April 29, 1969 T. J. MILLIKEN 3,441,458

METHOD OF APPLYING A VITREOUS DECALCOMANIA

Filed Feb. 10, 1966

Fig. 1.

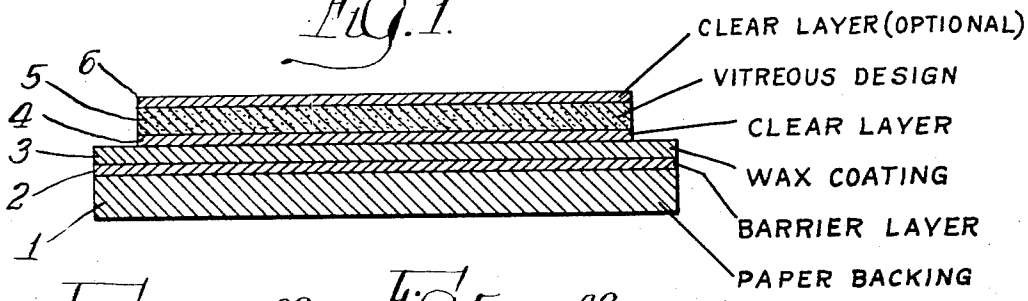


Fig. 4.

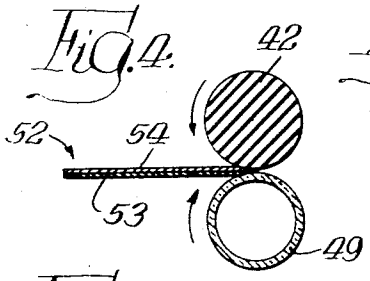


Fig. 5.

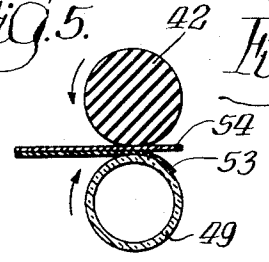


Fig. 6.

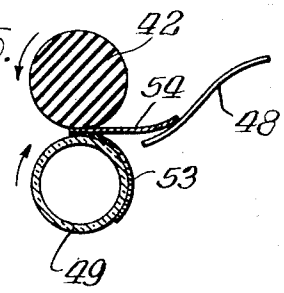
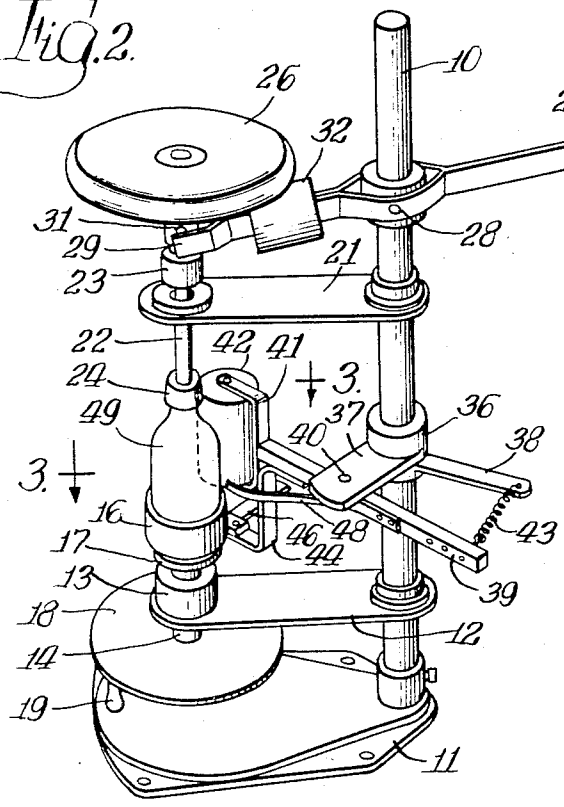


Fig. 2.



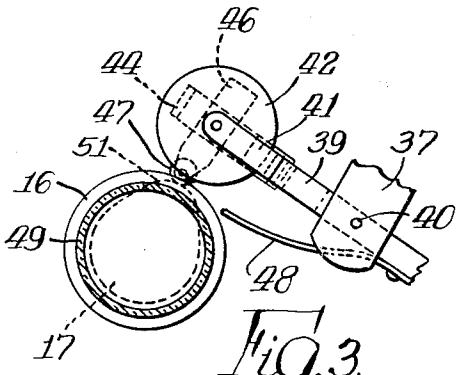


Fig. 3.

