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SINGLE FIRE ENAMELING PROCESS AND ARTICLE

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This application is a continuation-in-part of our copending application, Serial No. 612,720, filed August 25, 1945, and entitled Single Fire Enameling Process and Article, the said application being since abandoned; and the invention has to do with the problem of providing in a single firing an article having a commercial, smooth, continuous coating of vitreous or porcelain enamel of white or light color.

The solution of the problem involves two factors: (1) the use of an enameling stock or article which, when a coating of vitreous enamel is applied to its surface and fired, will be devoid of a tendency to produce bubbles, pits, oxide spots and the like visible through the coating, which tendency is generally known as "primary boiling," and (2) the provision of means or a procedure for obtaining high adhesion between the white or light colored vitreous enamel coating and the base metal.

Certain enameling stocks are available which are free from or have a greatly diminished tendency toward primary boiling. Developments in white or light colored enamels having sufficient smoothness and opacity for commercial purposes are in progress, and certain of these developments are directed toward enhancing the adhesion between such white or light colored enamel coatings and the base metal. The fact remains, however, that a white or light colored vitreous enamel coating having fully satisfactory adhesion to the usually relatively smooth surfaces of vitreous enameling stocks and articles has not been commercially developed, and this factor has delayed the commercial application of single fire white or light colored vitreous enamel processes.

Consequently, in commercial practice the art has produced white or light colored enamelware by a procedure involving a plurality of firings in the first of which a high adhesion ground coat is applied to the metal. High adhesion ground coats, by reason of the inclusion of cobalt or other adhesion promoting metal, are dark in color. After the article has cooled from the initial firing, a white or light colored frit is applied over the fused ground coat, and the article is again fired. The white or light colored enamel substance preferably has a firing temperature lower than that of the ground coat so that it may be fused to cover the ground coat without such softening of the latter as would lead to diffusion and the loss of the white or light color value of the overcoat. Under these circumstances the use of an enameling stock or

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ferrous base which is free from the primary boiling difficulty is not necessary since the white or light colored overcoat may be so applied and fired as to mask any imperfections existing in the ground coat. Then, too, the thickness of the conventional ground coat itself is such that it tends to mask boiling defects.

A fundamental object of our invention is the provision of satisfactory single fired coatings of enamel, particularly in white or light colors, with concurrent solution of the problems of adhesion, opacity, acid resistance and the like.

Another important object of the invention is the provision of improved white or light colored enamel coatings and of improved white or light colored enameled articles which, in particular, are superior to those hitherto known in the art in that they are thinner and hence have less tendency toward chipping, while preserving satisfactory opacity and adherence.

These and other objects of the invention, which will be set forth hereinafter or will be apparent to one skilled in the art upon reading these specifications, we acomplish in that procedure and article, of which we shall now describe exemplary embodiments.

Our invention embodies the discovery that it is possible, under the circumstances hereinafter taught, to produce a satisfactory white or light color porcelain enameled article in a single firing by the use of an exceedingly thin underlayer of a ground coat enamel which develops high bond and an overlayer of white or light colored porcelain enamel, while preserving gloss, opacity and reflectivity, if certain steps are taken amounting to a reversal of the techniques hitherto practiced and considered to be necessary by the art. In describing our invention, we shall take up in order the two factors involved in the problem.

In a copending application in our names entitled Enameling Stock, filed August 25, 1945, Serial No. 612,721, the provision of iron or mild steel sheet or strip stock or articles has been taught, where the stock is so prepared that it will receive single fired or initial coats of vitreous enamel without the primary boiling defects heretofore encountered in a single or initial coats.

