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ACID RESISTANT VITREOUS ENAMEL COMPOSITION

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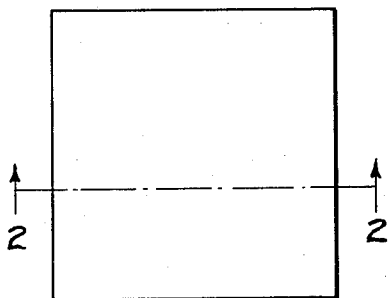


Fig. 1.



Fig. 2.

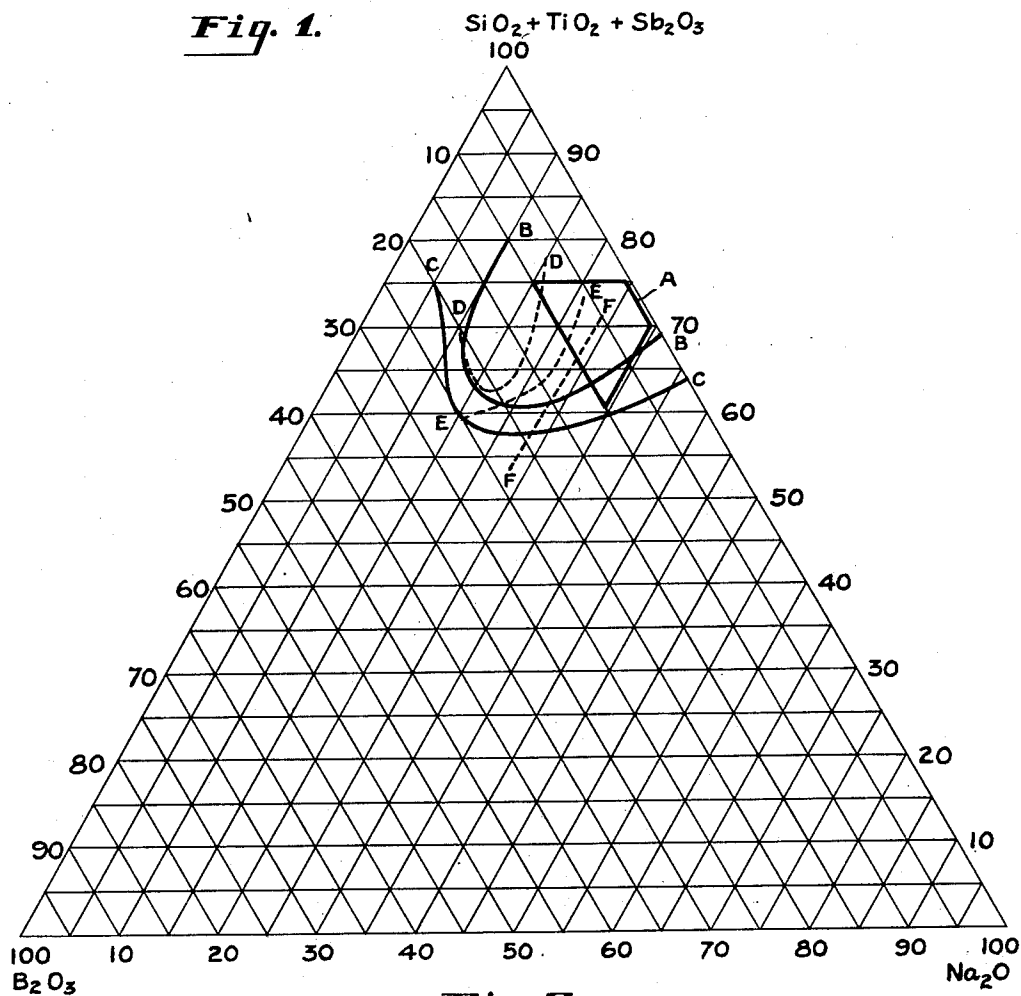


Fig. 3.

