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PORCELAIN ENAMEL FOR DIRECT APPLICATION TO METAL AND PROCESS FOR PRODUCING THE SAME

Eugene E. Bryant, Bedford, Ohio, assignor, by mesne assignments, to the United States of America as represented by the Secretary of the Army

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1

This invention relates as indicated to porcelain enamels for direct application to metal, and to a process for producing the same. It is primarily concerned with the provision of such an enamel characterized by improved density and strength, and, in its preferred embodiment, by the fact that it is also acid-resistant.

This application is a continuation-in-part of my application Serial No. 529,816, filed April 6, 1944, now abandoned.

Most porcelain enamels which are applied directly to the metal, and are accordingly generically defined as ground coats, even though no finished coat may be applied thereover, generally during the firing operation, have formed therein a substantial amount of bubbles of appreciable size. This bubble structure of ground coats is generally attributed to various causes such as the occurrence on the metal surface of a certain amount of oxide of the metal which may be present before the application of the enamel slip, or which is formed by an oxidation of the base metal prior to and during the firing stage.

The presence of oxygen in the atmosphere in which the enamel is fired, and also the possibility of oxygen liberation from slip components such as the normal clay content thereof, have also been charged with being the reason for bubble generation during the firing step.

The prior art has endeavored to overcome this difficulty by the use of a controlled atmosphere in the furnace in which the firing operation is performed. The use of a controlled or reducing atmosphere in the furnace is, however, an expensive expedient, and it is the principal object of my invention to avoid the necessity of using such atmosphere.

A further object of my invention is to provide a dense strong vitreous acid-resisting enamel coating, applicable to a ferrous base by direct firing thereon.

A further object of my invention is a high silica titanium dioxide enamel characterized by the inclusion in the mill charge of silicon in the form of uncombined silicon or ferrosilicon.

Other objects of my invention will appear as the description proceeds.

2

To the accomplishment of the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

Broadly stated, this invention comprises providing a porcelain enamel which is adapted for direct application to steel for the production of a dense and strong coating by the inclusion therein of a reducing agent.

Because the factors which are responsible for the generation of the objectionable structure apparently function in a relatively narrow range of conditions during the firing operations, the reducing agent which is selected for the purpose of counteracting the same must be effective in such narrow range. The reducing agent which I have found to be effective for the stated purpose is silicon metal which may be added to the enamel in the mill in the form of silicon metal, or in the form of ferrosilicon, the latter being an alloy of iron and silicon, and being the most economical form in which silicon metal is available for purposes such as this.

This particular reducing agent has been found to be effective for the stated purpose in only certain types of enamel. The enamels in which silicon metal has been found effective as a reducing agent during the firing operation are those generally identified in the trade as acid-resisting enamels. They have the common characteristic of containing silica of at least about 40% and up to about 65% as compared with a lower silica content of non-acid-resisting enamels. The enamels in which the use of silicon metal has been found effective have also had the common characteristic of containing a substantial amount, on the order of from about 2% to about 12% of titanium dioxide. It is not known whether there is some reaction between the silicon metal and the titanium content of the frit in the function of the former as a reducing agent during the firing step.

A raw batch mixture providing the desired silica and titanium dioxide for my enamel in accordance with the present invention, together with other suitable fritting agents, occupies the following ranges:

Table 1

	Parts by Weight (Percent)	
	From About—	To About—
Silica	40	65
Titanium Dioxide	2	12
Dehydrated Borax	15	25
Feldspar	0	15
Soda Ash	0	20
Sodium Nitrate	0	8
Cobalt Oxide	0.5	3
Potash Carbonate	0	20
Potash Nitrate	0	10
Lithium Carbonate	0	5
Sodium Fluosilicate	0	12
Manganese Oxide	1	3
Bone Ash	0	4
Calcium Carbonate (Calcspar or Whiting)	0	4
Fluospar	0	4
Cryolite	0	12
Barium Carbonate	0	4
Total	100	

It will be understood that the fritting agents in the above table, other than the silica and titanium dioxide are interchangeable in a manner well known to the expert in the enamel art, that is, where the lower limit of a fritting agent is indicated as 0, it may be substituted by suitably raising the amount of an equivalent fritting agent.

