

1

3,114,646

SINGLE COAT PORCELAIN ENAMEL

Thomas E. Currie, Louisville, Ky., assignor to Foote Mineral Company, Berwyn, Pa., a corporation of Pennsylvania

No Drawing. Filed May 16, 1960, Ser. No. 29,160
14 Claims. (Cl. 106—48)

This invention relates to vitreous enamels, and more particularly, relates to a frit composition adapted for use as a vitreous enamel and to a vitreous enamel comprising this frit.

The largest market for vitreous enamels is the finishing of appliances such as kitchen appliances. This use requires that the enamel be highly opaque, white and glossy, so that it will produce an attractive finish.

In the enamel industry, opacity was at first achieved by introducing opacifiers into the mill batch separately from the enamel frit. Subsequently it was discovered that super opaque enamels could be made by using titania as a component of the frit. Titania-opacified enamel frits have been made which produce coatings of a satisfactory degree of whiteness and opacity.

However, such enamels generally require relatively high firing temperatures, above the critical point of steel, which is about 1300° F. When thin, light gauge sheet steels are fired at elevated temperatures, above about 1300° F., they tend to warp and buckle. Since reducing the gauge of sheet steels lowers their cost, manufacturers desire to have available super opaque enamels which have low firing temperatures and thus make possible the use of light gauge steels.

Various vitreous compositions have been available hitherto which have relatively low firing temperatures. Some of these are ceramic glazes. Because the coefficients of expansion of ceramics and of steels are considerably different, such glazes cannot be used to enamel steel. Others of these low firing enamels contain lead compounds. Because lead compounds are toxic, enamels containing them are hazardous and are not considered desirable for use for many purposes, such as the finishing of kitchen appliances and like products. Thus, satisfactory super-opaque enamels having low firing temperatures have not been available hitherto.

A further object of research in the enamel industry has been the production of a single coat, super opaque enamel. Such an enamel is specifically desired for use on light gauge sheet steels, where the cost of the product to be given an enamel finish is sought to be minimized as much as possible. Conventional enamelling procedure consists in applying a ground coat to the prepared sheet steel, firing this, then applying the white cover coat enamel, and finally firing this. The cost of enamelling a product would be very much reduced if instead there could be used a "direct on" enamel, that is, a vitreous super opaque enamel which could be applied directly to the prepared sheet steel as a cover coat, dispensing with any need for a ground coat. Especially desired by the industry is a "direct on" vitreous enamel having a low firing temperature.

It is an object of this invention to provide a novel enamel having a low firing temperature.

A particular object of this invention is to provide a novel frit composition free of lead compounds which is adapted for use as a vitreous super opaque steel enamel having a low firing temperature.

Another object is to provide a novel, lead-free super opaque steel enamel having a low firing temperature.

Another object is to provide a novel, lead-free super opaque enamel having a low firing temperature and adapted for "direct on" application to sheet steel.

2

These and other objects will become evident from a consideration of the following specification and claims.

The discovery has now been made that a frit composition adapted for use as a vitreous super opaque steel enamel having a low firing temperature and free of lead compounds can be made by formulating the frit so that the types of oxides included in the frit are present in substantially fixed molar ratios to one another.

The oxides included in the frit composition of this invention are as follows:

SiO₂
R₂O₃ (B₂O₃, Al₂O₃)
R₂O (Li₂O, Na₂O, K₂O)
RO (ZnO, SrO, MgO, CaO)
TiO₂

Additionally, the frit composition will contain fluorine.

I have now found that a frit of extraordinarily low melting point, well below the critical point of steel, is obtained when the molecular ratios of these frit components are substantially as follows:

Of SiO ₂ to R ₂ O ₃ (B ₂ O ₃ +Al ₂ O ₃)	1:1-3:2
Of B ₂ O ₃ to Al ₂ O ₃	5:1-9:1
Of SiO ₂ to R ₂ O (Li ₂ O+Na ₂ O+K ₂ O)	1:1-3:2
Of Li ₂ O to Na ₂ O	1:1-7:4
Of Li ₂ O to K ₂ O	1:1-7:5
Of R ₂ O to RO (ZnO+R'O, where R'O=either SrO or MgO+CaO)	2:1-3:1
Of ZnO to R'O	1:1-7:4
Of MgO to CaO	About 1:1
F, as CaF ₂	1-5 mol-percent of total
TiO ₂	12-15 mol-percent of total

I have further found that when the frit of this composition is formulated as an enamel in a mill batch comprising lithium molybdate, the enamel is adapted for "direct on" application to sheet steel.