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ACID RESISTANT VITREOUS ENAMEL
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6 Claims. (Cl. 106—36.2)

This invention relates to vitreous enamels, and more particularly to an acid resistant frit from which an enamel may be prepared having a comparatively low fusion point, and is a continuation in part of application Serial No. 286,711 for Acid proof enamels, which was filed June 19, 1928.

The principal object of my invention is to provide an acid-proof and stain proof enamel which will be substantially resistant to the action of acids normally encountered in household use, and which is capable of being vitrified at a sufficiently low temperature to enable it to be applied to thin gauge sheet steel without causing a distortion of the sheet metal at the fusion temperature of the enamel.

A further object of my invention is to provide an article of manufacture composed of a base of thin gauge sheet steel, a non-acid resistant ground coat for the sheet steel, and an acid resistant and stain proof surface coat, the acid resistant surface coat having a sufficiently low fusion temperature and sufficient fluidity at its fusion point to enable it to be applied over thin gauge sheet steel at such a temperature that the steel will not be distorted.

Another object of my invention is to provide an enamel which is not only highly acid resistant but which is substantially stain proof; that is, no discoloration or iridescence of the enamel will remain after the acids have been applied.

An additional object of my invention is to provide an enamel containing sodium oxide, boric oxide, and silica as the principal ingredients, in which the relative amounts of these ingredients are maintained in such proportions that an enamel shall be produced having acid resisting and strain proof properties and a relatively low fusion point.

A further object of my invention is to provide an improved frit which has acid resistant properties, and which fuses at a sufficiently low temperature to permit of its being applied to sheet steel without causing distortion of the base metal.

Acid-proof enamels having a comparatively high fusion point have heretofore been utilized in the enameling industry. In view of the comparatively high fusion point of these enamels it has been necessary to utilize a base metal having a comparatively high softening point, such as cast iron or a special alloy, as the supporting surface upon which the enamel is applied. If a base metal having a comparatively low softening point, such as sheet steel, is employed, the high temperature required to vitrify the enamel causes a distortion of the base metal. When attempts have been made to add fluxes or to vary the proportions of the ingredients to lower the melting point of the enamel so that it can be applied to sheet steel, the results have not been satisfactory.

The general practice in such cases is to increase the amount of boric oxide and decrease the amount of silica or to add a relatively large amount of fluorspar. Such changes in proportions or the addition of other ingredients, however, while being effective in reducing the fusion temperature of the enamel, causes a substantial decrease in its chemical characteristics which substantially affects its ability to resist corrosion or acid stains. As a consequence, the enamels which have heretofore been utilized for kitchen ware having a sheet steel base have not been satisfactory because they have not been able to resist the effects of acids, such as citric or acetic, which are normally present in aqueous solutions of fruit juices.

I have made the discovery that if the relative proportions of the principal ingredients of acid-proof enamels are modified in a certain definite manner, an enamel frit will be produced that not only has acid resistant properties but which is also capable of being fused at a sufficiently low temperature to enable it to be successfully applied to a base metal, such as sheet steel, without causing a distortion of the base metal. In order to increase the fluidity of the frit at its fusion point and improve its opacity, I also prefer to add other ingredients, the characteristics and functions of which will be set forth as the specification proceeds.

My improved enamel is not only resistant to stains or discolorations produced from acids occurring in fruit juices but is also resistant against dilute or concentrated solutions of strong mineral acids, such as hydrochloric, sulphuric or nitric acid when cold. My enamel is also resistant to the above fruit acids and to the above strong mineral acids when hot if the strength of such acids do not exceed approximately 10% with the exception of hydrofluoric acid.

My invention will be better understood by reference to the accompanying drawing, in which:

Figure 1 is a plan view of a piece of enamel ware having an outer acid resistant coating;

Fig. 2 is a cross-sectional view on line 2—2 of Fig. 1; and

Fig. 3 is a graph showing how variations in the principal ingredients affect the fusion temperature and acid resistant properties of the enamel.