Those familiar with formulation will recognize that variations in the above ranges of such fritting agents may be used to supply essentially equal calculated yields and substitution of materials not listed may also be used to produce essentially equivalent melted compositions. It should be noted that this range allows for substitution of potash or lithium salts for soda. Additions of other materials such as nickel, copper and magnesium oxides can be used if desired.

These enamels are smelted in the usual way at temperatures from about 2000° F. to about 2500° F., and fritted in the conventional manner.

After the enamel has thus been smelted, the calculated oxide content of the yield will lie within the approximate ranges given in the following table:

Table 2

	Parts by Weight (Percent)	
	From About—	To About—
SiO_2	40	65
TiO_2	2	12
B_2O_3	10	18
Al_2O_3	0	3
Na_2O, K_2O, Li_2O—a total of	15	25
Co_3O_4	0.5	3
MnO_2	1	3
CaO	0	4
BaO	0	3

As illustrative of acid-resisting enamels of the character described, which are capable of use in carrying out my invention, the following specific examples are given:

A raw batch mixture is compounded according to Example A or B of Table 3:

Table 3

	Parts by Weight (Percent)	
	From About—	To About—
Silica	49.5	49.0
Titanium Dioxide	6.0	4.5
Dehydrated Borax	19.0	23.0
Feldspar	5.0	6.5
Soda Ash	8.0	17.0
Sodium Nitrate	6.0	4.0
Cobalt Oxide	2.0	2.0
Sodium Fluosilicate	9.0	2.5
Manganese Oxide	2.0	2.5
Bone Ash	3.0	

The titanium dioxide content of raw batch mixtures whose silica content is of the order of 45 to 50 percentage parts by weight, as exemplified by Examples A and B, is preferably between about 3 and about 6 parts by weight.

These enamels, after being smelted at a temperature on the order of about 2300° F. will be fritted in the conventional manner, and then used as a mill charge, of which the following is representative.

It will be observed that each of the examples given above is characterized by the presence of a large percentage of silica and an appreciable amount of titanium dioxide in the raw batch mixture, and consequently in the frit. In order to prepare from the above described frits an enamel slip which, when fired directly on steel, will have the characteristics which form the principal objects of my invention, I add thereto uncombined silicon (silicon metal or ferrosilicon) in the equivalent proportions of about .5 to about 2 parts by weight per 100 parts by weight of frit, together with other mill charge forming agents, including principally clay and water. The following table gives illustrative ranges of ingredients for such a mill charge:

Table 4

	Parts by Weight (Percent)	
	From About—	To About—
Frit	100	
Silocon metal or Electric furnace Ferrosilicon	.5	2
Clay	1	[1] 10
Hydrated Borax	0	1
Magnesium Carbonate	0	.5
Potash Carbonate	0	.5
Sodium Nitrite	0	.3
Feldspar	0	40
Silica	0	40
Water	40	60

[1] Including 0 to about 1 part of bentonite.

For instance, a mill charge may be formed by compounding the ingredients as follows:

Table 5

	Parts by weight
Frit	100.
Silicon metal	from about .5 to about 2.
Clay	about 7.
Hydrated borax	about .75.
Water	about 50.

Those skilled in the art will recognize the mill charge as a simple basic form. The usual changes may be made to adapt this to various

applications or operating conditions. For example, additions of quartz or feldspar may be made to increase resistance to firing. Bentonite may be added or changes in clay may be made to adjust the suspension. So called set-up electrolytes such as magnesium carbonate, sodium nitrite, potash carbonate may be added or substituted for hydrated borax.