The frit composition of this invention and enamels produced therefrom have many outstanding desirable characteristics. They are free of lead compounds, and thus non-toxic and non-hazardous. They are titania-opacified and super opaque, and although their titania content is quite low, compared to conventional enamels, they produce bright white finishes. The frit composition has an extremely low melting point, below about 1200° F. Enamels made from the frit can accordingly be fired at temperatures well below the critical point of steel. The enamels are therefore adapted for use on light gauge sheet steels, which are so thin that they would warp and deform if fired at the temperatures required by super opaque, lead-free enamels known hitherto.

When the mill batch in which the frit is formulated as an enamel comprises lithium molybdate, the resulting enamel has all of the above-stated advantages, and moreover, is adapted for "direct on" application to sheet steels. The necessity of providing a ground coat on the steel is thus obviated. A white, opaque enamel finish is obtained on the steel by a single application of the enamel to the steel surface and a single firing. Thus the process of providing an enamel finish on the steel is very much shortened, simplified and cheapened.

In my opinion, the fact that my novel frit composition gives enamels having low firing temperatures is due to the controlled molecular ratios of the oxide constituents of the frit to one another. It has been usual in the frit and vitreous enamel field hitherto to formulate frits in terms of the weight percent range to be observed for each constituent. This is essentially an empirical approach. I believe that there is a relation between the molecular ratios of the vitreous enamel components and the chemical and physical structure of the enamel. According to my research, specific advantages, particularly in re-

ducing the frit melting point, are found when the frit components are in the above-stated molecular ratios to one another.

In particular, it has been found especially advantageous to use substantially fixed molecular ratios as follows:

	Molecular ratio
SiO ₂ -----	10
R ₂ O ₃ (B ₂ O ₃ +Al ₂ O ₃)-----	10
B ₂ O ₃ :Al ₂ O ₃ -----	7:1
R ₂ O (Li ₂ O+Na ₂ O+K ₂ O)-----	10
Li ₂ O:Na ₂ O:K ₂ O -----	1:1:1
RO (SrO or MgO+CaO)-----	2
MgO:CaO -----	1:1
ZnO -----	2
F, as CaF ₂ -----	1
TiO ₂ -----	5

Nevertheless, a certain amount of deviation from the stated frit composition has been found to be permissible without so greatly altering the properties of the frit as to lose the advantages of this invention. It is essential only that the components of the frit be in substantially, and not necessarily precisely, the stated molecular ratios. Accordingly, in its broader aspects, this invention comprises the provision of a frit composition wherein the components are present within broader ranges, as herein disclosed.

The enamel frit composition of the invention will comprise, in terms of oxide analysis: silica (SiO₂); R₂O₃ oxides including B₂O₃ and Al₂O₃; R₂O oxides including Li₂O, Na₂O and K₂O; RO oxides including ZnO and either SrO or MgO and CaO; and titania (TiO₂). It will also include fluorine.

In terms of weight percent ranges, in its broader aspects, the frit composition of the invention will comprise silica in the range of from about 20 to about 30 weight percent.

The R₂O₃ oxide (B₂O₃ and Al₂O₃) content, considered as a whole, that is, as the total of the B₂O₃ and Al₂O₃ respective contents, will be in the range of from about 20 to about 25 weight percent. Further referring to the R₂O₃ oxide content, the ratio of the B₂O₃ content to the Al₂O₃ content will also be limited. Al₂O₃ will provide from about 10% to about 25% of the weight of the total R₂O₃ oxide content, made up of B₂O₃ and Al₂O₃ taken together.

Referring to the total R₂O oxide content (Li₂O, Na₂O and K₂O), this will provide from about 15 to about 25 weight percent of the frit composition. Of this total R₂O content, from about 10% to about 25% of the weight will be Li₂O, and from about 40% to about 60% of the weight will be K₂O. The remainder of the total R₂O oxide content of the frit composition will be Na₂O.

