Patented Oct. 17, 1944

2,360,413

UNITED STATES PATENT OFFICE

2,360,413

VITREOUS ENAMEL COATED OBJECTS AND METHOD OF PRODUCING THE SAME

Charles A. Getz, Glen Ellyn, and George Weidmann, Chicago, Ill.

No Drawing. Application November 13, 1940, Serial No. 365,556

19 Claims. (Cl. 117—70)

This invention relates to methods of applying vitreous enamels to non-ferrous metallic materials which are predominantly copper and are substantially free of lead, and the enameled objects produced by such methods.

The world of today is possessed of entirely satisfactory methods for applying vitreous enamels to both large and small surface areas of objects which are formed of ferrous metals. It has been impossible, however, to make the same assertions regarding methods for applying vitreous enamels to either large or small surface areas of objects which are formed of non-ferrous metallic materials, such as copper base alloys of the bronze group and commercially pure copper. With the market for objects formed of such material, which have an esthetic appeal, growing at an ever-increasing rate, the inability to further ornament these objects by applying an enamel coating to desired portions of their surfaces is a source of disappointment and embarrassment to their manufacturers.

A thorough study of the present, unsatisfactory methods of applying vitreous enamels to non-ferrous metallic materials, and the work produced thereby, has convinced us that these methods have been incapable of providing enameled surfaces which will not chip or scale off, as a result of the development of cracks or breaks in the coating, because workers in the art have failed to recognize or understand the reasons why such cracks or breaks develop. We have determined that one or more of the following practices may be held responsible for the development of these defects:

1. The use of non-ferrous metallic materials which include constituents that volatilize at the high temperatures employed in enameling processes causing the emission of gases which prevent proper fusion of the enamel binder to the metal surface.

2. The use of non-ferrous metallic materials which do not have their various constituents uniformly mixed and/or "married" during alloying and thereby develop localized spots to which the enamel binder will not properly become attached.

3. The failure to use temperatures which are high enough to cause the binder to penetrate the pores of the metal to a sufficient extent and depth to provide the proper anchorage and/or to cause the proper fusion of the binder and the enamel frit.

4. The failure to employ non-ferrous metallic materials which will retain their structural strength when subjected to the high temperatures required for a successful enameling process.

5. The use of furnaces which will not effect uniform heating of the objects throughout the entire areas to be enameled and which will not subject the objects, the binder, and the enamel frit to the same degree of heat.

6. The failure to recognize the importance of very accurate temperature and time control over the steps of bonding the binder to the objects and fusing the enamel frit to the binder.

7. The use of a binder which, because of its method of manufacture and/or the particular constituents combined to produce the same, undergoes further chemical changes or reactions when subjected to the high temperatures of a satisfactory enameling process and thereby prevents the formation of a perfect bond with the metal and the enamel.

8. The failure to overcome the difficulties arising from the difference in the temperature coefficient of expansion and contraction between the metal and the enamel when heated to such high temperatures.

9. The failure to provide an enamel coating which is of uniform thickness throughout its entire area and particularly the marginal edge portions.

The primary object of this invention is to provide methods of forming vitreous enamel coated objects produced of non-ferrous metallic materials which are predominantly copper and are substantially free of lead, said methods avoiding all of the aforementioned practices which have been responsible for the production of imperfect enameled objects.

A further important object of the invention is to provide methods for applying vitreous enamels to non-ferrous metallic materials, such as copper base alloys of the bronze group, and pure commercial copper, which will produce enamel coatings that will not chip or scale as a result of imperfections developed during application.

Still another important purpose of this invention is to provide vitreous enamel coated bronze or copper objects and to provide their coatings either of a solid or single color or of a mottled combination of several colors.

Other objects and advantages of the invention will be apparent during the course of the following description.

Prior workers in the art apparently have failed to recognize the importance of selecting the

proper types of non-ferrous metallic materials on which to apply coatings of vitreous enamel. The desire to enamel copper base alloys of the bronze type is most pronounced. This, apparently, is due to the fact that bronzes have the desired structural strength, uncoated portions are not easily scratched or marred, and the natural color of bronze is more pleasing than pure copper.

