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PRETREATMENT OF IRON OR STEEL BASE FOR SINGLE COAT VITREOUS ENAMELING

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This invention relates to a novel method of pretreating an iron or steel base to prepare the same for single coat vitreous enameling.

In order to obtain acceptable adherence between an iron or steel article and a light colored enamel it has been customary in the enamel trade for many years to utilize a so-called ground coat which contains certain dark colored adherence-promoting oxides such as cobalt oxide, nickel oxide or manganese oxide. Since such ground coats are dark in color, it has been necessary to employ one or more cover coats of light colored enamel over the ground coat in order to achieve an acceptable light colored enamel finish. Although the ground coat technique does not entirely solve the problem of eliminating surface defects in enameled articles, nevertheless, it is still widely used on a commercial scale in spite of the many efforts which have been devoted to the problem of eliminating the ground coat and providing a commercially acceptable single coat enameling procedure.

Obviously, the elimination of the ground coat in the production of light colored enameled articles would result in a substantially lower cost of production both from the viewpoint of materials used and also by the elimination of one or more process steps. Moreover, it has been found that iron or steel articles having only a single coat of enamel are highly resistant to chipping and crazing of the enameled surface as compared with multi-coated articles having two or more enamel coats.

Various attempts have been made to improve the adherence of cover coat enamels to iron or steel articles without the use of a ground coat. For example, certain of the prior art workers have devised special compositions for the enamel frit or special techniques in the preparation of the enamel slip which are said to improve adherence. Other workers in the art have advocated the provision of a substantial degree of surface roughness in the metal prior to enameling, the desired roughened surface being obtained by mechanical means, by scale annealing, by chemical pickling, or by some combination thereof. Although it is true that certain of these proposals may result in some degree of improvement in enamel adherence under some conditions, none of them has been consistently satisfactory in commercial practice or sufficiently economical to make possible the omission of dark colored adherence-promoting oxides from the enamel coat as a general practice. Thus, to a large extent the industry has continued to employ the dark colored ground coat and one or more super-imposed cover coats of light colored enamel.

Another approach to the problem has been by the use of enameling steels of special composition designed to eliminate surface defects and to improve the metal-enamel bond. Certain of these special steels have been highly successful to the extent that excellent single coat enamel adherence is obtained with a greatly reduced occurrence of surface defects and without the use of the conventional dark colored ground coat. However, wide

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scale use of such special steels is often limited largely by reason of their obviously higher cost.

Although enameled articles are subject to many different types of surface defects which are associated with poor adherence, perhaps the most critical requirement for a satisfactory single coat enamel is freedom from fish-scaling. Fishscaling is the expulsion, popping off or chipping off of small fishscale shaped pieces of the fired enamel coating and may occur during processing or some time after processing. According to the current theories, fishscaling is said to be caused by the release of hydrogen gas from the metal base upon cooling, the hydrogen presumably originating by the chemical reduction at enameling temperatures of water contained principally in the enamel frit. Generally speaking, fishscaling is associated with unsatisfactory enamel adherence so that the enamel coat is disrupted at various places under the excessive localized hydrogen gas pressure in the metal base. Consequently, the minimum prerequisite of any acceptable single coat enameling technique is substantial freedom from fishscaling.

A primary object of our invention is to provide a novel, relatively simple, and inexpensive solution to the long existent problem of producing enameled articles having a satisfactory enamel bond with only a single cover coat of vitreous enamel thereby eliminating the necessity for a dark colored ground coat.

Another object of the invention is to provide a novel method of pretreating an iron or steel base in order to prepare the same for enameling, said method being adapted to provide satisfactory single coat enamel adherence with a wide variety of irons or steels.

An additional object of the invention is to provide a novel iron or steel base for vitreous enameling with only a single light colored enamel cover coat which is substantially free of dark colored adherence-promoting oxides and having satisfactory adherence without fish-scaling or other surface defects.

We have found that satisfactory single coat enamel adherence and unusually good surface appearance are consistently obtained by pretreating the iron or steel base as follows: (1) providing on the surface of the metal base an oxide coating selected from the group consisting of titanium dioxide (TiO_2), antimony oxide (Sb_2O_3), and tungsten oxide (WO_3), and mixtures thereof, and (2) heating the oxide coated base in a non-oxidizing atmosphere to a temperature at which reduction of the oxide by reaction with the iron in the base takes place and thereby diffusing the surface of the base with titanium, antimony, or tungsten as the case may be. A third step which is optional comprises pickling the thus treated base under relatively mild conditions sufficient to "clean" the metal surface but without severely etching or roughening the same.