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METHOD OF APPLYING A VITREOUS DECALCOMANIA

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U.S. Cl. 156—89 10 Claims

This invention relates to improvements in the decoration of ceramic or vitreous articles, such as chinaware, glassware, pottery, porcelain ware, and the like, by means of a heat-release vitreous or ceramic decalcomania. More particularly, the invention relates to an improved method of applying a heat-release vitreous or ceramic decalcomania to glassware.

For many years, it has been customary to use decalcomania transfers prepared with special vitrifiable or ceramic colors in the decoration of articles of glassware, chinaware, or the like. For example, water release decalcomanias have been widely used which are either of the slide-off type or the varnish-applied duplex paper type, both of which will be familiar to those skilled in the art. In either case, soaking with water is necessary to effect separation of the backing from the design. After the design has been temporarily adhered to the ceramic article it is necessary to dry the article thoroughly to remove all traces of water after which a high temperature firing operation is employed in the usual manner.

Although water release vitreous decalcomanias have previously enjoyed extensive commercial use, it is well recognized that they have serious disadvantages arising primarily from the fact that a number of inconvenient and time-consuming manual steps are required. Furthermore, the use of water or varnish and the presence of water soluble gum introduces innumerable difficulties so that the water release transfers require considerable care and skill in the use thereof and do not lend themselves to high speed machine application.

In order to overcome the various disadvantages of the water release vitreous decalcomanias, there has been widespread commercial use in recent years of a heat release type vitreous or ceramic decalcomanias, e.g. as fully described in U.S. Patents Nos. 2,970,076 and 3,007,829. A heat release vitreous decalcomania is characterized by the use of a heat releasable backing at the face or front side of the vitreous design layer and an outermost thermoplastic or heat activatable adhesive surface at the opposite or rear side of the vitreous design. When the outermost thermoplastic or heat activatable surface of the decalcomania is pressed against the surface of a preheated vitreous or ceramic article, the heat of the article is sufficient to activate the adhesive surface of the decalcomania so that the design is temporarily adhered to the article being decorated, and at the same time the heat of the article is sufficient to soften or melt the heat release layer of the backing, thereby effecting release of the backing from the design layer. Both effects are accomplished in substantially a single application step in which the decalcomania is pressed against the preheated ware by means of a pressure platen which is sufficiently resilient or yieldable to conform to the configuration of the surface of the article. Usually, the released backing sheet can be fully disengaged from the article by means of a jet of air or the like. The ware with the temporarily adhered vitreous design layer is then fired in the usual manner so that the vitreous design becomes an integral part of the surface of the article.

One of the difficulties encountered in decorating vitreous and ceramic articles by means of heat release decalcomanias is the development of pinholes in the applied design during the firing step. If the pinholes are not too large and not excessive in number, they can often be tolerated depending upon the nature of the applied design and the type of ware being decorated. For example, in the case of translucent borosilicate glassware or opaque chinaware, a small number of minute pinholes in the applied design may not be readily noticeable by the average person. However, in the case of transparent glassware, such as bottles, tumblers and the like, even a small number of tiny pinholes may be objectionable.

Accordingly, a primary object of the present invention is to provide a novel and improved method of decorating vitreous or ceramic ware using heat release decalcomanias.

A further object of the invention is to eliminate pinholing and other related defects heretofore encountered in the decoration of vitreous or ceramic ware with heat release decalcomanias.

Other objects and advantages of the invention will become evident 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 vitreous decalcomania transfer of the heat release type used in the present invention;

FIG. 2 is a perspective view of a manually operated machine for applying the decalcomania of FIG. 1;

FIG. 3 is a fragmentary cross-sectional view taken substantially along the line 3—3 of FIG. 2; and

FIGS. 4–6 are schematic cross-sectional views showing various stages in the application of the decalcomania to a glass bottle using the machine of FIG. 2.

