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COLOR STABLE WHITE PORCELAIN ENAMEL
AND METHOD OF PRODUCING SAME
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The present invention relates to an improved white porcelain enamel, to a method of producing the improved product, and to a method of employing the improved enamel in the coating of metal articles.

The principal advantage of the enameling compositions of the present invention is their stability against change in color due to variations in processing.

It is well known that in the manufacture of porcelain enamel, the white titanium-opacified porcelain enamels are subject to an undesirable change in color over a range of firing conditions. For example, the load on the furnace may vary because there is an interruption in the sequence of articles passing through it on the conveyor mechanism. When this happens, different articles may be fired at significantly different temperatures, resulting in a noticeable color change between those articles.

Another process variable which must be taken into account arises because some articles have to be refired due to defects in the original enameling. Despite the fact that the refiring may be under exactly the same conditions as the original firing there will nevertheless be a detectable color change after refiring.

An object of the present invention is to provide an improved porcelain enameling frit stable toward color change over an extended firing range.

Another object of the present invention is to provide a porcelain enamel frit which can be fired onto the article in successive firings without a detectable color change occurring.

Still another object of the present invention is to provide an improved method for the manufacture of titanium-opacified porcelain enamel frits.

Still another object of the invention is to provide a method for applying the improved porcelain enamel frits to metal articles.

We have now found that substantially improved color stability results when porcelain enameling frits containing titania also contain small amounts of both cupric oxide and gold. The two materials cooperate to improve the firing and refiring stability without causing deviation from the particular white color desired in the enameled article.

More specifically, we have found that amounts of cupric oxide in the range from 0.01 to 0.20%, and amounts of gold from 0.0002 to 0.006% by weight provide a frit composition which, when applied in normal porcelain enameling processes, results in a material having excellent color stability toward temperature changes, excellent reflectivity and reproducibility of results.

It should be mentioned that it is not necessary to use cupric oxide or metallic gold as such to provide the improved results of the present invention. For example, materials which decompose under the conditions of smelting to provide the cupric oxide and metallic gold in the frit without adding objectionable impurities are satisfactory, provided that the amounts added yield the ranges of concentration of cupric oxide and gold previously set forth.

The porcelain enamels which results from the use of the frits of the present invention have reflectivities in the range of 74 to 84, which is deemed to be the most satisfactory for commercial use. They also have an "a" value in the range from 0.0 to -2.0 and a "b" value not in excess of +1.0. All of these values are measured on the

standard Hunter Color and Color-Difference meter. The "a" value is a measure of the degree of pink or green cast, the more negative values of "a" representing more green, and the more positive values representing more pink in the material. The "b" value is indicative of a blue-white cast when the value is negative, but at values over +1.0, the cast becomes yellowish.

The addition of cupric oxide and gold has been found to improve the color stability of a wide variety of titanium-opacified enameling compositions. The following table represents a typical range of ingredients used commercially in the manufacture of white titanium frit.

TABLE I

	Percent by weight
SiO ₂ -----	20-55
TiO ₂ -----	8-24
B ₂ O ₃ -----	5-25
Na ₂ O-----	0-25
K ₂ O-----	0-25
Li ₂ O-----	0-5
ZnO-----	0-5
Al ₂ O ₃ -----	0-4
MgO-----	0-3
P ₂ O ₅ -----	0-5
F-----	0-20
ZrO ₂ -----	0-10

In determining the improved color stability by the use of our invention, we did so in terms of ΔE units of the National Bureau of Standards. One ΔE NBS unit is actually about five times the smallest difference in color perceptible under the best experimental conditions. The ΔE was calculated from the reflectivity (Rd), the "a" and "b" values as determined from the Hunter Color and Color-Difference meter by means of the following approximation equation:

$$\Delta E \approx [(10\sqrt{Rd_1} - 10\sqrt{Rd_2})^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]^{1/2}$$

The foregoing equation is an accepted standard in the industry and is a modification of that described in the book "Color in Business, Science and Industry" by Deane B. Judd (John Wiley and Sons, 1952), pages 258-260.

In the foregoing equation, Rd₁ and Rd₂ are the reflectivities of the material produced under different firing temperatures, or upon refiring, as the case may be; "a₁" and "a₂" are the "a" values and "b₁" and "b₂" are the "b" values for the two materials being tested.

The following specific examples illustrate the improved results which are obtained from the process of the present invention.

Example I

A glass composition was made to have the following melted formula.

TABLE II

	Percent by weight
SiO ₃ -----	43.619
TiO ₂ -----	18.75
ZrO ₂ -----	1.21
B ₂ O ₃ -----	17.00
P ₂ O ₅ -----	1.25
Na ₂ O-----	7.87
K ₂ O-----	7.88
Li ₂ O-----	0.92
F-----	2.59
Au-----	0.001
	101.09
Less oxygen for fluorine-----	-1.09
	100.00

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The material was melted and fritted in the usual fashion to provide a titania opacified porcelain enameling frit. This frit was applied with the conventional wet process of application to sheet steel at a weight of 25 grams per square foot. The pieces were fired at three minutes each, one at 1360° F., and the other at 1450° F. with the following results:

TABLE III

Firing Temp.	1,360° F.	1,450° F.
Rd.....	80.9	83.1
a.....	-1.9	-0.9
b.....	-1.7	+1.2

$\Delta E = 3.3$ NBS units.

