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VITREOUS ENAMELING METHOD AND COMPOSITION

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1

This invention relates to vitreous enameling, more particularly to new and improved base stock for vitreous enamels and to a new and improved method of controlling the adherence of vitreous enamels to ferrous metals.

As is well known, one of the principal problems in the art of vitreous enameling is to secure proper adherence between the vitreous enamel coating and the base stock to which the enamel is applied, without the use of a "ground" or grip coat containing cobalt, manganese and usually nickel. It has long been recognized that it would be desirable to employ as the enamel base stock ordinary carbon steels containing the usual percentage of carbon (e. g., 0.10% to 0.20%), but such steels are characterized by rather poor warping properties as compared with the special enamel irons or enamel steels when exposed to heat during the burning operation. As a result, the most satisfactory vitreous enamel base stocks have been specially prepared low carbon steels (containing, say, 0.01% to 0.02% carbon) which are more expensive than many of the ordinary steels.

One of the objects of this invention is to provide a new and improved method of controlling the adherence of vitreous enamels to ferrous metal base stocks.

Another object of the invention is to provide a new and improved method of controlling the oxidation and reduction reactions which occur during the firing of a vitreous enamel.

A further object of the invention is to provide a new and improved type of material which is specially adapted to receive a coating of a vitreous enamel.

Generally stated, the invention relates to a new step in the process of enamel coating ferrous metals which consists of applying to the surface of the metal a bonding composition having as one of its essential ingredients an antimony compound which is preferably dispersed in an inert dispersion medium containing finely divided, preferably colloidal, particles. The invention also contemplates the addition to the above described ingredients of a substantial portion of a chloride, preferably barium chloride or nickel chloride. The bonding materials disclosed herein possess special utility as a spray to provide a thin evenly dispersed primer coat on the ferrous metal surface, said primer coat insuring complete adherence of the subsequently applied enamel color coat. The antimony compound and chloride in the dispersion medium are evenly dispersed over the surface of the metal so that minute particles

2

thereof are presented to the metal surface. The enamel frit or coat can be applied directly to the coated metal surface while still wet after which the firing of the enamel coated metal sheet may be carried out without intermediate drying.

The vitreous enamel firing temperatures will vary, depending upon the composition of the vitreous enamel. For example, a high firing vitreous enamel may be fired at temperatures as high as 1650 degrees F. while a low firing vitreous enamel may be fired at temperatures around 1250 degrees F. or below. The invention especially contemplates a vitreous enameling method which makes it possible to employ low firing vitreous enameling compositions which can be fired at much lower temperatures than heretofore considered feasible. The minimum firing temperatures will naturally vary, depending upon the type of vitreous enameling composition, but vitreous enameling compositions firing at temperatures as low as 800 degrees F. or lower are contemplated in accordance with the invention.

Example

Tartar emetic was dissolved with nickel chloride or barium chloride in water in the proportion of 7 parts by weight of tartar emetic, 7 parts by weight nickel chloride or barium chloride, and 86 parts by weight water. The solution was subjected to thorough agitation and then mixed with commercial sodium silicate in a ratio of 50 parts of said solution to 50 parts of sodium silicate. This resulted in the formation of a silica gel by the reaction of the sodium silicate with the tartaric acid radical of the tartar emetic.

The resultant composition together with the supernatant liquor was passed into a paste mill and then mixed with a bentonite suspension in the proportion of 28⅛ parts by weight to 71⅞ parts by weight of the bentonite suspension. The bentonite suspension was prepared by mixing 3 parts by weight of bentonite with 97 parts by weight of water with heating and agitation.

The foregoing composition was then introduced into a ball mill where it was ground to a superfineness so that the resulting thin colloidal suspension could be sprayed in a very thin film on a previously pickled metal sheet or article.

The bonding composition as thus prepared, when applied as a spray to the ferrous surface to be coated, will uniformly disperse over the surface of the metal, the antimony acting as a reducing agent to reduce the valence of the iron in the thermally formed iron oxide while the chloride phase of the composition functions to in-

crease the oxidation rate, particularly at the fusion temperature of medium and low firing enamels, thereby providing for a strong adherence of the vitreous body to the ferrous metal surface. The bentonite and silica gel function as a vehicle to hold the compound in a finely divided condition suitable for use in a spray gun, whereby the surface to be enameled can be sprayed evenly with the compound to prepare the metal surface immediately, without drying, for the application of the enamel color-coat to be fired thereon.

Tartar emetic, which is also known technically as potassium antimonyl tartrate, is the preferred antimony compound for the practice of the invention because it is a salt of an organic acid which will react with an alkaline silicate to form a silica gel as described in the previous example. It is also substantially water soluble and therefore readily dispersed in an aqueous dispersion medium. Other antimony compounds, such as potassium pyroantimonate and antimony oxide, can be employed for the purpose of the invention but are less desirable in that they do not have all of the aforementioned properties of tartar emetic. A coating of antimony trichloride on steel tends to explode under the impact of a sharp blow. Hence, it is preferable to employ the antimony and chlorine in separate components of the composition.

