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3,061,449

VITREOUS ENAMEL FRIT

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This invention relates to a new and improved enamel frit. More particularly it relates to vitreous enamel frits having sufficiently low maturing temperatures and coefficients of thermal expansion, and a sufficient resistivity to weathering to make them of outstanding utility for outdoor use on ordinary medium carbon steels and especially on aluminum-coated steels.

Aluminum-coated steels, particularly aluminum-silicon coated steel such as is produced by hot dipping decarburized steel in molten aluminum alloy after the method of T. Sendzimir (U.S. Patent No. 2,110,893) have proven very difficult to enamel with a vitreous enamel. The aluminum coating has a low melting point (melting point of aluminum 660° C.) and therefore the enamel must have a low maturing temperature. Vitreous enamels conventionally used for enameling steel are completely unsuitable since they have a too high maturing temperature. The aluminum coated steels have a linear coefficient of expansion approximately the same as the underlying steel base sheet, and therefore vitreous enamels customarily used for enameling aluminum are highly unsuitable since aluminum and aluminum-rich alloys have coefficients of expansion approximately twice that of steel. (By aluminum-rich alloys is meant alloys containing at least 80% of aluminum.) Moreover, as the temperature at the aluminum-steel interface increases the probability of formation of a brittle interfacial layer and subsequent failure of the bond on flexing becomes greater.

There is also a demand for a suitable low temperature maturing steel enamel. Ordinary medium carbon grade steel is difficult to enamel at conventional steel-enamel frit maturing temperatures, which vary from 1300° F. to 1600° F., because of extensive gas forming reactions and also because of a tendency of the steel to sag and warp. Premium priced enameling grade steels have therefore been required for the production of vitreous enamel coated steel products. These problems with the enameling of ordinary steel may be largely avoided if the steel is enameled at a maturing temperature of less than about 1100° F. Heretofore, however, no satisfactory glass frit compositions have been developed that have the desired maturing temperatures, thermal expansion properties and chemical resistance necessary for the enameling of medium carbon steel.

It is therefore an object of this invention to produce a new and improved vitreous enamel frit.

It is another object to produce an enamel frit that has the maturing temperature, thermal expansion coefficient and chemical resistance characteristics necessary for use as a vitreous enamel on medium carbon steel and aluminum-coated steel.

It is a further object of this invention to produce an enamel frit having a maturing temperature of aluminum enamels, a coefficient of expansion, corresponding to that of steel enamels and having outstanding utility for the enameling of aluminum-coated steel products.

Other objects of the invention will appear hereinafter.

It has now been found that a new and improved series of vitreous enamel frits can be prepared, that will have a good adherence with the aluminum or aluminum-rich alloy coatings on steel substrates, that will have a linear coefficient of thermal expansion suitable for use on either aluminum-coated steel or ordinary medium carbon steel, that will have a sufficiently low maturing temperature

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(below 1000° F.) to be suitable for use on an aluminum surface and that will have a sufficiently high chemical resistance to be suitable for use as outdoor surface coatings.

The new and improved vitreous enamels of this invention have the good adherence of conventional steel and aluminum enamels, a linear coefficient of thermal expansion of between 90 and 120×10⁻⁷ cm./cm./° C. a maturing temperature of below 1000° F. and contain the following ingredients within the following critical ranges and proportions:

	Mol percent
PbO	13-17
SiO ₂	34-42
TiO ₂	10-19
Na ₂ O	13-19
Li ₂ O	8-17
PbF ₂	1-3
Sb ₂ O ₃	0-1
BaO	0-3
CoO	0-2
CdO	0-3
B ₂ O ₃	0-6
Total R ₂ O (R=alkali metal)	23-30

and the ratio

$$\frac{\text{SiO}_2 + 2\text{TiO}_2}{\text{PbO} + \text{R}_2\text{O} + \text{PbF}_2} = 1.5-1.8$$

Small percentages of other oxide constituents, i.e. less than 4% of any one other constituent, than those mentioned above may be contained in these vitreous enamels, however at least 90% of the content thereof must consist of the above-named ingredients within the ranges stated. Moreover, these enamels should contain less than 1% of Al₂O₃ or CaO.

Since aluminum and aluminum-rich alloy coatings have minimal resistance to corrosion it is preferred to use enamel frits that have a low alkali content. Steel surfaces, on the other hand, generally need the presence in the enamel of CoO in order to obtain optimum adherence. The presence of CoO in the enamel frit produces a dark blue frit due to the cobalt ions. Therefore, if a color other than blue is desired, it may be necessary to provide the steel surface with two coatings, a blue ground coat and a cover coat of the desired color. If the steel is already covered with a high temperature firing ground coat containing CoO, then any frits of this invention, with or without CoO and firing below 1000° F. can be used, it being unnecessary to soften the ground coat to obtain adequate adherence.

