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MANUFACTURE OF DECORATED CHINA

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Heretofore, the usual method of decorating chinaware, such as table china, vases, etc., has been to subject the cast or jiggered ceramic composition object to a bisque burn, then apply a glaze to the object and subject the object to a glost burn before attempting to decorate the object. At this stage, the ceramic object is provided with a smooth, dense, impervious glazed surface. When the decoration to be applied thereto is in the form of lithographed decals, the surface of the glazed chinaware was first coated with a varnish, this varnish being allowed to set until tacky. The thin decal sheet with its lithographed decoration was then applied to the varnished piece. This system had numerous disadvantages in that it was difficult for the operators to properly estimate the thickness of the varnish and the dry decals had to be applied very carefully. If the varnish is too thick, it may bubble during the subsequent firing and impair or destroy the effect desired by the decoration. The dried decals do not conform easily to the curved or cylindrical surface of many pieces of china. Furthermore, after such decal has been applied to the dry, varnished piece, it is necessary to soak the entire piece in water and peel off the thin sheet of paper which constitutes the carrier member of the decal. At all events, it is necessary to again burn the piece after the decal is applied in order to properly render the decoration an integral and irremovable part of the finished piece of chinaware.

In some instances, the so-called wet transfer process has been used. In this method, the design or decoration in color is carried by a thin sheet of sized paper, the coloring being also covered on the other side by a thin film of a cellulose derivative. This particular type of transfer is first soaked in water, the paper is removed and the thin cellulose derivative film with its adhering decoration and color is then applied to the previously glazed and burned ware. This process has the advantage that the decal or transfer has been soaked in water before it is applied to the glazed surface and therefore can be slightly distorted and made to fit cylindrical or conical curved surfaces more readily.

It will be noted that in all of these processes the glaze on the ceramic object has been matured by burning prior to the application of the transfer or decoration, and after the application of the decoration it is again necessary to subject the ware to a still further heat treatment or burning in order to burn the decoration into the glaze. It has not been possible heretofore to apply a glaze composition to a dried but unburned piece of ware and apply decoration thereto by hand brushing, the silk scren process, or by the use of decals or transfers, because the glaze composition is weak, friable, and porous. The one-fire process has not been used heretofore on decorated ware.

It is an object of the present invention to disclose and provide improved methods of procedure whereby the decoration of ceramic objects is facilitated.

Another object is to disclose and provide means and methods whereby decoration can be applied to leather-dry ceramic objects or to such objects provided with a coating of unmatured glaze composition.

A further object is to disclose methods of producing decorated chinaware and the like by a one-fire process.

These and other objects and advantages will become apparent from subsequent description and a comparison of the procedures contemplated by this invention with the processes practiced heretofore.

The present invention distinguishes from the processes

described hereinabove in that it permits the application of decoration from transfers or decals (either lithographed or applied by the silk screen process) and by hand painting or brushing onto the surface of an unburned or unmatured glaze carried by a ceramic object. In accordance with the present invention, a ceramic composition can be molded or formed, subjected to a bisque burn, and then covered with a glaze composition. After such glaze composition has partially dried, the surface to be decorated may be brushed or sprayed with an emulsion or dispersion of a synthetic resin, preferably a methacrylate. Such emulsion or dispersion may contain from 20 per cent to about 50 per cent of the resin, the liquid phase of the dispersion being preferably aqueous or containing but a minor quantity of organic components. The aqueous, external phase is absorbed by the glaze and body and a resilient, virtually continuous resinous and resilient film is formed on the surface. Decoration can then be applied to this film and the object is fired to mature the glaze and fix the decoration.

The present invention also permits the use of a one-fire process in the production of decorated china or other ceramic objects. The object can be jiggered or formed, dried leather hard, sprayed with glaze, and the surface of the virtually dry, unmatured glaze then sprayed or brushed with a resin dispersion. The resinous film thus formed on the surface can then be used to receive desired decoration, applied by hand brushing, the silk screen process, or by use of transfers or decals, and the object then subjected to firing at a temperature sufficient to mature the body, the glaze and the decoration in a single operation.

