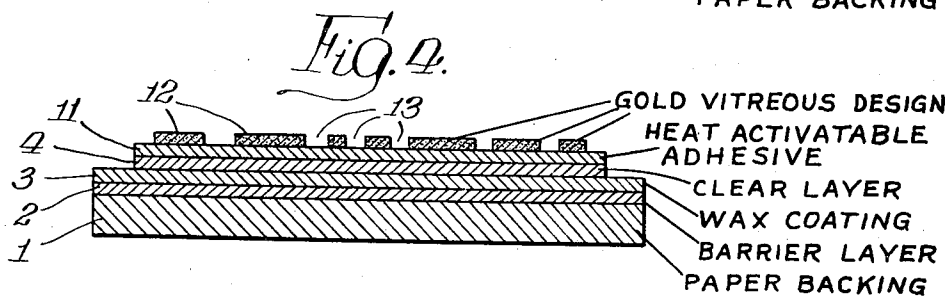
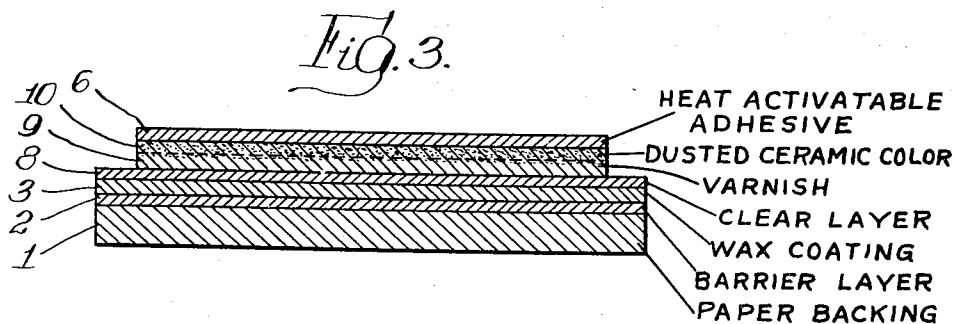
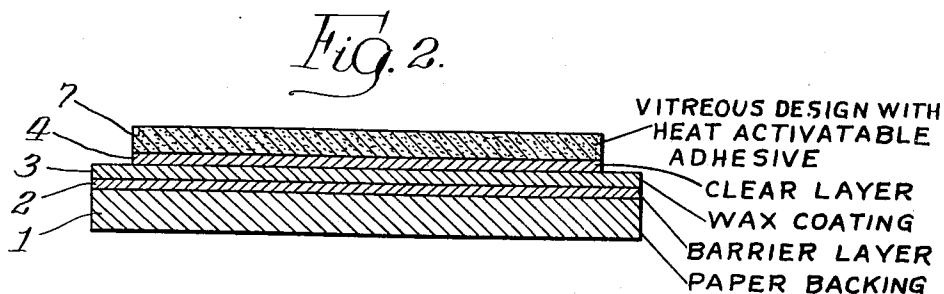
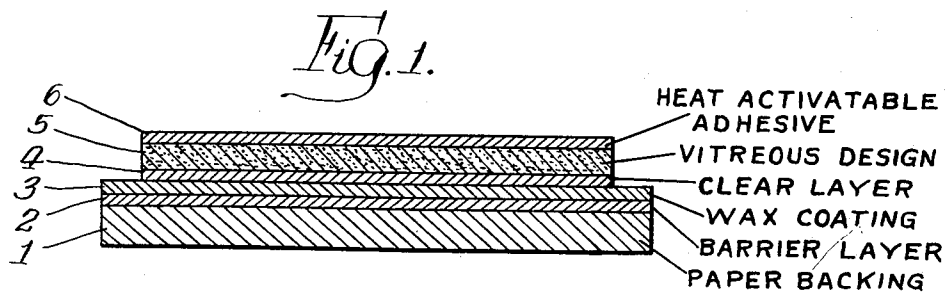


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VITREOUS DECALCOMANIA AND METHOD OF
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VITREOUS DECALCOMANIA AND METHOD OF DECORATING CERAMIC ARTICLES

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This invention relates to improvements in the decoration of ceramic articles such as chinaware, glassware, pottery, porcelain ware, and the like. The invention also involves a novel decalcomania or transfer for use in such decoration.

For many years, the ceramic industry has utilized decalcomania transfers prepared with special vitrifiable or ceramic colors in the decoration of articles of glassware, chinaware, or the like. The most familiar type of decalcomania for this purpose consists essentially of a paper carrier or backing having the desired design imprinted thereon in one or more vitrifiable enamel colors. The backing paper is a conventional water release type well known in the decalcomania art. For example, in the so called "slide-off" type of decalcomania the backing paper carries a thin layer of a water soluble gum and the vitreous design is imprinted face up upon this gummed surface. Another type of decalcomania backing paper is known in the industry as duplex paper and consists of a layer of thin tissue paper releasably mounted on a heavier paper sheet. The thin tissue paper carries a water soluble gum coating and the vitreous design layer is imprinted face down on the gum coating.