Coming now to the RO oxide content of the frit composition, at least two RO oxides will be included therein. One of these will be ZnO, and as to it, from about 1 to about 10 weight percent of the frit composition will be ZnO. The rest of the RO oxide content will be alkaline earth oxide, and will provide from about 5 to about 10 weight percent of the frit composition. The nature of this alkaline earth oxide content of the frit may vary. On the one hand, it may consist essentially of SrO. On the other hand, it may consist of a mixture of CaO and MgO. The use of CaO in substantial amounts in frits is generally limited, because if P₂O₅ is also present, the two can combine to precipitate a calcium phosphate from the enamel. Where P₂O₅ is absent, as in the present frit, CaO can be used as a substitute for SrO, in admixture with MgO. Use of a CaO-MgO mixture is advantageous in that these divalent oxides are substantially cheaper than SrO, and also because CaO promotes fluidity of the melt, while MgO promotes a blue-white color in the enamel, as compared to the cream white produced by SrO or CaO. MgO,

however, tends to lower the coefficient of thermal expansion of the frit, and the amount used thereof will be limited so that it will provide from about 20% to about 50% by weight of the MgO and CaO content of the frit.

Referring to the fluorine content of the frit composition, expressed as CaF₂, this will provide from about 2 to about 5 wt.-percent of the frit composition. As pointed out hereinafter, the fluorine may alternatively be introduced into the frit as some other compound, such as sodium fluoride. In such case, an equivalent amount of the selected fluoride compound will be used to supply a molar equivalent of fluorine to that provided by the stated amount of calcium fluoride. Where the fluorine is introduced as calcium fluoride, it is to be understood that the calcium introduced into the frit composition thereby is not to be considered as contributing to the calcium oxide content of the frit in the oxide analysis thereof, as referred to above.

The enamels of the present invention are titania-opacified, that is, the high opacity provided in the enamels prepared from the present frit compositions is due to the precipitation of titania during the enamelling operation. The titania is an integral part of the frit, dissolved therein, and is not incorporated with the frit as an additive during milling. To provide the high opacity mentioned above for the present enamel compositions, the TiO₂ content will provide between about 10 and about 18 wt.-percent of the frit composition. This is a relatively low titania content for a super opaque enamel, which is advantageous in view of the high cost of titania compared to other frit components.

As stated above, it is believed that the molar ratios of the oxide components of the present frit compositions to one another are of controlling significance in producing the desirable properties attained by this invention. It is therefore to be understood in considering the ranges of weight percentages stated in the preceding paragraphs that the preferred amounts of each constituent are to be selected with reference to the molar ratio thereof to the other components of the frit, desirably to approach as closely as possible to the specific molar ratios stated hereinabove.

The enamel frit composition of the present invention will consist essentially of the constituents discussed above, in the stated amounts. This does not mean, however, that small amounts of other materials not deleteriously altering the advantageous characteristics of the enamel are excluded. For example, small amounts, such as amounts up to about 1% by weight, of compounds such as Sb₂O₃, Sb₂O₅, BaO and the like can be included without significantly detracting from the desirable properties of the enamel.

The compositional ranges and amounts referred to above are in terms of percent by weight, and refer to the proportions of the constituents in the frit and not to the composition of the final enamel inasmuch as these may be altered somewhat due to the addition of certain compounds to the frit in making up the enamel coating composition.

The composition, in the form of a frit, having the above-described chemical composition, may be prepared in accordance with conventional practice. As is well known, in preparing the frit, compounds ultimately providing the desired oxide analysis—in the present case providing the above-described oxide analysis—are mixed together in fine particle size and melted, and the molten mass quickly cooled, as by water-quenching, and dried. Compounds which may be employed to provide the above chemical oxide analysis are well known in the art, and the provision of the above-described oxide analysis will present no problem to those skilled in the vitreous enamel art. SiO₂ may be provided by silica itself or by appropriate silicates, such as sodium silicates or minerals containing silica as well as one or more of the desired constituents. The B₂O₃ may be provided by borates, such

