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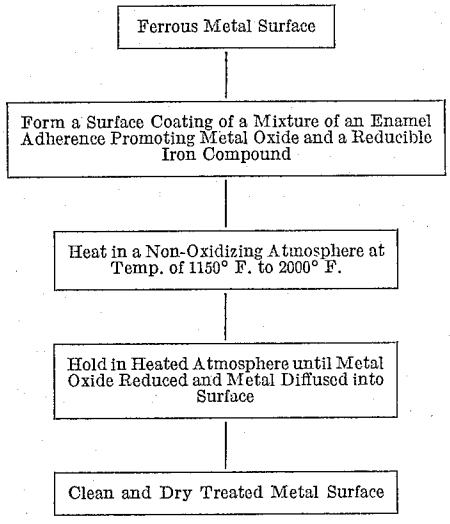
METHOD OF TREATING FERROUS METAL BASE FOR VITREOUS ENAMELING AND COATED METAL BASE PRODUCED

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This invention relates generally to a method of pretreating an iron-containing base to prepare the same for receiving a protective or decorative surface coating, and more particularly, to an improved process for pretreating an iron or steel base for single coat vitreous enameling.

A simplified flow diagram of the method is as follows:



In order to obtain satisfactory adherence between an iron or steel article and a surface coating, for example, such as a vitreous enamel, it has been customary for many years to utilize a so-called ground coat which contains certain adherence-promoting oxides. Although the ground coat does not entirely solve the problem of eliminating surface defects, nevertheless, it is still widely used commercially.

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 in 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 usage of such special steels is often limited because of their obviously higher cost.

More recently, it has been proposed to provide a thin diffused coating of a reducible metal oxide, such as an oxide of molybdenum, on the surface of an article to be enameled, as in the Bernick et al., U.S. Patent No. 2,862,842. With the foregoing technique, it has been found that satisfactory single coat enamel adherence and unusually good surface appearance are consistently obtained by pretreating the iron or steel base by providing on the surface of the metal base an oxide coating comprising molybdenum oxide (MoO_3) either alone or with other oxides, particularly nickel or cobalt 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 the base takes place and thereby diffusing the surface of the base with molybdenum. 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 surface. Obviously, the cost of producing the single coat adherent base could be substantially diminished and the coating improved if the rate of reduction of the metal oxide to the reduced state could be increased, and if the reaction with the base metal were more complete.

Accordingly, it is an object of the present invention to provide an improved process for pretreating an iron or steel base with an adherence-promoting metal.

It is a further object of the present invention to provide an improved method of pretreating an iron or steel base with a vitreous enamel adherence-promoting metal.

It is still another object of the present invention to provide a more economical process of producing a single-coat vitreous enamel coating on a ferrous metal.

It is also an object of the present invention to provide an improved single-coat vitreous enamel coating on ferrous metals.

Other objects of the present invention will be apparent from the detailed description and claims to follow.

The foregoing and other objects of the present invention are broadly achieved by co-depositing on a ferrous metal surface, such as an iron or steel base, a coating comprising: a mixture of (1) a reducible compound of a known adherence-promoting agent, such as the oxides of molybdenum, nickel, cobalt, tungsten, titanium, and antimony; and (2) a relatively non-volatile salt of iron which, on thermal decomposition in an atmosphere non-oxidizing to iron, yields free iron with the release of volatile decomposition products free of elemental carbon deposits, objectionable iron oxides, or other non-volatile products which interfere with the diffusion or subsequent enameling steps; and thereafter heating the iron or steel base having the foregoing coating in order to reduce the adherence-promoting agent to the metallic state and diffuse the metal into the base in substantially the same manner as described in the Bernick et al. Patent No. 2,862,842.

In general, my improved process comprises providing a ferrous metal with an adherence-promoting metal film diffused into the surface thereof by applying to an iron or steel base, a surface layer or deposit of an intimate, finely divided mixture of an iron salt of the above-specified type and one or more known reducible adherence-promoting agents from either a solution or suspension of the said mixture by spraying, dipping, brushing, or the like. Thereafter, the iron or steel base having the said mixture uniformly deposited on the surface thereof is subjected to a heating step, such as in a standard normalizing cycle in order to reduce the adherence-promoting agent to the metallic state and diffuse the metal thus formed into the base. The heating step may or may not include a brief preannealing oxidizing pass in a burn-off or scaling furnace to burn off the rolling oil which may be on the surface but without causing any appreciable degree of scaling or oxidizing of the metal. The heating step is carried out in an atmosphere substantially non-oxidizing to iron, and preferably in a neutral or reducing atmosphere, to facilitate reduction of the oxides and diffusion of the reduced metal into the iron or steel base without effecting surface oxidation.