The same test was carried out with the addition of cupric oxide and gold to provide a raw batch having the following composition:

TABLE IV

	Percent by weight
SiO ₂	43.548
TiO ₂	18.75
ZrO ₂	1.21
B ₂ O ₃	17.00
P ₂ O ₅	1.25
Na ₂ O.....	7.87
K ₂ O.....	7.88
Li ₂ O.....	0.92
F.....	2.59
CuO.....	0.07
Au.....	0.002
	101.09
Less oxygen for fluorine.....	-1.09
	100.00

It should be noted that the compositions are identical except for the addition of cupric oxide, a slight increase in the gold content, and a corresponding decrease in the silica content to compensate for the addition of the cupric oxide.

The composition of Table IV was then smelted, fritted, applied to the sheet steel, and fired under the same conditions and concentrations employed with the composition of Table II. With the enamel having the composition of Table IV, however, the following results were obtained:

TABLE V

Firing Temp.	1,360° F.	1,450° F.
Rd.....	79.6	81.0
a.....	-1.9	-1.1
b.....	-1.3	+0.5

$\Delta E = 2.1$ NBS units.

Example II

The compositions were also compared with regard to their ability to withstand color change due to refiring. The composition of Table II was again applied by the conventional wet process to sheet steel at a concentration of 25 grams per square foot. After one firing at 1420° F., the following values were recorded:

TABLE VI

Rd.....	83.2
a.....	-0.7
b.....	+0.6

This sample was then subjected to cooling followed by two additional firings, with intermediate cooling, the additional firings being at a temperature of 1420° F. The following values were obtained from this porcelain enamel coating:

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TABLE VII

Rd.....	81.9
a.....	-0.7
b.....	+1.4

The ΔE value for these two tests amounted to 1.1 NBS units.

The same conditions of firing and refiring were applied to the composition of Table IV. After one firing at 1420° F. the following results were obtained:

TABLE VIII

Rd.....	80.2
a.....	-1.5
b.....	-0.3

After the third firing at 1420° F. the composition of Table IV evidenced the following values:

TABLE IX

Rd.....	80.0
a.....	-1.4
b.....	+0.3

The ΔE value for these two samples amounted to 0.6 NBS unit.

Example III

A molten glass of the following composition was prepared:

	Percent
SiO ₂	41.23
TiO ₂	18.94
ZrO ₂	2.54
Al ₂ O ₃	0.50
ZnO.....	0.46
B ₂ O ₃	15.41
P ₂ O ₅	1.37
Na ₂ O.....	7.48
K ₂ O.....	8.05
Li ₂ O.....	1.23
F.....	4.82
	102.03
Less oxygen for fluorine.....	-2.03
	100.00

The values obtained after firing at 1380° F. and 1480° F. are given below:

TABLE X

Firing Temp.	1,380° F.	1,480° F.
Rd.....	82.3	85.7
a.....	-2.6	-1.5
b.....	-0.5	+2.5

$\Delta E = 3.7$ NBS units.

The glass formula given above in this example was modified to include cupric oxide and gold as follows:

	Percent
SiO ₂	41.0865
TiO ₂	18.94
ZrO ₂	2.54
Al ₂ O ₃	0.50
ZnO.....	0.46
B ₂ O ₃	15.41
P ₂ O ₅	1.37
Na ₂ O.....	7.48
K ₂ O.....	8.05
Li ₂ O.....	1.23
F.....	4.82
CuO.....	0.14
Au.....	0.0035
	102.03
Less oxygen for fluorine.....	-2.03
	100.00

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The corresponding values obtained under the same firing conditions are given below:

TABLE XI

Firing Temp.	1,380° F.	1,480° F.
Rd.....	77.3	77.6
a.....	-0.6	-0.5
b.....	-0.7	-0.5

$\Delta E = 0.3$ NBS unit.

The frit without the cupric oxide and gold evidenced the following values on refiring:

	One fire at 1,430° F.	Two additional firings at 1,430° F.
Rd.....	84.7	82.0
a.....	-2.4	-2.2
b.....	+0.8	+1.8

$\Delta E = 1.8$ NBS units.

Under the same conditions of refiring, the formula containing the 0.14% CuO and the 0.0035% Au evidenced the following values:

	One fire at 1,430° F.	Two additional firings at 1,430° F.
Rd.....	77.4	77.1
a.....	-0.6	-0.4
b.....	-0.7	-0.4

$\Delta E = 0.4$ NBS unit.

