July 20, 1943. M. J. BAHNSEN ET AL 2,324,812

PORCELAIN ENAMEL

Filed July 25, 1941 2 Sheets-Sheet 1

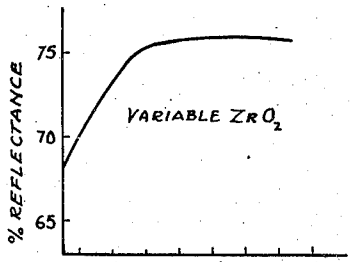

Fig. 1.

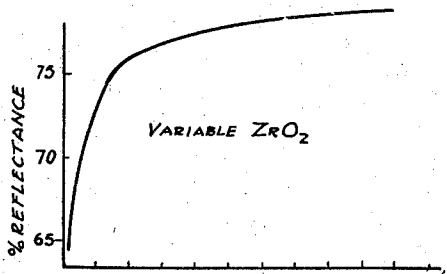

Fig. 2.

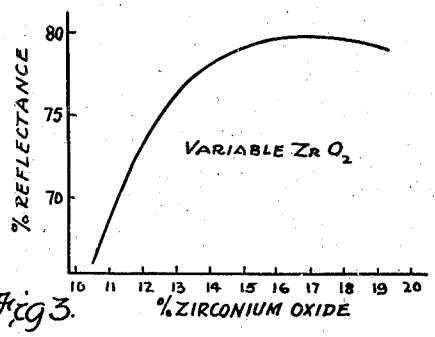

Fig. 3.

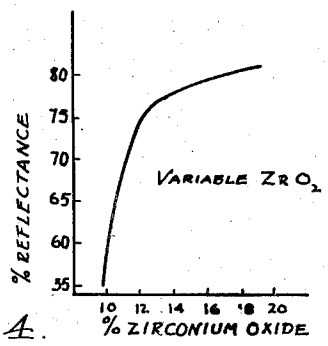

Fig. 4.

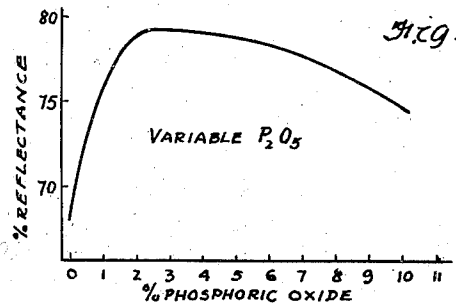

Fig. 5

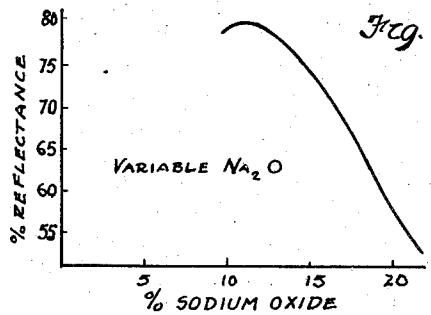

Fig. 6

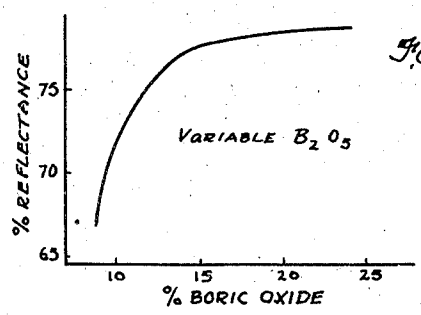

Fig. 7

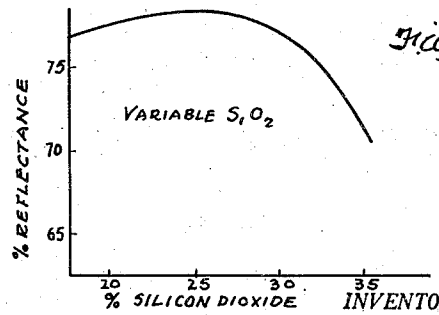

Fig. 8

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PORCELAIN ENAMEL

Filed July 25, 1941 2 Sheets-Sheet 2

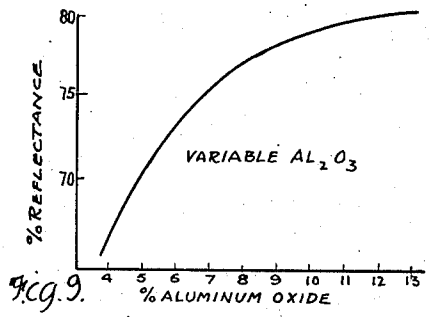

Fig. 9.

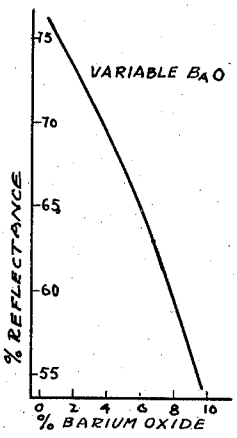

Fig. 13

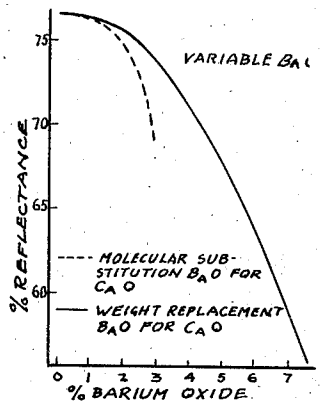

Fig. 14

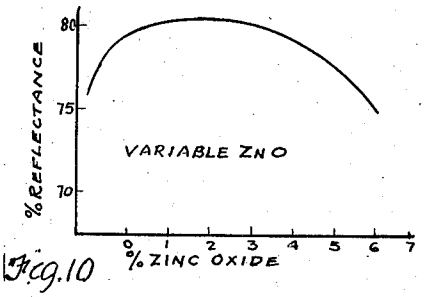

Fig. 10

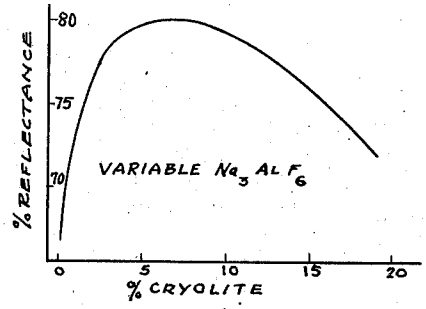

Fig. 15

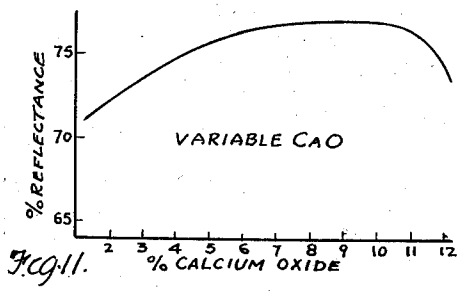

Fig. 11.