It has been found that the liquid component of the resin dispersion will become absorbed by the relatively porous and absorbent layer of glaze composition (and the underlying bisque) and the relatively large molecules or agglomerates of resin will be left upon the surface of the glaze composition thereby forming a slippery, thin, resilient and somewhat adhesive or lightly tacky layer of resin. This film of resinous material is nonporous, continuous and glossy and the decal or transfer may be placed thereon and shifted into desired position with great precision. Pigments applied by a paint brush can be easily and positively placed. Moreover, these films dry quickly so that the unburned ware, with its decoration adhering thereto, may be safely handled during placement in the kiln. Upon burning, the glaze is matured and, simultaneously therewith, the decoration is caused to become an integral and irremovable part of the ceramic object.

It has been found that thermoplastic resins produced by polymerization of acrylic acid derivatives, such as the methyl and ethyl esters of methacrylic acid, are eminently suited for use in this process. These polymers or mixed esters of methacrylic acid can be readily purchased in the form of emulsions or dispersions, one of the best known suppliers being Rohm and Haas. The emulsions or dispersions have a specific gravity of 1.06 to 1.07, and contain particles having an average size of between about 1 and 2 microns. The aqueous phase is slightly alkaline and contains a small amount of emulsifying agent. The solids content of the emulsions or dispersions as purchased is on the order of 40 per cent–50 per cent by weight. These emulsions may be diluted to a solids content of 20 percent–35 per cent when being sprayed or brushed upon the ware and it will be found that they will leave a clear, thin, resilient, continuous film upon the surface. This film is compatible with normal pigments and glaze colorings thereby permitting hand decoration to be applied to the surface. Furthermore, decoration can be applied by the silk screen process or by the use of transfers as previously stated. The aqueous phase of the emulsion is quickly absorbed so that no excess drying time is needed.

Although particular attention has been drawn to the use of emulsions and dispersions of the polymers of acrylic acid derivatives, dispersions and emulsions of other resins can also be used provided they form a continuous film and do not carbonize or form bubbles during subsequent firing. Emulsions of modified polystyrene resins (such as those modified with butadiene) form satisfactory continuous films. Co-polymers of vinyl-nitrile-

rubber or latex, polyamide emulsions, or acetate emulsions may also be used. Vinyl chloride resins do not appear to be satisfactory because they bubble and distort the decoration which has been applied. Furthermore, they appear to form excessive amounts of carbon during the firing. Because of the great number of various synthetic resins now available on the market, it appears desirable to test the resins and resin emulsions by applying a coating to a bisque and subjecting the coating and its superimposed decoration to firing in order to observe the behavior of the resin both as to its ability to form continuous films and its reactions under firing conditions. It appears that resins having molecular weight over 10,000 are better suited for the purposes of this invention; moreover, the average particle size of the emulsion or dispersion should be on the order of from about 1 to 4 microns. The effect obtained with the preferred resin dispersions is totally different from that obtained by the use of solutions of vegetable gums such as for example gum tragacanth; solutions of these gums are totally ineffective since they are absorbed into the coarse pores of the bisque or glaze composition. Similarly, methyl carboxy cellulose is ineffective.

The characteristics of the film deposited upon the surface of the ware, prior to the application of the decoration thereto, may be varied somewhat by changing the concentration of the emulsion used and by repeating the application of the emulsion to the surface being treated. As previously indicated, these resins emulsions may be applied either by spraying or by brushing and since the aqueous phase is very rapidly absorbed by the ware, two or even three successive brushings may be applied in very rapid succession.

In accordance with this invention, therefore, the manufacture of decorated chinaware and the like is greatly facilitated by (1) facilitating the application of decals and transfers to previously burned and glazed ware, (2) by permitting the application of decoration to bisque coated with an unmatured glaze composition, and (3) by permitting the manufacture of decorated chinaware and the like in a one-fire operation.