The improved enameling frits of the present invention can be applied by any of the conventional processes such as the wet process in which the frit is applied with a liquid vehicle in the manner of paint, and by the dry process in which it is dusted onto the surface of a heated metal article. Suitable firing temperatures for the enamels extend from about 1300 to 1550° F. and firing times of 1.5 to 6 minutes are normally adequate to secure a high quality, color stable enamel coating, the lower temperatures being used with the longer times, and vice versa.

It should be evident that various modifications can be made to the described embodiments as, for example, by including additional coloring agents in the smelt or combined with the frit.

We claim as our invention:

1. An opacified enameling frit having an enhanced color stability over an extended firing range, said frit consisting essentially of from 20-55% by weight SiO₂, from 8-24% TiO₂, from 5-25% B₂O₃, from 0-25% Na₂O, from 0-25% K₂O, from 0-5% Li₂O, from 0-5% ZnO, from 0-4% Al₂O₃, from 0-3% MgO, from 0-5% P₂O₅, from 0-20% F, from 0-10% ZrO₂, from 0.01 to 0.20% cupric oxide, and from 0.0002 to 0.006% gold.

2. An opacified enameling frit having enhanced color stability over an extended firing range, said frit consisting essentially of from 20-55% by weight SiO₂, from 8-24% TiO₂, from 5-25% B₂O₃, from 0-25% Na₂O, from 0-25% K₂O, from 0-5% Li₂O, from 0-5% ZnO,

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from 0-4% Al₂O₃, from 0-3% MgO, from 0-5% P₂O₅, from 0-20% F, from 0-10% ZrO₂, about 0.07% cupric oxide, and about 0.002% gold.

3. An enameled metal article having a color stable porcelain enamel coating resulting from firing onto said article a composition consisting essentially of from 20-55% by weight SiO₂, from 8-24% TiO₂, from 5-25% B₂O₃, from 0-25% Na₂O, from 0-25% K₂O, from 0-5% Li₂O, from 0-5% ZnO, from 0-4% Al₂O₃, from 0-3% MgO, from 0-5% P₂O₅, from 0-20% F, from 0-10% ZrO₂, from 0.01 to 0.20% cupric oxide, and from 0.0002 to 0.006% gold.

4. An enameled metal article having a color stable porcelain enamel coating resulting from firing onto said article a composition consisting essentially of from 20-55% by weight SiO₂, from 8-24% TiO₂, from 5-25% B₂O₃, from 0-25% Na₂O, from 0-25% K₂O, from 0-5% Li₂O, from 0-5% ZnO, from 0-4% Al₂O₃, from 0-3% MgO, from 0-5% P₂O₅, from 0-20% F, from 0-10% ZrO₂, from 0.01 to 0.20% cupric oxide, and from 0.0002 to 0.006% gold, said coating having a reflectivity in the range from 74 to 84 as measured on the Hunter Color and Color-Difference meter.

5. An enameled metal article having a color stable porcelain enamel coating resulting from firing onto said article a composition consisting essentially of from 20-55% by weight SiO₂, from 8-24% TiO₂, from 5-25% B₂O₃, from 0-25% Na₂O, from 0-25% K₂O, from 0-5% Li₂O, from 0-5% ZnO, from 0-4% Al₂O₃, from 0-3% MgO, from 0-5% P₂O₅, from 0-20% F, from 0-10% ZrO₂, from 0.01 to 0.20% cupric oxide, and from 0.0002 to 0.006% gold, said coating having a reflectivity in the range from 74 to 84, an "a" value in the range from 0.0 to -2.0, and a "b" value not over +1.0, all as measured on the Hunter Color and Color-Difference meter.

6. The method of preparing a porcelain enamel frit stable toward color change over an extended firing range which comprises providing a porcelain enameling composition consisting essentially of from 20-55% by weight SiO₂, from 8-24% TiO₂, from 5-25% B₂O₃, from 0-25% Na₂O, from 0-25% K₂O, from 0-5% Li₂O, from 0-5% ZnO, from 0-4% Al₂O₃, from 0-3% MgO, from 0-5% P₂O₅, from 0-20% F, and from 0-10% ZrO₂, adding to said composition from 0.01 to 0.20% by weight cupric oxide and 0.0002 to 0.006% by weight gold, and forming an enameling frit from the resulting mixture.

7. The method of enameling an article which comprises providing a porcelain enameling composition consisting essentially of from 20-55% by weight SiO₂, from 8-24% TiO₂, from 5-25% B₂O₃, from 0-25% Na₂O, from 0-25% K₂O, from 0-5% Li₂O, from 0-5% ZnO, from 0-4% Al₂O₃, from 0-3% MgO, from 0-5% P₂O₅, from 0-20% F, and from 0-10% ZrO₂, adding to said composition from 0.01 to 0.20% by weight cupric oxide and 0.0002 to 0.006% by weight gold, forming a frit from the resulting mixture, and firing the frit on said article at a temperature of from about 1300 to 1550° F. for a time of from 1.5 to 6 minutes.

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