One large use of the enamels of this invention is for the production of enameled steel or enameled aluminum-coated steel laminated to paper or other materials to form panels for use on large buildings or store fronts having the so-called "curtain-wall" construction. The enamels are thus exposed to corrosive weathering environment such as sulfurous gases dissolved in rain water. Citric acid solutions of a standard strength are used in accelerated tests for weather performance of vitreous enamels.

One such large group of vitreous enamels are disclosed in Deyrup U.S. Patent No. 2,467,114 for use on aluminum and aluminum-rich alloys. These frits are too high in thermal expansion for use on steel or aluminum-coated steel. Attempts to apply and fire these enamels on steel or aluminum-coated steel leads enamel crazing because of the difference in dimensional changes upon cooling from the firing temperatures. The use of these frits on aluminum, and their satisfactory outdoor performance for the past 15 years, provides the art with a standard of durability. The frits of the present invention have the

same order of corrosion resistance and durability as these previously known enamels.
Crazing on aluminized steel involves immediate frac-

The following three tables list twelve examples of useful frit compositions in mol percent, weight percent and weight percent of batches respectively:

TABLE I.—MELTED COMPOSITIONS, MOL PERCENT

	1	2	3	4	5	6	7	8	9	10	11	12
PbO.....	15.0	15.4	13.8	15.8	16.8	16.2	14.9	13.7	13.7	13.5	15.8	16.1
SiO ₂	40.2	40.1	40.1	41.6	38.6	40.1	41.3	34.5	40.6	38.9	40.6	40.6
TiO ₂	16.4	16.0	16.0	14.8	15.7	13.1	15.2	18.4	10.5	14.3	16.3	16.4
Na ₂ O.....	15.6	15.4	15.4	14.6	16.0	18.6	15.5	16.6	16.7	13.2	15.5	15.6
Li ₂ O.....	9.1	8.9	8.9	9.2	9.3	9.1	9.0	8.8	8.9	16.1	9.0	9.0
Sb ₂ O ₃	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.8	0.8	-----	-----
BaO.....	0.5	0.5	0.5	1.3	1.3	0.7	1.9	1.2	2.4	1.8	0.5	-----
PbF ₂	2.3	2.2	2.2	2.3	1.9	1.8	1.8	1.4	1.4	1.4	2.3	2.3
CoO.....	-----	1.2	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
CdO.....	-----	-----	2.8	-----	-----	-----	-----	-----	-----	-----	-----	-----
B ₂ O ₃	-----	-----	-----	-----	-----	-----	-----	5.0	5.1	-----	-----	-----
Total R ₂ O.....	24.7	24.3	24.3	23.8	25.3	27.7	24.5	25.4	25.6	29.3	24.5	24.6
Ratio: SiO ₂ +2TiO ₂ /R ₂ O+PbO+PbF ₂	1.7	1.7	1.8	1.7	1.6	1.5	1.7	1.8	1.5	1.5	1.7	1.7

TABLE II.—MELTED COMPOSITIONS, WEIGHT PERCENT

	1	2	3	4	5	6	7	8	9	10	11	12
PbO.....	38.3	38.3	34.3	38.3	40.3	39.8	36.8	34.5	34.5	35.5	39.1	39.8
SiO ₂	26.9	26.9	26.9	26.8	24.9	26.4	27.4	23.4	27.4	27.4	26.9	26.9
TiO ₂	14.5	14.5	14.5	12.5	13.5	11.5	13.5	16.5	9.5	13.5	14.5	14.5
Na ₂ O.....	10.7	10.7	10.7	10.7	10.7	12.7	10.7	11.7	11.7	9.7	10.7	10.7
Li ₂ O.....	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	4.2	2.2	2.2
Sb ₂ O ₃	0.8	0.5	0.8	1.3	1.3	1.3	1.3	1.3	2.6	2.6	-----	-----
BaO.....	0.7	0.7	0.7	2.2	2.2	1.2	3.2	2.2	4.2	3.2	0.7	-----
PbF ₂	6.0	6.0	6.0	6.0	5.0	5.0	5.0	4.0	4.0	4.0	6.0	6.0
CoO.....	-----	1.0	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
CdO.....	-----	-----	4.0	-----	-----	-----	-----	-----	-----	-----	-----	-----
B ₂ O ₃	-----	-----	-----	-----	-----	-----	-----	4.0	4.0	-----	-----	-----