as borax, boric acid, and the like. The Al_2O_3 may be provided by alumina itself, by a mineral like bauxite, or by a mineral also supplying one or more of the other constituents required to make up the desired oxide analysis. The alkali metal oxides may be supplied by various compounds, including compounds of the alkali metal with other desired constituents and compounds which decompose at the frit melting temperature to yield the alkali metal compounds. Thus for example, they may be provided by carbonates, nitrates, minerals and the like such as lithium carbonate, lithium nitrate, sodium carbonate, borax, potassium carbonate and the like. The divalent oxides including ZnO , SrO , MgO and CaO may be provided by suitable salts, such as carbonates, or the oxides themselves may be used. The fluorine will preferably be provided as calcium fluoride. It may alternatively, however, be supplied by any of the alkali metal fluorides, such as sodium fluoride, lithium fluoride, and the like, and more complex fluorides, for instance sodium silicofluoride, and the like. It will be understood, of course, that during melting in the preparation of the frit, a certain amount of fluorine is lost due to volatilization, the exact amount depending upon the fritting procedure followed. The amount of the source of fluorine, therefore, will be selected to provide a theoretical fluorine content in the frit as specified above, corresponding to the stated amount of fluorine expressed as calcium fluoride. The titania is normally provided by titania itself. In all cases, one compound may provide more than one of the above-mentioned frit constituents: for example, borax may be relied on to provide Na_2O and B_2O_3 . In any event, the compounds will be selected in accordance with well known practice to provide the proper oxide analysis, and in the event such compounds contain a constituent not desired in the ultimate frit, such constituent will be of a volatile nature so that it may be removed during heating and melting of the mixture. For example, where carbonates are employed, carbon dioxide is liberated.

The materials, in fine particle size, providing the desired chemical analysis upon heating and melting thereof, are mixed together in accordance with common practice, and heated to an elevated temperature to provide a molten, pourable mass. With the compositions of the present invention, temperatures in the neighborhood of from about 1800°F . to about 2150°F . may be employed to provide the molten mass. The molten mass is then quickly chilled, such as by pouring it into a water bath, and such quick chilling causes the glass-like mass to fracture into small pieces. These small pieces are recovered and dried.

The resulting frit is too coarse for direct use as an enamelling composition and may, therefore, be ground to the desired size in accordance with well known practice.

To prepare an enamel adapted for application to the surface of sheet steels or the like, the composition in the form of a frit described above will be formulated as an aqueous slip. The normal practice followed in vitreous enamelling composition formulation may be followed in this connection insofar as the physical steps of preparing the slip are concerned. This consists of milling the frit with various additives and water to provide a homogeneous, liquid enamelling composition.

There are two embodiments of the present invention provided hereby insofar as it relates to the enamelling compositions prepared in the stated manner. The first of these embodiments provides a vitreous enamel cover coat adapted to be applied over a ground coat as in conventional enamelling practice. The second embodiment provides a vitreous enamel adapted for "direct on" application to the metal surface.

In either embodiment, the enamelling composition is characterized by the low firing temperature conferred by the frit of this invention.

To prepare an enamelling composition of the nature of a cover coat, the frit of this invention will be milled with additives of the type normally incorporated in vitre-

ous enamelling compositions. For example, it is normally the practice to incorporate a suspending agent in the mill batch. Examples of suitable suspending agents are enamelling clays, bentonite, sodium silicate and the like. The suspending agent may be added to the frit either as a solid or as a dispersion in water. Similarly, an electrolyte salt is also normally added to the composition to flocculate the composition when water is added thereto controlling the viscosity of the resulting slip. Examples of such salts are the water-soluble—particularly the alkali metal—chlorides, carbonates, nitrites, phosphates and the like. A preliminary binder imparting strength to the coating until it is fired, such as gum tragacanth, may also be included in the composition. As stated, in the composition of the present invention, the titania in the frit serves as the ultimate opacifying agent. Hence, it is not necessary to add an opacifying agent to the frit, such as during milling.

To prepare a "direct on" enamelling composition, the frit of this invention will be milled with additives including lithium molybdate. The amount of lithium molybdate to be included in the mill batch in this embodiment of the invention may range from about 0.3% to about 2.0% by weight, calculated on the weight of the frit. Generally about 1% by weight, calculated on the weight of the frit, will be found to give satisfactory results. In addition to the frit and the lithium molybdate, the mill batch in which the enamelling composition is prepared in the form of an aqueous slip will normally comprise further additives of the general classes of those mentioned in the preceding discussion of conventional, cover coat vitreous enamelling composition formulation. Thus for example, a suspending agent such as an enamelling clay, bentonite, sodium silicate or the like will be included in the mill batch. The mill batch will also include flocculating agents comprising one or more water-soluble electrolyte salts, such as halides like KCl and LiF , carbonates like ammonium carbonate, alkali metal or ammonium nitrites, phosphates, and so forth. The proportion of water added to the mill batch to form the slip and the amounts of the additives included as suspending agents, flocculating agents and the like in the mill batch will in general conform to the amounts normally used of these components in cover coat enamelling composition formulating. As in the case of the cover coat enamelling compositions comprising the presently provided frit discussed hereinabove, it will be unnecessary to add any opacifying agent during milling to the enamelling compositions provided in this embodiment of this invention, since the frit itself includes titania which will act as the opacifying agent when the enamel is applied to metal surfaces and fired.