In preparing my acid resistant slip, I utilize raw materials of such character and in sufficient amounts so that the proportions of the ingredients in the fused frit will be present in the desired range. As the raw material I may utilize borax, sodium nitrate, soda ash, quartz, feldspar, titanium oxide, fluorspar, antimony oxide, and in certain cases litharge has been added. The following specific examples will serve to illustrate an example of my improved frit and the raw materials which may be employed in producing it.

Example 1

Raw materials		Composition of fused frit		
5	Borax	15.5	Na ₂ O	20.8
	Sodium nitrate	11.0	CaF ₂	3.1
	Soda ash	13.7	Al ₂ O ₃	4.0
	Quartz	32.5	Sb ₂ O ₃	3.8
	Feldspar	18.0	B ₂ O ₃	7.1
	Titanium oxide	3.8	TiO ₂	4.8
	Fluorspar	2.5	SiO ₂	56.4
	Antimony oxide	3.0		
	100.0			100.0

Example 2

Raw materials		Composition of fused frit		
15	Borax.....	19.4	Na ₂ O.....	20.8
	Feldspar.....	22.5	PbO.....	2.0
	Quartz.....	39.0	CaF ₂	3.1
	Sodium nitrate.....	10.4	Al ₂ O ₃	4.0
	Soda ash.....	19.3	Sb ₂ O ₃	4.5
	Titanium oxide.....	3.8	B ₂ O ₃	7.1
	Fluorspar.....	3.1	TiO ₂	3.8
	Antimony oxide.....	4.5	SiO ₂	54.7
	Litharge.....	2.0		100.0
		124.0		

It will be understood, however, that the above examples are only illustrative as the ingredients and proportions of the raw material will be naturally determined by the ingredients and proportions desired in the fused frit.

In preparing the frit, the raw material in the desired proportions are first thoroughly mixed in a coarsely powdered condition and then smelted in a furnace with frequent stirring until boiling has ceased. During fusion of the frit, nitrogen oxide and carbon dioxide are expelled. After the fusion is completed, the fused material is run into a stream of cold water and the frit ground with a mill addition comprising clay, water and a suitable acid in a suitable ball mill until it is capable of passing through a 60 mesh screen. In the mill addition I prefer to add six to eight parts by weight of clay, approximately one-half part by weight of boric acid, and forty-five parts by weight of water to 100 parts of frit. Other acids such as hydrochloric, sulphuric, or suitable salts such as calcium chloride, barium chloride and alum may also be employed. When mineral acids are utilized not such a large proportion is required, about 1/8 % to 1/4 % being sufficient. The clay is, of course, employed to keep the frit in suspension. The mill addition may also contain suitable coloring agents and small amounts of compounds which have opacifying properties such as sodium antimonate, zirconium oxide and tin oxide. The acid or salt increases the viscosity of the slip and aids in holding the enamel in suspension.

The same result as to the composition of the fused frit may obviously be accomplished, for example, by using potassium nitrate or a mixture of potassium nitrate and sodium nitrate. I may also utilize boric acid in place of borax. Sodium silicate may also be employed in place of quartz and soda ash. Other combinations of raw material may likewise be employed. As previously stated, however, it is highly essential to maintain the proportions of the alkali metal oxide, boric oxide, and silica within a definite desired range; otherwise an acid-proof enamel will not be produced which has a relatively low melting point.

If the alkali metal oxide, boric oxide and silica are maintained in the desired proportions, I have found that it is possible to produce a frit utilizing these three ingredients alone which will have acid resisting properties and which has a suffi-

ciently low fusion point to permit of its being applied to sheet steel. For example, if the boric oxide is maintained within proportions of 2% to 10%, and preferably within proportions of 4% to 8%, the sodium oxide is present in amounts ranging from 15% to 30% and preferably between 15% to 25%, and the silica within proportions ranging from 55% to 75% and preferably in amounts ranging from 55% to 65%, a frit may be produced having the desired properties.

