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COATING OF METAL SURFACES

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This invention relates to a process for coating metallic surfaces, specifically ferrous metal surfaces, with a vitreous and fused enamel coating and bonding the same to the metallic surface.

A further object of my invention is to provide a process of the character referred to which involves the use of agents or materials which, when used in accordance with the process of the present invention, operate to control the bond of the vitreous coating, to the ferrous metal surface, by controlling the nature and quantity of the nascent iron oxide produced during fusion.

A further and important object of the invention is to employ vitreous combinations having fusion points lower than the fusion points of sheet steel enamel ground or grip coats, thereby permitting the present invention to be carried out in connection with lighter gauge metal sheets and with a wider range of base metal compositions than heretofore possible.

Feldspathic, or metallic borosilicates, having fusion points in the range of 1000° F. to 1250° F. do not have sufficient adherence, when milled, sprayed, and fused on ferrous metal surfaces, to be used as decorative or corrosion resisting films without the preceding application of a higher firing ground or grip coat of the conventional cobalt, nickel and manganese wet-process enamel type. Whereas, according to the present invention, the addition to the mill or milled slip of an oxidizing agent, such as ferric sulphate, decomposing below the fusion temperature of the glass and forming stable decomposition products compatible with the vitreous body, aids in bonding these glasses to low carbon enamelling iron or steel, and in particular to those ferrous alloys slightly higher in silicon, phosphorus and manganese and known commercially as hot rolled steel.

Though it is necessary with enamel glasses firing on ferrous metal surfaces at the usual temperature ranges of 1500° F. to 1650° F. to use electric furnaces or fuel fired full muffle furnaces to insure burning atmospheres free from the products of combustion, however, according to the present invention, it is possible to utilize direct fired fuel furnaces, thereby materially decreasing equipment costs and operating expenses.

That is to say, according to the present invention, the coated metal is fired in an oxidizing atmosphere which is below 1260° F. Below this temperature there is no danger of warpage, strain and softening of the steel. With this process 30 gauge steel has been and is being successfully coated without warpage of the steel or hair-lining or crazing of the vitreous enamel coating.

Furthermore, the present invention can be used successfully with several glass or enamel frit formulae, and for purposes of the present application two such formulae may be given as examples of high lead borosilicate glasses with which the present process is particularly applicable:

Formula I:	Parts by weight
Litharge	73.6
Boric acid	11.1
Silica	15.3

and/or

Formula II:	Parts by weight
Litharge	46.80
Boric acid	9.45
Silica	13.10
Calcium carbonate	15.70
Fluorspar	10.20
Zinc oxide	4.75

Such high lead borosilicate glasses fuse at temperatures in the range of 1000° F. to 1260° F.

The mill additions for either Formula I or Formula II would be:

Frit	pounds	100
Bentonite	ounces	4
Ilmenite	do	6
Black iron oxide	do	4
Water	pounds	40

The above is to give a medium gray mill; the color may be changed by changing the oxide addition at the mill.

A distinctive feature of the present invention is to utilize with these glass or frit formulae an oxidizing agent compatible with the glass, such as ferric sulphate, as a further addition which acts as an agent to cause the fused glass or porcelain to be bonded to the ferrous metal surface over which it has been previously applied.

With normal hot rolled black iron as purchased from steel mills, it is found that the addition of ½ to 1½ cubic centimeters of a 20% aqueous solution of ferric sulphate to 100 cubic centimeters of milled slip of a high lead borosilicate glass having a specific gravity of 1.95 to 3.05, bonds this material to the metal surface when the metal is sprayed with this mixed slip and fired to a maturing temperature. This can be used with the frit of either Formula I or Formula II.

After the frit of Formula I or Formula II, with mill additions, is milled to appropriate fineness, it is measured and a 20% aqueous solution of ferric sulphate is added in the proportions of one part of sulphate solution to each one hundred parts by volume of milled slip. For some steels and some glasses different proportions of ferric sulphate will be found to work more satisfactorily.

Another oxidizing agent compatible with glasses of the type mentioned, and which may be advantageously employed in the process of the present invention, is sodium nitrite, which may be

added to the milled slip containing ferric sulphate in the proposition of 1 cubic centimeter of a 20% aqueous solution to 100 cubic centimeters of milled slip.