In the first step of the process the aforementioned oxide or oxides may be deposited as such or formed in situ on the surface of the iron or steel base. It is also within the scope of the present invention to use the above-mentioned oxides in combination with molybdenum, nickel, or cobalt oxides as disclosed in our co-pending application Serial No. 677,813, filed August 13, 1957.

One method of providing the oxide coating on the iron or steel base is to form a suspension or dispersion in water or other suitable liquid medium of the oxide or oxides in finely divided or powdered form and then apply the liquid coating material to the surface of the base by any convenient technique such as spraying, brushing, roll-coating, dipping, etc. Usually, water will be the most convenient liquid medium but other liquid vehicles such as glycerine, light oils, etc. can be used. In the case of an aqueous medium it is usually advantageous to employ

an added dispersing or suspending agent, such as starch or various surface active agents, in order to form a relatively stable suspension or dispersion of the finely divided oxide in the aqueous liquid. We have found that corn starch is highly satisfactory and economical for this purpose.

It is also within the scope of the invention to provide the oxide coating on the metal surface by means of a solution or suspension of a compound or salt which can be decomposed or oxidized to yield the desired oxide in situ. For example, ammonium tungstate, sodium tungstate, or tungstic acid can be deposited on the metal surface and are readily decomposable merely by heating to form the desired tungsten oxide.

The quantity of oxide provided on the metal surface is not highly critical but a certain minimum amount of oxide must be present in order to realize the benefits of the invention to any practical degree. For obtaining satisfactory enamel adherence it has been found that sufficient oxide should be present to yield, upon reduction thereof by reaction with the iron in the base, from about 0.2 to about 0.8 gram of titanium, antimony, or tungsten per square foot of surface. In other words, the contained titanium, antimony, or tungsten content of the oxide coating should be from about 0.2 to about 0.8 gram per square foot of surface. Although larger amounts may be used, there appears to be no additional benefit justifying the use of greater amounts of the several oxides.

Following the formation of the oxide coating on the surface of the iron or steel base, either by direct application of the oxide or in situ formation of the same, the next essential step of the invention is to heat the oxide coated base to an elevated temperature, which may be within the range of from about 1400° F. to about 2000° F., sufficient to obtain reduction of the oxide or oxides by reaction with the iron in the base. This step may sometimes be referred to as a normalizing or diffusing step. Although under very favorable circumstances, it may be possible to carry out this heating and reducing step in a somewhat oxidizing atmosphere, it will readily be understood that the heating of the oxide coated base should preferably be conducted in a non-oxidizing atmosphere, i. e. either neutral or reducing. A wide variety of atmospheres which are either neutral or reducing to a predetermined degree are well known in connection with the various normalizing, annealing, and heat treating operations which are frequently carried out in the steelmaking art. However, generally speaking, such atmospheres comprise specially prepared mixtures of inert gases containing none or a certain predetermined amount of hydrogen which determines the reducing character of the atmosphere.

As previously indicated, it will be desirable in most cases to subject the resultant pretreated base to a rather mild or light pickling operation solely for the purpose of "cleaning up" the metal surface in order to provide a salable product. However, it is to be understood that this pickling step is of relatively short duration so that there is no appreciable etching action or production of surface roughness of the nature which has previously been thought by some investigators to influence the adherence of a subsequent enamel coating. The usual acid pickle liquors may be employed, e. g. a suitable pickling operation in accordance with the present invention comprises treating the base with a solution of 8% sulfuric acid for a period of about one minute. However, it is to be understood that this final pickling step is not an indispensable part of the invention and in any given operation it may be omitted entirely since it has no significant effect on the subsequent enamel adherence. As a matter of practice, the enameler at a later date will ordinarily give the product a light pickle and a conventional nickel strike or flash before application of the enamel coat.

It has been postulated by some investigators that the presence of FeO is essential during the firing of vitreous enamels on iron bases because of the fact that FeO is soluble in iron and also forms a silicate with the enamel components thereby acting as a mutual bonding agent. Since the firing of the enamel takes place in an oxidizing atmosphere, it will be apparent that, in the absence of some regulating factor, either Fe_2O_3 or Fe_3O_4 or FeO may be formed. It is believed that the formation of Fe_2O_3 during the enamel firing is highly detrimental and will result in poor adherence since this compound is not soluble in the iron. Hence, it is our hypothesis that the titanium, antimony, or tungsten formed on or diffused into the metal surface of the iron or steel base by the above-described technique controls the oxidation of the iron of the base so that Fe_2O_3 is not formed during the firing of the enamel and so that Fe_3O_4 or preferably FeO are present to insure an adequate bond. However, it will be understood that the invention is not limited by this proposed explanation of the results obtained.

