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METHOD OF BONDING VITREOUS ENAMELS AND ARTICLES PRODUCED THEREBY

Allan E. Chester, Highland Park, Ill., assignor to Poor & Company, Chicago, Ill., a corporation of Delaware

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This invention relates to a method of bonding vitreous enamels to steel, cast iron, and other similar materials.

As is well known, vitreous enamels may be bonded to ferrous metals, such as iron and steel surfaces, by various methods. Thus, one of the principal methods involves the addition of cobalt and manganese to a vitreous enamel ground coat and firing at high temperatures, say 1520 to 1600° F. At these temperatures conventional hot rolled steels will warp permanently. Hence, it is necessary to employ special so-called "enamel steels" which will withstand such high temperatures without permanent warping. The use of such steels and high firing vitreous enamels substantially adds to the cost of vitreous enameled products. Furthermore, the addition of cobalt, manganese, or other bonding agents to the vitreous enamel has disadvantages in producing dark colors and other defects, thereby necessitating one or more additional enamel coats in order to produce objects having a pleasing appearance. The net result is an article having a relatively thick coat of enamel which is subject to chipping and cracking.

One of the objects of the present invention is to provide a new and improved method of bonding vitreous enamels to metallic surfaces whereby the foregoing disadvantages are avoided.

Another object of the invention is to provide a new and improved method of bonding vitreous enamels to metallic surfaces which depends upon a pre-treatment of the metallic surface as distinguished from a treatment of the enamel slip or the frit which is used in forming the enamel coating.

Another object is to provide a new and improved method for bonding vitreous enamels to metallic surfaces, particularly iron and steel surfaces, wherein conventional steels may be employed rather than special steels, and the ultimate cost of the products is reduced.

An additional object of the invention is to produce vitreous enameled articles containing a relatively thin coating of a vitreous enamel which presents a pleasing appearance and does not readily chip or crack.

Another object is to produce new and improved vitreous enameled articles from relatively low firing vitreous enamels.

A further object of the invention is to produce a new and improved ferrous metal base stock for vitreous enameled articles which eliminates the need for conventional bonding materials.

Still another object of the invention is to provide a method of preparing ferrous metal base stocks for vitreous enameling by covering the surface of the metal with certain selected materials.

In accordance with the invention it has been found that new and improved results in the bonding of vitreous enamels to ferrous metal surfaces can be obtained by pretreating the metallic surfaces to form thereon a thin, uniform film or coating of an elemental substance from the group consisting of sulfur and selenium and covering the film with a sealing layer of a metal from the group consisting of antimony, arsenic and bismuth.

After the metal coating has been applied, any suitable vitreous enamel may be applied thereover. If an enamel of the ground coat type is used, bonding agents such as cobalt, manganese, copper or nickel oxide may be omitted. In this manner, relatively thin vitreous enamel coatings are applied which present a pleasing appearance and do not tend to chip or crack off in large pieces, as

is usually the case with the ordinary type of vitreous enamel coating.

In the practice of the invention it has been found that the layer of elemental sulfur or selenium may be applied to the surface of the ferrous metal stock in any manner which will give a thin uniform coating. Spraying of the stock with a finely divided or colloidal solution of sulfur or selenium in a suitable carrier may provide satisfactory coatings. Likewise, the stock may be dipped in a colloidal solution of the type described. Electrochemical deposition may be used as well as decomposition of sulfur compounds to produce elemental sulfur. Another satisfactory method will be described in greater detail hereinafter and involves electroplating of the sulfur in a manner more fully disclosed in my copending application Serial No. 555,953, filed September 27, 1944 now Patent No. 2,615,836.

The invention also contemplates the application of thin, uniform layers or coatings of metals from the group consisting of antimony, arsenic and bismuth by any suitable method. Here again it may be possible to apply the coating by spraying, dipping, electrochemical or chemical deposition and by electroplating in a manner which will be described more fully hereinafter.

