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ENAMELED PRODUCT AND METHOD OF MAKING THE SAME

Oscar E. Harder and John D. Sullivan, Columbus, Ohio, assignors to Battelle Memorial Institute, Columbus, Ohio, a corporation of Ohio

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Our invention relates to an enameled product and a method of making the same. It has to do particularly with the application of vitreous enamels on metals. It relates particularly to the application of such enamels to alloys.

In the prior art, it has generally been customary to apply vitreous coatings to cast iron, sheet iron or steel. However, these metals are susceptible to corrosion and, if the surface of the vitreous material is cracked so as to expose the metal base, corrosion shortly sets in, with the result that the product is rendered unsightly and its life is materially shortened.

In order to overcome this disadvantage, some attempts have been made to employ certain metals and alloys that are resistant to atmospheric corrosion. For example, copper and some of its alloys have been used for this purpose. However, copper and many of its alloys, on heating to the temperature required to mature the vitreous frit, are annealed and become soft. Therefore, in order to insure sufficient strength, the coated metal must be thick. This results in an increased cost for the finished article.

One of the objects of this invention is to obtain an enameled metal object which possesses adequate resistance to atmospheric corrosion by the use of a metal or alloy which is inherently resistant to such corrosion, even in the event of cracking of the enamel and, at the same time, to use relatively thin sections of the metal which, nevertheless, have sufficient strength and rigidity in spite of the fact that they are relatively thin.

Another object of this invention is to produce enameled metal products of the nature indicated by a simplified and novel method which will serve to reduce the cost of manufacture.

Our invention preferably involves the use of an alloy as a base to which the vitreous enamel is applied and, more particularly, the use of an alloy of a class that may be hardened and strengthened by precipitation-hardening. For example, copper base alloys containing nickel and silicon are capable of hardening through precipitation of nickel silicide. Likewise, some of the copper-tin-nickel alloys may be hardened by precipitation. That the aluminum alloys of the duralumin type are precipitation-hardening is well known. These and many other alloys are of the precipitation-hardening type and our invention contemplates the use of an alloy of this type to which hardness and strength can be imparted by the precipitation-hardening process, preferably after the vitreous enamel has been applied thereto.

For example, we may take a copper-nickel-silicon alloy of a composition suitable for precipitation-hardening and subject it to a temperature sufficient to bring the metal of the alloy into complete solid solution. The preferred temperature is about 1400° F., or above, and the time of application thereof for the attainment of the desired result depends on the thickness and shape of the piece of metal and the type of the heating furnace. The metal which has thus been treated is then cooled with sufficient rapidity to maintain the metal in substantially complete solid solution. It is then preferably pickled in a suitable pickling agent, which, for example, may be an acid bath. After pickling, the article is thoroughly washed and dried.

With the article thus prepared, vitreous enamel may then be applied by one of the methods well known to the ceramic and enameling art. For example, this may be done by the use of a vitreous enamel frit and by spraying, dipping or by the dry dusting process. The frit-covered article is then fired in a suitable furnace for a sufficient time to effect fusion of the frit thereon to a continuous and more or less smooth vitreous layer which covers and protects the surface of the alloy.

The article may then be removed from the furnace and cooled to room temperature, this cooling being sufficiently rapid that the alloy composition remains in substantially complete solid solution throughout this cooling operation, so that the now-enameled material suffers no undue precipitation of the precipitation-hardening compounds or materials in the alloy. Air-cooling of comparatively thin sheets, such as are commonly used for most enameled products is adequate for this purpose.

The article may then be reheated to the precipitation-hardening range of temperature and held within this temperature range for a sufficient time to precipitate out in a solid state a certain phase or phases, such as will produce hardening of the alloy. The enameled article may then be removed from the furnace and cooled.

As indicated above, however, we may, after the firing to effect fusion of the enamel, omit the step of cooling to room temperature and transfer the hot article to a furnace which will be effective to maintain the temperature of the article within the precipitation-hardening range. It is held in this furnace at this suitable lower temperature for a sufficient time to effect the desired precipitation-hardening and may then be

removed from the furnace and cooled. This latter method of arrested cooling is particularly efficacious in handling objects that would otherwise require water-quenching in order to fully preserve the alloy in substantially complete solution in cooling from the enameling temperature. It avoids any danger of injury which the enamel might suffer from the use of a drastic quenching operation.