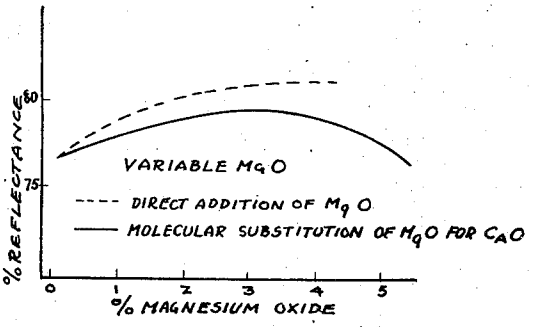

Fig. 16

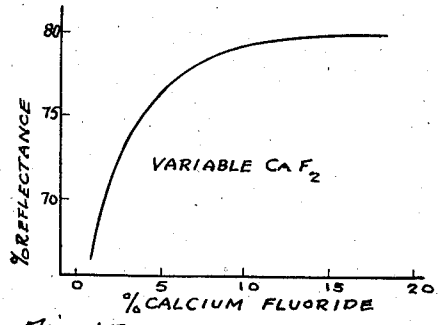

Fig. 12

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Patented July 20, 1943

2,324,812

UNITED STATES PATENT OFFICE

2,324,812

PORCELAIN ENAMEL

Monroe J. Bahnsen, Lakewood, and Eugene E. Bryant, Bedford, Ohio, assignors to Ferro Enamel Corporation, Cleveland, Ohio, a corporation of Ohio

Application July 25, 1941, Serial No. 404,048

8 Claims. (Cl. 106—48)

This invention relates as indicated, to porcelain enamel, and more particularly to procelain enamels characterized by the combined inclusion therein of zirconium oxide and phosphorus.

This application is a continuation in part of our co-pending applications Serial No. 311,362, filed December 28, 1939, now Patent No. 2,250,456, and Serial No. 361,448, filed October 16, 1940, now Patent No. 2,250,457.

From an inspection of our aforesaid co-pending applications it will be observed that we have disclosed and claimed therein the combined use in antimony-free porcelain enamels of zirconium oxide within a rather narrow range and phosphorus in the form of P_2O_5, likewise in a relatively narrow, although lower, range. Our investigations as disclosed and claimed in our aforesaid co-pending applications therefore extended to the discovery of an unexpected result produced by the combined presence within said percentage ranges of zirconium oxide and phosphorus in antimony-free enamels.

In the present application we shall give the results of considerable additional development work which has shown that when certain other factors are controlled in the manner hereinafter specified, this cooperative relationship between zirconia and phosphorus may be utilized in a much wider range of enamels than those disclosed in our said co-pending applications.

Our further development work, as reported in this continuation in part application, includes within its scope all of the work reported in our previous applications as well as a large amount of additional work, from a careful study of which it will be observed that this wider range within which the cooperative effect between zirconia and phosphorus is demonstrated is determined by certain balances between the constituents such as the monovalent basic oxides such as sodium and potassium oxide.

It is a principal object of our invention therefore to provide a wide range of enamel compositions within which the cooperative effect of zirconia and phosphorus may be utilized in the production of enamels which have superior properties, especially from the standpoint of opacity.

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

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter fully described and particularly pointed out in the claims.

The following description sets forth in detail certain approved combinations of ingredients embodying our invention, such disclosed means constituting, however, but representative examples in which the principles of the invention may be used. The several drawings comprise charts showing the effect upon the composition of the variance therein of certain basic components of the composition.

In said annexed drawings:

Fig. 1 is a chart showing the effect on the percentage of reflectance, i. e., the effect on opacity, of a representative enamel of our invention by varying the zirconia content thereof;

Fig. 2 is a chart similar to Fig. 1 showing the effect of varying the zirconia in an enamel composition generally similar to Fig. 1 but in which the sodium fluosilicate component of the composition of Fig. 1 is replaced by cryolite;

Fig. 3 is a chart similar to Fig. 1, utilizing however a somewhat different basic formula;

Fig. 4 is a chart similar to Fig. 3, showing the effect on opacity of variations in the amount of zirconia in a composition generally similar to that shown in Fig. 3, but in which the sodium fluosilicate of the composition shown by Fig. 3 has been replaced by cryolite; and

Figs. 5 to 16 are charts which show the effect on reflectance of opacity of variations in the concentration of other specifically identified components of the basic formula of Fig. 2, the same amount by weight of all constituents, excepting the one varied, being used for all of the compositions of Figs. 5 to 16, it being observed that when the same weight of each of the components excepting the one varied is maintained constant the percentage of the "constant" components changes slightly as their total percentages of the composition varies in accordance with variations in the variable.

For the reasons which will be explained later

and in greater detail, the compositions of our invention can best be identified by having reference to the oxide content of the resultant enamel produced by smelting the raw batch mixture. Throughout the following description the oxide content of the smelt has been given based on a theoretical calculation of the raw materials which enter into the smelt. At this point we should explain that these theoretical or computed oxide compositions have been arrived at in the following manner:

In all cases except the fluorides, the raw materials consist essentially of oxides or combinations of oxides and these materials are broken down in the normal manner as used by any chemist or ceramist, the volatile ingredients of these components are considered as lost, leaving the single oxide content. However, in case of fluorides, for the sake of simplicity, the metal ion or ions in these fluorides are calculated to be the chemical equivalent of the oxide and the fluorine is calculated as molecular fluorine, assuming no loss thereof. While there may be some loss of fluorine during the smelting operation, the amount is generally indeterminate, and while other workers in the art may employ a slightly different mode of calculation in determining the calculated oxide content, it is nevertheless general practice, whatever mode of computation is used, to assume no loss of fluorine.

In the following Table I we have set forth the ranges of percentages of the calculated oxide content of the enamels which comprise our invention.

