This invention relates to methods of printing and decorating (by spraying or otherwise) glass and other vitreous surfaces with gold and other precious metals with the purpose of having said decorations appear to be in relief of the precious metals. This application is a continuation-in-part of application Ser. No. 100,098, filed Mar. 16, 1949, moved Feb. 25, 1950.

In the past it has been customary in the industry to print a prepared formula of gold upon glass bottles, drinking glasses or other vitreous surfaces by means of a screen process and fire it on. However, all of these commercially available precious metal formulae are compounded so that the gold or other metal is associated with a heat dispersable binder whereby the said metal is dispersed or fixed in a vitreous body. The thickness of the decoration or lettering resulting from this conventional process is extremely small. When gold is the precious metal used the resulting layer averages approximately .00004 to .00001 inch in thickness. Naturally, this gives the appearance of the gold lying absolutely flat with the glass.

When using precious metal for this type of work, it is desirable to have the design give a raised or embossed effect which enhances its visual appearance. Gold lying flat or absolutely co-planar with a vitreous surface loses the effect of its beauty unless viewed along a line perpendicular to the surface due to the absence of appropriate reflecting surfaces. On the other hand, should the design or lettering be actually raised then the light rays are so reflected as to show off the gold from any position. Furthermore, the massive effect of precious metal applied in relief to such articles as drinking glasses, art pieces, etc. is extremely desirable and impressive.

A formula with sufficient precious metal cooperating with it to give the result of a relief or embossed effect has never been compounded commercially as the cost of such a composition would far exceed the market value of such precious metals as gold would be exorbitant and certainly not commercially feasible to the glass industry.

An object of this invention is to provide a method of printing or decorating (by spraying or otherwise) whereby it would be commercially practical to print or decorate a design having a raised or embossed or dimensional effect without the expense thereof being prohibitive.

In order to carry out our invention we first print the desired design through a stencil screen upon the glass or other surface using a material composed of glass, flux or flux which is dispersed in a heat binder such as what is known in the industry as squeeze oil. This material is available commercially and well known to the trade.

By way of clarification it is pointed out that in relation to ceramic decorating, flux means a prepared, low melting, powdered glass, usually colorless, which may be mixed with pigments to produce, upon firing, vitrifiable coatings on glass or clay ware. Most common fluxes contain large quantities of lead oxide and fuse at temperatures below 1200° F. The following is a typical formula for flux used with vitrifiable pigments, applied on glassware:

<table>
<thead>
<tr>
<th>Flux Ingredient</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead oxide</td>
<td>50</td>
</tr>
<tr>
<td>Boric oxide</td>
<td>10.8</td>
</tr>
<tr>
<td>Silica</td>
<td>35.2</td>
</tr>
<tr>
<td>Soda</td>
<td>4</td>
</tr>
</tbody>
</table>

The desired result is obtained due to the fact that the flux composition contains inexpensive solids that do not fire away and, also, to the fact that a screen stencil will permit a sufficient deposit of this material to achieve a raised effect. Additional relief may be obtained by dusting the wet print with a dry powder of the same or similar material which has been sifted through approximately 150 to 200 mesh. The dusting, of course, will be done while the screen print is still wet and tacky and before firing. However, sufficient relief may be obtained with the screen print alone, this relief being dependent upon the thickness of the stencil or screen. However, since the thickness of an efficient screen is limited, where a very high relief is desired the dusting process is useful.

The body bearing the flux image is then fired to the maturing point of the flux. It is then possible to print by the screen process over the relief image with the prepared precious metal formula such as bright gold. The gold paste or “squeeze gold” used in this process is a prepared formula sold commercially by various manufacturers. It is essentially an organic gold compound (about 11% gold) of resins and other materials dissolved in volatile oils and other solvents. When printed or painted on a ceramic glaze, or on glass, and heated to maturity, it yields, without further treatment, a highly specular gold film reflecting light like a mirror.

The thickness of the fired gold film is extremely small as previously mentioned. Such a thin film may volatilize at high temperatures, and in order to make it fire-resistant, a small amount of rhodium resinate is incor-
porated in the gold. Essentially the gold consists of the following material:

1. Gold (about 115%)
2. Volatile oils
3. Solvents
4. Resins
5. Rhodium resinate
6. Metal organic fluxes

The same screen may be used for the gold printing step, or, if desired, another one that is made in exact register with the one used for the flux. The metallic print is then fired to a point slightly below the maturing point of the flux that is used. This is important since, otherwise, the flux or frit, if fired too high, will absorb or craze the metal that was applied. While the gold or other metallic compound may be applied by the normal screen method, it is also possible to apply gold or other precious metals by spraying the same over the flux printed body and firing at or below the maturation point of the flux. This will give the appearance of the decoration being in metallic relief while the rest of the background remains in metallic.

A typical application of this process on a drinking tumbler, for example, would be as follows:

A silk screen stencil is prepared for a design to be printed on an opaque ground of glass having a softening point of about 1150°F. The stencil may be prepared in any conventional manner. The use of silk, steel, nylon or any other kind of suitable mesh is simply a matter of choice. In this case steel would be preferable since the screen for glass steel has a tendency to deposit a more substantial amount of flux on the ware. The design is then printed on the ware with a prepared flux composed of 80% lead oxide, 10% silicon dioxide and 10% boric acid which has been dispersed in a vehicle of squeegee oil. Squeegee oil is a temporary printing medium for the flux. It is completely combustible and will fire away completely before the flux reaches its maturation point. The flux chosen in this case is one that will mature at approximately 950°F. The ware is then fired to this temperature and then allowed to cool. A printed decoration in embossed relief is therefore achieved.

