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PLURAL COAT ENAMELING PROCESS

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5 Claims. (Cl. 117—70)

This invention relates to a process for providing a vitreous enamel coating on a metallic surface and, more particularly, to an improved process for providing a very thin mat ground coat for porcelain enameled steel articles.

Patent applications, Serial Nos. 409,539 and 453,424, now U. S. Patent No. 2,786,782, describe a method and preferred compositions for providing thin mat ground coats for porcelain enameling. These ground coats differ from the conventional ground coats in that they are extremely thin (approximately .0005 to .004 inch thick) and are not glassy in appearance. The advantageous features of this process over the methods now commonly employed are: much smaller amounts of enameling materials are required for a given area; expensive adherence-promoting oxides, such as the oxides of cobalt, nickel, and manganese, are unnecessary ingredients to the frit compositions; and no specific surface preparation, such as etching or metal plating, other than providing a clean surface, is required.

In applying vitreous enamel ground coats by means of prior art methods, including the methods disclosed above, it is considered necessary to prepare an enamel frit, then ball-mill the frit with clay and water plus minor mill additions to obtain the enamel slip with which to coat the article. When applying a glassy ground coat, it is necessary to first frit the enameling material in order to obtain an even, homogeneous adherent glassy coat. However, it has now been found that the step of fritting the enamel ground-coat composition is unnecsssary when applying a thin, mat-type ground coat of the nature described in patent applications, Serial Nos. 409,539 and 453,424.

It is, therefore, the object of this invention to provide an improved method of producing porcelain enameled articles.

It is also an object of this invention to provide a method of producing an enameling ground coat whereby the step of fritting enameling materials is eliminated.

Other objects and advantageous features can best be determined by the following specification and examples.

In general, the present invention relates to a method of producing a thin mat ground coat which comprises milling a slip directly from raw-batch enameling materials, omitting the step of first fritting these enameling materials, applying the slip to a metallic article to a dry weight of 8 to 17 grams per square foot, two sides, and firing to obtain a coating, .0005 to .004 inch thick.

When enameling steel parts by the conventional enameling processes, raw-batch enameling materials, such as flint, feldspar and borax are brought together and fritted by heating the materials to a temperature of about 2200° F. and quenching in water. The frit is then ball milled with clay, water and other mill additions to form a slip which is then applied to a steel article to such a weight or thickness that when fired a glassy ground coat is obtained. For example, when applying conventional ground coat to 20-gage steel sheets, a conventional enameling slip is applied at a dry weight of from 1¼ to 1¾

ounces per square foot and forms a glass when fired at a temperature of about 1600° F. for from about 3 to 5 minutes. In patent application, Serial No. 409,539 a process is disclosed whereby the slip is applied to a weight of from ⅛ to ⅜ ounce per square foot, dry weight, and fired at from 1300 to 1700° F. for from 2 to 8 minutes to form a nonglassy ground coat approximately .0005 to .002 inch thick. This ground coat may then be satisfactorily provided with a conventional enameling cover coat that is ordinarily applied to a glassy-type ground coat. Patent application Serial No. 453,424 discloses preferred theoretical enameling frit compositions when using the process of patent application Serial No. 409,539. These preferred ranges are disclosed in Table 1 below. In obtaining the thin mat ground coat it has been found that the enameling materials employed must be those that will form a glass when fired in the conventional manner but need not contain the conventional adherence promoting oxides. This is believed to be due to the fact that in providing the thin mat coat a conventional glass must first be obtained but that due to the thickness of application and the firing temperatures and times involved, the glass becomes saturated with iron oxide and converts into the desired mat coating.

It has now been found that the step of fritting may be eliminated when employing the process of patent application Serial No. 409,539. Raw-batch materials may be added directly to the ball mill or grinding apparatus in preparing an enamel slip.

In the practice of the present invention, where the step of fritting is omitted, highly refractory enameling compositions must be avoided. The necessary reactions between the raw materials are accomplished during the firing of the dried slip which is preferably performed within the temperature range of from 1200° F. and 1700° F. It is, therefore, essential that the raw-batch materials employed be predominantly made up of materials that will form a glass within the temperature range of from 1200° F. to 1700° F. For this reason, a conventional flint-, feldspar-, borax-type raw-batch composition may not be employed in the process of the present invention. Flint and feldspar are highly refractory materials and may be used as enameling materials for the present process only in minor quantities.

It is desirable when employing the process of the present invention to avoid using excessive amounts of enameling materials that tend to emit gas during firing. Examples of such materials are the carbonates which emit carbon dioxide when fired. The emission of excessive amounts of gas adversely affects the smoothness and continuity of the ground coat.

The enameling materials that may be used with the process of the present invention are those materials which will melt and form essentially the same calculated glass compositions as those obtained in conventional ground coats, when fired at a temperature of from about 1200° F. to 1700° F. Adherence-promoting oxides such as the oxides of nickel, manganese and cobalt are not necessary enameling ingredients but will not adversely affect the resulting ground coat if present in their usual concentrations.