Referring to FIG. 1, the releasable backing of the heat release vitreous decalcomania illustrated therein includes a paper sheet 1 having a barrier layer or coating 2 which renders one side of the paper less porous and retards penetration by molten wax or wax-like materials. Various inorganic seal coatings, such as starch, casein, glue, an alkali metal silicate with or without a clay filler, etc., may be used as the barrier layer 2, but an organic barrier material is preferred, particularly polyvinyl acetate. Superimposed over the barrier layer 2 is a coating 3 of a wax-like heat release material which is preferably a normally solid high molecular weight polyethylene glycol. For example, the materials known as Carbowax compounds sold by Union Carbide Corporation, Chemicals Division, are particularly useful, as more fully described in the aforementioned U.S. Patents Nos. 2,970,076 and 3,007,829.

By reason of the heat release layer 3, the remainder of the decalcomania(comprising the layers 4, 5 and 6) is releasable as a unit from the backing. The layer 4 is an unpigmented clear resinous film disposed over the heat release 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. If necessary to impart strength and integrity to the design layer 5 or to provide an outermost surface that can more readily be rendered tacky or adhesive, another layer 6 may be disposed over the vitreous design 5, such as a clear layer of resinous material or a layer of heat-activatable thermoplastic adhesive material. However, as hereinafter described in more detail, the optional outermost layer 6 is preferably omitted and will ordinarily be used only in those instances in which the nature of the design layer 5 is such as to require added strength or protection or more readily induced adhesive properties.

The clear resinous layer 4 which provides a base or

support for the vitreous design 5 is preferably formed from the same general type of organic medium or vehicle which provides the body portion of the various color prints in the vitreous design 5. More specifically, the film 4 comprises the residue from a lacquer containing a resinous film-forming ingredient, a solvent, and, in some cases, a plasticizer. The resinous film-forming ingredient is ordinarily a cellulose ester or ether (such as ethyl cellulose, cellulose acetate, or nitrocellulose) or an acrylic resin. The preferred materials are ethyl cellulose and the acrylic resins. For the decoration of glassware, in accordance with the preferred embodiment of the present invention, the methacrylate polymers give best results, particularly n-butyl methacrylate polymer, isobutyl methacrylate polymer, and copolymers of the same. Any suitable solvent system may be employed, but in the case of ethyl cellulose the preferred solvent is one of the ethylene glycol ethers, such as ethylene glycol monobutyl ether, and in the case of the acrylic resins the preferred solvents are aromatic petroleum hydrocarbon solvents, such as toluene and xylene fractions. Although plasticizers, such as castor oil, dibutyl phthalate, or chlorinated diphenyl, have generally been considered as desirable ingredients in vitreous decalcamonia films in order to provide the desired film flexibility, it is one of the advantageous of the present invention, as described in more detail below, that plasticizers can be omitted from the resinous films thereby avoiding certain difficulties which have been encountered, particularly when chlorine-containing plasticizers are employed.

The vitreous design 5 is usually a composite or compound layer formed by imprinting a plurality of successive ceramic color compositions in liquid form over the clear layer 4 by screen printing or other suitable printing techniques. The printing composition consists of a pigmented vitrifiable material or flux and an organic liquid vehicle or binder in which the pigmented flux is dispersed or suspended. The pigmented flux materials are supplied by ceramic color manufacturers and are added to the vehicle or binder by the manufacture of the decalcomania. The vehicle or binder may be any of the lacquers described above in connection with the clear resinous layer 4. The proportion of pigmented flux to vehicle or binder may be regulated in accordance with the requirements of the particular decalcomania. In general, the flux to binder ratio on a weight basis may range from about 2:1 to as high as about 5:1.

As previously described, in decorating a ceramic or glass article with a heat release vitreous decalcomania it has been customary heretofore to contact the entire outermost surface of the transfer with the heated article in a unitary step by pressing the entire transfer substantially uniformly against the surface of the article by means of a pressure platen. However, it has now been discovered that this method of application is responsible for entrapment of small pockets of air between the transfer and the article with the result that during subsequent firing the pockets of air are forced through the design layer resulting in minute pinholes. Careful analysis of photographs of applied transfers before and after firing shows a very close correlation between the pockets of air trapped under the transfer during application by the pressure platen method and the pinholes appearing after firing.