The adherence of vitreous white or light colored cover coat enamels to surfaces so treated is equal to or better than that ordinarily obtained in the enameling trade through the use of ground coats. Therefore, the fish-scaling difficulties ordinarily encountered when attempting to apply white or light colored vitreous enamel coatings to ordinary ferrous base metals are entirely eliminated. In addition, the technique of the present invention eliminates, to a large extent, the other more common vitreous enamel defects such as blistering, pitting, copper-heading, and so forth, which are objectionable from an appearance standpoint.

In order to illustrate some of the features of the invention, but not by way of limitation, the following specific examples are presented.

Example I

The test specimens comprised a cold reduced enameling iron having the following composition on a weight percent basis: .035% C, .07% Mn, .007% P, .029% S, .08% Cu.

The test specimens were subjected to the treatment hereinafter described and a white cover coat enamel was then applied by spraying and firing for approximately five minutes at about 1500° F. The enamel frit had the following composition on a weight percent basis:

	Percent
SiO_2 -----	42.8
B_2O_3 -----	15.8
Na_2O -----	10.5
K_2O -----	3.7
TiO_2 -----	19.6
Al_2O_3 -----	1.5
Li_2O -----	0.6
MgO -----	0.9
P_2O_5 -----	2.8
F -----	1.8
	100.0

The enamel slip was prepared by milling the following ingredients in the indicated proportions

	Grams
Frit -----	3400
Clay -----	84.5
Sodium nitrite -----	4.25
Sodium aluminate -----	8.5
Bentonite -----	17.0
Potassium carbonate -----	8.5
Gum tragacanth -----	2.1
Water -----	1300

After milling to a fineness of about 2 grams on a 200 mesh screen, the following mill additions were made:

	Grams
Sodium nitrite -----	2.1
Urea -----	12.7

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After enameling, the test specimens were evaluated for adherence by the well known impact test, the results being designated as poor, fair, good, or excellent by visual examination.

The cold reduced test strip was first treated for the removal of rolling oil by vapor degreasing or by means of an alkaline cleaner. The oil-free strip was then given an oxide coating by immersing the strip for a brief time in an aqueous starch-containing suspension of antimony trioxide (Sb_2O_3). The suspension contained 25 grams per liter of corn starch and 40 grams per liter of antimony trioxide. After removal from the treating solution the test strip was allowed to drain and dry leaving a coating on the strip which ranged from about 0.2 to about 0.8 gram per square foot of contained antimony. The thus treated strip was then subjected to heat treatment for five minutes in a reducing atmosphere containing 5% hydrogen at a temperature of from about 1400 to about 1850° F. whereby the antimony trioxide on the strip was reduced by the iron of the strip to effect diffusion of antimony in the surface of the strip.

Upon being enameled with white cover coat enamel in the manner described above, the test specimens were found to display good adherence and the other common vitreous enamel defects such as blistering, pitting, copper-heading, etc. were at a minimum.

Equally good results are obtained using a neutral atmosphere comprising nitrogen for the heating and reduction step.

In cases where the present invention is to be practiced with existing equipment it may not always be convenient to utilize a vapor degreasing or alkaline cleaning step for the removal of rolling oil from the cold reduced strip. In such case, we have found that the oily strip may be treated directly with the antimony trioxide suspension or treating liquid, but it will usually be desirable to incorporate in the treating liquid a suitable wetting agent to facilitate uniform wetting of the oily surface of the strip with the treating liquid. For example, to the aqueous suspension of antimony trioxide described above may be added about 0.1% of a non-ionic surface active agent of which many different kinds are well known. We have obtained good results with Kryo EO which is sold by Procter & Gamble Distributing Co. and comprises an alkylphenol-ethylene oxide condensate. Following the application of the antimony trioxide suspension, the strip is then placed in or passed through an oxidizing furnace at a temperature on the order of 700° F. for a very brief period of time which is merely sufficient to burn off the rolling oil but without causing any appreciable degree of scaling or oxidation of the metal. Thereafter, the treated strip is subjected to the same heating step in a neutral or reducing atmosphere as described above. Good enamel adherence is again obtained with minimum surface defects.

Example II

The same procedure described in connection with Example I was followed except that instead of an aqueous suspension of antimony trioxide we employed an aqueous starch-containing suspension of titanium dioxide (TiO_2). Good adherence and good surface appearance were obtained in the enameled test specimens.