In applying the milled enamelling compositions comprising the frit, the selected additives and sufficient water to give the composition the consistency of a slip, procedures such as brushing, spraying or the like may be used to coat the metal surface to be enamelled therewith. As is well known in the art, metal, particularly sheet steel, surfaces are ordinarily prepared for enamelling by nickel flashing, and the metal surface to be enamelled will accordingly normally have a very thin flashed nickel coating. A metal surface so prepared for enamelling will be adapted to have a ground coat applied thereto, and where a ground coat is used prior to applying an enamel as provided by this invention, conventional enamelling procedures to supply such a ground coat of vitreous enamel on the metal surface will be followed. The ground coat surface, after firing, will provide a suitable surface for the application thereto of an enamelling composition formulated for cover coat use as provided by this invention. The nickel flashed metal surface itself will provide a suitable surface for the application thereto of an enamelling composition formulated for "direct on" application as provided by this invention. Other suitably prepared metal surfaces may also be coated with the enamelling compositions of this invention, and by

using special procedures to prepare the metal surface, it may even be possible in some cases to utilize "direct on" application, omitting a ground coat, with the embodiment of this invention comprising an enamelling composition not including lithium molybdate in the mill batch. In any case, the metal surface, suitably prepared for the method of application selected, will be coated with the aqueous slip comprising the presently provided frit, and the coating will then be dried and fired to cause the coating to fuse and to vitrify into a continuous white, opaque, glassy coating. The firing of the coating follows well known procedures; however, as stated, an important feature of the compositions of the present invention is their ability to be fired at unusually low temperatures, in the neighborhood of 1100–1300° F.

The compositions of the present invention and their preparation as well as their advantageous properties will be more readily understood from consideration of the following specific examples, which are given for the purpose of illustration only and are not intended to limit the scope of the invention in any way.

Example 1

This example describes preparation of a frit in accordance with this invention.

The frit of this example is prepared to have the following oxide analysis:

	Mol. Percent	Wt. Percent
SiO ₂	30.1	26.1
B ₂ O ₃	20.9	21.0
Al ₂ O ₃	3.7	5.5
Li ₂ O.....	8.3	3.6
Na ₂ O.....	4.7	4.2
K ₂ O.....	6.6	8.9
ZnO.....	6.2	7.2
SnO.....	3.5	5.1
CaF ₂	2.6	3.0
TiO ₂	13.4	15.4

To prepare the frit, the following compounds and materials, in proportions adapted to provide the stated oxide analysis after melting and fritting, are melted together:

	Wt.-Percent
Silica	19.6
Boric acid.....	28.0
Titania	11.6
Lithium carbonate.....	6.7
Sodium carbonate.....	4.3
Sodium nitrate.....	2.7
Potassium carbonate.....	9.8
Strontium carbonate.....	5.5
Zinc oxide.....	5.4
Alumina	4.1
Fluorspar	2.3

The clear melt formed is poured into water to quench and shatter the glass into easily friable particles. The water is drained from the solids, and the frit is then dried. The frit has a melting point of 1120° F., and a fusion flow of 33 millimeters at 1275° F.

Example 2

This example describes preparation and testing of an enamelling composition adapted for "direct on" application.

The frit of Example 1 is prepared into a mill mix having the following composition:

	Parts by weight
Frit	100
Lithium molybdate.....	1
Sodium silicate	2
Lithium fluoride.....	1
Potassium chloride.....	0.25
Ammonium carbonate.....	0.25
Water	37

The mill mix is ball milled for about four hours until 2

grams (± 1 gram) of residue remains on a 200 mesh screen when 50 cc. of slip are washed through the screen. The slip is then removed from the ball mill and dipped or sprayed onto a nickel-flashed sheet steel panel at the rate of 30 grams of dry enamel per square foot of surface per side. The panel is then fired to 1175° F., in 4 minutes.