I have found that the pinholing problem can be eliminated by changing the application techniques in two important respects. First, there is interposed between the ware and the vitreous design layer of the decalcomania a suitable organic liquid material which tends to increase the extent of surface contact between the applied design layer and the ware and also causes the outer surface of the design layer to become slightly tacky at the temperature of the ware. Secondly, instead of pressing substantially the entire decalcomania against the surface of the ware in a single pressure application step, the application must be such that the decalcomania transfer is pressed progressively into contact with the surface of the ware in successive increments by applying pressure in a restricted area or narrow line moving across the transfer, preferably from one edge thereof to the opposite edge. This action is most conveniently achieved by means of a roller coacting with the ware so that the decalcomania is adhered to the ware by means of rolling pressure. The combined effect of the organic liquid material and the progressive application technique results in the elimination of air bubbles or pockets between the applied design film and the ware. Consequently, pinholing during the subsequent firing of the ware is also eliminated.

A simple manual machine for the purpose of illustrating the principle of the application method of the present invention is shown in FIGS. 2 and 3. The device comprises an upright supporting post or standard **10** mounted on a base **11**. An arm **12** extending outwardly from the post **10** supports a ball bearing journal **13**, and an upright shaft **14** is rotatably mounted in the journal **13** and extends above and below the arm **12**. At the upper end of the shaft **14** is mounted a cup-shaped bottom chuck **16** for supporting the lower end of the ware to be decorated, in this case a glass bottle **49**. An eccentric cam **17** is fixed to the shaft **14** between the journal **13** and the chuck **16**. A hand wheel or crank **18** having a handle **19** is secured to the lower end of the shaft **14** below the arm **12**.

An arm **21**, similar to the arm **12**, is secured on the post **10** in spaced relation above the arm **12**, and an upright spindle **22** is supported at the outer end of the arm **21** for vertical and rotary movement relative to the arm **21**. A stop collar **23** is affixed to the spindle **22** above the arm **21** for limiting the lowermost position of the spindle. An upper chuck **24**, preferably of rubber or the like, is mounted at the lower end of the spindle **22**, and the uppermost end of the spindle **22** carries a heavy weight in the form of a circular metal disk **26**. For raising and lowering the spindle **22**, a pivot arm or lever **27** is pivotally supported on the post **10** intermediate its length, as at **28**. A yoke **29** is provided at one end of the lever **27** and engages a pair of projecting pins **31** on the spindle **22** for raising the latter vertically. A weight **32** is affixed to the lever **27** between the pivotal mounting **28** and the yoke **29** for normally urging the yoke **29** downwardly. Thus, when there is no bottle mounted between the chucks **16** and **24**, the stop collar **23** engages the arm **21** and the spindle **22** is in its lowermost position (not shown). A wire or cable **33** is connected to the opposite end of the lever **27** for operating the latter, as by means of a foot pedal (not shown) connected to the lower end of the cable.

A bracket **36** is mounted on the post **10** intermediate the arms **12** and **21** and is provided with a pair of rigid radially extending arms **37** and **38**. The arm **37** comprises a support for an elongated lever **39** having an intermediate pivotal connection, as at **40**, to the support arm **37**. A yoke **41** is rigidly affixed to one end of the lever **39** and rotatably supports a rubber roller **42**. The outer ends of the rigid arm **38** and the pivotal lever **39** are interconnected by means of a spring **43** for normally urging the outer end of the lever **39** toward the arm **38**. A bracket **44** is rigidly secured to the lever **39** and depends therefrom. A support arm **46** is slidably and adjustably carried at the lower end of the bracket **44** and rotatably mounts a cam follower or roller **47** which is in rolling engagement with the cam **17**. A resilient deflecting finger **48** is affixed to the lever **39** and projects toward the roller end of the lever **39** for the purpose described below.