There are available on the open market several different bronze alloys which have been developed for ordinary and special uses. Ordinary commercial bronze consists of an alloy of copper, tin, lead, and zinc. The copper, of course, is the base element, and it comprises from 88% to 89% of the entire mixture. This basic element of the alloy is noted for its resistance to corrosion and, of course, is responsible for the color characteristics of the resultant alloy. It has a relatively high melting point in the pure state. As casting is the usual method employed for producing bronze objects, the lead constituent is employed primarily for the purpose of adding fluidity to the molten alloy and thus causing it to flow and more perfectly fill all portions of the mold cavity. This lead constituent comprises from 1% to 2% of the alloyed mixture. Neither copper nor lead is a very hard metal, and the surfaces of objects formed of either of these elements are easily scratched or marred. Therefore, to give the bronze the desired degree of hardness, the zinc and tin constituents are included. Tin comprises 8% of commercial bronze, and the zinc varies from 3% to 4%, depending upon the amount of lead employed.

A bronze, to be suitable for having a perfect vitreous enamel coating applied thereto, must be able to retain its structural strength when subjected to temperatures as high as 1600° F. When subjected to such high temperatures, it has been determined that the lead constituent of ordinary commercial bronze will volatilize and cause the emission of gases from the surfaces of the bronze objects being heated. These liberated gases, when emitted from a surface on which the enamel binder is being applied, interfere with the perfect bonding of the binder with the surface of the object. These gases not only form minute bubbles on the surface of the object, but they are trapped in the pores of the material which, as will be explained, should be filled with the binder to provide a perfect union between the binder and the material. To overcome this detrimental characteristic of lead, we have determined that this element must not be present to any substantial extent in bronze which is to be provided with a satisfactory vitreous enamel coating.

Copper, to be suitable for having a perfect vitreous enamel coating applied thereto, also must be as free of lead as is possible. So-called pure commercial copper contains from 0.4% to 0.1% impurities and one of these impurities is lead. However, the copper which has only the 0.1% of impurities contains such a small portion of lead that it has been found to be satisfactory.

It has been determined that the most perfect combination of elements for producing a bronze which has the desired characteristics regarding strength and hardness and which forms a perfect base to which vitreous enamel may be applied consists of 88% pure copper, 10% zinc, and 2% tin. Of course, when the non-ferrous metallic material to be enameled is pure copper, it constitutes 100% of the object being coated. Starting with 100% copper, we have found that the copper of the alloy can be reduced as low as 80% and still obtain a structure which may be properly enameled. Depending upon the percentage of copper employed, the zinc may be varied from 12% to 0% and the tin may be varied from 8% to 0%. Therefore, the limits for an acceptable non-ferrous metallic material will be from 100% copper to a mixture which includes 80% copper, 12% zinc, and 8% tin. All conceivable combinations falling within these limits which will provide a material that will retain its structural strength at temperatures up to 1600° F. will permit proper temperatures to be employed during the enameling process.

The alloying of the copper, zinc, and tin constituents should be carefully carried out to assure a thorough mixture of these elements and to provide a proper "marriage" between the same. Imperfect alloying of these elements will produce "spots" on the surfaces of objects molded therefrom. Such imperfect spots will not bond with the binder for the enamel in the same manner as or to the same extent as the perfectly alloyed surfaces and a defect in the enameled coating is the result.

The objects to be provided with the vitreous enamel coating are cast or molded from a bronze alloy of the proper proportions of copper, tin, and zinc, or from pure commercial copper, and the areas to be coated are thoroughly cleaned. These areas should be enclosed within or surrounded by a retaining rib which is cast integrally with the body of the object. These ribs are, of course, raised above the surface to be enameled and their height should be from $\frac{1}{16}$ to $\frac{1}{8}$ of an inch. Ribs of greater height can be employed, but they detract from the general appearance of the object, and they cause water to accumulate on the enameled surface if the object is placed in the open and is arranged horizontally. These raised boundaries or ribs may be of any desired cross-sectional shape, but it is preferred that their inner edges, i. e., the edges presented to the surface to be enameled, be arranged at right angles to said surface. These barriers or ribs function to retain on the involved area the melted binder and enamel frit. They prevent the enamel frit from running beyond the area to be covered and thereby prevent enameled edge portions or margins of reduced thickness from being formed. In actual use, these raised margins or ribs protect the edges of the enamel from damage as a result of rough handling, etc.