Ferrosilicon (electric furnace grade) with more than 50% silicon may be used to replace the silicon metal in the mill addition. I prefer the 75% material. Ferrosilicon (75% grade) will replace silicon metal on an equal weight basis.

This mill charge is ground for a sufficient length of time so that the slip has a fineness such that there will be a residue of from 4 to 8 grams on a 200 mesh sieve from an initial 50 cc. sample. The slip thus prepared is applied directly to clean sheet iron and fired at a temperature of from about 1480° F. to about 1700° F., depending on variations in formulation, for a period of about 4½ minutes when 20-gauge sheet iron is used as the base metal. For the mill charge set forth in Table 5, I prefer a firing temperature from about 1560° F. to 1600° F.

The foregoing illustrative examples of my invention will enable those skilled in the art to make the customary modifications in adapting the same to particular uses.

A fired enamel coating prepared in the manner described will, under the microscope, show a marked reduction, in many cases a total absence of, the bubble structure which characterizes most ground coats, and which is responsible for the low strength and other undesirable properties of conventional ground coats.

As indicated, my invention is applicable not only to the use of ground coats, over which a finished coat will ultimately be applied, but also, because of the improved characteristics of the ground coat, the same may be used as a finished coat, i. e. without the application thereover of an additional finished coat.

When the enamel coating of my invention is to be used as a ground coat, the normal dry weight of application will be on the order of about 20 grams per square foot of area covered. If the same enamel is to be used as the finished coat, then a second coat may be applied over the first, the second being applied at a normal dry weight on the order of about 40 grams per square foot of area covered, making a total of about 60. The foregoing values are intended merely as illustrative, and those skilled in the art may, for particular purposes, vary the weights of application which have been given as examples.

I claim:

1. An enamel slip providing a dense strong vitreous acid-resisting coat when directly fired on metal, such characteristics being imparted thereto by the presence of from about 40 to about 65 parts by weight of silica, from about 2 to about 12 parts by weight of titanium dioxide, from about 10 to about 18 parts by weight of boron oxide and from about 15 to about 25 parts by weight of at least one substance being a member of the group consisting of Na_2O, K_2O, and Li_2O, calculated per 100 parts by weight of frit; and by the addition to said frit in the mill charge of water and from about 1 to about 10 parts by weight of clay and from about .5 to about 2 parts by weight of a member of the group consisting of silicon and ferrosilicon.

2. An enamel slip providing a dense strong vitreous acid-resisting coat when directly fired on metal, such characteristics being imparted thereto by the presence of from about 45 to about 50 parts by weight of silica, from about 3 to about 6 parts by weight of titanium dioxide, from about 10 to about 18 parts by weight of boron oxide and from about 15 to about 25 parts by weight of at least one substance being a member of the group consisting of Na_2O, K_2O, and Li_2O, calculated per 100 parts by weight of frit, and by the addition to said frit in the mill charge of water and from about 1 to about 10 parts by weight of clay and from about .5 to about 2 parts by weight of a member of the group consisting of silicon and ferrosilicon.

3. An enamel slip providing a dense strong vitreous enamel coating when directly fired on metal, whose frit has a calculated oxide content of about

	Parts by weight
SiO_2	40 to 65
TiO_2	2 to 12
B_2O_3	10 to 18
At least one member of the group consisting of Na_2O, K_2O, Li_2O	15 to 25
Co_3O_4	0.5 to 3
MnO_2	1 to 3

said enamel slip further being characterized by the inclusion therein, as a mill addition to each 100 parts by weight of said frit of about

	Parts by weight
A member of the group consisting of silicon and ferrosilicon	.5 to 2
Clay	1 to 10

4. An enamel slip providing a dense strong vitreous acid-resisting coating when directly fired on metal and whose frit is produced by smelting a raw batch mixture comprising about

	Parts by weight
Silica	45 to 50
Titanium dioxide	3 to 6
Dehydrated borax	19 to 23
Feldspar	5 to 6.5
Soda ash	8 to 17
Sodium nitrate	4 to 6
Cobalt oxide	2
Sodium fluosilicate	2.5 to 9
Manganese oxide	2 to 2.5

said enamel slip further being characterized by the inclusion therein, as a mill addition to each 100 parts by weight of said frit of about