In using the "slide-off" type transfer the entire transfer is wetted with water to soften the gum layer and the transfer design is then slid from the backing paper and disposed face up on the surface of the article being decorated. A certain amount of the softened gum adheres to the back of the released design and serves to bond the design temporarily to the article. In the case of a vitreous decalcomania having a duplex paper backing the heavy paper sheet is first stripped from the thin tissue sheet and a special adhesive varnish or temporary binder is applied either to the surface of the article being decorated or to the exposed back surface of the vitreous design layer carried on the thin paper sheet. The back of the vitreous design layer is then pressed against the ceramic surface being decorated and the thin tissue paper is thereafter wetted with water to permit its removal whereby to expose the face of the design. In the case of either type of transfer, the ceramic article with temporarily adhered design is thereafter dried thoroughly to remove all traces of water and is then subjected to a high temperature firing operation which first destroys all of the combustible organic ingredients in the transferred vitreous design and the temporary binder and then fuses the vitrifiable components of the design layer so that they melt and form a permanent bond with the ceramic surface.

Although vitreous decalcomanias of the water release type have enjoyed wide-spread commercial use, it is well recognized that they have serious disadvantages which arise primarily from the fact that a number of inconvenient and time-consuming steps are required to effect temporary adherence of the design, release thereof from the paper backing, and drying prior to firing. The use of water also introduces difficulties with spotting or staining of the design due to mineral ingredients in the water, e.g., iron. With the "slide-off" type transfer, con-

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taminants in the dextrine or water soluble gum frequently cause disfiguration of the design. In the duplex type transfer the varnish which must be used is a cause of considerable trouble due to its tacky consistency, variations in composition, and sensitivity to changes in atmospheric conditions and ambient temperature.

My invention is concerned with a special combination of features by means of which the decorating procedure is greatly simplified and a highly satisfactory vitreous decalcomania is provided having unique advantages in this art. As will appear hereinafter, the decalcomania of the present invention is particularly suited for the decoration of an article of glassware or the like by preheating the article, contacting the decalcomania with the preheated article, and then firing. The construction of my vitreous decalcomania is such that the heat of the article effects both a preliminary bonding of the vitreous design layer to the article and also the release of the backing from the vitreous design layer. The water release and varnish application principles have been completely eliminated with consequent freedom from all of the attendant difficulties. Moreover, the decalcomania of the present invention is characterized by a readily releasable relationship between the vitreous design and its temporary support thereby overcoming one of the most serious sources of difficulty with a heat release vitreous decalcomania.

Accordingly, a primary object of the invention is to provide a novel and improved vitreous decalcomania or transfer for use in the decoration of ceramic articles such as glassware, chinaware, and the like.

A further object of the invention is to provide a novel vitreous decalcomania which can be applied either by machine or by hand in a very rapid and highly convenient manner as compared with the vitreous decalcomanias heretofore in commercial use and is particularly adapted for high speed machine application.

Another object of the invention is to provide an improved vitreous decalcomania involving a novel combination of heat responsive features and characterized by trouble-free release of the vitreous design layer from the backing under a wide variety of conditions.

An additional object of the invention is to provide a novel method of decorating an article of glassware, chinaware or the like.

Other objects and advantages of the invention will become apparent from the subsequent detailed description taken in conjunction with the accompanying drawing, wherein:

Fig. 1 is a diagrammatic cross-sectional representation on an exaggerated scale of a decalcomania comprising one specific embodiment of the invention;

Fig. 2 is a view similar to Fig. 1 but showing a modification of the invention;

Fig. 3 is a view similar to Figs. 1 and 2 but showing still another modification of the invention; and

Fig. 4 is a view similar to Figs. 1-3 but showing a further modification of the invention.

Generally speaking, the invention involves a ceramic decalcomania or transfer characterized by the use of a heat releasable backing at one side of the vitreous design and an outer thermoplastic or heat activatable adhesive at the opposite side of the vitreous design. As a result, when the decalcomania is subjected to heat the vitreous design layer is released from the backing and is also temporarily adhered to the article being decorated, both effects being accomplished in substantially a single step. By the combination of these two heat responsive features, I am able to provide an inexpensive and highly advantageous vitreous decalcomania which has not hitherto been available in this field. Furthermore, by the incorporation of certain preferred materials and features in

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the releasable backing and in the vitreous design, as hereinafter described in detail, a readily releasable relationship is provided which obviates the most troublesome problems associated with the heat release of ceramic colors from a paper backing.