After cooling, the fired panel is found to be coated with a continuous white, opaque, glassy adherent coating. The coating has an excellent gloss, and the appearance thereof is comparable to that of a titania-opacified enamel fired at above 1400° F. over a ground coat. Measurement of the opacity of the panel coating on a Hunter reflectometer using two color filters gives the following high values:

	Percent
Blue light.....	84
Green light.....	82
Blue minus green.....	2

Example 3

This example illustrates another composition in the form of a frit adapted for use as an enamel.

The procedure used in preparing this frit is the same as that described in Example 1, with appropriate adjustment of the nature and percentages of the compounds and minerals used to form the initial melt so as to result in a frit of the following oxide analysis:

	Mol. Percent	Wt. Percent
SiO ₂	25.00	22.3
B ₂ O ₃	21.85	22.5
Al ₂ O ₃	3.15	4.8
Li ₂ O.....	8.33	3.7
Na ₂ O.....	8.33	7.6
K ₂ O.....	8.33	11.6
ZnO.....	5.00	2.1
MgO.....	2.50	1.5
CaO.....	2.50	6.0
CaF ₂	2.5	2.9
TiO ₂	12.5	14.8

This frit has a melting point which is below 1100° F. Its fusion flow is 59 mm. at 1275° F.

Example 4

This example describes preparation of a "direct on" enamelling composition.

A mill batch is prepared having the composition described in Example 2, but substituting for the frit used in that example, the same weight of the frit of Example 3. This milled composition is applied to the nickel-flashed surface of sheet steel panels at rates of 25 and 35 grams per square foot per side and the panels are respectively fired at different temperatures ranging from about 1125° F. up to about 1275° F. Opacity of the fired panels is measured on a Hunter reflectometer using two color filters. The firing temperatures and the reflectance of the panels are shown in the following table.

Firing Temp., ° F.	Appln. Rate, g./sq. ft.	Blue Light	Green Light	Green-Blue
1,125.....	25	75.4	69.1	-6.2
	35	74.4	67.6	-6.8
1,150.....	25	77.9	70.5	-7.4
	35	78.2	72.4	-5.8
1,175.....	25	76.2	69.2	-7.0
	35	78.4	71.4	-7.0
1,200.....	25	78.0	72.8	-5.2
	35	79.4	74.0	-5.4
1,225.....	25	79.0	74.8	-4.2
	35	80.1	78.0	-2.1
1,250.....	25	80.0	78.7	-1.3
	35	80.3	80.2	-0.1
1,275.....	25	77.6	77.2	-0.4
	35			

The relatively small color difference in reflectance at the different rates of application indicates that the bias of the reflectance values towards blue is not due to lack

of opacity, but rather shows that the color of these enamels is actually blue-white.

The acid resistance of this enamel is slightly superior to that of the enamel produced as described in Example 2.

Example 5

This example describes preparation of enamelling compositions adapted for application over a ground coat.

Each of the frits of Examples 1 and 3 is made up into a mill batch of the following composition:

	Parts by weight
Frit	100
Enamelling clay	4
Bentonite	0.125
Potassium chloride	0.25
Potassium carbonate	0.25
Gum tragacanth	0.031
Water	42

The mill mixes are ball milled for about four hours until 2 grams (± 1 gram) of residue remain on a 200 mesh screen when 50 cc. of slip are washed through the screen. Each slip is then removed from the ball mill and sprayed onto one side of a ground-coated sheet steel panel at the rate of 25 grams of dry enamel per square foot of surface. Each panel is then fired at a temperature of between 1125° and 1250° F. A continuous white, opaque, glossy vitreous enamel surface finish is produced on each panel.

While the invention has been described with reference to various particular preferred embodiments thereof it will be appreciated that modifications and variations may be made within the scope of the invention and the appended claims.

What is claimed is:

1. A vitreous enamel composition having a firing temperature between about 1125 and about 1275° F., suitable for application to the surface of sheet steels, comprising a frit consisting essentially of from about 20 to about 30 weight percent silica; from about 20 to about 25 weight percent of R_2O_3 oxides consisting of B_2O_3 and Al_2O_3 , said Al_2O_3 providing from about 10 to about 25 percent of the weight of said weight percent of R_2O_3 oxides; from about 15 to about 25 weight percent of R_2O oxides consisting of Li_2O , Na_2O and K_2O , said Li_2O providing from about 10 to about 25 percent of the weight of said weight percent of R_2O oxides and said K_2O providing from about 40 to about 60 percent of the weight of said weight percent of R_2O oxides; from about 1 to about 10 weight percent of ZnO; from about 5 to about 10 weight percent of alkaline earth oxide selected from the group consisting of SrO and a mixture of CaO and MgO, said MgO providing from about 20 to about 50% of the weight of said weight percent of alkaline earth oxide; fluorine, in the amount of from about 2 to about 5 weight percent where said fluorine is calculated as calcium fluoride; and from about 10 to about 18 weight percent of titania; in which the molar ratios of said frit components to one another are substantially

