l. of water whereupon 3 l. of ammonia of 25% are added. The solution obtained is applied by means of a doctor on a paper prepared by means of gum arabic. After drying, the film is lightly sprayed, for hardening purposes, with a 5% solution of aluminum sulphate and again dried. The film of polymethacrylic acid ammonium thus prepared is imprinted with ceramic colors in a well known manner. In order to transfer the film onto the ceramic body, paper and film are moistened with water and the paper is placed, with the side bearing the film, on the ceramic body. Once the film has become adsorbed on the porous ceramic body, the carrier paper is withdrawn. An activation in a separate step is not necessary in this case. After firing in a conventional manner, an excellent underglaze picture is obtained.

The polymethacrylic acid used for the polyvinyl film, may also be replaced by a copolymer of 90% of methacrylic acid and 10% of vinyl acetate, or else, a homopolymer of acrylic acid may be employed to equal advantage.

Example 2

A lacquer mixture is prepared according to the following prescription:

18 kg. of a copolymer of 35% of methacrylic acid and 65% of methacrylic acid methylester
61.5 kg. of ethylglycol
20.5 kg. of tetralin
35.7 kg. of polyvinylmethyl ether (K=40) of 70%, dissolved in toluene

This lacquer solution is applied by silk-screen printing, on a carrier paper prepared with dextrin, using a fine silk gauze having 100 meshes per cm.². On this film there is applied a picture in ceramic, annealable colors, in the usual manner either by silk-screen printing or litho-printing.

After drying, the picture can be transferred on a non-glazed ceramic body. For this purpose, the picture with the carrier paper is immersed, for activation purposes, for 10-15 seconds, in an 0.2% aqueous solution of tri-ethanol amine. The picture, which has commenced to swell, is applied on a ceramic body which, because of its porosity, adsorbs the picture so that, following a brief application of pressure, it firmly adheres thereto. Subsequently the carrier paper is withdrawn. The picture is dried and the ceramic body immersed in the glaze material in the usual manner, or else the glaze material is sprayed on the ceramic body. The glaze material is permitted to dry whereupon the glazed ceramic body is placed in the kiln. The baking is effected at a temperature of 1100° C.

Example 3

A lacquer mixture according to Example 2 is prepared and dried, in the manner described with reference to Example 2, on a carrier consisting of a fine, dense, cotton fabric prepared by means of gum arabic whereupon the ceramic picture is applied as noted with reference to Example 2. On this picture, another film is applied by

silk-screen printing to serve as a masking lacquer. For this film the same lacquer mixture is employed as for the film disposed underneath the ceramic picture. The further treatment follows the directions of Example 2, the result being as excellent as that obtained by Example 2.

This method may also be modified by the inclusion of an activation using a mixture of ethanol and water. The same excellent results are obtained. The fabric carrier may be replaced by a paper prepared by means of gum arabic.

Example 4

A lacquer mixture according to Example 2 is used and applied, in the manner described with reference to Example 2, on a carrier consisting of a polyvinyl chloride foil coated with polyethylene glycol (melting point 65° C.) and on which the ceramic picture was applied as described with reference to Example 2. The application to the non-glazed ceramic body as well as the further treatment follows the directions of Example 2, with equally excellent results.

Example 5

A ceramic picture is printed on a paper coated with gum arabic (a so-called meta-paper), and on this picture, a film is applied from a solution of 20 kg. of polyacrylic acid in a mixture of 40 kg. of ethanol and 40 kg. of methanol by silk-screen printing. The finished picture with the film is withdrawn from the paper, activated by immersion in a 1% soda solution and then applied to the ceramic body to be ornamented, whereupon the glaze suspension is sprayed thereon. A single, conventional baking step then yields an excellent underglaze picture.

Instead of the aforementioned homopolymer of polyacrylic acid, copolymers of acrylic acid with 10, 25 or 33% of vinyl chloride may be used for the polyvinyl film, with equally advantageous results.

Example 6

A solution of a copolymer of maleic acid anhydride, vinyl acetate and vinyl chloride (acid No.=12) in an ester mixture, is applied by a doctor on a carrier paper coated with gum arabic, whereupon a ceramic picture is applied by silk-screen printing. The paper is removed, the picture activated in a 1% aqueous solution of alkali carbonate to which 20% of acetone is added, and is then applied to the still unglazed ceramic body. Following a conventional baking step, the thoroughly excellent underglaze picture is obtained.

Example 7

In accordance with Example 1, the solution of polymethacrylic acid in ammonia (or a corresponding solution of polyacrylic acid or a copolymer of 90% of methacrylic acid with 10% of vinyl acetate) was applied on a carrier paper coated with gum arabic or dextrin, hardened and printed with ceramic colors. On the ceramic colors an additional polyvinyl film of the same composition was applied in a similar manner (to serve as a masking lacquer) and hardened.

The transfer was effected as described with reference to Example 1. A conventional baking step yielded an excellent underglaze picture.