Referring first to Fig. 1, the embodiment of the invention therein illustrated comprises a vitreous decalcomania or transfer which is adapted for manufacture by any suitable printing method, e.g. silk screen printing, lithography, rotogravure or letter press printing. The decalcomania has a releasable backing comprising in this instance a paper sheet 1 with a barrier layer or coating 2 which renders one side of the paper less porous and substantially impervious to wax. The barrier coated paper is also provided with a superimposed coating 3 of wax or wax-like material. A clear resinous film 4 is disposed over the wax coating 3 and serves as an imprint receiving support for the subsequently applied vitreous design. The vitreous design, indicated at 5, is disposed directly against the clear layer 4, it being understood that the design 5 will usually comprise a compound or composite layer including a plurality of different ceramic color compositions arranged to provide the desired ornamentation or text matter. Over the outermost side of the vitreous design 5 is provided a layer 6 of a suitable thermoplastic or heat activatable adhesive material which serves as a temporary binder for securing the design 5 to the article being decorated. Although not shown in the drawing, the bottom or opposite side of the paper sheet 1 may also have a wax coating or the like in order to facilitate stacking of individual transfers one against the other without sticking or blocking and thereby avoiding the use of separate slip sheets when it is desired to stack a group of transfers.

Although for the sake of a detailed description of the drawing the composite design 5 is identified as the "vitreous design," it will be apparent that the clear layer 4 and the composite design 5 constitute a single unitary element comprising the transferable vitreous design portion of the decalcomania and as used in the claims the term "vitreous design" should be understood to include the clear layer 4 when such is present.

In attempting to provide a heat releasable vitreous decalcomania by utilizing a wax coated paper as the temporary backing, difficulty is sometimes encountered with proper release of the design layer from the backing upon application of heat. It has been found that such difficulty is accounted for at least in part by the fact that the molten wax under certain conditions tends to be absorbed into the porous paper sheet before the sheet and the vitreous design can be separated. Consequently, the ceramic colors have an opportunity to make direct contact with the paper sheet and tend to stick or adhere tenaciously to the same if there is no intervening film of wax or similar release material. In accordance with the present invention, the temporary backing comprises a suitable sheet material which is relatively non-porous and substantially impervious to the release layer of wax or equivalent material when the latter is in softened or molten condition. For example, the temporary backing may comprise a plastic film such as cellulose acetate or a thin metal foil. However, in most cases it will be found most economical to employ the paper backing sheet 1 with the barrier coating 2 of a character which will resist penetration by molten wax or the like.

Generally speaking, the barrier layer 2 may be in the nature of a surface sizing or seal coating such as starch, casein, glue, alkali metal silicate, etc., either with or without a clay type filler. A highly satisfactory barrier layer comprises water glass or other alkali metal silicate having dispersed therein talc, clay or like filler. As will be well understood, presence of the barrier coating 2 on the paper 1 prevents excessive penetration and absorption of the wax coating 3 when the latter becomes

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soft or molten under heat release conditions. Consequently, there is always a film of wax material between the design layer and the temporary backing so as to facilitate rapid and trouble-free release of the design layer and thereby avoiding bonding or adherence of the ceramic color components to the paper. Obviously, the material selected for the barrier layer 2 must be stable and relatively unaffected by the temperatures normally encountered during heat release application of the decalcomania. It has also been found that the presence of the barrier coating 2, which seals the pores of the paper, apparently results in a more uniform and smoother wax coating 3 with the result that it is possible to print on the wax coating designs having relatively fine and delicate details without sacrificing clarity.

The wax coating 3 may comprise a relatively high melting point wax of vegetable or mineral origin, e.g. vegetable wax having a melting point of from about 130° F. to about 160° F. or a mineral wax having a melting point of from about 180° F. to about 220° F. However, instead of the vegetable or mineral waxes, I prefer to employ one of the normally solid polyethylene glycols having a relatively high molecular weight of at least 1000. Such materials are wax-like solids and are sold for example by Carbide & Carbon Chemicals Corporation under the trademark "Carbowax." The materials known as Carbowax compounds 4000 and 6000 are particularly useful for the heat release layer 3. These wax-like materials can be applied in generally the same manner as ordinary wax coatings and are particularly advantageous for purposes of the present invention because of their relatively slight solubility in and their resistance to penetration by petroleum hydrocarbons, and because of their excellent firing qualities, particularly their ability to burn without excessive carbon deposition. At the same time, such normally solid polyethylene glycols have softening points in the range of from about 150° F. to about 350° F. so that they are capable of providing the desired heat release properties under a variety of practical operating conditions. Generally speaking, it is preferred to employ a polyethylene glycol polymer having a softening point in the lower portion of the aforementioned range so as to obtain the desired softening and heat release effect as rapidly as possible during use of the decalcomania. This is particularly important in the case of automatic or machine application of the decalcomanias. As described hereinafter in more detail, a particularly important advantage of the use of polyethylene glycols or the like for the wax coating 3 is found in the relative insolubility of such compounds in the solvents employed in the formulation of the ceramic color materials used for the vitreous design layer 5. As will readily be appreciated, under such conditions there is no tendency for migration or deterioration of the layer 3 when the vitreous or ceramic color formulation is applied as a fluid material during manufacture of the decalcomania. Consequently, when the vitreous design 5 is dry, it will be seen that it is disposed in readily releasable relation against the wax coating 3.

