

UNITED STATES PATENT OFFICE

2,680,085

METHOD OF MAINTAINING DIMENSIONAL TOLERANCES IN PARTIALLY ENAMELED METAL OBJECTS

Arthur Edward Raeuber, Jr., and James D. Sullivan, Milwaukee, Wis., assignors to A. O. Smith Corporation, Milwaukee, Wis., a corporation of New York

No Drawing. Application October 26, 1949,
Serial No. 123,786

6 Claims. (Cl. 148—6.35)

1

This invention relates generally to the art of vitreous enameling and particularly to the firing of a glass coating on a portion of a metal surface without any dimensional changes occurring in the uncoated metal resulting from the process. In order that this may be accomplished it is necessary that the uncoated metal surfaces remain free from any oxide scale.

There has long been need for an economical commercial method of firing a vitreous enamel to a portion of a bright metal surface and to have the uncoated remaining metal retain certain dimensional tolerances. To accomplish this end this invention provides a method whereby the firing and also the cooling of the fired vitreous enamel is carried out in a controlled atmosphere thereby in the first instance, preventing the formation of a hard oxide scale during the firing of the enamel and in the second instance, preventing the formation of an oxide scale while the partially enameled object is cooled down from the high temperatures of firing to a temperature where no oxide scale will form.

Experimental work carried out in connection with metal objects, a portion only of which was coated with vitreous enamel, and in which dimensional tolerances must be maintained, has disclosed that it is impossible to maintain the desired tolerances when a relatively thick coating of oxide is formed on the uncoated metal surface due to the process practiced. When the oxide is removed there is bound to be a change in the dimension of the workpiece.

It is known in the enameling art that a glass coating may be fused to a ferrous metal in a controlled atmosphere substantially devoid of free oxygen, water vapor and hydrogen. This procedure will prevent blistering, reboiling, and copperheading of the glass surface and is generally practiced when an entire ferrous surface is to be coated with glass. There is, however, no economical commercial method, except for this invention whereby glass may be fused to a portion of a metal surface and yet retain strict dimensional tolerances in the object after it has been partially coated. To do this it is necessary to prevent the formation of an oxide film on the uncoated metal during firing of the glass and to further prevent the formation of an oxide film between the time of completion of fusing of the glass to the metal and the time when it is removed from the furnace and is exposed to the air.

The object of the invention therefore, is to provide a method of enameling to produce a hard non-porous glossy enamel on a portion of a bright

2

clean metal surface and to permit the remainder of the metal surface to retain its original brightness to thereby maintain dimensional tolerances in the metal which has been partially coated with a vitreous enamel.

In accordance with the invention the enamel coating is fused to a selected portion of the metal in either a neutral or reducing atmosphere and is thereafter permitted to cool to a predetermined temperature in a reducing atmosphere. The cooling of the partially enamel coated article to a predetermined temperature in a reducing atmosphere prevents the formation of an oxide scale on the surface of the metal.

To produce a hard non-porous glossy enamel which is firmly adherent to ferrous metals, it is generally necessary to provide a film of oxide between the surface of the metal and the enamel to be secured thereto. Many theories have been advanced as to the composition of this induced oxide film and as to the manner in which it bonds the enamel to the metal but suffice it to say it is generally recognized that this film is relatively thin and substantially soft and easily reducible.

The provision of the oxide film is generally accomplished by preparing the metal to be coated in any appropriate manner as by cleaning, for example, either chemically or by sandblasting the surface thereof, applying the enamel mixture as by spraying or dipping, and then permitting the coated articles to dry, preferably in a drying oven or chamber. Upon becoming dried, the articles are preferably heated in an oxidizing atmosphere, such as air, to a temperature which is too low to fuse the enamel, but which is sufficiently high to cause some oxidation of the metal surface beneath the enamel. If the articles are held at this temperature for a sufficient time, an oxide film will form on the surface of the metal beneath the coating of enamel mixture or glass slip. It will be appreciated that the entire surface of the metal will have become slightly oxidized with a relatively thin and soft film of oxide and if it is desired to produce articles having only a portion of their surfaces covered by a fused-on enamel, with the remaining uncovered metal surface retaining a bright unoxidized surface, provision must be made to remove the thin oxide film from the metal surface not covered by the enamel mixture. This should be done during fusion of the enamel to the metal, otherwise the thin soft film will build up into a hard film and when later removed it will be found that dimensional tolerances have not been maintained. To accomplish the desideratum the firing of the enamel to the

metal surface is done in a controlled atmosphere, preferably a reducing atmosphere, and the fired articles are permitted to cool to a predetermined temperature in the controlled atmosphere.