We claim:

1. In a process of producing decorated chinaware, the steps of: applying a suspension of thermoplastic resin to the surface of an unmatured glaze composition carried by a ceramic object, to form a resilient film on the surface of such unmatured glaze, applying a desired decoration to said film, and then subjecting the ceramic object to firing to mature the glaze composition and permanently connect the decoration to the glaze, said resin having a molecular weight of over about 10,000, whereby the resin does not carbonize and the decoration is not distorted during said firing.

2. In a process of the character stated in claim 1, wherein said suspension contains between about 20% to 50% by weight of an ester of methacrylic acid in the form of particles having an average size of between about 1 and 4 microns.

3. In a process of producing decorated chinaware, the steps of: applying a suspension of a thermoplastic resin, said resin having a molecular weight of over about 10,000 to the surface of ware to be decorated to form a virtually continuous resilient film of resin thereon, and then applying a desired decoration.

4. In a process of the character stated in claim 3, wherein said suspension contains between about 20% to 50% by weight of an ester of methacrylic acid in the form of particles having an average size of between about 1 and 4 microns.

5. A process of facilitating the application of surface decoration to ceramic objects which comprises: forming a film of thermoplastic resin on the surface of the object to be decorated by applying a suspension of the object resin having a molecular weight of over about 10,000 in the form of particles having an average size of between about 1 and 4 microns, to the surface to be decorated, then applying a desired decoration to the film so formed, and subjecting the object to firing.

6. A process of the character stated in claim 5, wherein the object to be decorated is in the form of a bisque.

7. A process of the character stated in claim 5, wherein the object to be decorated is in the form of a formed, leather-hard, unburned body.

8. A process of the character stated in claim 5, wherein the object to be decorated is in the form of a formed, unburned body provided with a virtually dry, porous glaze composition covering.

9. A process of the character stated in claim 5, wherein the object to be decorated is in the form of a bisque provided with a virtually dry, porous glaze composition covering.

10. A process of the character stated in claim 5, wherein the object to be decorated is in the form of a formed and glazed ceramic object.

11. A process of the character stated in claim 5, wherein the decoration is applied as a transfer.

12. A process of the character stated in claim 5, wherein the decoration is applied by a silk screen process.

13. A process of the character stated in claim 5, wherein the decoration is applied by hand painting.

14. A process of facilitating the application of surface decoration to ceramic objects which comprises: forming a film of an ester of methacrylic acid on the surface of a ceramic object in the form of a bisque provided with a virtually dry, porous glaze composition covering, by applying thereto a suspension of such ester in the form of particles having an average size of between about 1 and 4 microns, to the surface to be decorated and then applying decoration in the form of a transfer to the film so formed and subjecting the object to firing.

15. A process of facilitating the application of surface decoration to ceramic objects which comprises: forming a film of an ester of methacrylic acid on the surface of a ceramic object in the form of a formed and glazed object, by applying thereto a suspension of such ester in the form of particles having an average size of between about 1 and 4 microns, to the surface to be decorated and then applying decoration in the form of a transfer to the film so formed and subjecting the object to firing.

16. A process of facilitating the application of surface decoration to ceramic objects which comprises: forming a film of an ester of methacrylic acid on the surface of a formed, unburned body provided with a virtually dry, porous glaze composition covering, by applying thereto a suspension of such ester in the form of particles having an average size of between about 1 and 4 microns, to the surface to be decorated and then applying decoration in the form of a transfer to the film so formed and subjecting the object to firing.

References Cited in the file of this patent

UNITED STATES PATENTS

2,433,259	Box et al.	Dec. 23, 1947
2,476,570	Van Horn et al.	July 19, 1949
2,566,735	Lepie	Sept. 4, 1951

FOREIGN PATENTS

303,679	Great Britain	Jan. 10, 1929
480,660	Great Britain	Feb. 25, 1938
491,562	Great Britain	Sept. 2, 1938
623,973	Great Britain	May 25, 1949