Example 8

A lacquer mixture according to Example 2 was used and applied on a polyvinyl chloride foil which had been coated with polyethylene glycol (melting point of 65° C.). Subsequently, the ceramic picture was applied and the further treatment effected as described with reference to Example 4. An excellent underglaze picture was obtained.

In the place of the lacquer mixture according to Example 2, a copolymer according to Example 6, or a meth-

acrylic acid homopolymer according to Example 1 may also be used. Also, an additional polyvinyl film serving as a masking lacquer may be applied on the ceramic picture. The underglaze pictures obtained are of excellent quality in any of these instances.

The invention is illustrated further by the drawing accompanying this specification and forming part thereof. In the drawing:

FIG. 1 is a diagrammatic representation of a multi-layer decalcomania according to the invention;

FIG. 2 is a similar showing of a modification, and

FIG. 3 is a similar showing of still another embodiment of the invention.

Referring to the drawing, and first to FIG. 1, this shows a multi-layer decalcomania comprising a top layer in the form of a hydrophilic masking coating 1, containing a film forming ingredient consisting of a hydrophilic polymer according to the invention, a design or picture layer 2 in ceramic color containing varnish, drying oil or similar binder, disposed underneath the coating 1, a water soluble coating 3 of dextrin or the like arranged below the picture layer 2, and a carrier 4 e.g. of paper constituting the bottom layer.

In the embodiment of the invention illustrated in FIG. 2, layers 5 and 7 are hydrophilic masking coatings containing a film forming ingredient according to the invention, which are disposed above and below the ceramic color design coating 6, the base being again composed of a water soluble coating 8 on a carrier 9 such as paper.

The modification shown in FIG. 3 has the ceramic color design coating 10 disposed at the top, a hydrophilic masking coating 11 containing a film forming ingredient located underneath the design layer 11, the base comprising the water soluble coating 12 on a paper or similar carrier layer 13.

The underglaze decalcomania according to the invention have the signal advantage that they have hydrophilic characteristics with the result that when the moist glaze material is applied on the decalcomania, it is not repelled so that the glaze may be directly applied on the picture without a previous baking process such as was necessary up to now. This advantage is particularly important as it implies the saving of an entire operation inasmuch as the annealing process is eliminated, the organic substance of the novel lacquer film according to the invention being burnt only during baking of the glaze. Accordingly, the novel method requires for the entire operation of applying the ornamentation and applying the glaze, a single baking process only. The glaze adheres to the places ornamented with the present decalcomania just as well as to other parts of the ceramic body which are not so ornamented. The pictures obtained after baking display no step at the margin, but blend beautifully with the glaze applied on top thereof.

I wish it to be understood that I do not desire to be limited to the exact details of procedure, composition or application as modifications within the scope of the appended claims and involving no departure from the spirit of the invention nor any sacrifice of the advantages thereof, may occur to workers in this field.

I claim:

1. The method of preparing a ceramic decalcomania, comprising applying a water soluble base coating on strong carrier paper, said water soluble coating selected from the group consisting of dextrin, gum arabic, water soluble starch, polyvinyl methyl ether and polyvinyl alcohol, thereafter coating a design in ceramic color, said ceramic color being in the form of a liquid composition containing a binder selected from the group consisting of varnish, drying oil and lacquer, then applying a hydrophilic masking coating over the ceramic design, said masking coating containing a film forming ingredient consisting of a hydrophilic polymer selected from the group consisting of polyacrylic acid, polymethacrylic acid and maleic acid polymer and copolymers of said acids with a substance selected from the group consisting of polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl alkyl ether, polymethacrylic acid ester, polyacrylic acid ester, polyvinyl acetals and styrene.

2. A decalcomania comprising a strong carrier paper, a water soluble releasable base coating on said strong carrier paper, said base coating selected from the group consisting of dextrin, gum arabic, water soluble starch, polyvinyl methyl ether, and polyvinyl alcohol, a ceramic color design coating on said base coating containing a ceramic coloring material in a binder selected from the group consisting of varnish, drying oil and lacquer, and a hydrophilic masking coating over the said ceramic design coating, said masking coating containing a film forming ingredient consisting of a hydrophilic polymer selected from the group consisting of polyacrylic acid, polymethacrylic acid and maleic acid polymers and copolymers of said acids with a substance selected from the group consisting of polymethacrylic acid ester, polyacrylic acid ester, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl alkyl ether, polyvinyl acetals and styrene, said masking swelling in water and dilute alkali to adhere to an unglazed surface of a ceramic base and provides a decorative film by a single firing operation after upper glaze application.

3. A decalcomania as claimed in claim 2 wherein said polymer is polyacrylic acid.

4. A decalcomania as claimed in claim 2 wherein said polymer is polymethacrylic acid.

5. A decalcomania as claimed in claim 2 wherein said polymer is a polymer of maleic acid.

6. A decalcomania as claimed in claim 2 wherein said masking coating underlies as well as covers said ceramic color design coating.

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