Experimental work done in connection with this invention has disclosed that there are various gases which may be employed during the process to produce an atmosphere to remove any slight film of soft oxide which might have become deposited on the metal surfaces not covered by the enamel mixture during an early step in the process and to prevent the formation of a hard tough film of oxide during fusion of the glass to a portion of the metal surface. The following example of gases which may be employed to provide a reducing atmosphere are given: (1) Any partially combusted hydro-carbon gas, (2) dissociated ammonia gas produced by passing NH_3 into an endothermic cracker while in contact with a nickel catalyst, the latter gas consisting of about 75% hydrogen and 25% nitrogen and (3) or a combination of the gases of (1) and (2). Any of the above gases may be employed in producing a suitable atmosphere to be introduced into a retort or furnace in which the enamel mixture is being fused to the metal. The choice of atmosphere is governed by the composition of the glass and the type of metal being coated.

As an example of an atmosphere which may be employed for the purposes of this invention, an atmosphere of the following approximate analysis has been found suitable:

	Per cent
CO_2 -----	10.2
CO -----	6.1
H_2 -----	6.1
N_2 -----	76.6
H_2O -----	1.0

The apparatus used in practicing the invention may consist of a single retort, or preferably a muffle furnace which has a cooling zone connected to it so as to permit transfer of the coated articles from the furnace proper to the cooling zone while maintaining a preferred reducing atmosphere at all times. The reducing atmosphere is preferably directed into the heating zone where the enamel mixture is fused to the metal surface and also into a suitable cooling zone where it is maintained until the articles being treated have cooled to a predetermined temperature. During the initial stages of fusion of the enamel mixture to the metal, any thin soft oxide film which might have formed on the uncoated metal surface is effectively removed by the reducing atmosphere. The presence of the requisite atmosphere during fusion and subsequently during cooling prevents the formation of any oxide film on the exposed metal surfaces. Experimental work done in connection with this invention has revealed that the atmosphere must be carefully controlled to prevent any attack on the oxide film disposed between the metal surface and the enamel mixture.

It is desirable to maintain an adequate atmosphere in the furnace during firing of the enamel mixture to prevent leakage of oxygen into the furnace and it may be desirable to enclose the articles being fired within an envelope or retort preferably of a material that will not collapse or contaminate the atmosphere maintained in the furnace. Enclosing the articles in this manner will tend to reduce any tendency for combustion gases to react on the surfaces of the pieces within the furnace.

In some instances, as with special enamels and steels, it has been found that it is possible to maintain a reducing atmosphere during all steps of the process, or likewise the atmosphere employed may be neutral.

As stated above, the entire process may be carried out in a single suitable retort rather than in individual units, one for firing and the other for cooling. In the event that it is desired to use a single heated retort, provision may be made to vary the gas analysis so that it may change from oxidizing to neutral or to reducing or it may be maintained as reducing or neutral. The factors governing the choice of atmosphere to be employed are the composition of the glass and the type of base metal being coated.

It is, of course, essential and in accordance with well established good enameling practice to exercise careful control of time and temperature in the various steps of the process. The following is an example of the preferred practice of this invention. Steel parts (SAE 1020) were first machined to finished tolerances except for the areas to be covered with an enamel coating. The parts were degreased and the areas to which the enamel mixture was to be bonded were sand-blasted. The enamel mixture was applied to the metal by spraying through a suitable fixture which masked all of the metal surface except that which was to be coated. The pieces were then placed in an electric furnace and heated to a temperature of approximately 1050° F. Air was permitted to penetrate into the furnace and after remaining in this furnace for a time suitable to form a thin soft oxide between the enamel mixture and the metal surface, the parts were removed and permitted to cool. The exposed steel surfaces took on the yellow to dark blue colors of the ferrous oxides which form at low temperatures in the presence of air. It is to be understood that these oxides form, if they may be said to form at all, into microscopically thin films, almost susceptible of being wiped from the surface of the metal.

The parts were then placed into a muffle furnace and heated to about 1600° F. in a controlled atmosphere of substantially the analysis given above. During the calculated time that the partially coated metal parts remained in the firing furnace, a strong tenacious bond was formed between the enamel mixture and the metal, while simultaneously the thin soft oxide film on the uncoated portions of the parts was being reduced by the atmosphere in the furnace until the metal surfaces resumed the bright clean surfaces they carried at the very beginning of the practice. The uncoated portions of the metal parts lose whatever oxide film they may have before the final fusion temperature is reached.

The coated metal pieces with their bright surfaces were then transferred to a cooling zone in the muffle furnace where they were permitted to cool to approximately 300° F. in the presence of the same reducing atmosphere. This procedure prevents the formation of oxide on the exposed metal parts which would undoubtedly happen if the parts, at 1600° F., which is fusion temperature, were suddenly exposed to air. Upon removal of the parts from the cooling zone the glass or enamel surfaces were found to be satisfactorily fired and the exposed metal surfaces to be bright and clean. It was also found that dimensional tolerances of the parts had been satisfactorily maintained.

