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ORNAMENTATION OF CERAMIC WARE

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This invention relates to the production of ornamented ceramic ware and particularly to a method of over glaze decoration of such ware, making possible the application of both decalcomania decorations and metallic lustre and other similar decorations without an intermediate firing operation.

It has been the custom to apply a linseed oil rosin size to the glazed ware, then the decalcomania decoration; then fire off the size, apply the metallic lustre or other color of the type which is applied in an essential oil vehicle and again fire. In this particular art, the term "size" refers to a material which, in drying, develops temporarily a tackiness which is lost on further drying. With the linseed oil varnish size now used, the intermediate firing operation is necessary to prevent the development of defects in the decoration such as bleeding, feathering, streaking, discoloration, etc. It is the object of the present invention to provide a process permitting the successful elimination of the firing step intermediate between the application to the ware of the two types of decoration.

Decalcomania decorations are designs in ceramic colors and vitreous fluxing material carried by paper backings and secured thereto by water soluble adhesive material. They are applied by first covering the ware to be decorated, in the region where the design is to be applied, with a water insoluble size, applying the decalcomania to the size and then washing off the paper and soluble adhesive with water and firing on the design to remove the size and establish a ceramic bond between the colored design and the glaze of the ware.

Metallic lustres and a number of other colors are applied as liquids, containing, as indicated, the desired colors, usually metallic compounds, in essential oil solvents, together with a flux adapted to establish a ceramic bond with the glaze of the ware upon firing.

I have now discovered that by proper manipulation and the use of proper materials, satisfactory results may be produced, without the intermediate firing step.

In accordance with the preferred practice of the invention, I apply to the glazed ware a special size composition and dry the same to a "tacky" or sticky condition, expelling most of the solvent. I then apply the decalcomania, wash away the paper backing and soluble adhesive and further dry the size beyond the tacky condition. Certain size compositions within the scope of the invention may be more resistant to water after they

have been dried beyond the tacky state. In such case the drying is partly or entirely carried out before washing off the decalcomania backing. I then apply the metallic lustre or other color of the liquid or essential oil carried type and fire the ware in the usual manner. The lustre or like liquid color may be applied over the size or on the uncoated glaze or partly over the size and partly on the glaze.

It is my belief that the essential feature of the new size composition is that it be capable, under the conditions of the process, of developing the requisite tack and then becoming inert to the essential oils which are used in the liquid colors; and that the essential feature of the manipulation is that it develop the proper tackiness of the size for application of the decalcomania decoration and then, after such decoration has been applied, the inertness necessary to resist attack by the essential oil vehicle of the lustre.

The lustres usually contain resins dissolved in a vehicle of an essential oil blend. Liquid bright gold, for example, is a gold-sulfur-resinate suspended in an essential oil blend, for example:

	Grams
Gold resinate with 45 per cent gold-----	267
Rosemary oil-----	230
Fennel oil-----	98

It may also contain small amounts of resins of other metals for special color effects, asphalts, resin and other essential oils, such as oil of lavender. Bright platinum and other liquid bright metals, likewise, usually contain the metal resins in an essential oil blend.

Colors as applied for certain types of decoration other than decalcomania designs, are essentially inorganic compounds of metals which are suspended in an essential oil vehicle and are applied to the glazed ware by various means in this liquid state. Various ceramic fluxing agents are also usually present with the coloring compounds to render them active and fusible with the glaze on the ware.

The essential oils, and other constituents of the vehicle, which are likely to be used in liquid colors and lustres, and the attack of which must be withstood by the properly dried size are:

Oil of lavender	Oil of sassafras
Oil of rosemary	Oil of turpentine
Oil of fennel	Linseed oil
Oil of clove	Tung oil

No single resin, so far as I am aware, is entirely suitable as a one-fire size. However, I

have discovered that a composition including one or more materials from each of three classes is quite satisfactory.

CLASS I

GLYCERYL-PHTHALIC ANHYDRIDE RESINS (ALKYD RESINS)

A. Modified by fatty acid

For example, a mixed glyceride of phthalic acid and castor oil fatty acid corresponding to 65% glyceryl-phthalate resin and 35% castor oil fatty acid glyceride. This material contains 20% of toluol as a solvent and is sold under the trade name "Rezyl 53." This material is further identified as follows: Sp. G., 1.15; acid No. 18 to 24; refractive index, 1.5; consistency at 20° C., liquid.

B. Unmodified

For example, Beckosol 1307 which is 50 per cent glyceryl-phthalate and 50 per cent xylene solvent. (This material has an undesirably high solvent content and preferably is reduced to 25 to 35 per cent solvent before use.)

CLASS II

CELLULOSE RESINS

- A. Cellulose nitrate
- B. Cellulose acetate
- C. Benzyl cellulose
- D. Ethyl cellulose

CLASS III

PLASTICIZERS (SOLVENTS FOR CLASSES I AND II)

- A. Dibutyl tartrate (B. P. 292°-312° C., M., P. 16°-19° C.)
- B. Butyl carbitol acetate (B. P. 245° C.)
- C. Iso amyl oxalate
- D. Butyl tartrate
- E. Dibutyl phthalate

EXAMPLES OF SIZE COMPOSITIONS

[1]

Rezyl 53	cc	2.0
Cellulose nitrate (15/30 sec., 11.5% N.)	gm	1.3
Butyl tartrate	cc	3.2
Solvent	cc	35.0

[2]

Rezyl 53	cc	2.2
Cellulose nitrate	gm	1.5
Butyl tartrate	cc	2.5
Solvent	cc	15.0

[3]

Rezyl 53	cc	22
Cellulose nitrate	gm	13
N-butyl-tartrate	cc	10
Solvent	cc	150

[4]

Rezyl 53	cc	22
Cellulose nitrate	gm	13
N-butyl tartrate	cc	10
Solvent	cc	105

The foregoing resin mixtures are dissolved in any suitable solvent, the following being preferred. The solvent is not very critical, very little of it remaining at the time of application of the metallic lustre or colored decoration.