Of silica to R_2O_3 oxides consisting of $B_2O_3 + Al_2O_3$	1:1-3:2
Of B_2O_3 to Al_2O_3	5:1-9:1
Of silica to R_2O oxides consisting of $Li_2O + Na_2O + K_2O$	1:1-3:2
Of Li_2O to Na_2O	1:1-7:4
Of Li_2O to K_2O	1:1-7:5
Of R_2O oxides to RO oxides consisting of ZnO + R'O oxide	2:1-3:1
Of ZnO to R'O oxide	1:1-7:4
F, as CaF_2	1-5 mol-percent of total
TiO_2	12-15 mol-percent of total

where R'O is alkaline earth oxide selected from the group

consisting of SrO and a mixture of CaO and MgO in the molar ratio of said CaO to said MgO of about 1:1.

2. The vitreous enamel composition of claim 1, in the form of a frit.

3. A "direct on" enamelling composition consisting of the composition of claim 1, containing lithium molybdate.

4. A vitreous enamel composition having a firing temperature between about 1125 and about 1275° F., suitable for application to the surface of sheet steels, comprising a frit consisting essentially of silica, R_2O_3 oxides, R_2O oxides, RO oxides, fluorine and titania in substantially fixed molecular ratios to one another, wherein the components of said frit and said molecular ratios are

Silica	10
$(B_2O_3 + Al_2O_3)$	10
$B_2O_3:Al_2O_3$	7:1
$(Li_2O + Na_2O + K_2O)$	10
$Li_2O:Na_2O:K_2O$	1:1:1
ZnO	2
$(CaO + MgO)$	2
CaO:MgO	1:1
F, as CaF_2	1
TiO_2	5

25 said frit having the following oxide analysis:

	Mol-percent
SiO_2	25.00
B_2O_3	21.85
Al_2O_3	3.15
Li_2O	8.33
Na_2O	8.33
K_2O	8.33
ZnO	5.00
MgO	2.50
CaO	2.50
CaF_2	2.5
TiO_2	12.5

5. The vitreous enamel composition of claim 4, in the form of a frit.

6. A "direct on" enamelling composition consisting of the composition of claim 4 containing lithium molybdate.

7. A vitreous enamel composition having a firing temperature between about 1125 and about 1275° F., suitable for application to the surface of sheet steels, comprising a frit consisting essentially of

	Mol-percent
SiO_2	30.1
B_2O_3	20.9
Al_2O_3	3.7
Li_2O	8.3
Na_2O	4.7
K_2O	6.6
ZnO	6.2
SrO	3.5
CaF_2	2.6
TiO_2	13.4

8. The vitreous enamel composition of claim 7, in the form of a frit.

9. A "direct on" enamelling composition consisting of the composition of claim 7, containing lithium molybdate.

10. A "direct on" enamelling composition having a firing temperature between about 1125 and about 1275° F., suitable for application to the surface of sheet steels, comprising about 100 parts by weight of the frit of claim 4, about 1 part by weight lithium molybdate, about 2 parts by weight sodium silicate, about 1 part by weight lithium fluoride, about $\frac{1}{4}$ part by weight potassium chloride, about $\frac{1}{4}$ part by weight ammonium carbonate, and about 37 parts by weight water.

11. A "direct on" enamelling composition having a firing temperature between about 1125 and about 1275° F., suitable for application to the surface of sheet steels, comprising about 100 parts by weight of the frit of claim

7, about 1 part by weight lithium molybdate, about 2 parts by weight sodium silicate, about 1 part by weight lithium fluoride, about 1/4 part by weight potassium chloride, about 1/4 part by weight ammonium carbonate, and about 37 parts by weight water.