It would be possible to pre-oxidize the surface

in the final firing furnace and to merely change the atmosphere from an oxidizing composition to a reducing composition as the rising temperature passes 1050° F.

The method of this invention has been particularly advantageous when employed with standard enamel mixtures. The invention provides an economical and efficient method of bonding a hard non-porous glossy enamel covering to a portion of a metal surface while at the same time it keeps the exposed metal bright and free of any oxide scale which might be caused by the high temperature of fusion and thereby maintains dimensional tolerances in the partially enameled part.

It will be understood that the atmosphere employed in the firing zone and in the cooling zone may be any suitable reducing or non-oxidizing atmosphere, the atmospheres mentioned in this application, namely partially combusted butane, dissociated ammonia and mixtures of hydrogen and nitrogen being by way of examples only.

Various embodiments of the invention may be employed within the scope of the accompanying claims.

We claim:

1. The method of maintaining dimensional tolerances in a ferrous metal article having a vitreous enamel coating applied to a portion of the article which comprises providing an oxide bond between the metal and the enamel by heating the same in an oxidizing atmosphere at about 1050° F., changing said atmosphere to a reducing atmosphere while gradually raising the temperature to substantially 1600° F. to fuse and bond the enamel to the metal and thereafter permitting the partially coated article to cool to substantially 300° F. in said last named atmosphere.

2. The method of maintaining dimensional tolerances in a ferrous metal article having a vitreous enamel coating applied to a portion of the article which comprises providing an oxide bond between the metal and the enamel by heating the same in an oxidizing atmosphere at about 1050° F., changing said atmosphere to one substantially comprising partially combusted hydro-carbon gas while gradually raising the temperature to substantially 1600° F. to fuse and bond the enamel to the metal and thereafter permitting the partially coated article to cool to substantially 300° F. in said last named atmosphere.

3. The method of maintaining dimensional tolerances in a ferrous metal article having a vitreous enamel coating applied to a portion of the article which comprises providing an oxide bond between the metal and the enamel by heating the same in an oxidizing atmosphere at about 1050° F., changing said atmosphere to one substantially comprising dissociated ammonia gas while gradually raising the temperature to substantially 1600° F. to fuse and bond the enamel to the metal and thereafter permitting the partially coated article to cool to substantially 300° F. in said last named atmosphere.

4. The method of maintaining dimensional tolerances in a ferrous metal article having a vitreous enamel coating applied to a portion of the article which comprises providing an oxide bond between the metal and the enamel by heating the same in an oxidizing atmosphere at about 1050° F., changing said atmosphere to one substantially comprising mixtures of partially combusted hydro-carbon gas and dissociated ammonia gas while gradually raising the temperature to substantially 1600° F. to fuse and bond the enamel to the metal and thereafter permitting the partially coated article to cool to substantially 300° F. in said last named atmosphere.

5. The method of maintaining dimensional tolerances in a ferrous metal article having a vitreous enamel coating applied to a portion of the article which comprises machining the metal article to finished tolerances, applying a coating of glass slip to the portion of the article to be coated, providing an oxide bond between the glass slip and the article by heating the same to a temperature of substantially 1050° F. in an oxidizing atmosphere, changing said atmosphere to a reducing atmosphere while gradually raising the temperature to substantially 1600° F. to fuse and bond the glass to the metal and thereafter permitting the partially coated article to cool to substantially 300° F. in said last named atmosphere.

6. The method of maintaining dimensional tolerances in a metal piece while applying an enamel coating to a portion only of the surface of the piece, which comprises applying a coating of enamel to the selected portion of the surface of an accurately dimensioned piece, heating the enameled piece in an oxidizing atmosphere to a temperature low enough to prevent fusion of the enamel but high enough to cause oxidation of the metal surface beneath the enamel and oxide bonding of the enamel to the metal, then heating the piece to a temperature high enough to fuse and bond the enamel to the piece while maintaining the piece in a reducing atmosphere, and thereafter cooling the partially enameled piece in the last named atmosphere to a temperature at which oxides will not form rapidly on the uncoated surface thereof upon exposure to air.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,156,170	Page	Oct. 12, 1915
1,996,840	Staley	Apr. 9, 1935
2,001,725	Harris	May 21, 1935
2,004,632	Martin	June 11, 1935
2,070,368	Martin	Feb. 9, 1937
2,109,487	Kreidl	Mar. 1, 1938
2,110,893	Sendzimir	Mar. 15, 1938
2,199,804	Matthes	May 7, 1940
2,354,123	Horstmann et al.	July 18, 1944
2,442,485	Cook	June 1, 1948