TABLE I

	Per cent
SiO_2	23.00 up to 35.00
ZrO_2	10.00 up to 20.00
B_2O_3	10.00 up to 20.00
Na_2O	0 up to 14.25
K_2O	0 up to 14.25
CaO	0 up to 12.00
Al_2O_3	5.50 up to 12.00
ZnO	0 up to 4.15
F_2	5.00 up to 13.00
P_2O_5	1.00 up to 7.50
TiO_2	0 up to 1.00
MnO_2	0 up to 1.00
BaO	0 up to 2.00
MgO	0 up to 4.50
Sb_2O_5	0 up to 5.00

It will be observed that a number of components have been identified as ranging from zero to a maximum stated amount. This means that satisfactory enamels may be made by omitting completely the particular component, and again certain components may be omitted entirely only if a substitute therefor, also included within the table of compositions, is included in the enamel. We shall hereinbelow refer specifically to each of the components mentioned in the foregoing Table I for a better understanding of the ranges given in such table and for a further explanation of such proportional relationship as should be maintained between the various components of the composition for best results.

Before proceeding with such explanation, however, it is deemed advisable to first include the following Table II which gives a range of possible raw batch compositions from which may be smelted enamels having the calculated oxide content included within the scope of our invention as given in Table I.

TABLE II

	Per cent
Silica sand	0 up to 17.98
Dehydrated borax	9.83 up to 26.40
Feldspar	6.15 up to 24.92
Zircon sand	16.42 up to 29.58
Sodium nitrate	0.99 up to 1.23
Fluorspar	3.54 up to 13.52
Sodium fluosilicate	0 up to 16.25
Bone ash	0 up to 5.94
Aluminum hydrate	0 up to 6.76
Zinc oxide	0 up to 4.22
Titanium dioxide	0 up to 0.81
Manganese dioxide	0 up to .094
Boric acid	0 up to 12.50
Calcium carbonate	0 up to 4.60
Cryolite	0 up to 16.51
Kaolin	0 up to 9.96
Magnesium carbonate	0 up to 8.80
Phosphoric acid	0 up to 8.96
Barium carbonate	0 up to 2.35
Sodium carbonate	0 up to 3.74

It is also believed desirable to set forth hereinbelow in Table III a sufficiently large number of representative specific examples of actual enamels which have been produced and which are identified both by their raw batch as well as calculated oxide composition.

TABLE III

Raw mix

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Silica sand	2.57	2.81	0.71	2.82	3.16	------	------	12.08	13.53	7.80	17.15	12.04	12.08	11.00	12.30	11.78	12.48	11.61
Dehydrated borax	16.37	16.45	15.79	17.96	18.08	16.30	16.98	23.80	24.35	22.20	18.37	16.95	23.80	21.70	9.83	23.22	17.48	22.90
Feldspar	22.55	22.65	21.75	24.75	24.92	22.48	23.40	6.77	6.92	6.30	11.07	10.21	6.77	6.15	6.88	6.60	6.98	6.50
Zircon sand	17.44	16.83	22.20	19.14	18.32	29.05	26.19	19.60	16.42	28.38	19.58	29.58	19.60	17.81	19.91	19.09	20.21	18.82
Sodium nitrate	1.01	1.01	0.99	1.11	1.12	1.01	1.05	1.11	1.14	1.04	1.14	1.05	1.11	1.01	1.13	1.08	1.15	1.07
Fluorspar	4.09	4.11	3.95	4.49	4.52	4.08	4.25	7.53	7.54	6.86	4.59	4.24	7.55	6.72	7.52	7.21	7.63	7.10
Sodium fluosilicate	14.72	14.80	14.21	16.15	16.25	14.67	15.25	------	------	------	------	------	------	------	------	------	------	------
Bone ash	4.79	4.82	4.62	5.26	5.30	4.78	4.97	5.37	5.50	5.01	5.37	4.96	4.41	4.88	5.46	5.23	5.54	5.16
Aluminum hydrate	4.44	4.46	4.24	4.87	4.90	4.42	4.60	------	------	------	2.70	2.50	------	------	------	------	------	------
Zinc oxide	2.41	2.42	2.33	2.65	2.67	2.41	2.50	2.70	2.77	2.52	2.70	2.50	2.70	2.46	2.75	2.64	2.80	2.60
Titanium dioxide	------	------	------	0.80	.805	.725	.756	------	------	------	.82	0.76	------	------	------	------	------	------
Manganese dioxide	.09	.094	.087	------	------	------	------	.065	.067	.063	------	------	0.048	.044	0.049	0.047	0.050	0.046
Boric acid	6.34	6.38	6.12	------	------	------	------	------	------	------	------	------	------	------	12.50	2.36	------	3.72
Calcium carbonate	3.17	3.19	3.06	------	------	------	------	------	------	------	------	------	.96	------	------	------	------	------
Cryolite	------	------	------	------	------	------	------	12.28	12.56	11.44	16.51	15.24	12.28	11.17	12.50	11.98	12.68	11.80
Kaolin	------	------	------	------	------	------	------	8.98	9.20	8.38	------	------	8.98	8.18	9.14	8.76	9.28	8.64
Magnesium carbonate	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
Phosphoric acid	------	------	------	------	------	------	------	------	------	------	------	------	------	8.96	------	------	------	------
Barium carbonate	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------
Sodium carbonate	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	3.74	------
Calcium antimonate	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------	------