In the use of the device, the spindle **22** and the upper chuck **24** are elevated by means of the lever **27** and its actuating cable **33** to permit a transparent glass bottle **49** to be inserted in the device with the base of the bottle in the bottom chuck **16** and the top of the bottle engaged by the upper chuck **24**, as shown in FIG. 2. In this position, the collar **23** is elevated above the arm **21**, and after the cable **33** is released it will be understood

that the bottle **49** is firmly clamped between the chucks **16** and **24** by reason of the force exerted by the weight **26**. During the insertion of the bottle **49** between the chucks, the rubber roller **42** is held in outwardly spaced relation away from the bottle **49** because the cam follower **47** is engaged by the peak of the lobe portion, indicated at **51** (FIG. 3), of the cam **17**, thereby pivoting the roller support lever **39** against the tension of the spring **43**. The hand wheel **18** is now rotated slightly so that the lobe portion **51** of the cam **17** is moved away from the cam follower **47**, thereby allowing the lever **39** to pivot under the action of the spring **43** and bring the rubber roller **42** into tangential or line contact with the outer surface of the bottle **49**.

The organic liquid material previously mentioned is now applied to the design layer side of a heat release vitreous decalcomania **52** (or to the bottle **49** or to both) and, as shown in FIG. 4, the forward edge of the decalcomania is inserted in the nip between the roller **42** and the bottle **49**. In FIGS. 4 to 6, the vitreous design of the decalcomania is designated at **53** and the releasable backing at **54**. The hand wheel **18** is now rotated through a complete revolution back to its original position (FIG. 3) in which the lobe **51** engages the cam follower **47** and the roller **42** is displaced outwardly from the bottle **49**. As seen in FIGS. 5 and 6, rotation of the bottle **49** in a clockwise direction causes the roller **42** to rotate in a counterclockwise direction, and the decalcomania **52** is fed or drawn therebetween and is pressed progressively against the bottle **49**. As will readily be understood, successive increments of the vitreous design **53** of the decalcomania **52** are thus brought into contact with the curved surface of the bottle **49** and pressure is applied along a relatively restricted area or narrow line extending across the decalcomania **52** and defined by the opposed portions of the curved surfaces of the roller **42** and the bottle **49**. Thus, a squeegee action is obtained which insures extrusion or displacement of air from the space between the design **53** and the bottle **49** in a direction opposite to the direction of movement of the decalcomania **52**, i.e. to the left as viewed in FIGS. 4–6.

It will be understood that the bottle **49** has been preheated to a suitable application temperature which may range from about 150° F. to 300° F. or higher but is usually from about 200° F. to about 250° F. As the decalcomania **52** is drawn between the pressure roller **42** and the bottle **49**, the heat of the bottle melts the heat release coating of the backing portion **54**. At the same time, the combined effect of the ware temperature and the applied organic liquid material causes the resinous film of the vitreous design portion **53** to become tacky or adhesive. Thus, the design **53** adheres to the bottle **49** and the released backing **54** automatically separates or parts from the design **53**, as shown in FIG. 5. In FIG. 6 the application of the decalcomania to the ware has been substantially completed, and the action of the spring finger **48** is shown schematically as it insures deflection of the released backing **54** away from the decorated bottle. When the rotation of the hand wheel **18** has continued through a complete revolution, the rolling pressure application of the decalcomania to the bottle **49** will be complete and the lobe portion **51** of the cam **17** will again coact with the cam follower **47** to displace the rubber roller **42** outwardly from the bottle **49**, and the bottle with the applied decoration can then be removed from chucks for firing in the usual manner.

Although the application method of the present invention has been illustrated by means of the simplified hand machine shown in FIGS. 2 and 3, it will be understood that the principles are equally applicable to high speed automatic machinery.

The organic liquid material used in this invention in the manner described above should possess several basic requirements. First, the liquid should have the ability to wet the surface of the design side of the decalcomania or the surface of the article being decorated and preferably it should wet both of these surfaces. The liquid should also have a suitable viscocity to facilitate displacement or squeezing out of air pockets as the decalcomania is pressed into contact with the hot ware by a traveling line of pressure, as heretofore described. In addition, the liquid material should have a partial solvent action on the resinous film forming ingredient of the vitreous design at the temperature of application so as to render the outermost surface of the design film slightly adhesive or tacky and thereby develop the necessary temporary adherence of the design to the ware, but at the same time the liquid material should not have an excessive solvent action on the resinous film which would result in smearing or distortion of the design. In general, the organic liquid should not have any appreciable solvent action on the film at room temperature. Finally, the liquid material should have a sufficiently high vaporization point so that there is no substantial vaporization at the temperature of application, thereby avoiding formation of blisters and bubbles in the applied design.