In the place of the conventional enameling materials such as flint and feldspar it is advantageous to employ alkali silicates such as sodium silicate. Other enameling materials which have proved to be highly satisfactory are the following:

Borax	Kyanite
Boric acid	Alumina
Sodium calcium borate	Aluminum silicate
Colemanite	Black iron oxide
Sodium aluminate	

Small amounts of refractory enameling materials may be employed so long as these materials are not present in such quantities that a satisfactory glass and mat coating cannot be attained within the firing range of from 1200° F. to 1700° F.

These enameling materials are mixed with the usual slip forming materials, such as clay and water. Slip materials commonly used to form vitreous enamel may be employed in the present process. When employing clay in the slip the clay should not exceed 15 weight percent of the slip because of the refractory nature of clay.

The preferred composition ranges disclosed in patent application Serial No. 453,424 apply equally to the process of the present invention. Therefore, it is preferable that any enameling materials used, including the above-mentioned materials, on calculated analysis, will fall within the preferred ranges. In the present invention these ranges are calculated enameling compositions instead of calculated frit compositions. Table 1 below describes these preferred ranges.

Table 1

Components of ground coat	Acceptable range, weight percent	Optimum range, weight percent
Fe_3O_4	1–15	5–13
ZnO	0– 9	2– 7
SiO_2	30–45	35–42
B_2O_3	17–28	20–25
Na_2O and/or K_2O	11–22	11–22
CaO	3– 8	4– 6
Al_2O_3	0– 7	3– 5

Minor additions of other enameling materials may be added to the raw-batch compositions and the theoretical calculated compositions of Table 1 which do not adversely affect the resulting mat ground coat and which do not throw the composition substantially outside of the preferred concentration ranges.

Due to the fact that the preferred firing period is of short duration, the reactions must take place rapidly. To aid in this it is desirable to have intimate contact between fine ground particles. It is advantageous to employ water soluble and finely ground materials. The use of coarse materials requires longer firing times to complete the necessary reactions while firing. It is, therefore, advantageous that even the insoluble enameling constituents possess an average particle size of about 200 mesh or less.

The enameling composition is ball milled or mixed with mill additions, such as clay and water, to form a liquid slip for enameling purposes. The liquid slip is applied to a steel surface by spraying, dipping, brushing, or other suitable means to form a coating. This coating is dried before firing. For best results the coating should be applied to a weight of from 8 to 17 grams per square foot dry weight two sides (4 to 8½ grams per square foot dry weight one side) to form a coating that will be approximately .0005 to .004 inch thick after firing.

The firing temperature may range from 1200° F. to 1700° F. and the time of firing may vary from 2 to 10 minutes depending on the enameling materials, the temperature used, and the thickness of the metal being enameled. If the coated steel surface is overfired, the coating will become mechanically weak, there may be excessive reaction with a cover coat, there will be a loss of the adhesive-promoting properties of the coating to the metal surface, and the resulting coat may exhibit a rough surface. If underfired, there will be a loss in the adhesion properties of the coating to the metal surface.

The optimum time and temperature within the ranges given are dependent upon the shape and gage of the steel-basis material, the composition of the coating and the thickness of the slip is applied.

After cooling to a handling temperature, the enameled articles may be given a cover coat of a porcelain enamel by coating and firing again in the conventional manner.

The following specific examples are given to illustrate more fully the process of the present invention. They are given merely as illustrations and are not meant to limit the scope of the invention.

Enameling slips were prepared by ball milling the compositions illustrated in Table 2, below. The slips thus prepared were applied to steel surfaces by dipping to form a coating. These coatings, after they had dried, weighed approximately 12 grams per square foot of surface area, both sides.

All samples were fired for approximately 4 to 6 minutes at a temperature of approximately 1500° F. All samples were coated with a conventional enamel cover coat and refired. All of these samples exhibited commercially acceptable vitreous enamel surfaces.

Table 2

Batch Composition

Material	Amount, parts by weight				
Sodium silicate, solution (36.6% solid sodium silicate; 1 Na_2O to 2.94 SiO_2 weight ratio)	27.0	27.0	27.0	27.0	27.0
Sodium silicate powder (1 Na_2O to 3.11 SiO_2 weight ratio)	29.5	45.0	26.4	26.4	35.0
Regular borax	37.1		29.8	29.8	29.8
Colemanite	20.4	20.4			
Boric acid		24.2			
Sodium calcium borate			31.0	31.0	31.0
Clay	10.0	10.0	10.0	10.0	10.0
Flint	8.0		10.7	10.7	2.0
Feldspar	2.0	2.0	2.0	2.0	2.0
Black iron oxide	9.1	9.1	9.1	4.5	9.1
Zinc oxide	3.6	3.6		3.6	
Sodium aluminate	5.3	5.3	5.3	5.3	5.3
Kyanite					5.3
Water [1]	130.0	130.0	130.0	130.0	130.0

[1] Additional water added after mixing to adjust to dipping consistency.

For convenience, the invention has been described in connection with its use on steel surfaces, but it can be used also on enameling iron, cast iron, and similar ferrous materials.

While certain preferred embodiments of this invention have been described, it will be obvious to those skilled in the art that various modifications may be made without departing from the true spirit and scope of the invention.

What is claimed is:

1. The process of producing a vitreous enameled metal body which comprises: mixing with clay and water unfritted enameling materials to form a slip, said enameling materials being capable of forming a glass within a temperature range of from 1200° F. to 1700° F., and said enameling materials being in such proportions as to yield, on calculated analyses, an enameling material consisting esssentially of:

	Weight percent
Fe_3O_4	1–15
ZnO	0–9
SiO_2	30–45
B_2O_3	17–28
At least one material selected from the group consisting of Na_2O and K_2O	11–22
CaO	3–8
Al_2O_3	0–7

applying the resulting slip to a steel body to a dry weight of from 8 to 17 grams per square foot two sides, and firing within a temperature range of from 1200° F. to 1700° F.; applying a vitreous enamel cover coat and refiring.

2. The process of producing a vitreous enameled metal body which comprises: mixing unfritted enameling materials selected from the group consisting of alkali silicates,

borax, boric acid, sodium calcium borate, colemanite, sodium aluminate, kyanite, alumina, aluminum silicate and black iron oxide, in such proportion as to yield, on calculated analyses, a material consisting essentially of:

	Weight percent
Fe_3O_4	1–15
ZnO	0–9
SiO_2	30–45
B_2O_3	17–28
At least one material selected from the group consisting of Na_2O and K_2O	11–22
CaO	3–8
Al_2O_3	0–7

applying the resulting material in an enameling slip to a steel body to a dry weight from 7 to 17 grams per square foot two sides, and firing within a temperature range of from 1200° F. to 1700° F. for a period of from 2 to 10 minutes; applying a vitreous enamel cover coat and refiring.

3. The process of producing a vitreous enameled steel body which comprises: preparing a slip by mixing enameling materials with water and up to 15 percent dry weight clay, said enameling materials selected from the group consisting of alkali silicates, borax, boric acid, sodium calcium borate, colemanite, sodium aluminate, kyanite, alumina, aluminum silicate and black iron oxide, and said enameling material being in such proportion and to yield, on calculated analyses, a material consisting essentially of:

	Weight percent
Fe_3O_4	1–15
ZnO	0–9
SiO_2	30–45
B_2O_3	17–28
At least one material selected from the group consisting of Na_2O and	
K_2O	11–22
CaO	3–8
Al_2O_3	0–7

applying the resulting slip to a steel body to a dry weight of from 8 to 15 grams per square foot two sides, firing within a temperature range of from 1200° F. to 1700° F. for a period of from 2 to 10 minutes; applying a vitreous enamel cover coat and refiring.

4. The process of providing a vitreous enameled steel body which comprises: preparing a slip by mixing enameling materials with water and up to 15 percent dry weight clay, said enameling materials selected from the group consisting of alkali silicates, borax, boric acid, sodium calcium borate, colemanite, sodium aluminate, kyanite, alumina, aluminum silicate and black iron oxide,

and said enameling materials being in such proportion as to yield, on calculated analyses, when fired at a temperature of from 1200° F. to 1700° F. for a period of from 2 to 10 minutes, a glass consisting essentially of:

	Weight percent
Fe_3O_4	1–15
ZnO	0–9
SiO_2	30–45
B_2O_3	17–28
At least one material selected from the group consisting of Na_2O and	
K_2O	11–22
CaO	3–8
Al_2O_3	0–7

applying the resulting slip to a steel body to a dry weight of from 8 to 17 grams per square foot two sides, firing within a temperature range of from 1200° F. to 1700° F. for period of from 2 to 10 minutes; applying a vitreous enamel cover coat and refiring.

5. The process of producing a vitreous enamel steel body which comprises: preparing a slip by mixing with water the following approximate composition:

Enameling material:	Approximate amount, parts by weight
Sodium silicate solution (36.6% solid sodium silicate, 1 Na_2O to 2.94 SiO_2 weight ratio)	27.0
Sodium silicate powder (1 Na_2O to 3.11 SiO_2 weight ratio)	35.0
Regular borax	29.8
Sodium calcium borate	31.0
Clay	10.0
Flint	2.0
Feldspar	2.0
Black iron oxide	9.1
Kyanite	5.3
Total	151.2

applying the resulting slip to a steel body for a dry weight of approximately 12 grams per square foot of surface area, both sides, firing at a temperature of approximately 1500° F. for a period of from 4 to 6 minutes; applying a vitreous enamel cover coat, and refiring.

References Cited in the file of this patent

UNITED STATES PATENTS

2,229,524 Rosenburg ---------- Jan. 21, 1941

OTHER REFERENCES

Andrews: Enamels, Twin City Printing Co., 1935, p. 295 relied on.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,864,721

December 16, 1958

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 16, for "dry weight from 7 to 17 grams" read -- dry weight from 8 to 17 grams --.

Signed and sealed this 14th day of April 1959.

(SEAL)

Attest:

KARL H. AXLINE
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