Raw mix—Continued

	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Silica sand	7.61	17.98	13.22	11.25	12.40	11.85	12.20	12.58	11.28	11.51	11.88	11.88	11.77	13.39	11.80	11.25	11.00	2.25
Dehydrated borax	25.00	22.10	24.00	22.20	24.45	23.37	24.08	24.80	22.21	22.70	23.40	23.40	23.21	26.40	23.28	22.20	21.70	16.10
Feldspar	7.10	6.30	6.83	6.30	6.95	6.64	6.83	7.04	6.31	6.44	6.66	6.66	6.60	7.50	6.61	6.31	6.16	21.25
Zircon sand	20.50	18.20	19.72	18.23	20.10	19.21	19.78	20.38	18.26	18.64	19.25	19.25	19.07	21.69	19.11	18.25	17.82	16.43
Sodium nitrate	1.17	1.04	1.13	1.04	1.14	1.09	1.12	1.16	1.04	1.06	1.09	1.09	1.08	1.23	1.09	1.04	1.01	0.97
Fluorspar	7.76	6.88	7.44	6.90	7.76	7.42	7.47	3.54	13.52	7.04	7.28	7.28	7.21	8.19	7.22	6.90	6.73	3.86
Sodium fluosilicate																		13.85
Bone ash	5.63	5.00	5.42	5.00	5.51	5.27	------	5.58	5.00	5.11	2.33	4.32	5.23	5.94	5.24	------	4.88	4.51
Aluminum hydrate				6.76														
Zinc oxide	2.84	2.52	2.77	2.52	------	4.22	2.73	2.82	2.52	2.58	2.66	2.66	2.64	3.00	2.65	2.54	2.46	4.19
Titanium dioxide																		2.35
Manganese dioxide	0.05	0.045	.048	.045	0.049	0.047	0.049	0.050	0.045	0.046	.047	.047	.042	0.050	0.050	0.045	0.044	0.04
Boric acid																		
Calcium carbonate																		5.99
Cryolite										4.60								2.90
Kaolin	12.89	11.42	12.37	11.43	12.60	12.05	12.40	12.78	11.45	11.70	12.05	12.05	11.95	2.67	14.17	11.44	11.18	
Magnesium carbonate	9.43	8.37	6.83	8.38	9.22	8.82	9.08	9.35	8.38	8.56	8.85	8.85	8.78	9.96	8.78	8.38	8.18	------
Phosphoric acid							4.33									7.66	8.80	------
Barium carbonate											2.47	.76				4.04		------
Sodium carbonate											1.99	1.85	2.35					------
Calcium antimonate																		4.84

Calculated oxide content

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
SiO_2	29.10	29.23	28.01	30.57	30.75	29.10	28.73	26.72	27.30	24.96	30.33	28.08	26.84	25.32	28.75	26.30	28.30	26.40
ZrO_2	11.91	11.50	15.14	12.50	11.95	19.07	17.80	12.71	10.69	18.48	12.71	19.25	12.86	12.13	13.75	12.60	13.54	12.65
B_2O_3	15.15	15.22	14.60	12.11	12.18	11.05	11.38	16.10	16.45	15.04	12.33	11.41	16.20	15.28	13.73	15.83	12.13	18.04
Na_2O	11.15	11.20	10.75	11.72	11.70	10.70	11.02	13.05	13.34	12.20	13.32	12.33	13.12	12.38	9.46	14.22	13.82	12.90
K_2O	2.30	2.31	2.22	2.42	2.43	2.20	2.27	.66	.67	.62	1.07	0.99	0.66	.62	0.71	0.65	0.70	0.65
CaO	7.43	7.47	7.16	5.92	5.96	5.40	5.57	8.02	8.20	7.50	6.03	5.58	8.05	7.60	8.65	7.93	8.46	7.90
Al_2O_3	7.05	7.09	6.80	7.42	7.46	6.77	6.98	7.58	7.75	7.08	7.54	6.97	7.63	7.20	8.16	7.49	8.03	7.50
ZnO	2.45	2.46	2.36	2.58	2.60	2.35	2.43	2.60	2.66	2.43	2.63	2.43	2.65	2.50	2.84	2.60	2.80	2.61
F_2	11.11	11.17	10.71	11.68	11.73	10.63	10.96	10.02	10.20	9.38	10.89	10.08	10.08	9.49	10.80	9.93	10.61	9.30
P_2O_5	2.23	2.24	2.15	2.35	2.36	2.14	2.21	2.40	2.45	2.24	2.39	2.21	1.92	7.50	2.56	2.34	2.54	2.37
TiO_2	0	0	0	0.78	.784	.71	.73	0	0	0	0.79	0.73	0	0				
MnO_2	.091	.092	.088	0	0	0	------	0.06	0.061	.056	0	------	.047	.044	0.05	0.05	0.050	0.046
BaO																		
MgO																		
Sb_2O_5																		

	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
SiO_2	23.00	31.50	27.00	25.58	27.42	26.30	27.47	28.08	24.67	25.04	26.72	26.51	26.24	30.30	26.05	26.42	25.60	27.20
ZrO_2	13.40	11.95	12.92	12.25	13.13	12.60	13.16	13.43	11.82	12.01	12.80	12.70	12.58	14.52	12.48	12.68	12.26	11.17
B_2O_3	16.82	15.00	16.25	15.40	16.50	15.84	16.58	16.93	14.90	15.13	16.10	16.00	15.82	18.30	15.71	15.93	15.42	14.72
Na_2O	13.70	12.20	13.15	12.50	13.40	12.85	13.42	13.71	12.05	12.24	13.05	12.95	12.83	9.92	13.67	12.90	12.50	10.69
K_2O	0.69	0.62	.67	.63	.68	.64	0.68	0.69	0.61	0.62	0.66	0.66	0.65	0.75	0.64	0.65	0.63	2.16
CaO	8.43	7.50	8.10	7.68	8.23	7.88	5.31	5.46	11.98	10.39	6.43	7.44	7.88	9.10	7.80	5.21	7.78	7.67
Al_2O_3	7.95	7.08	6.78	11.62	7.78	7.57	7.80	7.97	7.01	7.12	7.58	7.52	7.45	5.96	7.91	7.50	7.26	6.78
ZnO	2.76	2.46	2.65	2.49	0	4.15	2.71	2.77	2.44	2.48	2.60	2.58	2.55	3.00	2.57	2.57	2.49	2.29
F_2	10.55	9.40	10.12	9.59	10.28	9.87	10.30	8.52	12.38	12.56	10.02	9.94	9.84	5.45	10.92	9.92	9.60	10.44
P_2O_5	2.49	2.22	2.44	2.30	2.46	2.35	2.61	2.66	2.21	2.40	2.40	2.38	2.35	2.72	2.33	2.37	2.30	2.10
TiO_2																		0.65
MnO_2	0.05	0.04	.046	.044	.048	.046	0.048	0.050	.046	.046	.046	.046	.045	0.050	0.050	0.046	0.044	
BaO											1.63	1.41	1.80					
MgO																3.79	4.32	
Sb_2O_5																		4.18

Ratios of three critical components

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
P_2O_5	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Na_2O	5	5	5	4.99	4.96	5	5.22	5.44	5.44	5.44	5.57	5.58	6.83	1.65
ZrO_2	5.34	5.14	7.04	5.32	5.06	8.90	8.43	5.39	4.36	8.24	5.32	8.70	6.69	1.62

Now referring to the calculated oxide content as given in Table I, we have the following comments as to the ranges given for each of the components.