	Parts by weight
A member of the group consisting of silicon and ferrosilicon	.5 to 2
Clay	1 to 10

5. An enamel slip providing a dense strong vitreous acid-resisting coating when directly fired on metal and whose frit is produced by smelting a raw batch mixture comprising about

	Parts by weight
Silica	45 to 50
Titanium dioxide	3 to 6
Dehydrated borax	19 to 23
Feldspar	5 to 6.5
Soda ash	8 to 17
Sodium nitrate	4 to 6
Cobalt oxide	2
Sodium fluosilicate	2.5 to 9
Manganese oxide	2 to 2.5

said enamel slip further being characterized by the inclusion therein, as a mill addition to the

frit of about 7 parts by weight of clay, about .75 parts by weight of borax, and about .5 to about 2 parts by weight of a member of the group consisting of silicon and ferrosilicon, per 100 parts by weight of said frit.

6. An enamel slip providing a dense strong vitreous acid-resisting coating when directly fired on metal and whose frit is produced by smelting a raw batch mixture comprising about

	Parts by weight
Silica	49.5
Titanium dioxide	6.0
Dehydrated borax	19.0
Feldspar	5.0
Soda ash	8.0
Sodium nitrate	6.0
Cobalt oxide	2.0
Sodium fluosilicate	9.0
Manganese oxide	2.0
Bone ash	3.0

said enamel slip further being characterized by the inclusion therein, as a mill addition to each 100 parts by weight of said frit of about

	Parts by weight
A member of the group consisting of silicon and ferrosilicon	.5 to 2
Clay	1 to 10

7. An enamel slip providing a dense strong vitreous acid-resisting coating when directly fired on metal and whose frit is produced by smelting a raw batch mixture comprising about

	Parts by weight
Silica	49.5
Titanium dioxide	6.0
Dehydrated borax	19.0
Feldspar	5.0
Soda ash	8.0
Sodium nitrate	6.0
Cobalt oxide	2.0
Sodium fluosilicate	9.0
Manganese oxide	2.0
Bone ash	3.0

said enamel slip further being characterized by the inclusion therein, as a mill addition to the frit of about 7 parts by weight of clay, about .75 parts by weight of borax, and about .5 to about 2 parts by weight of a member of the group consisting of silicon and ferrosilicon, per 100 parts by weight of said frit.

8. An enamel slip providing a dense strong vitreous acid-resisting coating when directly fired on metal and whose frit is produced by smelting a raw batch mixture comprising about

	Parts by weight
Silica	49.0
Titanium dioxide	4.5
Dehydrated borax	23.0
Feldspar	6.5
Soda ash	17.0
Sodium nitrate	4.0
Cobalt oxide	2.0
Sodium fluosilicate	2.5
Manganese oxide	2.5

said enamel slip further being characterized by the inclusion therein, as a mill addition to each 100 parts by weight of said frit of about

	Parts by weight
A member of the group consisting of silicon and ferrosilicon	.5 to 2
Clay	1 to 10

9. An enamel slip providing a dense strong vitreous acid-resisting coating when directly fired on metal and whose frit is produced by smelting a raw batch mixture comprising about

	Parts by weight
Silica	49.0
Titanium dioxide	4.5
Dehydrated borax	23.0
Feldspar	6.5
Soda ash	17.0
Sodium nitrate	4.0
Cobalt oxide	2.0
Sodium fluosilicate	2.5
Manganese oxide	2.5

said enamel slip further being characterized by the inclusion therein, as a mill addition to the frit of about 7 parts by weight of clay, about .75 parts by weight of borax, and about .5 to about 2 parts by weight of a member of the group consisting of silicon and ferrosilicon, per 100 parts by weight of said frit.