It should be understood that both temperature and time are important considerations in the final step of precipitation-hardening, that is, the period wherein certain compounds or materials are precipitated out of the complete solid solution to bring about hardening of the alloy. Thus, a comparatively high temperature applied for a comparatively short time may accomplish the desired result and, at the same time, a comparatively low temperature for a comparatively long period of time may be effective to produce substantially similar results. Since the alloy is preferably enameled before this last step of precipitation-hardening, we utilize these variables to avoid injury to the enamel. In other words, we preferably select a temperature within the precipitation-hardening range which is sufficiently low that the enamel will not be injured and, if necessary, prolong the time at which this enameled article is subjected to such temperature sufficiently to complete the precipitation-hardening action.

In this specification, the terms "annealed" or "annealing" are used to designate that step of the process which, by the application of heat, brings the alloy into substantially complete solid solution.

The following example will demonstrate results which have been obtained in a test in which the alloy was annealed, coated with enamel, fired, cooled to room temperature, and then reheated to effect precipitation-hardening. An alloy sample .02 in. thick, containing about 97.65% of copper, 1.9% of nickel, and 0.45% of silicon, was heated (annealed) at 1472° F. for thirty minutes to effect solution and homogenizing. The alloy was then cooled to room temperature, cleaned, and pickled, and enamel frit applied. The piece was fired at 1600° F. for 3½ minutes to effect fusion of the enamel to a continuous layer. The enameled specimen was cooled to room temperature and then reheated to a temperature of 1000° F. for 30 minutes to effect precipitation-hardening. The hardening produced by this treatment is summarized as follows:

	Rockwell F, $\frac{1}{16}$" ball, 60 kg. load
Annealed	64
Annealed+1600° F. for 3 min.+1000° F. for 30 min.	93

As another example, one method which we have used in the production of our product has involved the selection of a copper-nickel-silicon alloy containing about 97.6% copper, 2% nickel and .4% silicon, and the application of our method thereto. The annealed alloy, in the form of a sheet approximately 0.02 inch thick, was cleaned in an alkaline cleaner and, after cleaning, it was pickled in a bath of $H_2SO_4.Na_2Cr_2O_7$ and, after pickling, it was washed and dried. Vitreous enamel frit of a composition suitable to mature at 1500° F. and to adhere to the alloy used was applied to the dried surface and the piece fired to fuse the frit to a vitreous layer that completely covered the metal surface. In the case of one vitreous enamel used, the firing was for 3½ minutes at 1500° F. The fired piece was then transferred without cooling to another furnace and held for one-half hour at 1000° F. After this treatment the piece was removed from the furnace and cooled in air. The hardening produced by this treatment is summarized as follows:

	Rockwell F, Number $\frac{1}{16}$" ball, 60 kg. load
Annealed	62
Annealed+3½ minutes at 1500° F.	63
Annealed+3½ minutes at 1500° F.+30 minutes at 1000° F.	98

The following example will demonstrate the method on another type of alloy. An alloy, in the form of a sheet approximately 0.02 inch thick, consisting of about 87% copper, 7.5% nickel and 5.5% tin was homogenized for one and three-quarters hours at 1400° F. It was then cleaned, pickled, washed and dried. A coating of vitreous frit was then applied and the piece fired at 1600° F. for 3 minutes to mature the frit to a continuous vitreous layer. After this treatment, the piece was transferred without cooling to another furnace and held for one hour at 700° F. The hardening produced by this treatment is summarized as follows:

	Rockwell F, Number $\frac{1}{16}$" ball, 60 kg. load
Annealed	89
Annealed+3 minutes at 1600° F.	90
Annealed+3 minutes at 1600° F.+1 hour at 700° F.	112

The above-mentioned alloys are given merely as examples and other alloys have been used. As indicated above, practically any alloy to which hardness and strength may be imparted by application of a precipitation-hardening process may be used, by varying the process to suit the particular alloy.

Other enamels may also be employed, as well as other methods of cleaning and pickling. These enamels and methods are well known in the art.

It is sometimes desirable to secure the maximum hardness possible with the particular alloy used and, in this case, complete solid solution should be obtained and maintained until the article is subjected to the final step which brings about the precipitation of the hardening phase or phases. However, maximum hardness is not always necessary and, in such a case, complete retention of solid solution may not be needed. In other words, even partial response to the final precipitation-hardening step may so improve the alloy over the fully annealed metals or alloys heretofore used for enameling as to render an alloy superior thereto, in spite of the fact that precipitation-hardening has been only partially effected. Thus, it is within the scope of our invention to bring the alloy into either complete solid solution or into partial solid solution, as long as the precipitation-hardening action is at least partially effective.