I have found it very highly desirable, however, to utilize titanium oxide or antimony oxide, and preferably a mixture of the two in combination with the silica, or as a substitution for a portion of it, so that the combined silica and titanium oxide, or combined silica, titanium oxide and antimony oxide content shall range from 55% to 75%. In such cases the amount of silica will vary from 50% to 65%. For example, by referring to the ternary diagram as disclosed in Fig. 3 of the drawing, all compositions falling within the quadrilateral area designated by the letter A, will not only have a low melting point but will also be acid resistant. All compositions falling within the heavy black line B—B of the drawing will be practically insoluble in ordinary acids, such as fruit juices, encountered in household use, and all compositions falling within the area C—C of the diagram will be only slightly soluble. All compositions falling in the area D—D will have a comparatively high fusion temperature and are therefore not desirable for application to sheet steel, while those compositions falling within the area extending to the right of that line will have a lower fusion temperature and may be applied to sheet steel having a U. S. standard gauge between 18 and 24. Frits having such a composition that they will fall within the area of the ternary diagram to the right of lines E—E and F—F, respectively, will have a still lower fusion temperature and will still be more adaptable for application to sheet steel.

If the boric oxide is above the proportions specified, the deposited enamel will have the tendency to craze and also lose its acid resisting properties, while if the amount is too low the fusion point of the enamel will be increased, a high fusion temperature will be required, and if sheet steel is utilized as the base metal it will be distorted during application of the enamel. It will be noted that the amount of sodium oxide, potassium oxide or sodium-potassium oxide in my improved enamel is maintained relatively high. I have found in practice that a high proportion of sodium oxide produces a non-corrosive enamel. A relatively high proportion of sodium oxide or equivalent oxide also reduces the melting point of the enamel, and since sodium oxide also has a higher coefficient of expansion than sheet steel, it enables the enameled article to be cooled without cracking and crazing the enamel. If too high a proportion of sodium oxide is added, however, the enamel loses its acid resisting properties.

It will be understood in practice that a feldspar is generally utilized which contains potassium as well as sodium, and in this connection it may be stated that either potassium oxide, sodium oxide, or a mixture of the two may be employed. For economical reasons, I prefer to utilize the mixture of the two which is obtained from ordinary potassium sodium feldspar.

As previously stated, although the composition of my frit may be composed entirely of boric

oxide, sodium oxide and silica in the proportions specified, I prefer to add titanium oxide or antimony oxide, or a mixture of the two, or substitute it for a portion of the silica. Titanium oxide and antimony oxide act as opacifiers and also increase the coefficient of expansion of the frit. In this connection it may be stated that antimony oxide and titanium oxide have a coefficient of expansion approximately five to six times higher than the coefficient of expansion of silica. Titanium oxide may be substituted for silica in amounts ranging up to 15%, but since titanium oxide is considerably more expensive than silica I prefer to maintain the titanium oxide content below 10%. It is highly desirable, however, to have some titanium oxide present because it increases the fluidity of the frit at its fusion point. Antimony oxide also improves the opacity and increases the expansion characteristics of the frit. If either titanium oxide or antimony oxide, or a mixture of the two, are added to or substituted for a portion of the silica, I prefer to maintain the combined silica, titanium oxide and antimony oxide of the fused frit between 55% and 75%.

I also prefer to add a refractory substance to the frit such as aluminum oxide, as it increases the resistance of the enamel to abrasion. Aluminum oxide also has a higher coefficient of expansion than silica which is also a very desirable characteristic.