By reason of the release layer 3, it will be understood that the transfer body comprising the layers 4, 5 and 6 is releasable as a unit from the wax coating 3. The layer 4 which provides a base or support for the vitreous design 5 is an unpigmented clear resinous film which is preferably formed from the same organic medium or vehicle which provides the body portion of the various color layers or prints in the vitreous design 5. More specifically, this film 4 comprises a plasticized acrylic resin layer such as a polymerized acrylic resin or a polymethyl methacrylate resin. The acrylic resin layer 4 may be formed over the wax surface 3 of the backing using a fluid formulation containing the acrylic resin in a solvent which has no substantial solvent effect on the wax coating 3 for the reasons described above. The acrylic resin formulation must also contain a suitable plasticizer such as a

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chlorinated diphenyl. When a polyethylene glycol compound is employed as the wax coating 3, the solvent for the acrylic resin formulation may conveniently comprise a petroleum hydrocarbon solvent. Merely by way of example, the following is a typical formulation of a material which may be used to form the clear acrylic resin layer 4:

Parts by wt.

"Lucite" acrylic resin (Du Pont L-46).....	1
Aromatic petroleum hydrocarbon solvent.....	1.3
Chlorinated diphenyl plasticizer (Monsanto Chemical Company, Aroclor 1262)	1

The above formulation provides a fluid having good screening properties and is, therefore, particularly adapted for application of the layer 4 by screen printing techniques. However, it will be appreciated that the relative proportions of acrylic resin, solvent, and plasticizer may be varied dependent upon the particular grade of acrylic resin which is employed and the physical or printing characteristics which are desired in the formulation.

As heretofore mentioned, the vitreous design 5 is usually a composite or compound layer formed by imprinting a plurality of successive ceramic colors over the clear layer 4. When the silk screen method of printing is used, the first vitrifiable color in the form of a relatively viscous liquid or paste is forced through the screen or stencil and onto the clear layer 4. When this first print is dried, subsequent printings are then similarly applied in predetermined sequence and registration to build up the desired final composite design 5. These printing pastes or inks consist of (1) a vitrifiable material or flux containing a suitable pigment or coloring material, and (2) a flowable vehicle or binder in which the pigmented flux is dispersed. The pigmented flux materials are well known to those skilled in the decoration of glassware and chinaware and are supplied by ceramic color manufacturers as complete vitrifiable or ceramic colors which are then dispersed in the vehicle or medium by the user in accordance with the requirements of the particular job at hand. As the vehicle or medium for the ceramic colors, lacquers are widely used containing a cellulose ester or ether (such as ethylcellulose, cellulose acetate, or nitrocellulose) in a low vapor pressure organic solvent such as ethylene glycol monobutyl ether (butyl Cellosolve) to which is added a suitable plasticizer such as castor oil, dibutyl phthalate, or a chlorinated diphenyl.

However, I have found that the usual lacquers have definite disadvantages in many cases as a vehicle for ceramic colors. For example, ethyl cellulose softens in the neighborhood of 200° F. and consequently if ethyl cellulose is used as the resinous ingredient of the binder for the vitreous design 5 difficulty will be encountered in attempting to apply the decalcomania transfer design at heat release temperatures above about 225° F. In other words, at such heat release temperatures the design layer itself tends to soften and does not release properly from the carrier or backing. In addition, the ordinary lacquer components, particularly ethyl cellulose, introduce difficulties in the firing stage after the vitreous design has been transferred to the article of glassware or chinaware. For example, ethyl cellulose unless fired quite slowly tends to pass through an exceedingly "runny" or low viscosity stage in the neighborhood of 600-700° F. with the result that there is a decided tendency for the applied design to smear or become disfigured during the firing operation.

Accordingly, as the vehicle for the ceramic colors I prefer to employ a resinous material having a softening point of not less than about 325° F. so that the decalcomania transfer can be used at relatively high heat release temperatures without interference with proper release of the transfer design. Moreover, the resinous material should be one which decomposes rapidly during firing and does not tend to pass through a liquefied or "runny" stage. Finally, the resinous material of the ce-

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ramic color vehicle should be one which volatilizes or burns off completely before the vitrifiable components of the ceramic color begin to soften or melt, i.e. below about 900° F. As heretofore indicated, I have found that the acrylic resins meet these requirements very satisfactorily and they are, therefore, the preferred materials for purposes of the present invention. For example, the du Pont acrylic resin known as Lucite has a softening point in the neighborhood of 325-350° F., decomposes or volatilizes completely before the vitrifiable ingredients begin to soften, and does not become liquid or "runny" during firing so that all difficulty with smearing and running of the applied design is avoided during the firing operation.