Reference is hereby made to the teachings of that case, because, as hereinabove indicated, the provision of iron or mild steel stock capable of receiving a single or initial coat of porcelain enamel without surface defects such as oxide spots, blisters, and black specks makes possible and effective the invention herein. In view of

such reference we shall not attempt to summarize the teachings of the copending application otherwise than to say that they include subjecting the stock or articles to a surface decarburization which is a brief, continuous heat treatment at temperatures between substantially 1250° and 1650° F. in an atmosphere, non-oxidizing to iron, and containing hydrogen and from 2% to 30% water vapor. This decarburization preferably follows such treatments as normalizing and the imposition of adhesion promoting coatings, e. g., coatings of nickel when they are used, as well as the pickling or other chemical treatments, wherever possible, to which the stock is subjected; and it has a number of effects: Among other things, it destroys gas forming residues, carbonaceous smudges and residues left by chemical treatments; it destroys massive carbides in the surfaces of the stock or articles as well as lowering the carbon content in the surfaces to a value such that carbon is no longer effective as a gas producer during the firing of vitreous enamel. Also, a sufficient lowering of surface carbon permits box annealing without diffusion of interior carbon to the surfaces in amounts productive of trouble, and also permits subsequent light pickling without the formation of carbonaceous smudges.

An exemplary routing for enameling stock in accordance with that invention is:

1. Hot roll the metal to thin bar.
2. Pickle.
3. Cold reduce to gauge.
4. Normalize.
5. Pickle.
6. Electroplate with nickel.
7. Decarburize.
8. Box anneal.
9. Temper roll.

Other routings may also be employed.

The teachings of the present application depend upon the provision of a stock capable of accepting an initial fired coating without the usual defects which in the past have necessitated the manufacture of enameled articles by processes involving plural firings of separately fired coats. We prefer a stock made in accordance with the procedures of the said copending application. The broader aspects of the teachings of this application are not confined to the provision of stock made by any particular procedure, but apply to any stock, however produced, which is capable of receiving an initial fired coat of vitreous enamel without exhibiting the coating defects to which reference has been made.

In our process it is necessary to make or select the two enamel substances in such a way that the firing temperature of the ground coat is no higher than, and is preferably lower than that of the cover coat. By firing temperature, we refer to the temperature at which an enamel becomes sufficiently fluid to flow on a metal sheet which has been prepared for enameling to form a smooth, glassy surface in an economically short length of time, such as three to five minutes on a 20 gauge sheet, when fired as a single coating of conventional thickness. Firing temperature is a characteristic of any given enamel, resulting from its particular compounding of ingredients, and is a property well understood by both enamelers and frit producers. It is related to the fusion temperature range of the enamel, but is a more useful term, since any enamel fuses and changes fluidity over a rather wide range of temperature, and since the extent of the enamel flow is also a function of time.

A second requirement for the ground coat in our process is that it be very thin; and we employ ground coats having a fired thickness ranging from substantially .0004 inch to substantially .001 inch.

A third requirement is that the ground coat especially be milled or ground finely as hereinafter taught. A fine and uniform milling of the cover coat is also of advantage.

In our process, only about one-eighth to one-fourth the former ground coat thickness is required. This permits consistent reduction of the total enamel thickness to .010 inch or less, with corresponding increase in resistance to chipping as the total thickness is lowered. This effect is already appreciable at a thickness of .010 inch, and becomes increasingly marked as total thickness is reduced to the minimum at which the ground coat will give good adherence and the cover coat good appearance. White coatings having good reflectance and appearance have been successfully produced as thin as .005 inch using commercial cover coat enamels, and still thinner coats, even as low as .003 inch can be made by the same practice, using more opaque cover coat enamels, or using commercial enamels for applications where high reflectance is not required.

The use of degassed stock or articles renders unnecessary the thicknesses of ground coating heretofore found necessary to take care of gas evolution and attendant troubles. It is only necessary to use sufficient ground coat to obtain the desired adhesion. While the thinnest ground coat which will give adherence is preferred for maximum resistance to chipping, a thin ground coat in our process, and having a firing temperature lower than that of the cover coat, has a special effect in our process which will be set forth hereinafter.