Two steels which were found to work very satisfactory with the ferric sulphate-enamel slip mixture described above had the following analysis:

	I	II
C	0.050	0.082
Mn	0.420	0.440
P	0.040	0.080
S	0.027	0.038
Cu	0.160	0.218
Si	0.061	0.003

The process may be further explained by stating that, at the low fusion temperatures employed, insufficient iron oxide is produced thermally and dissolved by the molten glass body to provide for a mutually soluble iron-glass interlocking layer between the vitreous coating and the base metal. For example, the metallic borosilicates, or majolica types of enamels, given in Formula I and Formula II are so strongly reducing in nature when fluid that when fired upon hot rolled steel at temperatures from 1000° F. to 1260° F. they have no adherence whatever. The surface of the steel exposed upon removing such glasses from the metal is white and clean, showing no indication of thermal oxidation during fusion. However, by the addition of an oxidizing agent which decomposes below the firing point of the enamel, and which does not form stable decomposition products harmful to the vitreous body, the quantity of the nascent iron oxide produced is increased sufficiently to insure adequate adherence. In particular, the addition of ferric sulphate as the oxidizing agent provides both additional iron oxide for solution in the melt, and a transitory oxidizing state at the interface of the enamel and the iron before fusion of the glass is complete. The necessary quantity of oxidizing agent is dependent upon the oxidizing characteristics of the steel, the chemical nature of the melt at the interface, and the quantity of iron oxide soluble in the ceramic composition being used.

Taking one phase of the process, the raw materials for the enamel are mixed and smelted at a temperature of approximately 2000° F. until reaction is complete, and immediately this molten glass is poured into cold water with agitation to quench the glass and break it into friable particles, producing the so-called "frit." This fritted glass is then ground in a ball mill with a suspending agent, water, an electrolyte, and color oxides if necessary, milled to a fineness of 0–25% residue on a 200 mesh screen from a 100 gram sample, preferably to a fineness of 3–7% residue on a 200 mesh screen from a 100 gram sample. The 20% solution of ferric sulphate is then added in the proportion of one part of sulphate solution to each one hundred parts by volume of milled slip, and if sodium nitrite is to be used as an auxiliary oxidizing agent it is added in the proportion of 1 cc. of a 20% aqueous solution to 100 cc. of milled slip containing the sulphate solution. This proportion may be varied somewhat for some irons or steels, and some glasses.

The metal articles to be coated are first cleaned, using commercial alkaline cleaning materials, then rinsed, pickled in acid, rinsed, neutralized and dried. Sand blasting may be substituted for cleaning and pickling in case of heavier gauge metals or cast iron. The metal article is then coated with the neamel slip, either by spraying, dipping, slushing or other known means; dried to remove moisture, and then fired at the proper temperature, which may be at 1070° F. for Example I and 1120° F. for Example II. In any case, the upper limit of the temperature range does not exceed 1260° F., thereby avoiding warpage and other physical change in the metal being coated.

Other oxidizing agents decomposing below a temperature of 1260° F., and forming stable decomposition products compatible with the enamels used in the present process are ferric chloride, potassium dichromate, sodium dichromate, and sodium sulphate.

By way of definition of certain terms employed herein it may be explained that the reference to neutralizing the rinsed metal articles preferably means immersion in a warm bath of mild alkali usually consisting of mixtures of sodium carbonate and borax in varying amounts, the total concentration being in general less than one ounce per gallon. In some cases where the water is extremely hard, phosphates or other water softeners are used. More specifically, there is a mixture of three parts of soda ash and one part of borax by weight in a total concentration of one-fourth ounce per gallon. The solution is used at 140° F. and the time of immersion is approximately four minutes.

It will be further understood that modifications in the process, materials employed, and the formulae thereof, proportions of ingredients and temperature ranges, falling within the scope of the appended claims may be resorted to without departing from the spirit or scope of the invention.

I claim:

1. In the process of enamel-coating ferrous metals, the new step of applying to the metal sheet a self-bonding milled slip containing a metallic boro-silicate having a fusing point in the range of 1000° F. to 1260° F. and a solution of ferric sulphate decomposable below the fusion temperature of the glass.

2. In the process of enamel-coating ferrous metals, the new step of applying to the metal sheet a self-bonding milled slip containing a metallic boro-silicate having a fusing point in the range of 1000° F. to 1260° F. and a solution of ferric sulphate and sodium nitrite.

3. A process of preparing a self-bonding enamel or glass composition for use in enamel-coating processes which consists in first preparing a lead boro-silicate glass frit having a fusing temperature in the range of 1000° F. to 1260° F., reducing the said frit to a milled slip, and then incorporating in said milled slip a solution of ferric sulphate.

4. A process of preparing a self-bonding enamel or glass composition for use in enamel-coating processes which consists in first preparing a lead boro-silicate glass frit having a fusing temperature in the range of 1000° F. to 1260° F., reducing the said frit to a milled slip, and then incorporating in said milled slip a solution of ferric sulphate and sodium nitrite.

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