It will be briefly pointed out at this time that the plate-like objects to be enameled will be molded or cast with reinforcing ribs formed on their rear faces. Preferably, these raised, reinforcing ribs will be arranged in two sets or groups that extend at right angles to each other and in parallelism with the four marginal edges of the plates. The function performed by these reinforcing ribs will be explained in detail when the difference in the temperature coefficient of expansion and contraction between copper or bronze and enamel is dealt with.

Of course, the surface of an object to be enameled must first be conditioned, such as by cleaning, to remove all impurities, foreign matter, and the like, therefrom. The vitreous enamel coating to be applied to the conditioned surface is attached thereto by means of a binder. It has been determined that care must be taken in selecting the binder. Many binders which have been used in the past to bond vitreous enamel to copper or copper base alloys have been found to be inef-

ficient because their methods of manufacture and/or the particular constituents combined to produce the same have resulted in leaving some of the starting materials in a chemically active state. Such materials undergo a further chemical reaction, when subjected to the high temperatures employed during the enameling process, and this reaction interferes with the bonding of the binder to the base material and the fusion of the enamel frit to the binder. We have determined that lead silicate, when prepared in accordance with one of the following methods, is an entirely satisfactory binder.

The lead silicate employed as a binder between the enamel and the base material should in general be of high purity for most efficient results. As stated above, various methods may be utilized to obtain a highly pure lead silicate which is satisfactory for use in accordance with this invention.

One method of preparing lead silicate of high purity is by chemical precipitation from an aqueous solution of lead salts, such as lead nitrate, by the addition of alkali metal silicate, such as sodium meta silicate. By the use of pure lead salts and pure alkali metal silicate, a high degree of purity of the resulting precipitate of lead silicate may be secured. The precipitate may be freed of the reactants from which it is formed by extensive washing with water, preferably hot water.

Another method of forming pure lead silicate comprises using lead salts with silicate materials. Various lead salts and various silicate materials may be used. For example, a lead oxide may, if desired, be fused with a silicic acid, or an alkali metal silicate, to form the desired lead silicate. The degree of purity of the resulting precipitate will depend upon the purity of the lead oxides and of the silicate materials.

As another example, a lead salt containing a volatile anion radical, such as lead nitrate, lead chlorate and the like, may be fused with silica or with silicates containing a volatile cation, to thereby form a lead silicate and volatile salts. During the fusion, the latter salts volatilize to leave the lead silicate free of impurities. Illustrative of this is the fusion of lead nitrate and ammonium silicate to yield lead silicate and volatile ammonium nitrate.

Fluxing materials of various kinds may be employed in the fusion methods above described. In general, however, only those fluxing materials which will volatilize away should be employed in order that the resultant lead silicate will be of a high degree of purity.

While a pure form of lead silicate is the desired binder in the preferred embodiment of the herein described invention, other similar materials may be employed. For example, lead oxides may be fused with silicious materials, such as quartz or flint in ground or powdered form. Borax, arsenic oxides, and alkali salts, such as sodium or potassium carbonates or nitrates, also may be utilized in connection with the fusion reactions, if desired.

A thin coat or layer of this lead silicate binder is sifted evenly over the cleaned area of the base material which is to receive the enamel coating. When sifted, the binder, of course, will be in a powdered or pulverized condition. If desired, however, the binder may be applied as a paste or a spray. This thin coat or layer of binder should have a thickness of from $\frac{1}{32}$ to $\frac{1}{8}$ inches to give the best results. During the first firing of the object, the binder melts and penetrates the expanded pores of the heated body material. The major portion of the binder should penetrate the surface portion of the object, but it is important that a small quantity of this glass-like binder be left as a film or layer on the surface being enameled at the first firing, because it is this excess film or layer which fuses with the enamel frit. It is important not to have too much excess material left on the surface, and for that reason the amount of binder applied to the surface of the object is important. The amount of binder to be used to obtain the desired result will depend on the firing temperature and the duration of this first firing operation. For example, if too large a quantity of binder is used and the firing temperature is not high enough or the firing period not long enough to cause the desired major portion of the binder to penetrate the pores of the base material, the degree and extent of penetration of the pores by the binder will not be proper, and too much of the binder will be left on the surface to be coated. The difference in the coefficiency of contraction of the binder and the enamel is rather large and weak spots or areas will be formed as a result of this difference if too much binder remains on the surface. If there is only a very small quantity of the binder material left on the plate, this small amount will be thoroughly blended with or diluted by the larger quantity of enamel frit with the result that the normal difference in the coefficiency of expansion between the binder and the enamel frit will be more or less completely eliminated and no weak spots or imperfections will be developed between the binder and the enamel.