A suitable compound containing fluorine is also a very desirable addition because it increases the fluidity of the fused frit and also aids in developing opacity. Compounds containing fluorine which have been found suitable are sodium-aluminum fluoride, sodium fluoride, calcium fluoride, or sodium fluosilicate. The amount of the fluorine-containing compound which is added is preferably sufficient so that the amount of fluorine in the frit will range from approximately .3% to 3%. Calcium fluoride has been found very satisfactory.

I may also add small proportions of litharge to the frit. Litharge has many of the desirable properties of boric oxide and consequently may either be substituted for a portion of the boric oxide or employed as an additional ingredient. In view of the poisonous characteristics of lead oxide, however, I prefer to limit its use to small quantities or to omit it altogether.

The following table shows the broad and narrow range of an improved frit in which the composition has been modified by the additions specified:

Broad range		Preferred	
	Percent		Percent
Na ₂ O	15 to 30	Na ₂ O	15 to 25
B ₂ O ₃	2 to 10	B ₂ O ₃	4 to 8
SiO ₂	50 to 75	SiO ₂	50 to 65
TiO ₂	1 to 10	TiO ₂	4 to 10
Sb ₂ O ₃	1 to 5	Sb ₂ O ₃	3 to 5
Al ₂ O ₃	.5 to 5	Al ₂ O ₃	3 to 5
CaF ₂	1 to 5	CaF ₂	3 to 5

While my improved frit may be applied to metals of various kinds, it is especially adaptable for application to sheet steel having a U. S. standard gauge between 18 and 24. As previously specified, it has heretofore been impossible to apply acid and stain-proof enamels to sheet steel of the gauge specified because the acid-proof frits which were formerly utilized contained the ingredients in such proportions that it was necessary to fuse the frit at such a temperature that

the base metal would be distorted, and frits which had a sufficiently low melting point could not be utilized because they were not sufficiently acid-proof to prevent the development of acid stains in service.

When aluminum oxide and the compound containing fluorine are employed, the amount of sodium oxide and boric oxide are maintained constant and the refractory substance and fluorine-containing compound is substituted for a portion of the silica or for a portion of the combined silica, antimony oxide and titanium oxide content, so that in the preferred form of my invention the silica or combined silica, titanium oxide and antimony oxide content may be less than that indicated in the quadrilateral area designated by the letter A.

In applying my improved frit to sheet steel, the metal is first immersed in a suitable pickling bath, such as a 5% solution of hot sulphuric acid or hydrochloric acid, flushed in water and then immersed in a dilute alkaline solution, such as sodium carbonate, and dried. A suitable non-acid resisting ground coat is applied in the usual manner, such as by dipping or spraying. Non-acid resisting ground coats are usually prepared from compositions containing borax, feldspar, quartz, soda ash, sodium nitrate, fluorspar, and a small amount of cobalt oxide. The fused ground frit usually contains between 45% and 51% silica, 19% to 21% sodium oxide, 14% to 15% boric oxide, 7% to 10% calcium fluoride, 6% to 8% aluminum oxide, .5% to .6% cobalt oxide, and may also contain from .5% to 1% of manganese oxide, iron oxide or nickel oxide. The following shows specific examples of two typical ground coats:

Example I		Example II	
Na ₂ O	19.4	Na ₂ O	20.6
CaF ₂	7.7	CaF ₂	9.8
CoO	.6	CoO	.5
MnO ₂	1.0	Fe ₂ O ₃	.5
Al ₂ O ₃	6.4	NiO	1.1
B ₂ O ₃	14.0	Al ₂ O ₃	7.4
SiO ₂	50.7	B ₂ O ₃	14.8
		SiO ₂	45.0

After the ground coat has been applied and the metal permitted to cool, my improved acid-proof enamel is applied in any suitable manner such as by spraying or dipping, and is then burned. The burning of the enamel is closely controlled, the temperature preferably not being allowed to exceed 1600° F. and is desirably maintained within a temperature of 1500° to 1550° F. My improved frit may be satisfactorily applied to sheet steel of the gauge specified without in any manner distorting the base metal. An article of manufacture comprising a base metal 1 composed of sheet steel or similar metal having a comparatively low melting point, a ground coat 2 and my improved acid-proof coating, are shown in Figs. 1 and 2 of the drawing, in which the numeral 1 represents the sheet metal base, 2 the ground coat, and 3 my improved cover coat. The enamel, thus applied, is resistant to the action of acid and acid stains. It has excellent gloss and opacity and is substantially free from craze and blisters.