A satisfactory ground coat is one designed to give good adherence. The best of such ground coats today contain, along with nickel, cobalt in small amounts, wherefore the coatings are deep blue in color. Work is being done on ground coats of lighter or white color, and such coats are available for our invention. As the enameler will understand, the ground coat frit is milled with water to form a slip and then applied to the article in any suitable way, spraying being an excellent mode of obtaining uniformly thin coatings. Similarly, the frit for the white or cover coat is milled with water, opacifier and clay to form a slip and is applied over the ground coat. Intermediate drying is not necessary and is not preferred, though it may be practiced if desired.

It will be useful at this point to contrast our procedure with that hitherto obtaining in the art. In the conventional commercial practice the blue ground coat is approximately .003 to .004 inch thick after firing. This results from the application of 18 grams of dried enamel per square foot of article surface. The ground coat cannot be substantially thinner than this on regular enameling stock or articles, or oxide spots and other defects produced during the primary boil will not be masked by the subsequent white coat. The firing temperature of the conventional ground coatings is 1560° to 1590° F.

Also, in the conventional practice, the subsequent white coat is usually about .006 to .008 inch in thickness after firing. When two white

coats are imposed upon a ground coat, the second one is about this thickness, while the first one is usually reduced to a thickness of about .004 to .005 inch. The firing temperature of conventional white cover coats is about 1500 to 1520° F. or even up to 1560° for some acid resisting enamels, which is slightly lower than that of the usual ground coat.

In the conventional practice, the ground coat is applied and fired at a suitably high temperature, after which the white cover coat is applied and fired at a somewhat lower temperature, the attempt being to apply and fire the white coat and cause it to mask the imperfections in the ground coat while disturbing the ground coat as little as possible and while preventing excessive diffusion of the two coats.

Thus in the conventional practice, the white or light colored cover coat is fired onto the previously fired ground coat at a temperature such that the ground coat does not soften appreciably, and hence diffusion of the ground coat into the cover coat is minimized. The ground coat is made to have sufficient thickness to flow and release bubbles produced by primary boiling; and while the ground coat absorbs some oxide from the surfaces of the ferrous base, its thickness is such that its fusion temperature is not greatly affected thereby. The white or light colored cover coat is made thick enough to mask the imperfections of the ground coat due to the primary boiling, and it generally has a fusion temperature definitely below that of the ground coat.

While it might be supposed that a saving in cost would be obtained if both coats could be fired at one time, attempts to do this hitherto have proved impractical. With the combination of enamels described, the firing of the enamels at a sufficiently high temperature to fuse the ground coat and obtain good adherence, would spoil, the gloss, reflectivity and opacity of the white cover coat. White cover coats have to be fired at temperatures low enough to avoid a tendency for the opacifying agent to dissolve excessively in the glass, or transparency and darkening will result. Furthermore, the concurrent firing of a conventional thickness ground and of a cover coat having a firing temperature lower or even the same as that of the ground coat would result in intermingling and diffusion of the two and the production of a defective article. Yet again, with the total thicknesses of enamel hitherto current in the art, the firing would give rise to flow and displacement problems, since it is frequently the practice to fire the articles with some or all of their enamel-coated surfaces in the vertical position.

Given a degassed stock, the key concept which makes it possible for us to fire simultaneously a ground and a cover coat in accordance with this invention is the new relationship of firing temperatures of the two coatings, providing these coatings are thin. As indicated, the ground coat must have a firing temperature not higher than, and preferably lower than the firing temperature of the cover coat. In practice this usually and preferably amounts to a reduction of the firing temperature of the ground coat rather than an increase in the firing temperature of the cover coat.