TABLE III.—BATCHES, WEIGHT PERCENT

	1	2	3	4	5	6	7	8	9	10	11	12
PbO.....	34.7	34.3	31.1	34.7	36.5	35.5	33.2	30.3	29.8	31.6	35.2	35.0
SiO ₂	24.4	24.2	24.4	24.3	22.5	23.7	24.7	20.5	23.6	24.5	24.3	24.4
TiO ₂	13.1	13.0	11.3	11.3	12.2	10.3	12.2	14.5	8.5	12.1	13.1	13.1
Na ₂ CO ₃	16.5	16.3	16.5	16.5	16.5	19.4	16.4	17.4	17.8	14.7	16.4	16.4
Li ₂ CO ₃	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.6	4.7	9.0	4.8	4.8
Sb ₂ O ₃	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.7	0.7	-----	-----
BaCO ₃	0.8	0.8	0.8	2.6	2.6	1.4	3.8	2.5	4.9	3.8	0.8	-----
PbF ₂	5.4	5.4	5.4	5.4	4.5	4.5	4.5	3.5	3.6	3.6	5.4	5.4
CoO.....	-----	0.9	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
CdO.....	-----	-----	3.6	-----	-----	-----	-----	6.3	6.4	-----	-----	-----
H ₃ BO ₃	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----

ture perpendicular to the enamel layer surface without failure of the bond between oxide film and glass. A fine pattern of cracks develops which requires a strong light for detection. On exposure to weather or to mild acidic environments, simulating weathering conditions, such as ammonium chloride solutions, the cracks allow the oxide interlayer to be attacked with gradual dissolution. As attack proceeds on this interlayer the enamel begins to lose adherence and to flake off the substrate. The first portions of enamel to lose adherence are those isolated between three intersecting craze cracks in such a fashion that a small island of enamel is formed. Gradually larger and larger islands flake off and an unattractive pattern of areas of metal and enamel develops.

In some cases, aluminum-coated steel is enameled for reasons of corrosion resistance. In these cases the presence of crazing cracks and "flick-outs," as the de-enameled portions have been called in the trade, are extremely deleterious as they allow penetration of the corroding solution down to the readily soluble aluminum oxide interlayer.

The frits described in this application avoid crazing on both steel and aluminum-silicon coated steel by possessing proper thermal expansion allowing rapid cooling from the maturing temperature of the enamel with the development of compressive rather than tensile stresses in the glass layer.

PbF₂ is listed as such in the tables even though it is not definitely known to be present in this form. It has been discovered, however, that PbF₂ is a superior source of fluorine introduction in the frit. The addition of fluorine in the form of other fluorides, e.g. CaF₂, Na₂AlF₆, Na₂SiF₆, NaF, LiF, BaF₂, or ZnF₂ leads to the production of inferior frits.

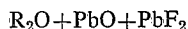
Some of these compounds are deleterious to these frit compositions because of a low tolerance of the frit for the cation introduced with the fluorine. Calcium and aluminum ions are presently regarded as harmful to these compositions when present to the extent of one percent or more. Fluorspar and cryolite are thus poor sources of fluorine. Introducing Na₂SiF₆, NaF, LiF, or BaF₂ in such a fashion as to yield the equivalent amount of fluorine as the PbF₂ and adjusting the other components for equivalency of the other cationic constituents proved to produce inferior melted compositions to those made from PbF₂. The reasons for this lie in the low melting point, extremely rapid solution of SiO₂ and TiO₂ in PbF₂, and the formation of a eutectic composition between PbO and PbF₂ producing liquid very early in the frit melting process.

PbF₂ as a batch component makes it possible to produce the desired low firing temperature (540° C., 1000° F.) coupled with low enough thermal expansion to fit the substrate metals and adequate weathering resistance.

The basic reasons for this are in the kinetics of the frit melting but PbF_2 is shown in the melted compositions to lend emphasis to its essentiality. Less than about 1 mol percent PbF_2 is ineffective and more than about 2.5 mol percent gives low weathering and chemical resistance.

PbO is an essential component in providing fluxing and dissolving action upon the more refractory components. Li_2O and Na_2O also are fluxes and the presence of both is considered essential. K_2O is an undesirable constituent because it raises the thermal expansion out of proportion to its contribution in lowering maturing temperature. SiO_2 is an essential component providing the glass forming properties of high melt viscosity. TiO_2 is essential in yielding good weathering resistance without raising expansion or maturing temperature unduly.