With regard to the silica (SiO_2) content, attention is directed to Fig. 8. From an inspection of the actual enamels produced, as well as the values given in Fig. 8, it has been found that in the lower silica range, that is from about 23% to about 26%, the enamels have a fairly high opacity although there is a tendency to produce matte surfaces. In the intermediate range, that is from about 26% to about 33%, the enamels are characterized by good surface and best opacity. In the upper end of the range, that is, above 33%, the surface and gloss characteristics increase at a sacrifice of reflectance. It may be observed that example 19 of Table III gives the low silica content and example 20 gives an example of near the upper limit of silica content.

The effect of varying boric oxide (B_2O_3) is given in Fig. 7. The low end of the range is determined largely by the tendency of the enamel to fail to produce a fully vitreous surface. This is sometimes referred to as the tendency of the enamel to "scum." The upper range of B_2O_3 is determined by the fact that the enamel becomes matte on the surface and also has increased water solubility. The production of the matte surface following the use of too large a percentage of B_2O_3 may be a devitrification. By referring to Table III it will be found that specific example 17 is representative of the low end of the B_2O_3 range and specific example 19 is representative of the upper end of the B_2O_3 range.

The effect of varying alumina (Al_2O_3) is shown

in Fig. 9 and from the curve there given, as well as from actual observation of the enamels produced, it may be noted that when the alumina is dropped to very much below the low range specified the enamel has a tendency to tear, and as the upper end of the range is approached or passed the enamel tends to produce a matte finish. The range specified in Table I is the range within which best reflectance was observed. Specific example 21 is representative of the enamel having an alumina content near the low end of the range and specific example 22 is representative of the upper end of such a range.

It is economically desirable to omit zinc oxide from enamels if at all possible. The addition of zinc oxide must therefore be justified, and while the addition of up to about 4% has produced a slight increase in opacity as is shown by Fig. 10 with good surfaces maintained throughout the range, the enamels in the low zinc oxide range will be found to give best results when the zinc oxide is replaced with an equal weight of alumina (Al_2O_3).

Example 23 of Table III is an example of an enamel which contains no zinc oxide and specific example 24 shows an enamel containing zinc oxide near the upper end of the range.

The effect of varying titanium dioxide (TiO_2) has not been shown by any chart. Titanium dioxide is added to this class of enamels to control color when desired. It is not necessary in most enamels of this class and it will be noted that when too high a concentration is used the enamel has a tendency to be yellowish.

The same comments made in connection with titanium dioxide apply equally to manganese oxide. However, when too large an amount of manganese oxide is used the enamel turns pink.

Barium oxide may be used in enamels of this character for the purpose of softening the same if this should be desired. By referring to Figs. 13 and 14 it will be noted that as the barium oxide is increased opacity falls off sharply. Fig. 14 shows the effect of barium oxide in replacing calcium oxide in these glasses. The solid line shows a weight for weight replacement of barium oxide for calcium oxide, and it will be noted that the reflectance drops off rapidly when more than 2% barium oxide has been added. The dotted lines of the same figure shows the effect of molecular replacement with barium oxide for calcium oxide and the drop in reflectance is even more rapid than in the previous case. Fig. 13 shows the direct addition of barium oxide to enamels of this type and it is observed that the reflectance is lowered tremendously. This would preclude the use of barium oxile except when it is used as a replacement material for calcium oxide. Specific examples 29, 30 and 31 are enamels which show these three types of substitution.

Fig. 16 should be referred to in studying the effect of the addition of magnesium oxide. Magnesium oxide should be expected to increase opacity. However, when added to the enamels in the form of magnesium carbonate ($MgCO_3$) a tendency to produce matte finishes results. Fig. 16 shows the reflectance change caused by the addition of magnesium oxide. The dotted line shows direct addition of magnesium oxide to this type of enamel (added as magnesium carbonate). It is seen that the reflectance increases slightly with this addition. The solid line which shows less increase in reflectance is based upon a molecular substitution of magnesium oxide for calcium oxide. Specific examples 34 and 35 of Table III may be referred to for enamels containing in both cases magnesium oxide near the upper limit of the range given.

No chart has been drawn showing the effect of the addition of various amounts of antimony oxide on the opacity of the enamels of the character to which this invention relates. However, it has now been found that amounts up to 5% of antimony oxide may be added (see specific example No. 36 for an enamel of this character) without impairment of the reflectance. Ordinarily antimony need not be added as an intentional raw batch constituent. However, the importance of the data on this material relates to the possible inclusion of antimony in cases where reclaimed enamel is melted as a part of the raw batch composition. In other words, it has been found that the enamels of our invention can tolerate up to as high as 5% of antimony when it thus finds its way into the smelt. In studying the effect of the presence of antimony, i. e., in producing specific example No. 36, antimony was intentionally added to the smelter in the form of calcium antimonate. It should be observed, however, that when antimony is present in the composition the sodium content of the enamel should be maintained as low as possible within the ranges above given.

No chart has been given for the effect of variations on the opacity by variations in the amount of fluorine present in the smelt. The low fluorine enamels were obtained by use of lower amounts of cryolite and can thus be more clearly discussed later under this raw material. The normal fluorine range for enamels of this type, from about 5% to about 13%, can be obtained by the use of either fluorspar, sodium fluosilicate or sodium aluminum fluoride (cryolite). The two latter raw materials are more or less interchangeable by making correct molecular substitutes. The normal enamels of this series will in general contain fluorine near the upper end of this range.

The main function of fluorine (fluorides) is to act as a flux and produce enamels of low enough melting temperature to be useful commercially. According to some authorities, fluorine also affects the opacity and it is generally thought that the higher the fluoride content the higher the opacity.

For the effect on reflectance or opacity of various amounts of calcium oxide, reference may be had to Fig. 11. The curve of Fig. 11 shows that as the calcium oxide content is increased from zero there is a more or less progressive increase in the amount of reflectance in the enamel until the upper range of 12%, given in Table I, is reached. Amounts of calcium oxide above 12% produce no appreciable increase in the amount of reflectance and are further accompanied by a hardening of the glass. It may be observed that as the upper end of the range for calcium oxide is approached the enamel has a tendency to produce a matte surface. Reference may be had to specific examples Nos. 25 and 28 which are respectively examples near the low and high ends of calcium oxide range given in Table I.