The invention will be further illustrated but is not limited by the following examples, in which the quantities are stated in parts by weight unless otherwise indicated:

Example I

In 1 gallon of commercial 18° Bé. hydrochloric acid there were dissolved

6 ounces of antimony trioxide (Sb_2O_3)
2 ounces of arsenic trioxide (As_2O_3)
½ ounce of metallic selenium and
0.10%, based on the total weight of the mixture, of lauryl sulfate.

The resultant mixture is an acid electrolyte or plating bath suitable for use in accordance with the invention, thereby to produce a ground coat to which the vitreous enamel is applied. The article, preferably made of a conventional type steel, is immersed in the foregoing electrolyte as the cathode and is subjected to a superimposed asymmetric alternating current obtained by an electrical hook-up of the type described in my copending application, Serial No. 555,953, filed September 27, 1944 now Patent No. 2,615,836. The electroplating operation is preferably effected by superimposing a voltage of 3.2 A. C. (root mean square) on 2.5 volts D. C., with a current density of 10 amperes per square foot for 8 to 15 seconds, or sufficient to produce a deposit on the order of 2 mgs. per square foot.

The resultant product is then removed from the plating bath and treated with a vitreous enamel milled slip of the following composition:

	Parts by weight
Frit	100
Clay	7
Silica	2
Sodium nitrite	0.125
Opacifier (optional)	6
Water	42

A typical frit formula which can be used has the following composition:

	Parts by weight
Borax	31.8
Feldspar	29.5
Silica	20.1
Fluorspar	4.1
Soda ash	9.0
Sodium nitrate	5.5

This material is blended, smelted, and fritted in the usual way.

The complete coating formula is milled to the fineness of 0 to 25% residue on a 200 mesh screen, usually to 4 to 9% residue, and is then sprayed, slushed or dipped on the previously prepared ferrous metal surface to the desired weight or thickness, usually 1 to 2 ounces per square foot of metal.

After drying this coated metal article, the same is fired to the maturing temperature of the glass, which is preferably within the range of 1320 to 1440° F.

It will be understood that the article may be washed and dried between the plating operation and the enameling operation. As indicated by the foregoing example, the use of an opacifier is optional, depending upon whether a clear or opaque enamel is desired.

In the preparation of the foregoing electroplating bath the metallic selenium is added simultaneously with the antimony. It may however be applied as a separate coating directly to the steel by any suitable method such as by electrical or chemical deposition, by spraying or by dipping so long as a substantially uniform coating of selenium is obtained. The metal coat of antimony, arsenic or bismuth is thereafter applied by suitable means such as electroplating to seal the selenium coat.

The lauryl sulfate is employed as a surface active agent in order to enhance the smoothness of deposit, which otherwise would be affected by fine dirt particles. Its use is not absolutely necessary but is desirable and preferable, in accordance with the practice of the invention. As will be understood, other acid stable wetting agents may be used in an acid type of electroplating bath. Any suitably resistant type of anode may be used, such as for example, a carbon anode. The type of electroplating bath just described may be described as a chloride bath, and represents a preferred type of bath for the practice of the invention.

Example II

The plating bath may be the same as in Example I except that elemental sulfur is substituted in place of the selenium and the arsenic trioxide may or may not be eliminated.

Example III

A cold rolled sheet metal base stock consisting of S. A. E. 1020 carbon steel was placed in an acid pickling bath for a period of three to twelve minutes.

The acid pickling bath was an aqueous bath containing 8% by weight of sulfuric acid, 1% of lactic acid, and 1 ounce per gallon of sodium acid fluoride (NaHF) heated at a temperature of 140 degrees to 150 degrees Fahrenheit.

The pickled sheet was then rinsed and put into a sodium polysulfide solution. The sodium polysulfide solution was made by dissolving 12.5 pounds of sodium sulfide (Na_2S) in 4.5 gallons of warm water together with 4.25 pounds of elemental sulfur, and refluxing for two and one-half hours at 228 degrees Fahrenheit. This bath was then allowed to cool and the pickled metal sheet was placed therein at room temperature (75 degrees Fahrenheit).