The firing of the binder should be performed in a furnace which has been heated to a temperature of from 1400° F. to 1500° F. The preferred temperature in this range is 1450° F. The object is placed in the furnace and is allowed to heat up to the furnace temperature and then to remain at this temperature for from 3 to 5 minutes, depending upon the temperature of the furnace. If the furnace temperature is 1450° F., the object should maintained at that temperature for 4 minutes. If the temperature of the furnace is higher, less time is required. That is to say, 3 minutes will be sufficient for a furnace temperature of 1500° F. and 5 minutes will be required for a furnace temperature of 1400° F.

It is important to employ a furnace temperature and a heating time which fall within the above noted ranges; otherwise the binder will not have the proper degree of fluidity and will not penetrate the pores of the base material to a desired depth or to a sufficient extent. This will be apparent from the fact that the higher the temperature to which a metal is heated, the more porous it becomes, and if the object is not heated to a sufficiently high temperature, the object will not possess the desired degree of porosity to permit proper penetration of the binder.

After the binder has been properly fired, the metal oxide formed during the firing should be removed. Such oxide will form on exposed surfaces of the object to which no binder has been applied. Preferably, the object should be removed from the furnace and allowed to cool before undertaking the removal of the oxide.

The binder coated surface of the object now is ready to receive the enamel frit. The enamel frit in granular or powdered form is applied evenly over the thin coating or layer of fused

binder and the depth of the enamel frit should be approximately from 1/8 to 1/4 inch.

The object is then placed in a furnace having a temperature of from 1380° F. to 1480° F. The preferred temperature is 1430° F. The object is permitted to remain in the furnace and be subjected to the furnace temperature for a sufficient length of time to permit the enamel frit to be properly melted and fused with the binder, which is remelted during this second firing period. The length of time required to melt and fuse the binder and the enamel frit varies with the particular enamel frit used. The periods found to be satisfactory for the various enamels, and enamel frit mixtures, which have been employed fall within a range of from 1/2 to 5 minutes.

In addition to using plain or solid colored vitreous enamels, we have developed a method of producing a mottled effect. From a distance the mottled enamel appears to be of some particular single shade or color, but upon close inspection, it will be seen to consist of a mixture of small points or areas of a variety of colors which give life, sparkle, and depth to the enamel. This unusual appearance is quite pleasing and differs from plain flat colors. This mottled, or multi-colored, enamel gives somewhat the effect of changeable silk which varies with different light exposures.

Without any intention of limiting this invention to any particular color combinations produced by certain enamel frit mixtures, it will be explained that a wide variety of blue-gray-green color combinations so far have been used extensively. One very pleasing combination involves several shades of green which in combination simulate the antique verdi green that is seen on old bronze statues, etc.

Merely by way of example, and without attempting to identify the color or color effects produced in each instance, three different typical examples of mixtures will be set forth as follows:

A

Parts	Description
1	Delicate gray-blue (opaque).
2	Medium green (opaque).
5	Grey (transparent).
2	Grey (opaque).

B

Parts	Description
6	Medium green (opaque).
1	Grey (opaque).
1/2	Delicate grey-blue (opaque).
4	Grey (transparent).

C

Parts	Description
5	Medium green (opaque).
5	Colorless (buff) (transparent).
1	Delicate grey-blue (opaque).

The mottled or multi-colored effects will differ with different enamel particle sizes. If even distribution of the mottled effect is the result desired, it is particularly important that each colored enamel that is used should be of the same particle size. The particle sizes of the different colors of enamels may differ one from the other if an uneven mottled effect is desired.

The particle sizes which should be used will fall between 60 mesh and 100 mesh; that is, the smallest size will be retained by a 100 mesh screen, while the largest size will pass through a 60 mesh screen. With regard to these particle sizes, the coarse particles of the range give a more marked mottled effect, while the finer particles will give a less mottled effect.