R_2O concentration is critical with respect to thermal expansion. This has been more critically defined by calculating the total R_2O content which lies between 23 and 30 mol percent. Higher total R_2O leads to crazing and lower R_2O to too high maturing temperatures. The ratio of acidic to basic constituents is also presented as is common practice. $\text{SiO}_2 + 2\text{TiO}_2$ divided by



is seen to lie between 1.5 and 1.8. This further defines the useful compositions.

The frits of this invention as exemplified in the tables have maturing temperatures below 1000°F . and have a linear thermal expansion between 110 and 120×10^{-7} cm./cm./ $^\circ\text{C}$. and are prepared in a conventional manner. Specifically, the batch ingredients are weighed and thoroughly mixed. The batch is then placed in a crucible, e.g. a fire clay-grog crucible and placed in a furnace preheated to about 1200°C . The actual melting temperature may vary between about 1100°C . and 1300°C . More time is, of course, required at the lower temperatures. For example, all the gas evolution and the batch dissolution in Example 1 of the table will be substantially complete in 20 minutes at 1300°C . or in 85 minutes at 1200°C . Completion of melting of all of the batch ingredients may be determined by well-known tests. A drop of the molten frit may be placed on a metal plate and examined when cool for the presence of undissolved matter; or a thread or string may be slowly drawn from the molten frit and examined visually and by feel for lumps or aggregates of unmolten batch material.

Upon completion of the melting of the frit the molten mass is commonly quenched or fritted by pouring it into water or between water-cooled rolls. The cooled fritted material is then ground in a ball or pebble mill. At this point any desired mill addition agents are added, such as pigments or coloring agents, anti-tearing agents and the like. As anti-tearing agents may be mentioned those disclosed in Deyrup, U.S. Patent No. 2,653,877, borax, sodium silicate, urea, and sodium fluoride. The grinding may be carried out wet or dry and the wetting agent may be water, alcohol, glycol or other similar materials or mixtures thereof.

The finely ground frit is made of the desired consistency with the wetting agent for application by brushing, dipping, spraying or stencilling as desired. The frit slurry for application is referred to as an enamel slip. The slip may, if desired, contain binder agents such as ethyl or methyl cellulose, soya lecithin terpeneol or the like for good adherence before firing. So-called thermo-fluid media may also be employed in enamel application to a substrate. Such thermo-fluid vehicles are commonly used and constitute no part of this invention.

Application on Steel Surfaces

Steel or iron conventionally requires a surface preparation before enameling. Such surface preparation may be accomplished by cleaning the surface, as needed, with a chlorinated hydrocarbon degreasing liquid such as trichlorethylene, with a hot acid treatment sulfuric acid,

chromic acid, hydrochloric acid of the desired strength or in any other conventional manner.

The steel may then be deoxidized by immersing in 7% H_2SO_4 at 70°C . for about 5 minutes; rinsed in water; dipped for 10 minutes in $70-80^\circ\text{C}$. nickel sulfate solution, 3 oz. per gal. NiSO_4 ($\text{pH}=3$); again rinsed in water; neutralized in 1 oz. per gal. solution of NaOH at room temperature; rinsed and dried.

Any other commonly used steel cleaning method can be used as well, it being only necessary to provide a clean steel or iron surface.

The enamel slip is then applied to the steel surface. For the direct application of a vitreous enamel to a steel surface it is highly desirable that it be one containing CoO for adequate adherence to the steel. Frit example 2 of the tables is satisfactory for direct application to a steel surface. It should be applied in an amount of about 40 grams per square foot to yield a fired thickness of about 0.001 inch, although considerable variation in application thickness is possible.

After application of the enamel slip it is allowed to dry and is then fired at about 1000°F . for a period of about 7 minutes. Higher temperatures and shorter firing periods or lower temperatures and longer firing periods may, of course, be used.

Application to Aluminum-Silicon Coated Steel

This substrate metal generally needs no surface preparation other than liquid cleaning with a degreasing liquid or a possible preparing at enamel firing temperature of about 1000°F . to remove any oil or grease present. The aluminum-coated steel may be enameled with one or two coats as desired. To produce the best appearance it may be necessary to apply slightly heavier enamel slip coatings than when enameling steel. 50 grams per square foot of surface area has been found to be satisfactory.

The application and drying and firing of the enamel is the source above-described with reference to steel.