10. A process for producing a slip adapted to provide an acid-resisting vitreous enamel capable of being directly fired on metal, comprising adding to each 100 parts of frit having a calculated oxide content of about

	Parts by weight
SiO_2	40 to 65
TiO_2	2 to 12
B_2O_3	10 to 18
At least one member of the group consisting of Na_2O, K_2O, Li_2O	15 to 25
Co_3O_4	0.5 to 3
MnO_2	1 to 3

mill charge forming agents comprising water and about

	Parts by weight
A member of the group consisting of silicon and ferrosilicon	.5 to 2
Clay	1 to 10

and grinding said frit and additives together until not more than 8 grams per 50 cc. are retained on a 200 mesh sieve.

11. A process for producing a slip adapted to provide an acid-resisting vitreous enamel capable of being directly fired on metal, comprising smelting a mixture comprising about

	Parts by weight
Silica	45 to 50
Titanium dioxide	3 to 6
Dehydrated borax	19 to 23
Feldspar	5 to 6.5
Soda ash	8 to 17
Sodium nitrate	4 to 6
Cobalt oxide	2
Sodium fluosilicate	2.5 to 9
Manganese oxide	2 to 2.5

at a temperature on the order of 2300° F., fritting the smelted mixture; adding to the frit: water, about 7 parts by weight of clay, about .75 part by weight of borax, and about .5 to 2 parts by weight of a member of the group consisting of silicon and ferrosilicon, per 100 parts by weight of said frit; and grinding said frit and additives together until not more than 8 grams per 50 cc. are retained on a 200 mesh sieve.

12. A process for producing an acid-resisting vitreous enamel coating directly fired on metal

comprising fritting a raw batch mixture comprising about

	Parts by weight
Silica	45 to 50
Titanium dioxide	3 to 6
Dehydrated borax	19 to 23
Feldspar	5 to 6.5
Soda ash	8 to 17
Sodium nitrate	4 to 6
Cobalt oxide	2
Sodium fluosilicate	2.5 to 9
Manganese oxide	2 to 2.5

adding to each 100 parts by weight of said frit: water and about

	Parts by weight
A member of the group consisting of silicon and ferrosilicon	.5 to 2
Clay	1 to 10

grinding said frit and additives together to form a finely divided intimate mixture, applying the ground mixture to a ferrous base and firing the same in a non-reducing atmosphere at a temperature on the order of about 1480° F. to about 1700° F.

13. A process for producing an acid-resisting vitreous enamel coating directly fired on metal comprising fritting a raw batch mixture comprising about

	Parts by weight
Silica	49.5
Titanium dioxide	6.0
Dehydrated borax	19.0
Feldspar	5.0
Soda ash	8.0
Sodium nitrate	6.0
Cobalt oxide	2.0
Sodium fluosilicate	9.0
Manganese oxide	2.0
Bone ash	3.0

adding to each 100 parts of said frit: water, about 7 parts by weight of clay, about .75 part by weight of borax, and .5 to 2 parts by weight of a member of the group consisting of silicon and ferrosilicon; grinding said frit and additives together, applying the ground mixture directly to a metal base and firing the same in a non-reducing atmosphere at a temperature of about 1560° F. to about 1600° F.

14. A process for producing an acid-resisting vitreous enamel coating directly fired on metal comprising fritting a raw batch mixture comprising about

	Parts by weight
Silica	49.0
Titanium dioxide	4.5
Dehydrated borax	23.0
Feldspar	6.5
Soda ash	17.0
Sodium nitrate	4.0
Cobalt oxide	2.0
Sodium fluosilicate	2.5
Manganese oxide	2.5

adding to each 100 parts of said frit: water, about 7 parts by weight of clay, about .75 part by weight of borax, and .5 to 2 parts by weight of a member of the group consisting of silicon and ferrosilicon; grinding said frit and additives together, applying the ground mixture directly to a metal base and firing the same in a non-reducing atmosphere at a temperature of about 1560° F. to about 1600° F.