After the enamel frit is properly fired, the object is removed and allowed to air cool. The oxide, which was formed during firing, should be removed from the surfaces of the object which were not coated. If desired, lacquer, or the like, may be applied to the entire surface of the object.

Enamel has a lower coefficiency of expansion and contraction than the non-ferrous metallic materials being coated. This difference must be overcome or a proper bond will not be provided. The filling of the pores of the front face portion of the plate-like object by the penetration of the binder during its firing prevents this front portion from contracting to a normal extent; i. e., it lowers its coefficiency to approximately that of the enamel.

However, the above noted effect has a tendency to cause the object to bend or curve. This tendency to bend or curve is not desirable for two reasons: first, the appearance is objectionable, and second, it causes the hardened enamel to bend, thereby subjecting it to destructive stresses and strains. The reinforcing bars formed on the rear face or back of the plate-like objects have been found to overcome any tendency for them to bend or curve. It is believed that these reinforcing ribs prevent the bending of the plates because they cooperate with the pore-filled top surface portions to lower the coefficiency of contraction of the entire object. In other words, the back portion of the plate-like object cannot contract to its normal degree because the reinforcing ribs compel this rear portion to contract only to the same extent as the front portion. As the pore-filled front portion cannot contract to its normal degree, the rear or back portion will not be permitted to contract to its normal degree. The final result is that the coefficiency of contraction has been lowered for the entire plate-like object to approximately that of the enamel.

Regarding the type of furnace to be used for the two firing operations, it is important that the plate-like objects be supported in a horizontal plane within the heating chamber of the furnace and the heating elements should be located above and below the plates to effect an even distribution of heat over their entire area. In other words, opposed sources of heat should be provided for the plate-like objects, and these sources should be parallel with the plane of the plate.

It is obvious that if the sources of heat were arranged at right angles to the plane of the plate-like object, and beyond its edges, the marginal portions of the object would heat up much faster than the central portion. This would be true even though the furnace were permitted to reach the desired temperature and the center of the plate be given time to reach the proper temperature for, under such conditions, the marginal portions would still be hotter than desired.

It is extremely important that the entire area of the plate be heated uniformly because:

(*a*) For the first firing, the binder is sifted on the surface to be coated in an even layer. By subjecting this binder to an uneven fusing heat, it has been determined that the penetration of the binder into the pores of the base material will

be equally uneven. The only way such an uneven heating condition could be remedied would be to vary the depth of the layer or coating of binder in accordance with variations in heat applied to different areas of the object.

(b) During the second firing, the enamel frit is fused to the binder. To obtain the colors desired, especially the mottled colors, it is essential that all of the enamel frit be subjected to the same temperature. The blending of the different colored enamels to produce the mottled effect is dependent upon the amount of heat applied to the enamel frit. If certain portions of the object were subjected to higher temperatures than other portions, the blending would be uneven and the desired effect would not be obtained.

It is very important that accurate control be maintained over the furnace temperatures during the two firing operations and the timing of these periods. For this reason, suitable temperature and time control devices should be applied to the furnace.

Without any intention of limiting this invention to the enameling of any particular types of objects, it will be noted that this enameling method is particularly suited for ornamenting grave markers, interior and exterior signs, memorial placques, etc.

It will be obvious that various changes in the proportions, materials, and other details, which have been herein described in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims.

Having thus described the invention, we claim:

1. A method of producing vitreous enamel coated objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a non-ferrous metallic material consisting of from 80% to 100% copper and substantially lead-free, firing all portions of the object and the binder to a uniform temperature falling between 1400° F. and 1500° F., applying enamel frit to the binder treated surface of the object, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F.

2. A method of producing vitreous enamel coated objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a non-ferrous metallic material consisting of from 80% to 100% copper and substantially lead-free. firing all portions of the object and the binder to a uniform temperature falling between 1400° F. and 1500° F. for a sufficient length of time to cause the binder to melt and the major portion to penetrate the pores of the object leaving the remainder as a film of uniform thickness over the surface, applying enamel frit to the remaining binder film, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F. for a sufficient length of time to cause the binder film and enamel frit to melt and uniformly fuse.