The proportion of pigmented flux to vehicle or organic medium in the vitreous ink or paste which is necessary to give satisfactory color values, firing characteristics and shelf life will depend to a large extent on the specific gravity and other properties of the particular pigmented flux or ceramic color. For example, in many instances a suitable paste formulation can be made by grinding about 2 parts by weight of the pigmented flux or ceramic color with about 1 part by weight of organic medium. The organic medium is provided with a sufficient quantity of plasticizer to enable the printed film to maintain proper flexibility even though carrying a heavy quantity of pigmented flux. In other instances, e.g. where a color deposit of reduced intensity is desired, the relative quantity of pigmented flux may be decreased by combining about two parts by weight of pigmented flux with about three parts by weight of organic medium. In the latter case, the plasticizer content of the organic medium will usually be reduced. For certain applications of the vitreous decalcomania herein described improved firing qualities and avoidance of surface disfiguration may be realized by arranging the respective color layers of the design 5 in a predetermined sequence so that the color print adjacent the clear layer 4 constitutes the hardest or most difficultly fusible layer with each successive color layer thereafter being progressively softer or more readily fusible so that the outermost or uppermost color layer of the decalcomania is the softest or most easily fusible. Generally speaking, the degree of hardness or fusing temperature of the respective ceramic colors can be readily controlled by regulation of the composition and quantity of the flux content of the color.

For purposes of illustration, but not by way of limiting the scope of the invention, typical ceramic color formulae for the vitreous design 5 in Fig. 1 may comprise the following:

(1) A white color layer may have a flux consisting of 62.8% lead oxide or litharge, 17.8% boric oxide, 14.1% silicon dioxide, and 5.3% cadmium oxide (all percentages by weight). To this formula 16% by weight of titanium dioxide is milled in as an opacifier.

(2) A red color layer may include a flux containing 56.0% lead oxide or litharge, 29.8% silicon dioxide, 3.2% boric oxide, 2.1% lithium oxide, 4.1% cadmium oxide, 3.0% titanium dioxide, and 1.8% sodium oxide (all percentages by weight). To this flux formula about 9% by weight of red pigment comprising cadmium sulfoselenide and cadmium oxide is milled in.

(3) In the case of a black color layer the flux formulation may include 78.0% lead oxide or litharge, 10.3% boric oxide, and 11.7% silicon dioxide (all percentages by weight). This formula is combined with about 16% by weight of black pigment composed of a mixture of cobalt, chromium and iron oxides.

Each of the foregoing pigmented fluxes is ground in an organic medium, preferably an acrylic resin vehicle of the type hereinbefore described, the proportion of organic medium and its plasticizer content being regulated to provide the desired color and storage and firing characteristics in the finished transfer. The clear acrylic resin formulation described heretofore for the layer 4 is a highly satisfactory medium for use with the foregoing ceramic

color formulations and may be composited in the proportion of 2 parts by weight of ceramic color to 1 part by weight of clear acrylic vehicle.

The thermoplastic or heat activatable adhesive layer 6, which constitutes the temporary bonding agent for effecting preliminary adherence of the vitreous design 5 to the article being decorated, may consist of any suitable thermoplastic resinous adhesive such as a maleic modified or maleate resin, an acrylic resin, a vinyl resin, polyvinyl methyl ether, etc. I have found that excellent results are obtained with a modified ethyl cellulose lacquer residue containing a suitable plasticizer, such as chlorinated diphenyl, and an ester gum, e.g. the glyceryl, methyl, or ethyl esters of rosin acids. One such product known commercially as Reslac 1218-45 and manufactured by Reslac Chemicals Inc. of Chicago, Illinois, is particularly suitable for forming the layer 6. I have also found that in many cases it is advantageous to include in the adhesive layer 6 a minor amount of a clear unpigmented flux or vitrifiable material. The inclusion of the flux assists in anchoring or retaining the design 5 in place on the ware during firing and also helps to avoid pin holes or the like in the final fired design. The flux may comprise a mixture of unpigmented inorganic oxides of the general character described above and is preferably a somewhat lower melting flux as compared with the pigmented fluxes in the design 5. With the Reslac adhesive mentioned above a ratio of 1 part by weight of flux to 15 parts by weight of adhesive gives good results.

The vitreous decalcomania described above is employed in decorating a ceramic article, such as an article of chinaware, glassware or the like, preferably by first preheating the ceramic article and then contacting the outermost thermoplastic layer 6 of the transfer with the preheated article. The heat thus applied to the transfer accomplishes two effects in a single step. In the first place, the thermoplastic layer 6 is activated or rendered tacky so that the vitreous design 5 is temporarily adhered or bonded to the ceramic surface. At the same time, the application of heat to the decalcomania from the design side thereof causes the wax coating 3 to melt or soften thereby automatically releasing the barrier coated paper backing. Of course, it will be understood that the clear layer 4 is released as a unit with the design 5 and is disposed outermost when the design 5 is on the ceramic article. Thereafter, the ceramic article is fired at a high temperature in the usual manner so that the vitreous design 5 is melted and permanently fused into the ceramic surface. The clear layer 4, the organic components of the vitreous design 5, and the temporary binder 6 are completely consumed during the firing operation so that only the pigmented flux component of the vitreous design 5 remains. It will, of course, be appreciated that the foregoing technique may be applied either to glazed or unglazed ware. In the case of the latter, the so-called bisque or unglazed article is preheated and the transfer applied as described above. Thereafter the bisque with the temporarily adhered design is heated to dispel the organic components of the design and a liquid glaze is then applied by dipping or spraying. After an initial drying period, the ware is then fired to produce the finished article having a very durable underglaze decoration.