Example III

The same procedure as described in Example I was followed with the exception that the coating liquid was an aqueous starch-containing suspension of tungstic acid. During the heat treatment step the tungstic acid decomposed to tungsten trioxide which was in turn reduced by reaction with the iron of the strip to diffuse tungsten in the strip surface. Good adherence and highly satisfactory surface appearance were again realized.

Example IV

The procedure was the same as described in Example

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III with the exception that sodium tungstate was employed instead of tungstic acid. Although sodium tungstate is soluble in water to a limited degree, the starch suspension technique was used to insure the desired 0.2 to 0.8 gram per square foot of contained tungsten on the strip surface. Good adherence and good surface appearance were again obtained in the enameled specimens.

We claim:

1. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of providing on the surface of the metal base a coating comprising at least one oxide selected from the group consisting of titanium, antimony, and tungsten oxides, and heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature at which reduction of the oxide by reaction with the iron in said base occurs.

2. The process of claim 1 further characterized in that said temperature is within the range of from about 1400° F. to about 2000° F.

3. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of providing on the surface of the metal base a coating comprising titanium oxide, and heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature within the range of from about 1400° F. to about 2000° F. sufficient to effect reduction of the oxide by reaction with the iron in said base.

4. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of providing on the surface of the metal base a coating comprising antimony oxide, and heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature within the range of from about 1400° F. to about 2000° F. sufficient to effect reduction of the oxide by reaction with the iron in said base.

5. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of providing on the surface of the metal base a coating comprising tungsten oxide, and heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature within the range of from about 1400° F. to about 2000° F. sufficient to effect reduction of the oxide by reaction with the iron in said base.

6. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of applying to the surface of the metal base a liquid suspension of at least one oxide selected from the group consisting of titanium, antimony, and tungsten oxides, and thereafter heating the coated base in a non-oxidizing atmosphere at a temperature within the range of from about 1400° F. to about 2000° F. sufficient to effect reduction of the oxide by the iron in said base.

7. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of applying to the surface of the metal base a liquid coating material comprising a compound selected from the group consisting of titanium, antimony, and tungsten compounds capable of being

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thermally decomposed to the corresponding titanium, antimony, and tungsten oxides, and thereafter heating the coated base in a non-oxidizing atmosphere at a temperature within the range of from about 1400° F. to about 2000° F. sufficient to effect decomposition of the compound to the corresponding oxide and reduction of the oxide by the iron in said base.

8. The process of claim 7 further characterized in that said compound comprises tungstic acid.

9. The process of claim 7 further characterized in that said compound comprises a tungstate.

10. A process for preparing an iron or steel base for vitreous enameling so as to obtain satisfactory enamel adherence with a single cover coat of a light colored vitreous enamel applied directly to the base, said process comprising the steps of providing on the surface of the metal base a coating comprising at least one oxide selected from the group consisting of titanium, antimony, and tungsten oxides, heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature at which reduction of the oxide by reaction with the iron in said base occurs, and thereafter pickling the base.

11. The process of claim 6 further characterized in that said atmosphere comprises a neutral atmosphere.

12. The process of claim 6 further characterized in that said atmosphere comprises a reducing atmosphere.

13. The process of claim 7 further characterized in that said atmosphere comprises a neutral atmosphere.

14. The process of claim 7 further characterized in that said atmosphere comprises a reducing atmosphere.

15. The process of claim 6 further characterized in that said liquid suspension comprises a dispersion of the oxide in water with starch as a dispersing agent.

16. The process of claim 1 further characterized in that said oxide is present on the metal surface in an amount sufficient to provide, after reduction thereof, from

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about 0.2 to about 0.8 gram of titanium, antimony, or tungsten per square foot of surface.

17. An iron or steel base having a coating produced according to the process of claim 1.

18. An iron or steel base having a coating produced according to the process of claim 3.

19. An iron or steel base having a coating produced according to the process of claim 4.

20. An iron or steel base having a coating produced according to the process of claim 5.

21. A process for enameling an iron or steel base with a single cover coat of a light colored vitreous enamel comprising the steps of providing on the surface of the metal base a coating comprising at least one oxide selected from the group consisting of titanium, antimony, and tungsten oxides, heating the oxide coated base in a substantially non-oxidizing atmosphere to a temperature at which reduction of the oxide by reaction with the iron in said base occurs, applying to the surface of the base a cover coat of light colored vitreous enamel which is substantially free of dark colored adherence-promoting oxides, and firing said enamel thereon.

22. The process of claim 21 further characterized in that said oxide is present on the metal surface in an amount sufficient to provide after reduction thereof, from about 0.2 to about 0.8 gram of titanium, antimony, or tungsten per square foot of surface.

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