3. A method of producing vitreous enamel coated objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a non-ferrous metallic material consisting of from 80% to 100% copper and substantially lead-free, firing all portions of the object and the binder to a uniform temperature falling between 1400° F. and 1500° F. for from 3 to 5 minutes to cause the binder to melt and the major portion to penetrate the pores of the object leaving the remainder as a film of uniform thickness over the surface, applying enamel frit to the binder film, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F. for from ½ to 5 minutes to cause the binder film and enamel frit to melt and uniformly fuse.

4. A method of producing vitreous enamel coated objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a non-ferrous metallic material consisting of from 80% to 100% copper and substantially lead-free, firing all portions of the object and the binder to a uniform temperature falling between 1400° F. and 1500° F. for a sufficient length of time to cause the binder to melt and the major portion to penetrate the pores of the object leaving the remainder as a film of uniform thickness over the surface, cooling the object, removing metallic oxide formed during firing, applying enamel frit to the binder film, firing all portions of the object, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F. for a sufficient length of time to cause the binder film and enamel frit to melt and uniformly fuse, air cooling the object, and removing metallic oxides formed during the second firing period.

5. A method of producing vitreous enamel coated objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a non-ferrous metallic material consisting of from 80% to 100% copper and substantially lead-free, firing all portions of the object and the binder to a uniform temperature of 1450° F., applying enamel frit to the binder treated surface of the object, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature of 1430° F.

6. A method of producing vitreous enamel coated objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a non-ferrous metallic material consisting of from 80% to 100% copper and substantially lead-free, firing all portions of the object and the binder to a uniform temperature of 1450° F. for a sufficient length of time to cause the binder to melt and the major portion to penetrate the pores of the object leaving the remainder as a film of uniform thickness over the surface, applying enamel frit to the binder film, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature of 1430° F. for a sufficient length of time to cause the binder film and enamel frit to melt and uniformly fuse.

7. A method of producing vitreous enamel coated objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a non-ferrous metallic material consisting of from 80% to 100% copper and substantially lead-free, firing all portions of the object and the binder to a uniform temperature of 1450° F. for four minutes to cause the binder to melt and the major portion to penetrate the pores of the object leaving the remainder as a film of uniform thickness over the surface, applying enamel frit

to the binder film, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature of 1430° F. for 3 minutes to cause the binder film and enamel frit to melt and uniformly fuse.

8. A method of producing vitreous enamel coated objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a non-ferrous metallic material consisting of from 80% to 100% copper and substantially lead-free, firing all portions of the object and the binder to a temperature of 1450° F. for a sufficient length of time to cause the binder to melt and the major portion to penetrate the pores of the object leaving the remainder as a film of uniform thickness over the surface, cooling the plate, removing metallic oxides from the exposed surfaces of the object, applying enamel frit to the binder film, firing all portions of the object, the binder, and the enamel frit to a uniform temperature of 1430° F. to cause the binder film and enamel frit to melt and uniformly fuse, air cooling the object, and removing metallic oxides formed during the second firing step.

9. A method of producing vitreous enamel coated copper base alloy objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a mixture consisting of not less than 80% copper, not more than 12% zinc, and not more than 8% tin, with the elements so proportioned as to provide an alloy that will retain its structural strength at firing temperatures up to 1600° F., firing all portions of the object and the binder to a uniform temperature falling between 1400° F. and 1500° F., applying enamel frit to the binder treated surface, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F.

10. A method of producing vitreous enamel coated copper base alloy objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a mixture consisting of not less than 80% copper, not more than 12% zinc, and not more than 8% tin, with the elements so proportioned as to provide an alloy that will retain its structural strength at firing temperatures up to 1600° F., firing all portions of the object and the binder to a uniform temperature falling between 1400° F. and 1500° F. for a sufficient length of time to cause the binder to melt and the major portion to penetrate the pores of the object leaving the remainder as a film of uniform thickness over the surface, applying enamel frit to the binder film, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F. for a sufficient length of time to cause the binder film and enamel frit to melt and uniformly fuse.

