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ENAMELING PROCESS

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2 Claims. (Cl. 106—48)

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This invention relates to vitreous enamel coatings and particularly to colored vitreous enamel coatings for application over a conventional, previously fired, ground coat.

In the past, colored vitreous enamel coatings have customarily been produced by applying to an article carrying a previously fired ground coat, one or more coats of a slip made of a clear frit suitably pigmented to render it opaque or a slit made of highly opaque, generally white frit, firing the same after each coat, and then applying a second slip of translucent frit suitably pigmented to produce the desired color. This produced undesirably thick coatings, often as thick as $^{18}/_{1000}$ of an inch or more, on top of the ground coat, which is objectionable from the standpoint of durability because of its tendency to chip and, from the economic standpoint, because of the amount of material in the coating and the plurality of separate applications and firings required to produce the finished coating.

Attempts to produce thin, suitably colored coatings of the required opacity with a single application of a pigmented slip have generally been quite unsuccessful, because the opaque frits could not be pigmented to produce uniform colors of acceptable depth, richness, and gloss. Upon recrystallization during firing the opaque frits seem to envelop the pigments employed so as to render them only partially and unevenly visible. Also, attempts to reduce the thickness of the separate finishing coats in the customary two-coat finishing process have failed because of insufficient opacity or color strength. Moreover, this still did not reduce the number of firings required.

As a result of these difficulties, insofar as I am aware, there have been no commercially successful processes for producing a high quality colored finish coat of vitreous enamel having high opacity by the application and firing of a single slip. Colored vitreous enamel coatings having satisfactory color quality and opacity for most purposes have, therefore, been objectionably thick, fragile, and expensive.

By "colored" coatings I mean coatings having chromatic colors (colors possessing chroma) and neutral grays, as distinguished from white and black.

The principal object of the present invention is to make it possible to produce colored porcelain enamel coatings with minimum application weight and maximum color depth, richness, gloss, and acid-resistance when desired.

A further object of the invention is to accomplish the foregoing objective by the application of a single coating over a previously fired ground coat.

These objectives have been accomplished in accordance with the invention by employing a

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novel mixture of frits, comprising a high opacity frit and a clear, or near clear, color-carrying frit, together with one or more conventional color compounds to give the desired pigmentation. When these ingredients are combined in a single slip, the opaque frit provides the necessary hiding power and the clear frit somehow carries the color so that it is not masked by the opaque frit, giving a richness, depth, and intensity of color together with a degree of hiding power far exceeding anything heretofore obtainable with a single pigmented slip. The proportions of the two types of frits may be varied considerably, depending upon the depth of color desired and the opacity required to give the best coverage with minimum application.

The two types of frits may also have other frits combined with them in minor amounts to produce special surface textures or increased acid-resistance and to obtain a greater measure of control over firing time and temperature.

For a better understanding of the invention and the method of applying it in practice, the following typical examples are given to illustrate suitable formulations:

Example 1

The following ingredients may be milled together, or mixed after milling, to produce a one coat pastel blue, acid-resisting enamel:

Titanium frit (opaque)	lbs.	80
Antimony frit (clear)	lbs.	20
Clay (clear)	lbs.	4
Blue oxide	lbs.	4
Sodium aluminate (electrolyte)	oz.	4
H_2O vehicle	lbs.	40

Example 2

An acid-resisting red enamel may be similarly prepared from the following ingredients:

Titanium frit (opaque)	lbs.	25
Antimony frit (clear)	lbs.	75
Clay (clear)	lbs.	5
Quartz	lbs.	3
Red pigment	lbs.	8
Sodium aluminate	oz.	6
Water	lbs.	40

Example 3

The following ingredients may be milled together, or mixed after milling, to produce a one coat acid-resisting enamel having a deep, rich, blue color:

Titanium frit (opaque)	lbs.	50
Antimony frit (clear)	lbs.	50
Clay (clear)	lbs.	4
Blue oxide	lbs.	4
Sodium aluminate (electrolyte)	oz.	4
H_2O vehicle	lbs.	40

Example 4

A non-acid-resisting yellow enamel may be similarly prepared from the following ingredients:

Zirconium frit (opaque)	lbs.	25
Antimony frit (clear)	lbs.	75
Clay (clear)	lbs.	5
Yellow pigment	lbs.	6
Sodium aluminate	oz.	6
Water	lbs.	40