In the practice of our process it is believed that an entirely different mechanism occurs. The ground coat, as has been indicated, has a firing temperature not higher than and preferably lower than that of the cover coat. As the double-coated article is raised in temperature during the firing, the ground coat is first melted and attains that degree of fluidity which enables it to make a good bond with the base metal. In doing so it absorbs oxide from the base metal surfaces; but by reason of the exceeding thinness of the ground coat this absorption of oxide affects its softening point appreciably, and the ground coat, we believe, almost instantaneously sets up to a condition of very much greater viscosity. During the initial highly fluid condition of the ground coat, the cover coat, if softened, was at least in a relatively viscous condition not tending toward diffusion. By the time the cover coat has attained its maximum fluidity under the particular firing conditions, the ground coat will have attained a higher viscosity again tending to prevent diffusion. We believe that this mechanism explains the surprising fact that diffusion does not destroy the appearance of our product despite the thinness of our coatings and the lower firing temperature of the ground coat as compared with the cover coat.

For example, we may use a conventional white cover coat in a thickness of .006 to .008 inch, and having a firing temperature of 1500 to 1560° F. With this, however, we use a blue ground coat having a firing temperature of about 1400 to 1500° F. The two layers are fired simultaneously at the firing temperature of the cover coat. With such a combination we obtain good bond without lowering the gloss or reflectivity of the white coat on degassed stock.

The thickness of the ground coating is preferably reduced at the same time its firing temperature is lowered. As has been explained, the use of a degassed stock makes it unnecessary to employ a heavy ground coat, and the advantages of thin over-all enamel surfacing can be realized. Our preferred surfacing is made up of a ground coat with a firing temperature between substantially 1400 and 1500° F. of such weight as to produce a fired layer about .001 inch thick or less, and a white cover coat with a firing temperature of substantially 1500 to 1560° F. of such weight that it will form a layer about .006 to .008 inch after firing, both layers being simultaneously fired, at the firing temperature of the cover coat, for a length of time properly to fuse the enamel, which is of the order of 3 to 5 minutes on 20 gauge metal, for example.

With such a combination, we obtain in one firing good adhesion, gloss, high reflectivity, increased chipping resistance and a good white color. The thinner ground coating is more easily fired to give good adherence without damaging the cover coat, just because of its smaller mass. We have noted no tendency for the two coatings to diffuse into each other to the detriment of the qualities of the cover coat. The use of a high adherence ground coat permits the use of cover coats of widely different kind and character, and in particular the use of cover coats (desirable for some other reason, such as opacity) of such poor adherence to iron and steel as to be impossible of use as a first coat.

The firing temperature of the ground coat must not be higher than the firing temperature of the cover coat. We prefer to have the firing temperature of the ground coat from 20° to 100° F. lower than that of the cover coat, and to have the ground coat as thin as possible to obtain good adherence, which will be about .0004 inch to .001 inch thick rather than the conventional .003 or .004 inch.

High adhesion ground coats and cover coats of white or light colored enamel constitute well recognized classes of enamel substances familiar to the enameler and readily ascertainable from standard texts. For example, reference is made to the publication entitled "Enamels" by Andrew I. Andrews, first edition, published 1935 by the Twin City Printing Company. Beginning at page 165, this publication has an extensive section on ground coats and their analyses, pointing out that there are white and gray ground coats as well as the more common cobalt blue ground coat and giving analyses of various ground coats. A conventional cobalt blue ground coat contains feldspar, borax, quartz, soda ash, soda nitre, fluorspar, cobalt oxide and manganese dioxide. The firing temperatures of ground coats depend upon their relative contents of such materials as borax, feldspar and quartz, generally expressible in triangular composition diagrams, such as those to be found in the above publication on pages 172, 173 and 174. For example, the greater the quantity of quartz, the higher the firing temperature will be, while an increase in the quantity of borax will lower the firing temperature. Thus it is well understood by the skilled worker in the enameling art how the firing temperature of any particular type of ground coat can be raised or lowered by controlling the relative percentages of its ingredients. Our process is applicable to all of the grount coat compositions set forth in the publication above noted, without exception, as well as to all ground coat compositions we have encountered in practice.