12. A vitreous enameled body comprising a steel base, a vitreous ground coat adherent thereto, and a vitreous cover coat adherent to said ground coat, said cover having a firing temperature between about 1125° F. and about 1275° F. and comprising a frit consisting essentially of from about 20 to about 30 weight percent silica; from about 20 to about 25 weight percent of R_2O_3 oxides consisting of B_2O_3 and Al_2O_3 , said Al_2O_3 providing from about 10 to about 25 percent of the weight of said weight percent of R_2O oxides; from about 15 to about 25 weight percent of R_2O oxides consisting of Li_2O , Na_2O and K_2O , said Li_2O providing from about 10 to about 25 percent of the weight of said weight percent of R_2O oxides and said K_2O providing from about 40 to about 60 percent of the weight of said weight percent of R_2O oxides; from about 1 to about 10 weight percent of ZnO; from about 5 to about 10 weight percent of alkaline earth oxide selected from the group consisting of SrO and a mixture of CaO and MgO, said MgO providing from about 20 to about 50 percent of the weight of said weight percent of alkaline earth oxide; fluorine, in the amount of from about 2 to about 5 weight percent where said fluorine is calculated as calcium fluoride; and from about 10 to about 18 weight percent of titania; in which the molar ratios of said frit components to one another are substantially

Of silica to R_2O_3 oxides consisting of	
$B_2O_3 + Al_2O_3$ -----	1:1-3:2
Of B_2O_3 to Al_2O_3 -----	5:1-9:1
Of silica to R_2O oxides	
consisting of $Li_2O + Na_2O + K_2O$ -----	1:1-3:2
Of Li_2O to Na_2O -----	1:1-7:4
Of Li_2O to K_2O -----	1:1-7:5
Of R_2O oxides to RO oxides consisting	
of ZnO + R'O oxide -----	2:1-3:1
Of ZnO to R'O oxide -----	1:1-7:4
F, as CaF_2 -----	1-5 mol-percent of total
TiO_2 -----	12-15 mol-percent of total

where R'O is alkaline earth oxide selected from the group consisting of SrO and a mixture of CaO and MgO in the molar ratio of said CaO to said MgO of about 1:1.

13. A super opaque vitreous enameled body comprising a steel base and a vitreous enamel composition adherent thereto, said enamel composition having a firing

temperature between about 1125° F. and 1275° F. and comprising a frit consisting essentially of from about 20 to about 30 weight percent silica; from about 20 to about 25 weight percent of R_2O_3 oxides consisting of B_2O_3 and Al_2O_3 , said Al_2O_3 providing from about 10 to about 25 percent of the weight of said weight percent of R_2O oxides; from about 15 to about 25 weight percent of R_2O oxides consisting of Li_2O , Na_2O and K_2O , said Li_2O providing from about 10 to about 25 percent of the weight of said weight percent of R_2O oxides and said K_2O providing from about 40 to about 60 percent of the weight of said weight percent of R_2O oxides; from about 1 to about 10 weight percent of ZnO; from about 5 to about 10 weight percent of alkaline earth oxide selected from the group consisting of SrO and a mixture of CaO and MgO, said MgO providing from about 20 to about 50 percent of the weight of said weight percent of alkaline earth oxide; fluorine, in the amount of from about 2 to about 5 weight percent where said fluorine is calculated as calcium fluoride; and from about 10 to about 18 weight percent of titania; in which the molar ratios of said frit components to one another are substantially

Of silica to R_2O_3 oxides consisting	
of $B_2O_3 + Al_2O_3$ -----	1:1-3:2
Of B_2O_3 to Al_2O_3 -----	5:1-9:1
Of silica to R_2O oxides consisting	
of $Li_2O + Na_2O + K_2O$ -----	1:1-3:2
Of Li_2O to Na_2O -----	1:1-7:4
Of Li_2O to K_2O -----	1:1-7:5
Of R_2O oxides to RO oxides consisting	
of ZnO + R'O oxide -----	2:1-3:1
Of ZnO to R'O oxide -----	1:1-7:4
F, as CaF_2 -----	1-5 mol-percent of total
TiO_2 -----	12-15 mol-percent of total

where R'O is alkaline earth oxide selected from the group consisting of SrO and a mixture of CaO and MgO in the molar ratio of said CaO to said MgO of about 1:1.

14. An enameled body according to claim 13 wherein the enameling composition is a "direct on" enameling composition containing lithium molybdate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,293,146	Kautz -----	Aug. 18, 1942
2,396,856	King -----	Mar. 19, 1946
2,660,531	Fraser et al. -----	Nov. 24, 1953
2,930,713	Hoffman -----	Mar. 29, 1960