As a convenient method of carrying out our invention, we match the maturing temperature of the enamel with the temperature necessary for bringing the alloy into complete solid solution and accomplish the two operations simultaneously. The enameled article whose alloy has been brought into complete solid solution and whose enamel has been fused by the same heat may then be brought into the precipitation-hardening range either by arrested cooling or by cooling and

reheating and retained at the proper temperature within this range for a sufficient time to effect the desired precipitation-hardening.

In another modified form of our invention in which maximum hardness is not required, we may heat the alloy to effect solution and then subject it to a desirable precipitation-hardening treatment to effect hardening thereof. The hardened alloy is then cleaned and pickeled and enamel frit is applied to the surface in the usual manner. It is then fired in a suitable furnace at a sufficient temperature for a suitable time to effect fusion of the enamel to a vitreous layer. Since the time required to fuse the enamel is short, only partial resolution of the precipitation-hardening phase will result, and the alloy base may still possess adequate hardness and rigidity.

We have produced by our invention a highly satisfactory porcelain enameled product. By taking advantage of precipitation-hardening, we have been enabled to use less metal than hitherto possible with non-corrosive metals while, at the same time, attaining satisfactory strength and rigidity. Because the sheets are thinner, they have greater flexibility and there is less danger of cracking the enamel in handling. We have combined the advantages of porcelain enamel for preserving, decorating, ornamenting, and enhancing the beauty of the surface of alloys with the precipitation-hardening treatment which permits of the use of a corrosion-resistant metal of less thickness than hitherto possible and, yet, of adequate strength. The product which we have produced is a better and cheaper product and a marked advance in the art.

It will be seen from the above that the precipitation-hardening of the alloy metal, to which the enamel is to be applied in accordance with our process, may be effected either after the enamel is applied or before the enamel is applied. Likewise, the application of the heat necessary to bring the alloy metal into substantially complete solid solution may be effected either before the application of the enamel or during the firing of the product to effect fusion of the enamel. Variation of the times of occurrence of such steps as these may, obviously, be resorted to without departing from the spirit of our invention and such variations are within the scope of our invention.

Having thus described our invention, what we claim is:

1. The method of producing a vitreous enameled product which comprises applying vitreous enamel on a precipitation-hardening alloy, heating such enamel to effect fusion thereof, and then subjecting said enameled article to a temperature within the precipitation-hardening range for a period of time adequate to effect hardening of the alloy by precipitation.

2. The method of producing a vitreous enameled product which comprises applying a covering of vitreous enamel to an alloy which is capable of being precipitation-hardened and which is in substantially complete solid solution, subjecting the article to such a temperature and for such a period of time as to effect fusion of the vitreous enamel in a continuous layer, and then subjecting the enameled article to such a temperature and for such a period of time as will effect precipitation-hardening of the alloy.

3. The method of producing a vitreous enameled product which comprises applying a covering of vitreous enamel to an alloy which is capable of being precipitation-hardened and which is in substantially complete solid solution, subjecting the article to such a temperature and for such a period of time as to effect fusion of the vitreous enamel in a continuous layer, cooling the enameled article to room temperature at a rate adequate to maintain the metal in substantially solid solution, and then reheating said article and maintaining it at a temperature and for a period of time adequate to effect hardening of the alloy by precipitation.

4. The method of producing a vitreous enameled product which comprises applying a covering of vitreous enamel to an alloy which is capable of being precipitation-hardened and which is in substantially complete solid solution, subjecting the article to such a temperature and for such a period of time as to effect fusion of the vitreous enamel in a continuous layer, cooling the enameled article at a rate adequate to maintain the metal in substantially solid solution to a temperature within the precipitation-hardening range for such metal, and maintaining the article within such range for a period of time adequate to effect hardening of the metal by precipitation.

5. The method of producing a vitreous enameled product which comprises applying a covering of vitreous enamel to an alloy of a type which will be subject to precipitation-hardening, subjecting the alloy with the enamel thereon to a temperature which will mature the enamel and simultaneously produce substantially complete solid solution of the alloy, and then subjecting such enameled product to a temperature within the precipitation-hardening range for such a period of time as will effect hardening of such alloy metal by precipitation.

6. The method of producing a vitreous enameled product which comprises selecting an alloy of a type that may be precipitation-hardened, heating such alloy metal to effect substantially complete solid solution of the metal, then subjecting it to a temperature within the precipitation-hardening range for a period of time sufficient to produce hardening of the alloy by precipitation, applying a vitreous enamel to the alloy, and then firing at a sufficient temperature for a time adequate to effect fusion of the enamel to a vitreous layer, but terminating the first period before complete resolution of the precipitation-hardening phase.

OSCAR E. HARDER.
JOHN D. SULLIVAN.