The same publication, beginning at page 178, has a section on white cover enamels. In general, these consist of such materials as feldspar, borax, quartz, soda ash, soda nitre, fluorspar and cryolite. The metallic ingredients designed to promote adhesion, and which ordinarily darken the color of a ground coat, are omitted in white or light colored cover coat enamels; and an opacifying agent is added to give the desired opacity and color. There are a number of such opacifying agents and we mention without limitation such exemplary ones as antimony oxide, titanium oxide, tin oxide, zirconia, and the like. A section on acid resisting enamels begins on page 182 and a section on colored enamels on page 185 of the above entitled publication.

Again, in the case of ground coats, the firing temperature may be controlled by controlling the relative proportions of certain ingredients, usually borax, feldspar and quartz. The relationship of these may be expressed in a triangular diagram, such as that shown on page 182 of the publication. The same considerations apply as in the case of ground coats. In the practice of our invention we may employ any of the white or light colored cover coat compositions, without exception, set forth in the said publication and any others of which we are aware.

The above publication also contains a section beginning at chapter 12, page 325, on the properties of enamels, giving various tests by which their thermal behavior may be determined, including their fusion temperatures as set forth in this specification.

In the practice of our process we have found it advisable to grind the frits finely, and we prefer to employ both ground coats and cover coats of such fineness that they will pass through a 200-mesh sieve, as set forth on page 384 of the above entitled publication. In such a sieve having 200 meshes per lineal inch, the size of the sieve opening is .0029 inch. The fineness of subdivision of the frit makes for smooth, uniform and continuous coatings and tends to prevent diffusion, inasmuch as larger particles may result in some actual interlocking of the particles in the applied coatings in a single fire process.

The thicknesses of the coatings given hereinabove are the fired thicknesses. It will be understood that finely ground frits dispersed in water are normally applied by means of a spray gun, and control of the thickness of a layer is usually accomplished by spraying a given weight of the solids on a given area of the surface to be enameled. Upon firing this will provide a coating of given weight and hence of determined thickness.

We are not restricted to the simultaneous firing of a total of two superposed coats of porcelain enamel. In addition to a ground coat and a cover coat, we may employ one or more intermediate coats for various purposes. The number of coats simultaneously fired is not a limitation upon our invention, keeping in mind the following matters. The firing behavior of enamel is not only a function of temperature but also of time, which is rather critical. The firing must be long enough to develop bond and strength, whether the enamel be attached to the base metal or to an underlying coat of other enamel. But the time must be short enough to prevent the loss of opacity due to solution of opacifier in the glassy matrix and due to diffusion of iron oxide from the base metal into the enamel. While the time interval between the fusion of the surface and the fusion of the interior of even a thick layer of enamel is short, it is nevertheless appreciable. Even a single white coat cannot be put on too thickly or opacity may be lost by an overfiring of the surface before the proper maturing and bond of the underlying portion of the enamel is achieved.

In view of these considerations there is a maximum total thickness of enamel which should be fired at any one time. Under ordinary conditions, if the total thickness of the enamel layers employed exceeds around .015 inch, overfiring of the surface is likely to result. For this and for other reasons which have been given above, it is preferred that the total or combined thickness of all layers of enamel to be simultaneously fired be not over .010 inch.

The greater the difference between the firing temperature of the ground coat and that of the cover coat within practical limits, the greater can be the total or combined thickness of all coatings to be simultaneously fired. While excellent results can be attained with a ground coat and a cover coat of the same firing temperature if the layers are kept quite thin, difficulty is frequently encountered at total thicknesses approaching .015 inch, whereas the thicker coats can readily be fired if the ground coat has a substantially lower firing temperature than the cover coat. Similarly in simultaneously firing more than two coats, it is well to have a firing temperature gradient as between the coats, those lying inwardly of the surface having progressively lower firing temperatures.