Although it is also possible to apply the transfer by placing the design side of the transfer against an unheated article and then applying heat to the backing side of the transfer, the above described technique of preheating the ceramic article before contact with the transfer is found to be highly advantageous because it affords better release of the design from the backing and lends itself very readily to high speed machine application. In the case of machine application of the transfers to the ware at high speeds, it is particularly important that the transfer body comprising the layers 4, 5 and 6 be rapidly and effectively released from the temporary

carrier. The features of the decalcomania transfer described herein cooperate in a novel and highly effective manner in meeting this objective. In the first place, the presence of the wax impervious barrier layer 2 on the paper backing 1 prevents or retards excessive absorption of the molten or softened wax coating 3 by the paper 1 so that the wax material is retained at the surface of the carrier during the release step. Secondly, the fact that the wax coating 3 is insoluble in the solvent materials employed during printing of the transfer layers 4 and 5 contributes to the rapidity and ease of release of the transfer body 4-5-6 since there is substantially no migration or physical merging of the adjacent layers 3 and 4 under these conditions. Finally, rapid heat release of the transfer body is facilitated by the fact that the acrylic resin or other resinous component of the layers 4 and 5 has a relatively high softening point so that there is little chance for the development of thermoplastic properties in the layers 4 and 5 during the relatively brief time required for the heat release operation. The combined effect of each of these factors is such that my invention provides for the first time an inexpensive vitreous transfer which can be applied by a machine at high speeds with consistently good results under a wide variety of operating conditions.

In Fig. 2 I have illustrated a modification of the vitreous decalcomania described above. In this instance, the paper backing 1, the barrier coating 2, the wax coating 3, and the clear layer 4 may be substantially the same as described in connection with Fig. 1. However, the vitreous design, designated at 7, includes as an integral component thereof a thermoplastic or heat activatable adhesive ingredient which makes it possible to omit the separate adhesive layer 5 shown in Fig. 1. In use, the layer 7 is contacted with the preheated ceramic article and develops sufficient tackiness at the relatively low perheat temperature to adhere directly to the article.

In Fig. 3, a modification of the invention is shown wherein the vitreous design is formed by a different technique. In this case, the paper backing 1 with its barrier layer 2 and wax coating 3 may be the same as previously described. A clear layer 8 is also applied over the wax coating 3. Whereas in the Fig. 1 embodiment the clear layer 4 serves primarily as a supporting film for the compound vitreous design 5, in this instance the clear layer 8 also serves the additional important purpose of protecting the wax coating 3. Consequently, the clear layer 8 is preferably of sufficient extent to completely cover the wax coating 3.

Over the protective clear layer 8 a binder or varnish 9 is applied in the desired design configuration by any suitable technique, preferably by the lithographic printing process or the like. Such binders or varnishes are well known in the art, e.g. linseed oil with a suitable plasticizer may be used. After application of the layer 9 and while the latter is still wet or tacky, the desired ceramic color or vitrifiable color formulation in pulverized or subdivided form is dusted or sprinkled, as at 10, onto the preformed design layer 9. Obviously, the particles of vitrifiable color 10 will adhere only to the tacky coated areas, and the dry non-tacky protective layer 8 prevents the vitreous particles from adhering to the wax coating 3. After the layer 9 is dry, the loose vitrifiable or ceramic color particles can be readily removed and thereafter the outermost thermoplastic layer 6 is applied in the same manner as hereinbefore described. For purposes of simplicity, Fig. 3 shows only a single layer 9 having the ceramic color particles 10 dusted thereon. However, any number of superimposed layers may be provided in the vitreous design, each layer being formed by the same application and dusting technique and being dried before the next succeeding layer is applied.

In Fig. 4 a special embodiment of the invention is shown wherein the design comprises a metallic colored

ornamentation or text, e.g. gold, silver, platinum, palladium, etc. Generally speaking, the metallic color components, e.g. the so-called "screening gold," are quite different in character and composition from the more conventional ceramic colors heretofore mentioned. Among other things, the gold ceramic color has a substantially lower melting point than the usual ceramic colors and as a result during firing of an applied gold decoration there is a tendency to trap carbon particles between the applied gold color and the ware if an intermediate adhesive layer is used such as the heat activatable adhesive 6 heretofore described. In other words, as a result of the relatively lower melting point of the gold color, the heat activatable adhesive material 6 does not always have an opportunity to completely volatilize or decompose before the gold melts with the result that some of the adhesive or carbon residue thereof can become trapped in the gold color during firing. Obviously, this results in poor adherence of the gold and also imparts an unsatisfactory speckled appearance to the decorated ware. Also, the metallic colors often exhibit an undesirable tendency to shrink during firing if an adhesive material is present between the color and the surface of the ware. In Fig. 4, the layers 1, 2, 3 and 4 are exactly the same as in the Fig. 1 embodiment. However, immediately over the clear layer 4 the heat activatable adhesive layer is applied, as at 11, and the gold colored or other metallic vitreous design is superimposed, as at 12, over the adhesive layer. Thus, the gold design comprises the outermost portion of the transfer in this embodiment of the invention. In order to insure contact of at least a portion of the heat activatable adhesive layer 11 with the preheated ware so as to obtain temporary adherence of the transfer design before firing, it is important that the gold design layer 12 be of a discontinuous nature so as to provide a number of openings or gaps, as indicated at 13, between the various parts of the gold design. With such arrangement, the exposed heat activatable adhesive 11 in the open spaces or gaps 13 between the gold colored areas 12 can make direct contact with the surface of the heated ware and this contact area is sufficient to achieve the necessary temporary adherence of the transfer body to the article. At the same time, the gold color areas 12 are disposed in direct contact with the ware so that during subsequent firing there is no adhesive or other material interposed between the gold color and the surface of the ware.