The metal chloride should preferably contain at least two atoms of chlorine per molecule so that the proportion of chlorine to metal is relatively high. Otherwise, large quantities of unnecessary elements are present in the coating composition and too great a bulk of material is required to supply the necessary chlorine. Examples of suitable chlorides are barium chloride, strontium chloride, nickel chloride, cobalt chloride, manganese chloride and magnesium chloride. The chloride should also be substantially neutral for the best results. Acidic chlorides may be used where they are neutralized by the alkaline silicate.

The employment of the chloride component of this composition as nickel chloride has the advantage that nickel, being below ferrous iron in the electrochemical series and being nonvolatile at the vitreous enamel firing temperatures, functions as an added reducing component in the oxidation and reduction reactions that occur when the enamel is fired.

An example of glass or frit which can be used with the bonding method is as follows:

	Parts by weight
Feldspar	20.9
Borax	40.2
Silica	22.9
Soda ash	5.1
Sodium nitrate	4.8
Fluorspar	6.1

This material is mixed, smelted, fritted and dried in the usual manner, and to produce a light grey coating the mill additions of the above will be as follows:

Frit	parts by weight	100
Clay	parts by frit weight	7
Opacifier	do	3
Ilmenite	do	5/8
Black oxide iron	do	1/16
Borax	do	3/4
Water	do	40

This material is ground or milled to a fineness of 0–25% residue on a 200 mesh screen, preferably 4–8% residue, and the metal as previously sprayed with the new bonding compound described is then coated with this milled slip by spraying. Finally the coated piece is dried and fired at a temperature below 1580 degrees F., e. g., in a range between 1100 degrees F. to 1580 degrees F.

An important advantage of the invention lies in the simplicity with which the process may be carried out. The bonding composition is simply and inexpensively prepared into a colloidal suspension which is particularly useful as a spray. The application of the new bonding composition is a one-step process which does not require drying before the application of the enamel frit. All of these advantages result in a lessening of the cost of application of the enamel coating, while at the same time providing adherence which is as good or better than that obtained by the use of a conventional vitreous enamel ground coat.

This application is a continuation-in-part of my co-pending application Serial No. 680,835, filed July 1, 1946, now abandoned. This former application was a continuation as to common subject matter of application Serial No. 400,103, filed June 27, 1941, now abandoned.

That portion of the subject matter of the present invention which is directed toward the employment of chlorides of metals from the group consisting of barium, strontium, manganese and magnesium in conjunction with potassium antimonyl tartrate is claimed in divisional application Serial No. 379,287 filed September 9, 1953.

The invention is hereby claimed as follows:

1. In a method of coating ferrous metals with vitreous enamels, the step which comprises pretreating the ferrous metal with a substantially uniform thin coating containing potassium antimonyl tartrate and a chloride of a metal from the group consisting of nickel and cobalt.

2. In a method of coating ferrous metals with vitreous enamels, the step which comprises pretreating the ferrous metal with a substantially uniform thin coating containing tartar emetic and nickel chloride.

3. In a process of coating ferrous metals with vitreous enamels, the step which comprises pretreating the ferrous metal with a substantially uniform thin coating containing tartar emetic, nickel chloride and a suspending agent.

4. The method of coating ferrous metals with vitreous enamels which comprises applying tartar emetic intimately dispersed with nickel chloride to the metal surface, thereafter applying a low firing enamel composition capable of being converted to a vitreous enamel by firing at temperatures within the range of 1100 degrees F. to 1580 degrees F., and then firing said enamel composition.

5. A bonding composition for pretreating ferrous metals to bond vitreous enamels thereto consisting essentially of a dispersion in an inert aqueous dispersion medium of potassium antimonyl tartrate and a chloride of a metal from the group consisting of nickel and cobalt.

6. A bonding composition for pretreating ferrous metals to bond vitreous enamels thereto consisting essentially of a dispersion in an inert aqueous dispersion medium comprising silica gel together with potassium antimonyl tartrate and a chloride of a metal from the group consisting of nickel and cobalt.

7. A bonding composition for processes of

enamel-coating ferrous metals composed of tartar emetic, nickel chloride, sodium silicate and a spspending agent.

8. A bonding composition for processes of enamel-coating ferrous metals composed of tartar emetic, nickel chloride, sodium silicate and bentonite.

9. A bonding composition for pretreating ferrous metals to bond vitreous enamels thereto which comprises tartar emetic, nickel chloride, and an inert aqueous dispersion medium therefor, said dispersion medium being effective to disperse said tartar emetic and said chloride over the surface of said ferrous metal.

10. A bonding composition for pretreating ferrous metals to bond vitreous enamels thereto, which comprises tartar emetic, nickel chloride, and an aqueous dispersion medium effective to disperse said tartar emetic over the surface of said ferrous metal, said dispersion medium comprising silica gel.

11. A process of preparing a bonding composition for use in enamel-coating processes which consists in preparing a solution of tartar emetic, chloride of nickel and water, subjecting the said solution to agitation and then adding to the mixture sodium silicate thereby forming silica gel as a part thereof, then subjecting the silica gel combination to the action of a paste mill followed

by introducing into said mixture an aqueous bentonite suspension to complete the composition, and finally grinding the complete composition to a fineness for use as a spray.

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