15. A process for producing an acid-resisting vitreous enamel coat directly fired on metal, comprising fritting a raw batch mixture characterized by the presence of from about 40 to about 65 parts by weight of silica, from about 2 to about 12 parts by weight of titanium dioxide and from about 15 to about 25 parts by weight of dehydrated borax calculated per 100 parts by weight of raw batch mixture, adding to each 100 parts of said frit: water, from about 1 to about 10 parts by weight of clay and from about .5 to about 2 parts by weight of a member of the group consisting of silicon and ferrosilicon; grinding said frit and additives together to form a finely divided intimate mixture; applying the ground mixture directly to a metal base and firing the same in a non-reducing atmosphere.

16. An enamel slip providing a dense vitreous enamel coating when directly fired on metal and whose frit is provided by smelting a raw batch mixture comprising about

	Parts by weight
Silica	40 to 65
Titanium dioxide	2 to 12
Dehydrated borax	15 to 25
Cobalt oxide	0.5 to 3
At least one member of the group consisting of soda ash, sodium nitrate, potash carbonate, potash nitrate, lithium carbonate, and sodium fluosilicate (calculated as oxides)	15 to 25
Manganese oxide	1 to 3

said enamel slip further being characterized by the inclusion therein, as a mill addition to each 100 parts by weight of said frit of about

	Parts by weight
A member of the group consisting of silicon and ferrosilicon	.5 to 2
Clay	1 to 10

17. A process for producing an enamel slip adapted to provide an acid-resisting vitreous enamel capable of being directly fired on metal, comprising smelting a mixture which comprises about

	Parts by weight
Silica	40 to 65
Titanium dioxide	2 to 12
Dehydrated borax	15 to 25
Cobalt oxide	0.5 to 3
At least one member of the group consisting of soda ash, sodium nitrate, potash carbonate, potash nitrate, lithium carbonate and sodium fluosilicate (calculated as oxides)	15 to 25
Manganese oxide	1 to 3

at a temperature between about 2000° F. and about 2500° F., fritting the smelted mixture, adding to each 100 parts by weight of said frit: water and about

	Parts by weight
A member of the group consisting of silicon and ferrosilicon	.5 to 2
Clay	1 to 10

and grinding said frit and additives together to form a finely divided intimate mixture.

18. A process for producing an acid-resisting vitreous enamel coat directly fired on metal, com-

prising fritting a raw batch mixture comprising about

	Parts by weight
Silica	40 to 65
Titanium dioxide	2 to 12
Dehydrated borax	15 to 25
Cobalt oxide	0.5 to 3
At least one member of the group consisting of soda ash, sodium nitrate, potash carbonate, potash nitrate, lithium carbonate and sodium fluosilicate (calculated as oxides)	15 to 25
Manganese oxide	1 to 3

adding to each 100 parts of said frit: water and about

	Parts by weight
A member of the group consisting of silicon and ferrosilicon	.5 to 2
Clay	1 to 10

grinding said frit and additives together, applying the ground mixture directly to a metal base and firing the same in a non-reducing atmosphere.

19. A process for producing an acid-resisting vitreous enamel coat directly fired on metal, comprising fritting a raw batch mixture comprising about

	Parts by weight
Silica	40 to 65
Titanium dioxide	2 to 12
Dehydrated borax	15 to 25
Cobalt oxide	0.5 to 3

At least one member of the group consisting of soda ash, sodium nitrate, potash carbonate, potash nitrate, lithium carbonate and sodium fluosilicate (calculated as oxides)	15 to 25
Manganese oxide	1 to 3

adding to each 100 parts of said frit: water and about

	Parts by weight
A member of the group consisting of silicon and ferrosilicon	.5 to 2
Clay	1 to 10

grinding said frit and additives together, applying the ground mixtures to a ferrous base and firing the same at a temperature on the order of about 1480° F. to about 1700° F.

EUGENE E. BRYANT.

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