In the foregoing formulations any of the numerous conventional, highly opaque acid-resistant or non-acid-resistant frits may be substituted for the titanium frit. Similarly, any of the numerous, clear frits commonly employed as a separately applied, color-carrying coat may be substituted for the antimony frit, including both acid-resisting and non-acid-resisting types. As is well known in the art, these conventional frits are composed of silica combined in various proportions with one or more metal oxides as complex metal silicates, together with any of a variety of smelter batch addition compounds for controlling reflectance or opacity, promoting adherence, producing a desired surface texture and/or pigmentation, etc. A variety of opaque titanium, antimony, and zirconium frits of both acid-resisting and non-acid-resisting types and a variety of clear antimony frits are available on the market under different trade-mark or brand names, and these may be employed as desired with only the normally expected differences in results.

The proportions of opaque to clear frits may range generally from as high as about 4:1 to as low as about 1:4, depending principally upon the color to be produced and the hiding power required. The color intensity and depth varies directly with the amount of clear frit employed and inversely with the amount of opaque frit employed, whereas the hiding power varies inversely with the amount of clear frit and directly with the amount of opaque frit. In general the lighter colors permit the use of considerably higher percentages of opaque frits than dark colors. Thus, the proportions employed will vary widely according to the color used and the particular hiding power and color quality required, and no absolute limits on the proportions of opaque and clear frits can be prescribed. While very small amounts of either the opaque frit or the clear frit may have a considerable effect under some circumstances, approximate practical limits for most purposes are those set forth above.

The color intensity will also vary with the particular kind and quantity of pigment employed. Any of the conventional color compounds employed in porcelain enamels may be substituted for the oxide blue in Examples 1 and 3 with only the expected normal variations in the hue, chroma, and intensity of the applied enamel after firing.

The sodium aluminate electrolyte in Examples 1 to 4 may be replaced by any of the many electrolytes conventionally used for their known effects upon the selected oxide color during the firing operation, namely, to produce an ionized solution of the color and a flotative action on the solid particles of the mix.

Potassium chloride, sodium nitrite, ammonium carbonate, and potassium carbonate may be mentioned as typical examples of suitable electrolytes.

The clay, or clay substitute, acts as a floating agent and a bonding agent. Though a desirable ingredient, its presence is not essential.

The mixture selected in accordance with the considerations discussed above and including sufficient volatile liquid to produce a slip of flowable liquid consistency, will cover well with good hiding and excellent color uniformity when applied as a thin coat over a conventional ground coat. The application may be by spraying or dipping and regulated to give a final fused coating of from $^{5}/_{1000}$ to about $^{8}/_{1000}$ of an inch for light colors, compared to thicknesses of $^{10}/_{1000}$ to $^{12}/_{1000}$ when employing the same colors in the prior two finish coat process; and $^{9}/_{1000}$ to $^{14}/_{1000}$ for dark colors, compared to thicknesses of $^{15}/_{1000}$ to $^{25}/_{1000}$, when employing the same colors in the prior two finish coat process.

The firing procedure is conventional. The temperature and time of firing are regulated according to the requirements of the particular frits employed, being selected at values between their individual requirements in accordance with their proportions in the mix.

From the foregoing description of the invention, it will be appreciated that it is not governed by any critical limits as regards the particular opaque and clear frits that may be combined, the proportions in which they are mixed or the firing conditions employed, provided only that each type of frit is employed in a substantial amount. Similarly, the suitability of all of the conventional color compounds renders their selection entirely a matter of choice, based on the color effects desired. Accordingly, the scope of the invention as defined in the appended claims is not limited to the particular ingredients, proportions, and processing conditions mentioned for illustrative purposes.

Having described my invention, I claim:

1. A coating composition for use in producing colored fused enamel coatings comprising from 4 to 1 parts of a fusible frit selected from the class of opaque titanium, zirconium, and antimony frits mixed with from 1 to 4 parts of a clear fusible antimony frit as the essential fusible constituents and a relatively small amount of a vitreous enamel color compound.

2. An enamel slip for use in producing colored fused enamel finishes with a single application over a ground coat comprising a mixture of from 4 to 1 parts of an opaque fusible frit selected from the class consisting of titanium, zirconium and antimony frits with from 1 to 4 parts of a clear fusible antimony frit in 5 parts of said mixture as the essential fusible constituents, a minor amount of a clear fusible clay, a minor amount of a vitreous enamel color compound, a minor amount of a fusible electrolyte, and sufficient water to give the slip a flowable liquid consistency.

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