The effect of sodium and potassium may be conveniently considered together if for no other reason than each may be employed in total or partial substitution for the other. The effect of varying the amount of sodium is strikingly illustrated in Fig. 6. Sodium is present in most commercial enamels of the type to which this invention relates because sodium borate (borax) is

the normal source of the B_2O_3 radicle, also soda and potash both are contained in feldspar which is one of the most generally used commercial sources of alumina. Sodium nitrate is also selected as an oxidizing material in the enamel batches because of its cheapness, and the two fluorides which are used to contribute most of the fluorine to this type of enamel, namely cryolite and sodium fluosilicate, both contain high percentages of sodium oxide. For these reasons no data on commercial glasses with less than about 8% sodium oxide are given in Fig. 6, and such amount represents the minimum necessary in order to include in the composition the material with which it is combined in the raw materials available. The curve above about 8% shows, however, that if the soda content of the composition is raised intentionally or by lack of careful control of the selection of raw materials used, the reflectance drops off very rapidly. It is for this reason that the amount of soda included in the composition should for best results be not greater than about 14%. If it should be possible to secure raw materials which could cheaply contribute the other components of the composition above identified with which soda is usually associated in the raw materials presently available, and if it were possible to omit soda completely or to reduce it to a very small percentage, this would be a desirable improvement. The range of soda has, therefore, been given as extending to not more than about 14%.

The comments made above with respect to soda apply also to potassium oxide when the two elements are treated on a molecular equivalency basis. Thus it is highly desirable to keep the mono-basic metal oxide content of the enamel as low as possible, that is, as low as feasible in view of commercial considerations.

As previously indicated, the enamels of the present invention are all characterized by the combined presence therein and the cooperative effect between ZrO_2 and phosphorus which is conveniently present in the form of P_2O_5. As likewise previously indicated, the chart of Fig. 1 shows the effect of varying the zirconia content of an enamel which has a basic composition similar to specific example 1. In other words, the various points which were determined and which fixed the curve of Fig. 1 were arrived at by holding constant the values for all of the other components of specific example 1 and varying only the amount of zirconia. This was accomplished by varying the amount of zircon sand and at the same time varying the amount of silica sand so as to maintain in the composition a substantially constant amount of silica. Fig. 3 similarly shows the effect of variations in the amount of zirconia in the basic formula as represented by specific example No. 4, and in arriving at the various points which determine the curve of Fig. 3 all of the raw batch components with the exception of zircon sand and silica were held constant. Zircon sand was varied to yield various amounts of zirconia, and the silica sand was varied so as to maintain a substantial amount of silica in the composition. The results given in Figs. 1 and 3 have been verified by other data, not shown, in which the raw batch constituents were all held constant with the exception of variations in the amount of pure zirconia added to the smelter. Inasmuch as zirconia is available in the enamel more economically as zircon sand, it was felt desirable to base the data herein on variations in the amount of zircon sand.

Various commercial and political considerations may make one or the other of cryolite or sodium fluosilicate the most economical to use, hence it was felt desirable to give data in the case where sodium fluosilicate was used and a corresponding curve where cryolite was used in substitution for sodium fluosilicate. Fig. 1, it will be observed by having reference to specific example 1, is based on enamels containing sodium fluosilicate. Fig. 2, as previously indicated, is based on a comparable composition (see specific example 8) in which sodium fluosilicate was substituted by cryolite. Similarly, the chart of Fig. 3 is based on an enamel containing sodium fluosilicate (see specific example 4) and for a comparison Fig. 4 is based on an enamel (see specific example 11) in which sodium fluosilicate is substituted by cryolite. The effect of zirconia as an opacifier, both in the form of a smelter addition as well as a mill addition, has been under investigation by workers in the art for many years. Hartmann thirty years ago explored the use of zirconia in concentrations up to more than 20% as an opacifier in conventional enamels. The use of zirconia by itself has, however, been accompanied by certain difficulties, which difficulties are becoming increasingly acute according to the increasingly rigid requirement to which porcelain enamels are subjected. While a zirconia opacified enamel as produced by Hartmann was satisfactory in meeting the requirements of enamels thirty years ago, such requirements can no longer be met by the use of zirconia alone. It may be observed that about 1910 Hartmann proposed enamels containing approximately 15% zirconia (see Grunwald's "The Raw Materials for the Enamel Industry and Their Chemical Technology," Charles Griffin & Co. Ltd., London, 1914, page 129), and other workers in the art (see, for example Kinzie Patents Nos. 1,848,567 and 1,944,936), have proposed using zirconia in amounts of about 15%. These enamels judged by present day rigid standards, however, are not entirely satisfactory and our invention is therefore concerned with the combined use with such zirconia bearing enamels of substantial amounts of phosphorus which is conveniently present in the composition in the form of P_2O_5.

By having reference to Fig. 5, the powerful cooperative effect of P_2O_5 on the opacity of the enamel will be observed. At this point it may be well to mention that all of the other enamels, that is, the enamels on which the other charts of the several figures were based, all contained the zirconia phosphorus combination.

This was felt desirable because it is only possible to secure consistent results in zirconia bearing enamels when the zirconia phosphorus combination is used.

At this point we should explain that the curves of Figs. 5 to 16 were all determined by first selecting a particular enamel having a composition of specific example 8 of Table III and varying only that component the effect of whose variation on the opacity is shown in a particular curve. This variation was achieved variously by a change in those raw batch components which contribute the variable to the smelt. It is believed that from an inspection of the various specific examples given it can readily be determined by those skilled in the art the manner in which variations were made in the raw batch composition in order to effect the required variation in the calculated oxide content in order to

produce the variations represented by the several curves. In other words, specific examples 1 to 35 are representative of a vary large number of smelts which were made up in determining the points on the various charts or figures which determine the curves thereon. Specific examples 1 to 12 represent various smelts in which changes were made in the zirconia content and specific examples 13 to 35 represent smelts made holding the zirconia substantially constant and varying certain other components. Attention is directed to the bottom of Table III where a series of figures are given for each of specific examples 1 to 14 indicating the proportional relationship between the amounts of P_2O_5, sodium oxide and zirconia present in the calculated oxide composition of such specific examples. It was felt unnecessary to include in the table the proportional relationship which exists between these three critical elements in the remaining specific examples. That information can be determined readily from the values given in the table.