The metal sheet was then connected to one pole of alternating current transformer having a potential of 6 volts (R. M. S.) and the other pole was connected to a graphite electrode. The sheet was subjected to a current having a density of 80 amperes per square foot for one minute, thereby forming a sheet having a surface layer of sulfur thereon. Alternatively, both legs of the transformer can be connected to graphite electrodes and the sheet suspended between the electrodes in the polysulfide solution.

The metal sheet turned in a brownish black color during the deposition of the sulfur, and the latter was probably entrained in a light hydrated and spongy iron oxide layer on the surface of the metal. When the sheet was taken out of the bath, it was spray-rinsed with water, then immersion-rinsed. It is my belief that iron salts, mainly ferrous sulfate, are entrained in the pickle pits formed by the attack of the acid on the ferrous metal surface and that they are not completely removed by the rinsing operations, that these iron salts are hydrolyzed upon immersion in the sulfide bath and that colloidal sulfur is precipitated and a certain amount of iron sulfide is formed.

The sulfur coated base stock is thereafter immersed in an acid electrolyte containing 1 gallon of commercial 18° Bé. hydrochloric acid in which has been dissolved about 6 ounces of antimony trioxide. If desired 2 ounces of arsenic trioxide may be added as well as about 0.10% of lauryl sulfate, based on the total weight of the mixture. The plating is thereafter carried out according to the method more fully disclosed in Example I. Thereafter the article is enameled according to the method disclosed in Example I.

If desired an alkaline plating bath may be used instead of the acid bath, in which case a steel anode is employed, preferably made of cold rolled steel. A typical composition for such an alkaline bath comprises 4.4 ounces potassium carbonate and 2.11 ounces antimony sulfide in 1 quart of water, boiled for one hour and then filtered, the water lost by evaporation being replaced.

In general, in the practice of this invention a proper ground coat for enameling can be obtained with one or more of the metals previously described by employing a ratio of A. C. (R. M. S.) to D. C. of 2–4 volts R. M. S.: 2.5 volts D. C., with a current density preferably within the range of 2 to 15 amperes per square foot for a period of time within the range of about 8 seconds to 1½ minutes. The direct current values may be varied rather widely provided the alternating current values are correspondingly changed within the foregoing ratios. Usually, the minimum of direct current voltage will be around 0.5 volt, the maximum value will be governed by practical considerations, including the object being plated, the surface area thereof, the positions of the anodes and the available electric power. The frequency of the alternating current may be varied, but good results have been obtained with 25 to 60 cycle A. C. current.

The invention is not limited to the particular type of vitreous enamel disclosed in Example I and other types of enamel coatings may be employed with good results. Thus, the enamel may consist of a blend of a raw glass batch of relatively high maturing temperature with a eutectic frit of a relatively low maturing temperature of the types described, for instance, in United States Patents Nos. 2,321,656 and 2,321,657. Low firing vitreous enamels (e. g., those firing at 1100° F. to 1500° F.) are preferred for the purpose of the invention.

The invention has the advantage that it is no longer necessary to apply a primer coat of enamel containing manganese, cobalt, or nickel, or other bonding materials. The omission of these bonding materials makes it possible to produce new and improved results in enameling because these materials ordinarily diffuse throughout the body of the enamel and injure the texture or gloss. Further, the present invention makes it possible to produce enamel ware or enameled objects with fewer coats of enamel or with a less over-all thickness of enamel. At the same time, it produces superior products in that there is a much greater bond between the enamel and the steel, cast iron, or other material being treated. Thus, a sharp blow against objects prepared in accordance with this invention will not crack off large particles of enamel, as is generally the case with present day types of enamels.