In this specification the term "stain proof" is used to mean an enamel which will not discolor, become iridescent, or show marks as the result of contact with fruit acids, such as citric, malic, acetic and the like, or with cold mineral acids, such as hydrochloric, sulphuric or nitric,

or with such mineral acids in concentrations of approximately 10% or less, even when hot.

From the foregoing specification it will be apparent that my improved frit has marked advantages over those that have been previously utilized because it has a high thermal expansion, a comparatively high fluidity upon melting, and when applied as an enamel to suitable base metals is characterized by having high acid and stain resistant properties. Its low fusion point and comparatively high thermal expansion also permit of its being utilized on kitchen ware having a sheet metal base.

To those skilled in the art many modifications of and widely different embodiments and applications of my invention will suggest themselves without departing from the spirit of my invention and the scope thereof. My disclosures and descriptions herein are purely illustrative and are not intended to be in any sense limiting.

What I claim is:

1. An enamel frit comprising boric oxide, sodium oxide, silica, titanium oxide and antimony oxide, the boric oxide being present in amounts ranging from 2% to 10%, the sodium oxide in amounts ranging from 15% to 25%, and the combined silica and titanium oxide and antimony oxide ranging from 54% to 75%, the titanium oxide being present in the amount not greater than 10%.

2. An enamel frit comprising boric oxide, sodium-potassium oxide, silica, titanium oxide, antimony oxide, aluminum oxide, and a fluorine-containing compound, the boric oxide being present in amounts ranging from 4% to 8%, the sodium-potassium oxide in amounts from 15% to 25%, silica in amounts from 50% to 65%, titanium oxide in amounts from 4% to 10%, antimony oxide in amounts from 3% to 5%, aluminum oxide in amounts from 3% to 5%, and the fluorine-containing compound in amounts from 3% to 5%.

3. An enamel frit comprising boric oxide, sodium oxide, silica, titanium oxide, antimony oxide, and a compound containing fluorine, the boric oxide being present in amounts ranging from 2% to 10%, the sodium oxide in amounts ranging from 15% to 30%, and the combined silica, titanium oxide and antimony oxide in amounts ranging from 54% to 75%, of which amount the titanium oxide constitutes not more than 10% and the antimony oxide not more than 5%, the compound containing fluorine being present in such proportions that the amount of fluorine will not be present in an amount greater than 3%.

4. An enamel frit comprising from 2% to 10% boric oxide, 15% to 30% of an alkali metal oxide selected from a group consisting of sodium oxide, potassium oxide and sodium-potassium oxide, 1% to 10% of titanium oxide, 1% to 5% of a fluorine-containing compound and more than 50% silica, the combined titanium oxide and silica content ranging from 54% to 75%.

5. An enamel frit comprising 2% to 10% boric oxide, 15% to 30% of an alkali metal oxide selected from a group consisting of sodium oxide, potassium oxide and sodium-potassium oxide, 50% to 75% silica, 1% to 10% titanium oxide, 1% to 5% antimony oxide, .5% to 5% aluminum oxide, and 1% to 5% of a fluorine-containing compound.

6. An enamel frit comprising 4% to 8% boric oxide, 15% to 25% of an alkaline metal oxide selected from a group consisting of sodium oxide, potassium oxide, and sodium-potassium oxide, 50% to 65% silica, 4% to 10% titanium oxide, 3% to 5% antimony oxide, 3% to 5% aluminum oxide, and 3% to 5% calcium fluoride.

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