The reflectance values for the 36 specific examples given in Table III are available but it is believed that such information instead of being included in Table III can be much more intelligently studied if reference is had to the several charts in the drawings. In other words, the reflectance values if entered on Table III would give only single points on the curve whereas by having reference to the charts themselves the full picture of the effect on reflectance of the particular component may be more readily determined.

In Table I certain components have been indicated as being permissibly absent. It is believed that the previous discussion of the effect on reflectance of variations in each of such components has explained the reason why Table I indicates the permissible absence of certain of such components.

Now with respect to Table II, it will be observed that the same indicates the permissible absence of a rather large percentage of the available raw materials, and with respect to that table the following comments may be observed.

Silica sand may be omitted entirely if there is included in the composition other silica bearing materials which will supply in the calculated oxide content of the resultant smelt the 23% minimum of Table I. Sources of silica may be zircon sand, sodium fluosilicate, kaolin and feldspar. This manner of varying the raw batch mixtures in making available a particular component of the calculated oxide content from various sources is common practice and well known to those familiar with the art.

While zircon sand is specifically mentioned as one of the raw materials, it is well known that other sources of zirconia may be substituted for the zircon sand. Such possible sources include pure zirconia and baddeleyite, a crude zirconium oxide which may soon become available in this country in commercial quantities. Sodium zirconium silicate and other compounds of a similar nature may also be substituted in place of the zircon sand.

The partial or complete substitution one for the other of sodium fluosilicate and cryolite has already been explained.

Bone ash is used as the source of P_2O_5 in the smelt. At this point it may be well to state that throughout this specification where reference has been made to phosphorus, it is of course understood that reference to the oxide was intended, since phosphorus will not occur in its pure state in the smelt. Instead of bone ash any other available source of phosphorus may be used, even to the point of using pure phosphoric acid, although phosphoric acid will be found uneconomical in view of the more economically available raw materials like bone ash which can contribute phosphorus.

In adding alumina to these enamels, feldspar is generally considered as the principal source, and the permissible maximum of feldspar is determined by the alkali content thereof. After as much feldspar as is possible has been added, the remainder of the alumina is added in the form of kaolin unless the total amount of kaolin required to contribute the remaining alumina would raise the silica content too high, in which latter event the necessary deficiency in alumina can be contributed by the addition of aluminum hydrate. Since cryolite is also a source of alumina, those enamels which employ cryolite may not require the addition of any aluminum hydrate in order to supply the required minimum of Al_2O_3 in the calculated oxide content as given in Table I.

The total omission of zinc oxide from the enamel and its replacement with an equal weight of alumina has already been discussed so that further reference to the omission of zinc oxide is believed unnecessary. The same is true with respect to titanium dioxide and manganese dioxide.

Boric acid is quite expensive and need be added only to soften the enamel in cases of hard enamel which require to be softened and which hard enamel already contains the maximum permissible amount of sodium which is usually relied upon to provide the softening effect for which boric acid is used.

Calcium carbonate is used only as an auxiliary source of calcium where the other raw materials added to the smelt are not sufficiently high in calcium to provide that amount desired in the enamel. Since Table I shows that calcium oxide may be omitted entirely from the enamel, it is obvious that calcium carbonate may likewise be omitted entirely from the raw batch mixture.

Kaolin is, as previously indicated, employed as an auxiliary source of alumina to the extent that the maximum silica content of the smelt permits. If the other alumina containing raw materials provide sufficient of that component, then kaolin is not required.

Magnesium carbonate, barium carbonate and sodium carbonate are added only if for some reason the corresponding oxide should be desired. Reference to the discussion of the effect of such corresponding oxides, previously given, may be had for a full understanding of the reasons why these three carbonates may be omitted entirely from the raw batch mixture.

Phosphoric acid is mentioned as a possible raw batch constituent. However, as previously indicated, since bone ash is a more economical source of phosphorus, the latter will usually be employed and phosphoric acid omitted entirely.

Fig. 12 shows the important effect of fluorspar (CaF_2) on the reflectance of this type of enamel. Fluorspar is used as the basic source of fluorides and as much of it as possible is usually employed without producing an enamel of too high a firing temperature. It will be noted that the reflectance increases with increase in the percentage of fluorspar. On comparing this curve with Fig. 11, which refers to the effect of variable calcium

oxide content, the importance of fluorine in producing opacity is quite obvious.

Reference to Fig. 15, which shows the effect of variable sodium aluminum fluoride or cryolite on reflectance, is of interest because of the definite peak that is obtained. At less than 2% cryolite the reflectance is low, undoubtedly due to the low fluorine content of the enamel. From 2% to 12% cryolite the reflectance is high and enamels of excellent surface are obtained. When the cryolite percentage becomes greater than 14% the reflectance is appreciably lower and this is undoubtedly caused by the fact that while we are adding appreciable quantities of fluorine we are also adding large quantities of sodium oxide which has a stronger deopacifying effect than fluorine has an opacifying effect.

All of the charts, i. e. Figs. 5 to 16, have, as previously indicated, been based on enamels which have the basic formula of specific Example 8 and are characterized by the combined presence within the desirable proportional relationship of this invention of phosphorus and zirconia. Other data, which it is believed unnecessary to include in this description, shows that the various curves which have been given for modifications in the specific composition of Example 8 are representative of results which would be secured from similar modifications in other compositions falling within the broad range of our invention. A considerable number of smelts have been made and the reflectances thereof determined where the phosphorus component was omitted and zirconia used without the auxiliary effect thereon of the phosphorus. Such enamels have two pronounced characteristics different from those of our invention. In the first place, the auxiliary effect of phosphorus definitely increases the opacifying effect of zirconia with which it is combined and accordingly the phosphorus containing enamels have a uniformly higher reflectance than those enamels containing the same amount of zirconia and from which the phosphorus has been omitted. The second principal characteristic of the phosphorus-free zirconia bearing enamels is their lack of uniformity with respect to reflectance which may be due in a measure to their apparent extreme sensitivity to the conditions under which they are smelted. An attempt was made to correlate the data obtained on a large number of smelts of phosphorus-free zirconia containing enamels in order to show a curve indicative of the variation in reflectance due to variations in the zirconia content. All of these smelts were made under most carefully controlled conditions by the same worker and in the same equipment. As a matter of fact, the same careful control of conditions in the manufacture of these phosphorus-free enamels was observed as in the phosphorus containing enamels as to which the reflectance curves are given herein. A variation of not more than 4% in reflectance is permitted between separate smelts if they are to be considered as check results. In the preparation of the very large number of smelts of the phosphorus containing enamels which were prepared in compiling the data given by the curves of the figures herein, as many as twenty-six smelts of the same composition were manufactured and in those twenty-six smelts the total variation in observed reflectance was within the 4% limit above given. However, in the manufacture under identical conditions and with the same degree of control the reflectance of the phosphorus-free enamels varied so widely that it was impossible to draw a single curve representative of the reflectances which might be secured over a range of concentration of zirconia in the absence of phosphorus. In connection with this comparative work, two series of smelts under identical conditions in the same apparatus by the same worker showed differences in observed reflectance of as great as 10%. For this reason no attempt has been made to include in the figures a curve which is representative of the effect of zirconia in varying proportions when used without the auxiliary amount of phosphorus.