Solvent A

Toluene	cc	10
Methyl isobutyl ketone	cc	15
Butyl acetate	cc	10
Ethylene glycol monoethyl ether	cc	7

Solvent B

Toluene	cc	10
Xylene	cc	10
Ethyl carbonate	cc	10
Butyl propionate	cc	20
Cellulose acetate	cc	4

This application is a continuation-in-part of my application Serial No. 106,190, filed October 17, 1936.

Having thus described my invention, what I claim is:

1. Process of ornamenting glazed ceramic ware comprising applying thereto a size having the property of drying to a tacky state and upon further drying becoming inert to essential oils, said size consisting essentially of an alkyd resin, a cellulose resin, a minor amount of an organic plasticizer, in which said resins are soluble and a solvent for the composition, drying to a tacky state, applying decalcomania decoration, drying beyond the tacky state and washing off the backing of the decalcomania, applying a decoration at least a part of which overlies said size and which is carried by an essential oil vehicle and thereafter firing the ware.

2. A process as recited in claim 1, characterized in that the essential oil decoration contains a metallic resinate.

3. A process as recited in claim 1, characterized in that the essential oil decoration is liquid bright gold.

4. Process of ornamenting glazed ceramic ware comprising applying thereto a size having the property of drying to a tacky state and upon further drying becoming inert to essential oils, said size consisting essentially of a fatty acid modified glyceryl phthalate, a cellulosic resin, a minor amount of a plasticizer and a solvent for the composition, drying to a tacky state, applying a decalcomania decoration while said size is in such tacky state, further drying beyond the tacky state and removing the decalcomania backing, applying a color decoration at least a part of which overlies said size and which is dissolved in an essential oil vehicle and thereafter firing the ware.

5. A process as recited in claim 4, characterized in that the essential oil decoration is a metallic lustre.

6. A process as recited in claim 4, characterized in that the size contains castor oil fatty acid modified glyceryl phthalate, cellulose nitrate and dibutyl tartrate.

7. A process as recited in claim 4, characterized in that the size contains castor oil fatty acid modified glyceryl phthalate, cellulose nitrate and dibutyl tartrate, and said essential oil decoration is liquid bright gold.

8. Process of ornamenting glazed ceramic ware comprising applying thereto a size having the property of drying to a tacky state and upon further drying becoming inert to essential oils, said size consisting essentially of an alkyd resin, a cellulose resin of the class consisting of cellulose nitrate, cellulose acetate and ethyl and benzyl celluloses, a minor amount of an organic plasticizer, in which said resins are soluble and a solvent for the composition, drying to a tacky state, applying decalcomania decoration, drying beyond the tacky state and washing off the backing of the decalcomania, applying a decoration at least a part of which overlies said size and which is carried by an essential oil vehicle and thereafter firing the ware.

9. A process as recited in claim 8, characterized in that the essential oil decoration contains a metallic resinate.

10. A process as recited in claim 8, characterized in that the essential oil decoration is liquid bright gold.

11. Process of ornamenting glazed ceramic ware comprising applying thereto a size having the property of drying to a tacky state and upon further drying becoming inert to essential oils, said size consisting essentially of an alkyd resin, cellulose nitrate, a minor amount of an organic plasticizer, in which said resins are soluble and a solvent for the composition, drying to a tacky state, applying decalcomania decoration, drying beyond the tacky state and washing off the backing of the decalcomania, applying a decoration at least a part of which overlies said size and which is carried by an essential oil vehicle and thereafter firing the ware.

12. Process of ornamenting glazed ceramic ware comprising applying thereto a size having the property of drying to a tacky state and upon further drying becoming inert to essential oils, said size consisting essentially of an alkyd resin, cellulose acetate, a minor amount of an organic plasticizer, in which said resins are soluble and a solvent for the composition, drying to a tacky state, applying decalcomania decoration, drying beyond the tacky state and washing off the backing of the decalcomania, applying a decoration at

least a part of which overlies said size and which is carried by an essential oil vehicle and thereafter firing the ware.

13. A process as recited in claim 11, characterized in that the essential oil decoration contains a metallic resinate.

14. A process as recited in claim 11, characterized in that the essential oil decoration is liquid bright gold.

15. A process as recited in claim 12, characterized in that the essential oil decoration contains a metallic resinate.

16. A process as recited in claim 12, characterized in that the essential oil decoration is liquid bright gold.

17. A process of ornamenting ceramic ware comprising applying thereto a size characterized in that in drying it passes through a tacky state and then upon further drying becomes inert to essential oil solvents, drying such size to such tacky state, applying a decalcomania decoration over such size while it is in such tacky state, drying such size to the inert state and then applying thereover a color decoration in an essential oil solvent to which such size is inert and thereafter firing the ware, whereby a firing step between said decalcomania decoration and said color decoration is eliminated and with production of ware carrying a color decoration free from bleeding, feathering and streaking.

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