11. A method of producing vitreous enamel coated copper base alloy objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a mixture consisting of not less than 80% copper, not more than 12% zinc, and not more than 8% tin, with the elements so proportioned as to provide an alloy that will retain its structural strength at firing temperatures up to 1600° F., firing all portions of the object and the binder to a uniform temperature falling between 1400° F. and 1500° F. for from 3 to 5 minutes to cause the binder to melt and the major portion to penetrate the pores of the object leaving the remainder as a film of uniform thickness over the surface, applying enamel frit to the binder film, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F. for from ½ to 5 minutes to cause the binder film and enamel frit to melt and uniformly fuse.

12. A method of producing vitreous enamel coated copper base alloy objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a mixture consisting of 88% copper, 10% zinc, and 2% tin, firing all portions of the object and the binder to a uniform temperature falling between 1400° F. and 1500° F. for a sufficient length of time to cause the binder to melt and the major portion to penetrate the pores of the object leaving the remainder as a film of uniform thickness over the surface, applying enamel frit to the binder film, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F. for a sufficient length of time to cause the binder film and enamel frit to melt and uniformly fuse.

13. A method of producing vitreous enamel coated copper base alloy objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a mixture consisting of 88% copper, 10% zinc, and 2% tin, firing all portions of the object and the binder to a uniform temperature falling between 1400° F. and 1500° F. for from 3 to 5 minutes to cause the binder to melt and the major portion to penetrate the pores of the object leaving the remainder as a film of uniform thickness over the surface, cooling the object, removing metallic oxides formed during firing, applying enamel frit to the binder film, firing all portions of the object, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F. for from ½ to 5 minutes to cause the binder film and enamel frit to melt and uniformly fuse, air cooling the object, and removing metallic oxides formed during the second firing period.

14. A method of producing vitreous enamel coated objects, comprising applying a binder composed essentially of substantially pure lead silicate to the cleaned surface of an object formed of a non-ferrous metallic material consisting of from 80% to 100% copper and substantially lead-free, firing all portions of the object and the binder to a uniform temperature falling between 1400° F. and 1500° F., applying to the binder treated surface of the object a layer of a mixture of different colored enamels as a frit, the particle size of which will fall between 60 mesh and 100 mesh, and firing all portions of the object, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F.

15. A method of enameling non-ferrous metallic materials which are consisting of from 80% to 100% copper and are substantially free of lead, comprising applying a binder composed essentially of substantially pure lead silicate to a cleaned surface of the material, firing all portions of the material and the binder to a uniform temperature falling between 1400° F. and 1500° F., ap-

plying enamel frit to the surface of the fired binder, and firing all portions of the material, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F.

16. A method of enameling non-ferrous metallic materials which are consisting of from 80% to 100% copper and are substantially free of lead, comprising applying a binder composed essentially of substantially pure lead silicate to a cleaned surface of the material, firing all portions of the material and the binder to a uniform temperature falling between 1400° F. and 1500° F. for a sufficient length of time to cause the binder to melt and the major portion to penetrate the pores of the material leaving the remainder as a film of uniform thickness over said surface, applying enamel frit to the binder film, and firing all portions of the material, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F. for a sufficient length of time to cause the binder film and enamel frit to melt and uniformly fuse.

17. A method of enameling non-ferrous metallic materials which are consisting of from 80% to 100% copper and are substantially free of lead, comprising applying a binder composed essentially of substantially pure lead silicate to a cleaned surface of the material, firing all portions of the material and the binder to a uniform temperature falling between 1400° F. and 1500° F. for from 3 to 5 minutes to cause the binder to melt and the major portion to penetrate the pores of the material leaving the remainder as a film of uniform thickness over the surface, applying enamel frit to the binder film, and firing all portions of the material, the binder, and the enamel frit to a uniform temperature falling between 1380° F. and 1480° F. for from ½ to 5 minutes to cause the binder film and enamel frit to melt and uniformly fuse.

18. A vitreous enamel coated object, comprising a body formed of non-ferrous metallic material consisting of from 80% to 100% copper and substantially lead-free, a vitreous enamel coating covering a surface area of said body, and a binder composed essentially of substantially pure lead silicate bonding the enamel coating to the body.

19. A vitreous enamel coated object, comprising a body formed of an alloy consisting of not less than 80% pure copper, not more than 12% zinc, and not more than 8% tin, a vitreous enamel coating covering a surface area of said body, and a binder composed essentially of substantially pure lead silicate bonding the enamel coating to the body.

CHARLES A. GETZ.
GEORGE WEIDMANN.