Zirconium enamels generally, of which those of our present invention are representative, generally have the characteristic of developing opacity by the formation of a crystalline phase in a glass matrix, which crystalline phase has a different index of refraction than the matrix, and accordingly impart opacity thereto. As smelted, these enamels are relatively clear and the development of this crystalline phase occurs during the fusion of the enamel on the work. We have now discovered that by annealing the enamel after smelting and while it is in a semi-viscous or solid state and prior to its application to the work the ultimate opacity developed by the enamel during the fusion thereof to the work may be materially increased. We believe that this discovery that the ultimate reflectance or opacity of the enamel may be thus increased by annealing the same at a temperature where the enamel is not flowable, is new with us. The enamel, after smelting, may be annealed prior to fritting, or the conventional frit may be annealed. We have successfully annealed enamels of this character in a temperature range of from about 1100° F. to about 1400° F. in time intervals which vary largely due to the condition of the enamel glass prior to heating. If the enamel glass is in the form of cold frit, a longer time will be required than when the annealing period starts upon a reduction in temperature of the enamel glass from a higher temperature to the annealing temperature range.

The annealing of the enamel glass, as indicated, makes possible the attainment of a higher ultimate reflectance in the enamel as fused on the work than when such annealing step is not employed. Accordingly, by the employment of such annealing step the same ultimate reflectance may be achieved by the use of cheaper materials, thinner weights of application and lesser amounts of opacifier mill additions. It is also possible to achieve the desired reflectance in furnaces which fuse the enamel on the work in such a short length of time that without preannealing the necessary opacity could not be obtained.

It is within the contemplation of our invention to pour the enamel glass from the smelter and instead of immediately fritting the same by projecting the stream into a water bath, to roll the stream into a thin sheet much as in the process used for the manufacture of sheet glass. The rolled sheet is then passed through a furnace or annealing chamber where it may be maintained at an annealing temperature for a period which may vary from about ½ to 5 minutes. After the sheet issues from the annealing chamber it may be conveniently broken up by the projection thereagainst of a high velocity stream of water or steam or by the immediate projection of the sheet into a cold water bath. When a high velocity stream of water is employed as the fritting means, and particularly when such

stream is in finely divided form, the amount thereof may be so regulated that it will be just sufficient to cause the necessary fracture of the glass sheet at the same time that the water is all evaporated by the heat of the glass sheet so that the shattered sheet or frit is substantially dry. The temperature of the glass at which the stream of water is projected thereagainst for best results will be on the order of about 800° F., i. e., the glass will be sufficiently hot to properly shatter and at the same time sufficiently cool so that it is in a non-plastic state.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

We, therefore, particularly point out and distinctly claim as our invention:

1. The method of making a porcelain enamelled article having an opaque coating which comprises smelting a raw batch mixture of porcelain enamel forming ingredients characterized by being able to yield from the smelt a frit containing from about 10% to about 20% ZrO_2 and from about 1.00% to about 7.50% of P_2O_5 based on the total weight of the frit, milling a slip containing said frit, coating the ware with said slip, and burning the same to yield said opaque surface.

2. An opaque vitreous enamel characterized by high reflectance and containing about:

	Per cent
ZrO_2	From 10.00 to 20.00
P_2O_5	From 1.00 to 7.50

based on the total weight of the enamel.

3. An opaque vitreous enamel characterized by high reflectance and having a mono-basic metal oxide content based on the total weight of the enamel of not more than about 14.00% and containing about:

	Per cent
ZrO_2	From 10.00 to 20.00
P_2O_5	From 1.00 to 7.50

based on the total weight of the enamel.

4. An opaque vitreous enamel characterized by high reflectance and containing about:

	Per cent
ZrO_2	From 10.00 to 20.00
P_2O_5	From 1.00 to 7.50
SiO_2	From 23.00 to 35.00
B_2O_3	From 10.00 to 20.00
Al_2O_3	From 5.50 to 12.00
F_2	From 5.00 to 13.00

based on the total weight of the enamel.

5. An opaque vitreous enamel characterized by high reflectance and having a mono-basic metal oxide content of not more than about 14.00% based on the total weight of the enamel and containing about:

	Per cent
ZrO_2	From 10.00 to 20.00
P_2O_5	From 1.00 to 7.50
SiO_2	From 23.00 to 35.00
B_2O_3	From 10.00 to 20.00
Al_2O_3	From 5.50 to 12.00
F_2	From 5.00 to 13.00

based on the total weight of the enamel.

6. An opaque vitreous enamel of high reflectance characterized by the presence of about:

	Per cent
ZrO_2	From 10.00 to 20.00
P_2O_5	From 1.00 to 7.50

based on the total weight of the enamel and a mono-basic metal oxide content of approximately the same as the ZrO_2 content but not substantially in excess of about 14.00% based on the total weight of the enamel.

7. An opaque vitreous enamel of high reflectance characterized by the presence of about:

	Per cent
ZrO_2	From 10.00 to 20.00
P_2O_5	From 1.00 to 7.50

based on the total weight of the enamel and a mono-basic metal oxide content such that its proportional relationship to the ZrO_2 and P_2O_5 content is approximately:

P_2O_5	1
ZrO_2	5
Mono-basic metal oxide	5

based on the total weight of the enamel.

8. An opaque vitreous enamel of high reflectance comprising based on the total weight of the enamel from about 10% to about 20% ZrO_2 and P_2O_5 in an amount equal to about 20% of the amount of ZrO_2 present.

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