The term "vitreous design," as used in the claims, refers to a design comprising one or more inorganic colors and vitrifiable flux ingredients in an organic resinous film or medium, as contrasted with the Fig. 4 embodiment just described wherein the design comprises a metallic component of the precious metal type.

From the foregoing it will be evident that my invention provides a decorating technique for ceramic ware and a heat applied vitreous transfer which have very important and valuable advantages over the methods and transfers heretofore used in the art. The use of water during application of the transfer to the ware is completely eliminated so that there are no difficulties with water stains or spotting. Likewise the drying periods necessary with water release transfers prior to firing are completely eliminated. My invention utilizes thermoplastic adhesives which are simple to use and which fire out completely so as to avoid the difficulties heretofore mentioned in connection with gum coatings and varnishes. Also, the great simplicity and ease of application of my transfer makes it possible for the first time to employ high speed machine application techniques in this field with consequent savings in labor and other production costs.

Although the invention has been described with particular reference to certain specific embodiments thereof, it is to be understood that various modifications and equivalents may be resorted to without departing from

the scope of the invention as defined in the appended claims.

I claim:

1. A vitreous decalcomania comprising a paper backing having a substantially wax-impervious barrier coating, a wax layer comprising a normally solid high molecular weight polyethylene glycol over said coating, a vitreous design carried on the wax layer, and a thermoplastic material at the outermost surface of said design whereby upon application of heat said thermoplastic material is activated for adhering the vitreous design to an article and said wax is melted for simultaneously releasing the vitreous design from said backing, said vitreous design comprising a vitrifiable ceramic color in a resinous organic film which is readily releasable from said backing upon melting of said wax layer, and said film having a softening point not less than about 325° F. and being completely destructible upon firing while the firing temperature is below about 900° F. without passing through a relatively fluid and readily flowable stage during firing.

2. A vitreous decalcomania comprising a paper backing having a substantially wax-impervious barrier coating, a wax layer comprising a normally solid high molecular weight polyethylene glycol over said coating, a vitreous design carried on the wax layer, and a thermoplastic material at the outermost surface of said design whereby upon application of heat said thermoplastic material is activated for adhering the vitreous design to an article and said wax is melted for simultaneously releasing the vitreous design from said backing, said vitreous design being initially formed from a fluid composition comprising a vitrifiable ceramic color dispersed in an acrylic resin vehicle including a plasticizer for the resin and a solvent for the resin in which said polyethylene glycol is substantially insoluble whereby upon subsequent drying of the composition the vitreous design is formed on the wax coated surface in readily releasable relation therewith.

3. The decalcomania of claim 2 further characterized in that said solvent comprises a petroleum hydrocarbon solvent.

4. A vitreous decalcomania comprising a paper backing having a substantially wax-impervious barrier coating, a wax layer comprising a normally solid high molecular weight polyethylene glycol over said coating, a vitreous design carried on the wax layer and readily releasable from said backing upon melting of said wax layer, and a thermoplastic material at the outermost surface of said design whereby upon application of heat said thermoplastic material is activated for adhering the vitreous design to an article and said wax layer is melted for simultaneously releasing the vitreous design from said backing, said vitreous design being initially formed from a fluid composition comprising a vitrifiable ceramic color dispersed in an organic medium including a resinous film-forming material, a plasticizer for the resinous material, and a solvent, and said wax layer being relatively insoluble in said solvent whereby upon subsequent drying of the composition the vitreous design is formed on the wax surface in readily releasable relation therewith.

5. A vitreous decalcomania comprising a paper backing having a substantially wax-impervious barrier coating, a wax layer comprising a normally solid high molecular weight polyethylene glycol over said coating, a vitreous design carried on the wax layer, and an outermost thermoplastic layer over said design whereby upon application of heat said thermoplastic layer is activated for adhering the vitreous design to an article and said wax is melted for simultaneously releasing the vitreous design from said backing, said barrier coating preventing excessive absorption of the molten wax by the paper backing and thereby facilitating release of the design, said design comprising a vitrifiable ceramic color contained in an acrylic resin medium having a softening point not less than about 325° F., and said design being

initially formed from a fluid composition containing said ceramic color, said acrylic resin, and a solvent for the resin in which said polyethylene glycol layer is relatively insoluble whereby upon subsequent drying of the composition the vitreous design is formed on said polyethylene glycol layer in readily releasable relation therewith.