In addition to the foregoing requirements of the organic liquid material, it is also desirable that the material be capable of being fired without leaving an objectionable residue and that it be relatively inert with respect to the flux ingredients of the design layer so as not to cause any undesirable change in the appearance or properties of the ceramic colors during firing or subsequent use of the decorated article. Moreover, it is desirable that the liquid material have a high flash point so as to minimize the possibility of fire and explosion, and preferably it should not produce toxic or unpleasant vapors during its use.

As previously pointed out the primary advantage of the use of the organic liquid material and the progressive pressure method of application is that air pockets are excluded and pinholing difficulties during firing are eliminated. However, a further important advantage of the invention is that in most cases it is unnecessary to provide a separate heat-activatable thermoplastic adhesive material over the vitreous design layer of the decalcomania. Although it has been considered desirable heretofore to use a separate thermoplastic adhesive layer at the outermost surface of the vitreous design to insure the desired temporary adherence of the design to the preheated ware, nevertheless, the decomposition and vaporization of the separate adhesive material during subsequent firing is sometimes a source of difficulty in that it tends to produce minute pinholes in the design in much the same manner as entrapped air. The pinholes attributable to decomposition and vaporization of the adhesive layer have an adverse effect on the ceramic colors by giving them a matte appearance.

In accordance with the present invention, the partial solvent effect or tack-inducing action of the organic liquid material at the application temperature is sufficient in most cases to impart the required tackiness to the resinous film of the design layer and thereby achieve the desider temporary adherecene to the ware without the use of a special thermoplastic adhesive layer. However, the invention does not completely exclude the use of a separate heat-activatable layer, such as the clear resinous layer **6** of FIG. 1 or other equivalent thermoplastic material. For example, in those instances where the ratio of flux to binder in the vitreous design **5** is relatively high and/or where the contact time of the design with the ware is relatively short, it may be advantageous to provide a thin layer such as the layer **6** in order to obtain rapid development of tack at the design surface.

It has also been found that the partial solvent and tack-inducing effect of the aforementioned organic liquid material makes it possible to omit the usual plasticizers from the resinous films of the vitreous design **5** and the supporting clear layer **4**. As previously mentioned, ethyl cellulose and acrylic resins are the most acceptable

film-forming materials in heat release ceramic or vitreous decalcomanias. In addition, it has been preferred heretofore to include a plasticizer of the chlorinated diphenyl type (e.g., one of the Aroclor plasticizers manufactured by Monsanto Chemical Company). However, chlorine-containing plasticizers decompose at the elevated temperature of the firing step and the resultant atmosphere is often detrimental to certain ceramic colors resulting in bleaching and other defects unless elaborate ventilation precautions are taken to insure removal of the chlorine-containing vapors. In accordance with the present invention, the use of chlorine-containing plasticizers in the binder or film portion of the vitreous design layer or in the clear supporting layer is unnecessary and consequently the attendant firing difficulties are eliminated. Ample plasticity is imparted to the design film by the action of the organic liquid at the elevated temperature of the ware, and the ware can be flash fired, i.e. subjected to peak temperature immediately, with minimum ventilation.

In general, the organic liquid materials which have been found to be most suitable for use in applying heat release decalcomanias in accordance with the present invention are oils, including mineral oils (such as petroleum hydrocarbon oils), vegetable oils (such as soybean oil), and oils of animal origin. In the case of decoration of glassware by means of a heat release vitreous decalcomania in which the resinous film-forming ingredient of the vitreous design comprises an acrylic resin, the preferred liquids are petroleum lubricating oils. As a specific example, the petroleum oil designated as Indoil Industrial Oil No. 7 by American Oil Company gives excellent results. This material has the following specifications:

Viscosity, S.U.S. at 100° F	70
Viscosity, S.U.S. at 210° F	35.8
Flash point, °F., min	275
Pour point, °F., max	−40
Color, ASTM	½–2

In some cases, it will be desirable to employ a mixture of two more ingredients as the organic liquid material to be interposed between the decalcomania and the ware. For example, a petroleum lubricating oil, such as Indoil Industrial Oil No. 7 mentioned above, may have added to it a small percentage of a suitable plasticizer for the purpose of creating greater tackiness and adherence in the design film. For the reasons already mentioned, chlorine-containing plasticizers should be avoided, and in the case of a vitreous design film comprising an acrylic resin, it has been found that a plasticizer comprising a hydrogenated methyl ester of rosin is quite effective. Plasticizers of this character are sold by Hercules Powder Company under the trademark Hercolyn. Mixtures of oils may also be used with good results. For example, linseed oil, which has a marked solvent effect on acrylic resin films, can be used to best advantage when mixed with a suitable proportion of a weaker solvent, such as a highly refined mineral oil which, by itself, has only limited solvent effect on the resinous film.

Although the oil or other organic liquid material used in the method of the present invention can be applied to the decalcomania or to the ware by any suitable technique, it will generally be preferred to apply the oil or other liquid by spraying, particularly in the case of high-speed automatic machine application. As previously explained, the oil or other organic liquid material should not have any appreciable effect on the design film of the decalcomania at room temperature. However, when the decalcomania is contacted with the preheated ware with the organic liquid interposed therebetween, the resinous film component of the design layer is rendered tacky by the liquid so as to obtain the desired temporary adherence to the ware. After the vitreous design layer has been completely transferred to the ware and has assumed the temperature of the ware, the residual oil or other organic liquid is completely absorbed by the resinous film and eventually, during firing of the ware, will be completely vaporized along with the resinous ingredients without leaving any objectionable residue.

As will be appreciated by those skilled in the art, the thickness or coating weight of the heat release material (such as the layer 3 in FIG. 1) must be regulated in accordance with the other factors involved in a particular application in order to obtain the desired rapid heat release of the vitreous design from the backing. In general, the most appropriate coating weight will depend upon the speed of application or contact time between the decalcomania and the ware, the type of ware being decorated, the temperature of the ware at the time of application, and the composition of the heat release material. In the case of relatively high molecular weight polyethylene glycol compounds, such as Carbowax 4000 and Carbowax 6000 or mixtures thereof, coating weights of about 7 lbs./ream (a ream being 3000 square feet) or higher have been found to be most effective for the method of the present invention. In the case of mixtures containing lower molecular weight polyethylene glycols such as Carbowax 1540, a coating weight of less than about 7 lbs./ream can be used.

Although the primary effect of the partial solvent action of the organic liquid material at the elevated temperature of the ware is to induce tackiness or adhesive properties at the outer surface of the vitreous design, there is also a tendency in some cases to soften or diminish the tensile strength of the underlying clear resinous supporting film, such as the layer 4 in FIG. 1. To avoid such difficulties it is desirable that the clear supporting film be formulated to provide adequate high temperature tensile strength so as to avoid distortion of the design when subjected to progressive pressure, as by roller application. In general, such difficulties can be avoided if the clear supporting layer has a heat distortion temperature of at least about 25° C. as measured by ASTM test D648–45T. By way of example, the E. I. du Pont de Nemours & Co. materials identified as Lucite 45 or Elvacite 2045 (isobutyl methacrylate polymer) and Lucite 46 or Elvacite 2046 (n-butyl methacrylate/isobutyl methacrylate copolymer) have been found most suitable for this purpose.

For purposes of further illustration, but not by way of limiting the scope of the invention, the following is a complete description of a heat release vitreous decalcomania which was successfully applied to glass bottles by means of the device shown in FIGS. 2 and 3.

Referring to the layup shown in FIG. 1, a paper backing 1 was provided with a polyvinyl acetate barrier layer 2 and was coated with a layer 3 of Carbowax 4000 at a coating weight of 10 lbs./ream.

An unpigmented and plasticizer-free acrylic lacquer was then screened onto the Carbowax coated barrier paper 1–2–3 to provide, after drying, the clear resinous layer 4. The lacquer formulation was as follows:

	Wt. percent
n-Butyl/isobutyl methacrylate copolymer (du Pont-Elvacite 2046)	34
Aromatic petroleum hydrocarbon solvent (Central Solvents & Chemicals Co.—SC 100)	61
Cyclohexanol (du Pont-Hexalin)	5

The vitreous design layer 5 was formed by screen printing over the clear layer 4 a plurality of ceramic color formulations in predetermined sequence and registration to provide the desired design. The ceramic colors consisted of a selected pigmented flux in an acrylic resin vehicle or binder, the weight ratio of flux to binder being 2¼:1. The vehicle or binder composition was as follows:

	Wt. percent
n-Butyl methacrylate polymer (du Pont Elvacite 2044)	45
Aromatic petroleum hydrocarbon solvent (Central Solvents & Chemicals Co.—SC 150)	55

Typical pigmented flux formulae are as follows:

(1) *White.*—The flux consists of 62.8% lead oxide or litharge, 17.8% boric oxide, 14.1% silicon dioxide, and

5.3% cadmium oxide (all wt. percent). To this flux 16% by weight of titanium dioxide pigment is milled in.

(2) *Red.*—The flux consists of 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 wt. percent). To this flux 9% by weight of red pigment comprising cadmium sulfoselenide and cadmium oxide is milled in.

(3) *Black.*—The flux consists of 78.0% lead oxide or litharge, 10.3% boric oxide, and 11.7% silicon dioxide (all wt. percent). To this flux 16% by weight of black pigment comprising a mixture of cobalt, chromium, and iron oxides is milled in.

The vitreous design layer **5** was the outermost layer of the decalcomania and no outer clear layer **6** was necessary.

The decalcomanias were applied to glass bottles using the machine shown in FIGS. 2 and 3 at a ware temperature of approximately 250° F. and applying to the design layer **5** a petroleum oil (American Oil Co. Indoil No. 7) before contacting the same with the hot ware. The bottles were then fired in the usual manner and the resultant decorated articles had pinhole-free designs.

I claim:

1. A method of decorating an article of glassware, chinaware, or the like by means of a heat release vitreous decalcomania having a backing, a meltable heat release coating on said backing, and a vitreous design disposed over said coating, said vitreous design including a vitrifiable ceramic color in a resinous film, said method comprising:

preheating said article;

interposing between the article and the vitreous design side of the decalcomania an organic liquid material having a partial solvent action on said film and capable of rendering the same tacky at the elevated temperature of the preheated article without vaporization of said liquid material; and

pressing the vitreous design side of said decalcomania progressively into contact with the surface of the preheated article by applying pressure along a restricted area therebetween and moving said area across said decalcomania, said vitreous design being thereby temporarily adhered to said article and being released from said backing upon melting of said coating by the heat of said article, and said liquid material facilitating displacement of air during progressive application of the decalcomania whereby to prevent entrapement of air between said article and said vitreous design.

2. The method of claim **1** further characterized in that said article with the temporarily adhered vitreous design is thereafter fired to obtain a permanent pinhole-free design on the surface of said article.

3. The method of claim **1** further characterized in that said resinous film is selected from the group consisting of ethyl cellulose and acrylic resin films.

4. The method of claim **1** further characterized in that said organic liquid material comprises an oil.

5. The method of claim **1** further characterized in that said organic liquid material comprises a petroleum oil.

6. The method of claim **1** further characterized in that said article comprises glassware, said resinous film comprises a methacrylate polymer, said resinous film comprises a methacrylate polymer, and said organic liquid material comprises a petroleum oil.

7. The method of claim **1** further characterized in that said pressure is applied by means of a roller.

8. The method of claim **1** further characterized in that said article comprises glassware, said resinous film comprises a methacrylate polymer, said organic liquid material comprises a petroleum oil, and said pressure is applied by means of a roller.

9. The method of claim **1** further characterized in that said heat release coating comprises a normally solid polyethylene glycol.

10. The method of claim **8** further characterized in that said heat release coating comprises a normally solid polyethylene glycol.

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