The same screen or another one which is in exact register to the first, is then used for the printing of the gold. The gold is printed in register and on top of the image of the flux. The ware is then fired to a temperature of about 50° below the maturation point of the flux. If it is fired any higher the movement of the flux at its maturing point will absorb and absorb the very thin film of gold which has formed itself at the surface of the flux. After cooling, the ware is then complete and the design imprinted will appear to be a vitreous surface. We also find that we can spray gold onto opalware with good results. Hereafter, it has been impossible to secure a good gold coverage on opalware by directly spraying or printing on it due to the fact that the opal gives off fluorides that destroy the appearance of the gold, but in our method we first spray the opalware with a flux or frit and fire to the maturation point of such flux or frit. We then spray with gold and fire below the maturation point of the flux or frit.

The result of the use of all our processes described is a gold decoration or letter which gives the effect of having considerable thickness and dimension which gives the effect of a heavily embossed gold letter or decoration.

Our process is a process for mechanically producing embossed gold designs on ceramic materials. Our process increases the production per day per person several thousand fold. Also, since machines can be employed, our process will in the future be capable of producing characters of appearance normally expected only in articles of great value. This makes it possible for an average household to possess richly gold-encrusted ceramic objects. Up to this time, were considered to be museum pieces only.

It will be appreciated that in describing our invention we have used gold as an example, but our method is applicable to printing with other precious materials such as platinum and silver, etc.

We claim:

1. A method of forming on a vitreous surface a precious metal character raised substantially above the plane of the vitreous surface to give the appearance of a glossy solid precious metal character attached to said surface consisting of printing the character through a screen onto the surface with a paste comprising a ceramic flux having a volatile binder, firing the flux at a temperature below the maturation point of the flux but below the softening point of the vitreous surface to give a glossy smooth surface character raised substantially above the plane of the vitreous surface, coating the raised character by printing over the raised portions thereof with a screen having identical printing areas as the first screen and with said areas in exact register with said raised character with a metallic composition in colloidal suspension in a heat dispersible binder and firing the metal composition at a temperature below the maturation point of the flux, but of sufficient heat to cause maturation and adhesion of the applied precious metal compound to the previously formed raised character to produce an article having glossy smooth raised characters of coated metal extending above the plane of said surface.

2. A method of forming on a vitreous surface a precious metal design raised substantially above the plane of the vitreous surface to give the appearance of a glossy solid precious metal design attached to and extending above said surface consisting of printing the design through a screen with a substantial amount of a paste consisting of a vitreous flux having a volatile binder, printing a lower melting flux to give the vitreous surface, thus forming a design raised substantially above said surface, firing the design to the melting point of the flux thus causing the flux to fuse to the surface and casting a smooth surface raised substantially above the surface, coating the raised design so formed by printing over the raised design with a screen having identical printing areas as the first screen and with said areas in exact register with said raised design and with a prepared solution of precious metal in a heat dispersible binder then firing the solution to a point just below the maturing point of the flux with sufficient heat to cause maturation and adhesion of the applied metal, thus producing an article having a glossy smooth raised design of coated metal extending above the plane of said surface.

3. A method of forming on a vitreous surface a precious metal character raised substantially above the plane of the vitreous surface to give the appearance of a glossy solid precious metal character attached to said surface consisting of printing the character through a screen onto the surface with a wet paste comprising a ceramic flux having a volatile binder, dusting the character while wet with a dry ceramic flux powder, firing the metal composition at a temperature equal to the maturation point of the flux but below the softening point of the vitreous surface to give a glossy smooth surface character raised substantially above the plane of the flux and fired character so formed by printing over the raised portions thereof with a screen having identical printing areas as the first screen and with said areas in exact register with said raised character with a metallic composition in colloidal suspension in a heat dispersible binder and firing the metal composition at a temperature below the maturation point of the flux, but of sufficient heat to cause maturation and adhesion of the applied precious metal compound to the previously formed raised character to produce an article having a glossy smooth raised character of coated metal extending above the plane of said surface.

4. A method of forming on a vitreous surface a precious metal character raised substantially above the plane of the vitreous surface to give the appearance of a glossy solid precious metal character attached to said surface consisting of printing the character through a screen onto the surface with a wet paste comprising a ceramic flux having a volatile binder, dusting the character while wet with dry ceramic flux powder sifted through approximately a 150 to 200 mesh, firing the flux at a temperature equal to the maturation point of the flux but below the softening point of the flux thereby forming a smooth surface raised substantially above the plane of the vitreous surface, coating the raised character so formed by printing over the raised portions thereof with a screen having identical printing areas as the first screen and with said areas in exact register with said raised character with a precious metal composition in colloidal suspension in a heat dispersible binder and firing the metal composition at a temperature below the maturation point of the flux, but of sufficient heat to
cause maturation and adhesion of the applied precious metal compound to the previously formed raised character to produce an article having a glossy smooth raised character of coated metal extending above the plane of said surface.

5. A method of forming on a vitreous surface a gold character raised substantially above the plane of the vitreous surface to give the appearance of a glossy solid gold character attached to said surface consisting of printing the character through a screen into the surface with a paste comprising a ceramic flux having a volatile binder, firing the flux at a temperature equal to the maturation point of the flux but below the softening point of the vitreous surface, thus forming a smooth surfaced character raised substantially above the plane of the vitreous surface, coating the raised character so formed by printing over the raised portions thereof with a screen having identical printing areas as the first screen and with said areas in exact register with said raised character with a gold composition in colloidal suspension in a heat disperseable binder and firing the gold composition at a temperature below the maturation point of the flux, but of sufficient heat to cause maturation and adhesion of the applied gold to the previously formed raised character to produce an article having a glossy smooth raised character of gold extending above the plane of said surface.

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