The expression "bonding materials," as used herein, is intended to cover cobalt, manganese, nickel, and compounds thereof such as are ordinarily employed in the vitreous enamel art for bonding vitreous enamels or glasses, steel, cast iron, and the like. As will be understood, the invention makes it possible to use vitreous enamels free from bonding materials in any amounts normally required for bonding. Although it is preferable to eliminate such materials entirely, the addition of such materials for some purposes is not negatived for the practice of the invention.

This application is a continuation-in-part of my copending application, Serial No. 555,953, filed September 27, 1944 now Patent No. 2,615,836.

The invention is hereby claimed as follows:

1. A method of controlling the adherence of vitreous enamels to ferrous metals which consists essentially in forming a layer of an elemental substance from the group consisting of sulfur and selenium on a ferrous metal base stock, covering said layer with a thin coating of a metal from the group consisting of antimony, arsenic and bismuth, applying a coating of a vitreous enamel over said metal coating, and firing said enamel.

2. A method of controlling the adherence of vitreous enamels to ferrous metals which consists essentially in forming a layer of elemental sulfur on a ferrous metal base stock, covering said layer with a thin coating of a metal from the group consisting of antimony, arsenic and bismuth, applying a coating of a vitreous enamel over said metal coating, and firing said enamel.

3. A method of controlling the adherence of vitreous enamels to ferrous metals which consists essentially in forming a layer of elemental selenium on a ferrous metal

base stock, covering said layer with a thin coating of a metal from the group consisting of antimony, arsenic and bismuth, applying a coating of a vitreous enamel over said metal coating, and firing said enamel.

4. A vitreous enamel base stock consisting essentially of a ferrous metal, a thin surface layer of an elemental substance from the group consisting of sulfur and selenium on said metal and a thin coating of a metal from the group consisting of antimony, arsenic and bismuth over said layer.

5. A vitreous enamel base stock consisting essentially of a ferrous metal, a thin surface layer of elemental sulfur on said metal and a thin coating of a metal from the group consisting of antimony, arsenic and bismuth over said layer.

6. A vitreous enamel base stock consisting essentially of a ferrous metal, a thin surface layer of elemental selenium on said metal and a thin coating of a metal from the group consisting of antimony, arsenic and bismuth over said layer.

7. In a method of preparing ferrous metals for vitreous enameling, the steps which consist essentially in acid pickling a steel having an average carbon content between 0.02% and 0.20%, depositing a layer of an elemental substance from the group consisting of sulfur and selenium on the steel and covering said layer with a thin coating of a metal from the group consisting of antimony, arsenic and bismuth.

8. In a method of preparing ferrous metals for vitreous enameling, the steps which consist essentially in acid pickling a steel having an average carbon content between 0.02% and 0.20%, depositing a layer of elemental sulfur on the steel and covering said layer with a thin coating of a metal from the group consisting of antimony, arsenic and bismuth.

9. In a method of preparing ferrous metals for vitreous enameling, the steps which consist essentially in acid pickling a steel having an average carbon content between 0.02% and 0.20%, depositing a layer of elemental selenium on the steel and covering said layer with a thin coating of a metal from the group consisting of antimony, arsenic and bismuth.

10. A vitreous enamel coated article obtained by firing a vitreous enamel on a steel having an average carbon content between 0.02% and 0.20% which has had a layer of an elemental substance from the group consisting of sulfur and selenium deposited on the surface thereof, and a coating of a metal from the group consisting of antimony, arsenic and bismuth over said layer.

11. A vitreous enamel coated article obtained by firing a vitreous enamel on a steel having an average carbon content between 0.02% and 0.20% which has had a layer of elemental sulfur deposited on the surface thereof, and a coating of a metal from the group consisting of antimony, arsenic and bismuth over said layer.

12. A vitreous enamel coated article obtained by firing a vitreous enamel on a steel having an average carbon content between 0.02% and 0.20% which has had a layer of elemental selenium deposited on the surface thereof, and a coating of a metal from the group consisting of antimony, arsenic and bismuth over said layer.

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