Throughout the specification and claims, any reference to parts, proportions and percentages refers to parts, proportions and percentages by weight unless otherwise specified.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

I claim:

1. A vitreous enamel frit, suitable for use as a protective coating on aluminum coated and aluminum-rich alloy coated steel, having a maturing temperature of less than 1000°F . and a linear coefficient of thermal expansion between 90 and 120×10^{-7} cm./cm./ $^\circ\text{C}$. at least 90 mol percent of the frit consisting of

	Mol percent
PbO -----	13 to 17
SiO_2 -----	34 to 42
TiO_2 -----	10 to 19
Na_2O -----	13 to 19
Li_2O -----	8 to 17
PbF_2 -----	1 to 3
Sb_2O_3 -----	0 to 1
BaO -----	0 to 3
CoO -----	0 to 2
CdO -----	0 to 3
B_2O_3 -----	0 to 6
Total R_2O ($\text{R}=\text{alkali metal}$) -----	23 to 30

and the ratio;

$$\frac{\text{SiO}_2 + 2\text{TiO}_2}{\text{PbO} + \text{R}_2\text{O} + \text{PbF}_2} = 1.5 \text{ to } 1.8$$

said enamel frit containing less than 4% of any one other oxide constituent and less than 1% of an oxide taken

from the group consisting of Al_2O_3 and CaO , all of said oxides being melted in said enamel frit composition.

2. A process for applying a vitreous enamel layer on a metal substrate taken from the group consisting of steel and aluminum-coated steel which comprises fusing thereon a vitreous enamel having a maturing temperature of less than 1000°F . and a linear coefficient of thermal expansion between 80 and $120 \times 10^{-7} \text{ cm./cm./}^\circ\text{C}$. at least 90 mol percent of the frit consisting of

	Mol percent
PbO -----	13 to 17
SiO_2 -----	34 to 42
TiO_2 -----	10 to 19
Na_2O -----	13 to 19
Li_2O -----	8 to 17
PbF_2 -----	1 to 3
Sb_2O_3 -----	0 to 1
BaO -----	0 to 3
CoO -----	0 to 2
CdO -----	0 to 3
B_2O_3 -----	0 to 6
Total R_2O (R=alkali metal) -----	23 to 30

and the ratio;

$$\frac{\text{SiO}_2 + 2\text{TiO}_2}{\text{PbO} + \text{R}_2\text{O} + \text{PbF}_2} = 1.5 \text{ to } 1.8$$

said enamel frit containing less than 4% of any one other oxide constituent and less than 1% of an oxide taken from the group consisting of Al_2O_3 and CaO , all of said oxides being melted in said enamel frit composition.

3. A metal substrate taken from the class consisting of steel and aluminum-coated steel containing fused to

the surface thereof a vitreous enamel having a maturing temperature of less than 1000°F . and a linear coefficient of thermal expansion between 80 and $120 \times 10^{-7} \text{ cm./cm./}^\circ\text{C}$. at least 90 mol percent of the frit consisting of

	Mol percent
PbO -----	13 to 17
SiO_2 -----	34 to 42
TiO_2 -----	10 to 19
Na_2O -----	13 to 19
Li_2O -----	8 to 17
PbF_2 -----	1 to 3
Sb_2O_3 -----	0 to 1
BaO -----	0 to 3
CoO -----	0 to 2
CdO -----	0 to 3
BaO -----	0 to 3
Total R_2O (R=alkali metal) -----	23 to 30

and the ratio;

$$\frac{\text{SiO}_2 + 2\text{TiO}_2}{\text{PbO} + \text{R}_2\text{O} + \text{PbF}_2} = 1.5 \text{ to } 1.8$$

said enamel frit containing less than 4% of any one other oxide constituent and less than 1% of an oxide taken from the group consisting of Al_2O_3 and CaO , all of said oxides being melted in said enamel frit composition.

References Cited in the file of this patent

UNITED STATES PATENTS

2,255,044	Deyrup -----	Sept. 9, 1941
2,356,317	Harbert et al. -----	Aug. 22, 1944
2,467,114	Deyrup -----	Apr. 12, 1949

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,061,449

October 30, 1962

Lewis C. Hoffman

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 67, before "enamel" insert -- to --;
line 71, for "of" read -- for --; columns 3 and 4, TABLE II,
opposite " Sb_2O_3 ", column 8 thereof, for "1.3" read -- 1.6 --;
column 8, line 3, for "80" read -- 90 --; line 16, for
"BaO -----O to 3" read -- B_2O_3 -----O to 6 --.

Signed and sealed this 6th day of August 1963.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents