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METHOD OF BONDING VITREOUS ENAMELS

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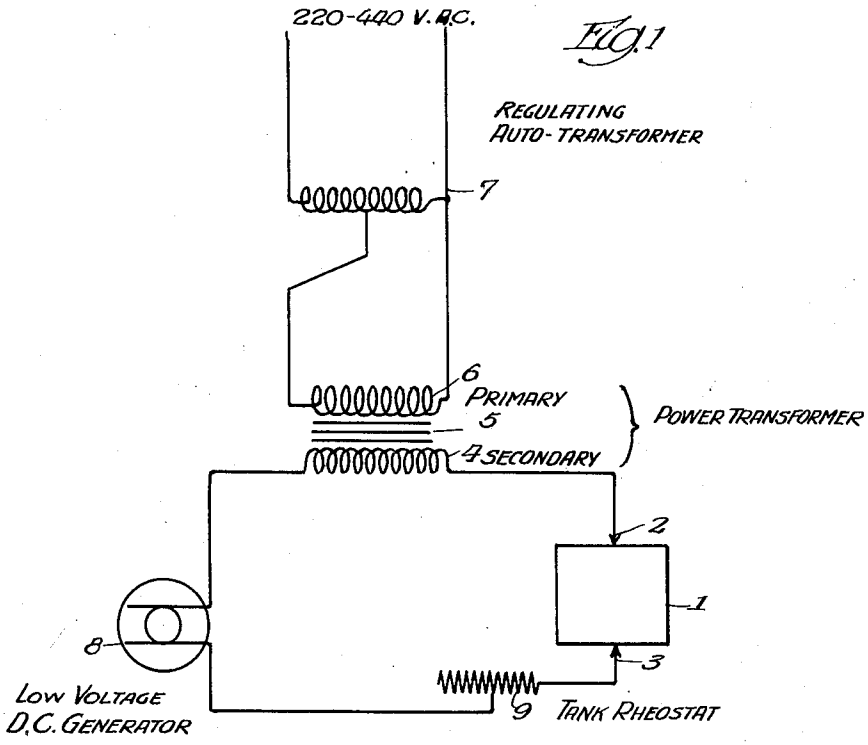


FIG. 1

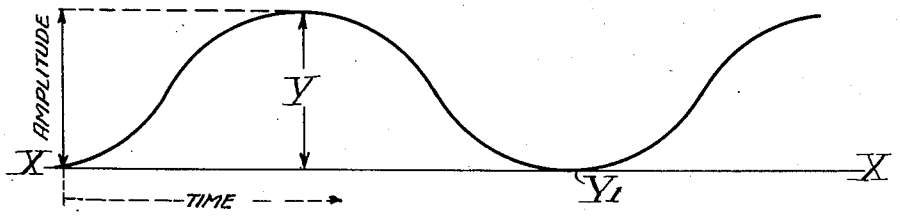


FIG. 2

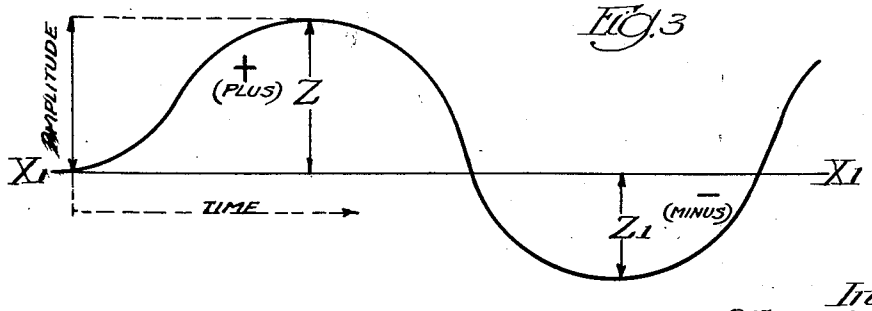


FIG. 3

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## METHOD OF BONDING VITREOUS ENAMELS

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1 Claim. (Cl. 204—38)

1

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. Other objects will appear hereinafter.

In accordance with the invention, it has been

2

found that new and improved results in the bonding of vitreous enamels to metallic surfaces, especially surfaces of ferrous metals such as steel, can be obtained by pre-treating the metallic surfaces to form thereon a very thin, substantially uniform, film or coating of a metal selected from the group consisting of antimony, arsenic, bismuth, cerium, lanthanum, and thorium. Especially good results are obtained with antimony.

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 there are certain minimum and maximum thicknesses of the metallic ground coat which should be applied in order to obtain the optimum results. A monomolecular metallic film such as is formed by treating the metallic surface with a solution of a metallic salt or oxide to cause the deposition of the metal by overvoltage is insufficient for the purpose of the invention. It is important, therefore, that the metallic ground coat be uniformly distributed over the metal surface with average thickness substantially greater than a monomolecular film of the metal, preferably within the range of .000005 inch to .00005 inch (five millionths to five hundred thousandths). If the thickness of the metal ground coat is insufficient, the desired bonding action will not occur, and the same is true if the thickness is too great. It will be recognized that the application of a uniform coating of a metal or a metallic material to thicknesses within the range mentioned is in itself a problem. It is well known, for example, that in ordinary electroplating methods the thickness of the electroplated material will vary, depending upon the configuration of the object being plated and numerous other factors. Thus, in plating flat objects and in plating other types of objects, the electrodeposited material will tend to build up around the edges to a greater extent than in the center.

Accordingly, a further feature of this invention is the provision of a method and apparatus for

electrodepositing metals uniformly on surfaces, such as flat surfaces or other types of surfaces, where uniform electrodeposition has been heretofore difficult to attain. This is accomplished in accordance with the invention by electrodepositing the metal on the electrically conducting surface, using a current comprising an alternating current superimposed upon direct current in a predetermined ratio effective to produce a plating current which may be described as an asymmetric alternating current, in which the negative peak value of the wave form varies from zero to $-\frac{2}{3}$ of the positive peak value.

In the accompanying drawings,

Fig. 1 illustrates diagrammatically one form of apparatus suitable for the application of a metallic ground coat, in accordance with the invention;

Fig. 2 illustrates graphically the wave form of the plating voltage when the negative peak is at zero; and

Fig. 3 illustrates the wave form of the plating voltage when the negative peak is at $-\frac{2}{3}$ of the positive value.

Referring to Fig. 1, the apparatus illustrated comprises a suitable plating bath 1 provided with one or more electrodes, generally indicated at 2, and a work piece or metallic surface to be plated, generally indicated at 3. The anode 2 is connected by suitable conductors to the secondary 4 of a power transformer having a core 5 and a primary 6. The primary 6 is connected to a regulating auto-transformer, generally illustrated at 7, which in turn is connected to a suitable source of electrical energy, such as a 220 or 440 volt alternating current. Direct current is supplied by means of a low voltage direct current generator, generally shown at 8, one side of which passes to the work piece 3 through a rheostat 9 and the other side of which is connected to the secondary 4 in the manner shown.

In Fig. 2, as will be recognized by those skilled in the art, the wave form illustrated is shown graphically by plotting amplitude in terms of current or voltage against time. Thus, X—X is the zero axis, Y represents the combined voltage or current of the positive peak, and $Y_1$ represents zero voltage or current at the negative peak. A wave form of this type wherein the negative peak $Y_1$ is above the X—X axis may be described as pulsating direct current. If $Y_1$ is below the X—X axis, the wave form is referred to herein as asymmetric provided the positive and negative peaks are unequal values from the X—X axis and Y is positive or above the X—X axis.

Fig. 3 illustrates graphically the minimum permissible wave form shown by plotting amplitude in voltage or current against time in which the value $Z_1$ between the zero axis ($X_1$—$X_1$) and the negative peak is $\frac{2}{3}$ of the value Z.

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
$\frac{1}{10}$%, based on the total weight of the mixture, of lauryl sulfate.



The resultant mixture is an acid electrolyte or plating bath suitable for the deposition of antimony on steel or other conducting surfaces 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 with reference to Fig. 1. 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 compositions:

| | 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 as an oxidizing agent. Other examples of suitable oxidizing agents are dissociable sulphur compounds such as ferric sulfide, polysulfides, and other metals of the oxygen group of metals, such as tellurium.

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 with the omission of the oxidizing agent (metallic selenium), the surface tension reducing agent (lauryl sulfate), and/or the arsenic trioxide, although the results are less desirable for reasons previously indicated.

*Example III*

In the procedure described in Example I, 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 an alkaline bath is the following:

4.4 ounces potassium carbonate
2.11 ounces antimony sulfide ($Sb_2S_3$)

in one quart of water boiled for one hour and then filtered, the water lost by evaporation being replaced.

With an alkaline bath of this type the ratio of alternating current to direct current may be varied from that described in Example I in order to obtain the optimum plating conditions and to retain a wave form within the preferred range previously described, as indicated by the minimum and maximum limits of Figs. 2 and 3.

*Example IV*

Instead of the antimony plating bath, an arsenic plating bath may be used having the following composition:

1¾ ounces sodium arsenate
0.8 ounce 98% potassium cyanide
1 quart of water

These are boiled together for ½ hour, then filtered and used at a temperature of 167° to 176° F. with a strong current. The ratios of alternating to direct current may be varied in order to obtain the optimum wave form.

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 material," 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.

The method of controlling the adherence of vitreous enamels to ferrous metals by forming on the ferrous metal base stock a layer of an elemental substance from the group consisting of sulfur and selenium, then covering said layer with a thin coating of a metal from the group consisting of antimony, arsenic and bismuth, and firing a vitreous enamel over said metal coating, is disclosed and claimed in my copending application Serial No. 260,577, filed December 7, 1951.

The invention is hereby claimed as follows:

A method of preparing vitreous enamel coated articles which consists essentially of electrodepositing on a ferrous metal article to be enameled a substantially uniform thin coating of a metal from the group consisting of antimony, arsenic and bismuth, said electrodeposition occurring from an electroplating bath containing a salt of said metal with an asymmetric alternating plating current comprising as one component an alternating current of a frequency within the range of 25 to 60 cycles and as the other component a direct current, the ratio of A. C. : D. C. being 2 to 4 volts R. M. S. : 2.5 volts D. C., at current densities within the range from about 2 to 15 amperes per square foot for a period of time within the range from about 8 seconds to 1½ minutes, thereafter applying over said metal coating a coating composition of a vitreous enamel substantially free from bonding materials, and then firing said enamel.

ALLAN E. CHESTER.

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