6. A decalcomania comprising a paper backing having a substantially wax-impervious barrier coating, a wax layer comprising a normally solid high molecular weight polyethylene glycol over said coating, a thermoplastic adhesive layer over said wax layer, and a discontinuous metallic design disposed against said adhesive layer and having design portions with open spaces therebetween, said adhesive material being adapted to protrude through said open spaces into contact with the surface of an article when the design side of the decalcomania is placed thereagainst, and said thermoplastic material being activatable by application of heat for temporarily adhering the design to the article and said wax coating being melted simultaneously for releasing the design from the backing.

7. The method of decorating an article of glassware, chinaware, and the like which comprises forming a vitreous design on the wax-coated surface of a paper backing having a substantially wax-impervious barrier coating with a wax coating over the barrier coating, said wax coating comprising a normally solid high molecular weight polyethylene glycol, applying a thermoplastic material over the outermost surface of the vitreous design, preheating the article being decorated, contacting the preheated article with the thermoplastic material whereby to activate the latter for temporarily adhering the vitreous design to the article and simultaneously to melt the wax coating for releasing the vitreous design from the paper backing, said barrier coating preventing excessive absorption of the molten wax by the paper backing and thereby facilitating release of the design, and subsequently firing the article for permanently fusing the vitreous design to the surface of the article.

8. A vitreous decalcomania comprising a paper backing having a substantially wax-impervious barrier coating, a wax layer comprising a normally solid high molecular weight polyethylene glycol over said coating, a vitreous design carried on the wax layer, and a thermoplastic material at the outermost surface of said design whereby upon application of heat said thermoplastic material is activated for adhering the vitreous design to an article and said wax is melted for simultaneously releasing the vitreous design from said backing, said barrier coating preventing excessive absorption of molten wax by the paper backing whereby to facilitate release of the design, and said vitreous design comprising a vitrifiable ceramic color in an acrylic resin medium.

9. A heat releasable carrier for use in a vitreous decalcomania comprising a paper backing having a substantially wax-impervious barrier coating, and a wax layer over said coating comprising a normally solid high molecular weight polyethylene glycol.

10. The article of claim 9 further characterized in that said barrier coating comprises a surface sizing selected from the group consisting of starch, casein, glue, and alkali metal silicate.

11. The article of claim 9 further characterized in that said polyethylene glycol has a molecular weight of at least 1000.

12. The article of claim 9 further characterized in that said polyethylene glycol has a softening point in the range of from about 150° F. to about 350° F.

13. A vitreous decalcomania comprising a paper backing having a substantially wax-impervious barrier coating, a wax layer comprising a normally solid high mo-

lecular weight polyethylene glycol over said coating, a vitreous design carried on the wax layer and readily releasable from the backing upon melting of said wax layer, and a thermoplastic material at the outermost surface of said design whereby upon application of heat said thermoplastic material is activated for adhering the vitreous design to an article and said wax is melted for simultaneously releasing the vitreous design from said backing, said barrier coating preventing excessive absorption of molten wax by the backing whereby to facilitate release of the design.

14. The decalcomania of claim 13 further characterized in that said vitreous design is initially formed by depositing on the wax layer a fluid composition containing a colored vitrifiable flux, a resinous film-forming material, and a solvent for the latter, said wax being substantially insoluble in said solvent whereby upon subsequent drying of the composition the vitreous design is provided on the wax layer in readily releasable relation.

15. The decalcomania of claim 13 further characterized in that said thermoplastic material comprises a separate layer of thermoplastic material disposed over said vitreous design.

16. The decalcomania of claim 13 further characterized in that said thermoplastic material is included as a component of said vitreous design.

17. The decalcomania of claim 13 further characterized in that said thermoplastic material also contains a minor amount of a relatively low melting point vitreous flux for facilitating retention of the vitreous design on the surface of the article during subsequent firing.

18. The decalcomania of claim 6 further characterized by the provision of a clear resinous layer interposed between said wax layer and said thermoplastic adhesive layer.

19. The method of decorating an article of glassware, chinaware, and the like by means of a vitreous decalcomania including a paper backing having a substantially wax-impervious barrier coating, a wax layer comprising a normally solid high molecular weight polyethylene glycol over said coating, a vitreous design on the wax layer which is readily releasable from said backing upon melting of said wax layer, and a thermoplastic material at the outermost surface of said design; said method comprising the steps of contacting the article in heated condition with the thermoplastic material side of said decalcomania whereby to activate said thermoplastic material for temporarily adhering the design to the article and simultaneously to melt said wax for releasing the design from said backing, said barrier coating preventing excessive absorption of the molten wax by the backing and thereby facilitating release of the design; and subsequently firing the article for permanently fusing the vitreous design to the surface of the article.

20. The method of claim 19 further characterized in that said vitreous design comprises an acrylic resin.

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