Modifications may be made in our invention without departing from the spirit of it. Having thus described our invention in certain exemplary embodiments, what we claim as new and desire to secure by Letters Patent is:

1. In a process of producing smooth, continuous, light colored porcelain enamel coatings on

ferrous enameling sheet stock free from gas forming substances productive of pits and spots, the coatings having a high degree of adherence to the stock, the steps of imposing upon the surface of said stock a thin continuous coating of high adherence ground coat enamel of such thickness that after firing it has a thickness substantially between .0004 and .001 inch, applying at least one subsequent continuous coating of white or light colored cover coat enamel of such thickness that the total thickness of all said coats after firing is substantially .003 to .010 inch, drying, and firing such coats simultaneously at the firing temperature of the cover coat, the firing temperature of the ground coat being not higher than the firing temperature of the cover coat.

2. The process claimed in claim 1 in which the ground coat has a firing temperature substantially 20° to 100° lower than the firing temperature of the cover coat.

3. A process of making a single fired white or light colored enameled article having good adhesion, which comprises imposing upon the surface of ferrous material freed of substances productive of gas and oxide spots upon firing, a ground coat of such thickness that after firing it will have a thickness substantially between .0004 in. and .001 in. and of high adhesion vitreous enamel substance having a firing temperature of between substantially 1400° to 1500° F. and a cover coat of vitreous enamel substance of such thickness that the total thickness of both coats after firing will be substantially .003 in. to .010 in. and having a firing temperature of between substantially 1500° to 1560° F., and firing both coatings at the same time, at the firing temperature of the cover coat.

4. A process of making a single fired white or light colored enameled article having good adhesion and enhanced chipping resistance, which comprises imposing upon the surface of ferrous material freed of substances productive of gas and oxide spots upon firing, a ground coat of high adhesion vitreous enamel substance having a firing temperature of between substantially 1400° to 1500° F. and a cover coat of vitreous enamel substance having a firing temperature of between substantially 1500° to 1560° F., and firing both coatings at the same time at the firing temperature of the cover coat, the weight of ground coat so applied being such as to produce a fired layer of substantially .0004 to .001 inch in thickness and the total weight of both coatings so applied being such as to produce a total thickness of fired enamel of substantially .003 to substantially .010 inch.

5. The process claimed in claim 1 in which the ferrous enameling stock is a ferrous sheet stock having its surfaces decarburized to the extent of being freed of carbonaceous smudges, massive carbides and gas producing carbon.

6. A single fired white or light colored enameled article having low cost, high gloss, reflectivity and opacity, comprising a base of ferrous material having surfaces free of substances productive of gas upon firing, and a single fired plural layer coating of porcelain enamel comprising a high adhesion ground coating next the surface of the ferrous material and an overlying light colored cover coating, both of vitreous enamel, the ground coating having a thickness to give, upon firing, a layer substantially between .0004 in. and .001 in. in thickness, the firing temperature of the ground coating being not higher than that of the cover coating, the total thickness of said fired coatings being substantially from .003 to .010 inch.

7. A single fired white or light colored enameled article having low cost, high gloss, reflectivity and opacity, comprising a base of ferrous material having surfaces free of substances productive of gas upon firing, and a single fired plural layer coating of porcelain enamel comprising a high adhesion ground coating next the surface of the ferrous material and an overlying light colored cover coating, both of vitreous enamel, the firing temperature of the ground coating being not higher than that of the cover coating, the total thickness of said fired coatings being substantially from .003 to .008 inch, the said ground coating being a blue, cobalt-containing coating and the said cover coating being a white coating of high reflectance.

8. A single fired white or light colored enameled article having low cost, high gloss, reflectivity and opacity, comprising a base of ferrous material having surfaces free of substances productive of gas upon firing, and a single fired plural layer coating of porcelain enamel comprising a high adhesion ground coating next the surface of the ferrous material and an overlying light colored cover coating, the ground coating having a thickness to give, upon firing, a layer substantially between .004 in. and .001 in. in thickness, the firing temperature of the ground coating being not higher than that of the cover coating, the total thickness of said fired coatings being substantially from .003 to .008 inch, the said ground coating being a blue, cobalt-containing coating having a firing temperature substantially between 1400° to 1500° F. and the said cover coating being a high reflectivity, white coating having a firing temperature substantially between 1500° to 1560° F.

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