It has been found that by providing a suitable iron compound of the foregoing type which serves as a source of free metallic iron in a finely dispersed form intimately mixed throughout the reducible adherence-promoting metal compound, a particularly significant and unexpected improvement in the pretreatment of iron or steel for single coat enameling is achieved. Thus, in the present invention, there is made available during the heating of the reducible adherence-promoting compound, a source of finely divided free metallic iron with which the reducible

adherence-promoting compound can react to reduce the adherence-promoting agent to the metallic state. And, in the preferred embodiment of the present invention, a sufficient amount of the said iron compound is admixed with the adherence-promoting metal compound to provide a stoichiometric amount of free metallic iron which will reduce the adherence-promoting metal compound to the metallic state by combining with the oxygen thereof to produce ferrous oxide (FeO). Thus, when the adherence-promoting compound is nickel oxide (NiO), for example, the ratio of the equivalent weight of nickel to iron used is substantially 1:1, and when the adherence-promoting compound is molybdenum oxide (MoO_3) the ratio of the equivalent weight of molybdenum to iron is substantially 3:1, since in the latter instance there are three molar equivalences of oxygen to be converted to FeO while reducing the molybdenum oxide to metallic molybdenum. No advantage is obtained by providing substantially greater than a stoichiometric amount of iron compound and a significant benefit is obtained even when less than stoichiometric amounts are employed. Thus, the inclusion of a small amount of a said iron compound which is capable of producing free metallic iron in a finely divided form dispersed throughout the adherence-promoting compound, produces a beneficial result even when a portion of the adherence-promoting compound is reduced by the metallic iron of the base, and is within the scope of the present invention.

The iron compounds which have been found to be most useful in the present invention are the organic iron salts containing carbon and oxygen or carbon, hydrogen, and oxygen, and particularly the oxalate, tartrate, and formate salts of iron, including ferric oxalate, ferric formate, ferrous tartrate, and ferrous oxalate. When the latter iron salts are subjected to pyrolysis or thermol decomposition during the heating step of the foregoing treating process prior to applying a vitreous enamel surface coating, the iron salts decompose to yield free iron and volatile products consisting of carbon monoxide or carbon dioxide, and water vapor. The volatile decomposition products of the iron compounds used in the present invention, in addition to leaving the base surface without forming residual deposits, should avoid the formation of objectionable oxides, and should preferably hasten the reduction of the adherence-promoting compounds. Typical examples of the organic iron compounds which are useful in the present invention and the chemical equations which represent the thermal decomposition reactions which are believed to take place as follows:

(1) Type A:

$$\overline{M}(CO_2)_x(OH_2)_y \rightarrow \overline{M} + xCO_2 + yH_2O$$

Example:

(*a*) ferric oxalate pentahydrate

$$Fe_2(C_2O_4)_3.5H_2O \rightarrow 2Fe + 6CO_2 + 5H_2O$$

(*b*) ferrous oxalate dihydrate

$$FeC_2O_4.2H_2O \rightarrow Fe + 2CO_2 + 2H_2O$$

(2) Type B:

$$\overline{M}(CO)_x(OH_2)_y \rightarrow \overline{M} + xCO + yH_2O$$

Example:

(*a*) ferrous tartrate

$$FeC_4H_4O_6 \rightarrow Fe + 4CO + 2H_2O$$

(3) Type C:

$$\overline{M}(CO)_x(CO_2)_y(OH_2)_z \rightarrow \overline{M} + xCO + yCO_2 + zH_2O$$

Example:

(*a*) ferric formate

$$2Fe(CHO_2)_3 \rightarrow 2Fe + 3CO + 3CO_2 + 3H_2O$$

In each of the foregoing reactions, the free iron which must be first formed by the thermal decomposition of the organic salt immediately reacts with the metal oxide to reduce the adherence metal oxide to the metallic form and permits the adherence-promoting metal to diffuse into the surface of the base. The chemical reactions which are thought to take place between the free iron from the organic salt and an adherence-promoting metal oxide are illustrated by the following equations:

(*a*) Ferric oxalate and nickel oxide deposit

$$Fe_2(C_2O_4)_3 \xrightarrow{\Delta} 2Fe + 6CO_2$$

$$Fe + NiO \xrightarrow{\Delta} FeO + Ni$$

(*b*) Ferric oxalate and molybdenum trioxide deposit

$$Fe_2(C_2O_4)_3 \xrightarrow{\Delta} 2Fe + 6CO_2$$

$$3Fe + MoO_3 \xrightarrow{\Delta} 3FeO + Mo$$

(*c*) Ferric oxalate and cobalt oxide deposit

$$Fe_2(C_2O_4)_3 \xrightarrow{\Delta} 2Fe + 6CO_2$$

$$3Fe + Co_2O_3 \xrightarrow{\Delta} 3FeO + 2Co$$

It will be evident that the presence of a heat decomposable organic iron salt in intimate contact with a reducible adherence-promoting metallic oxide on the surface of the iron or steel base promotes the kinetics of the reduction step by providing substantial amounts of free iron for the reduction of the said adherence-promoting oxide over and above the iron in the base. Moreover, the iron from the organic salt being in a finely dispersed form reacts more readily than does the iron of the base. The ferrous oxide (FeO) formed in the reduction of the metal oxide, being soluble in the iron of the base and being also capable of forming a silicate with a vitreous enamel, acts as a bonding agent between the subsequently applied vitreous enamel coating and the metal base. In addition, it has been found that the finished reduced surface produced by the new base treatment process after the heat treatment step has a topography which is more acceptable as a supporting or retaining surface for an enamel coating because of its roughened surface and porosity, a result which is essentially a mechanical or physical effect inherent in the process.

It has also been found that for the same degree of enamel adherence smaller amounts of an adherence-promoting oxide, such as nickel oxide, are required in the presence of an organic iron salt, such as iron oxalate, than are required when using nickel oxide alone. It is postulated that this surprising beneficial result is at least in part due to the fact that the resulting wustite (FeO) is more uniformly dispersed in a diffused layer than is the case in the previous process where it is confined largely to the reaction boundary between the iron or steel base and the adherence-promoting oxide coating. Thus, where it is necessary to use nickel oxide in an amount sufficient to provide between .15 and .20 grams of nickel per square foot of base in order to obtain good to excellent adherence of a single vitreous enamel coating, it is possible to obtain good to excellent adherence with only about .04 to .10 grams of nickel per square foot when a small amount of the organic iron salt, such as ferric oxalate, is present along with the nickel oxide.

The adherence-promoting agents which have been found most satisfactory for producing single coat enamel adherence and unusually good surface appearance are the reducible oxides or anhydrides of molybdenum, nickel, cobalt, titanium, antimony and tungsten, and include such compounds as molybdenum oxide (MoO_3), nickel oxide (NiO), cobalt oxide (CoO), titanium oxide (TiO_2), antimony oxide (Sb_2O_3), and tungsten oxide (WO_3). Combinations of the foregoing oxides can also be used. It is also within the scope of the invention to provide the oxide of the adherence-promoting metal on the ferrous metal base 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 molybdate or molybdic acid can be deposited on the base metal surface and is readily decomposed or oxidized by heating to yield molybdenum trioxide. Similarly, ammonium tungstate or tungstic acid can be deposited on the metal surface and readily decomposed by heating to form tungsten oxide. A convenient method of utilizing molybdenum and nickel oxides together comprises forming an aqueous solution of nickel nitrate or chloride or other water soluble nickel salt and ammonium molybdate or molybdic acid to obtain molybdenum-nickel complex. Ammonium hydroxide should also be added in order to maintain the molybdenum-nickel complex in solution. The resultant aqueous solution is applied to the metal surface and is thermally decomposed to yield the desired mixture of molybdenum and nickel oxides.

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 molybdenum oxide should be present to yield, upon reduction thereof by reaction with the iron, from about 0.05 to about 0.4 gram of molybdenum per square foot of surface. In other words, the contained molybdenum content of the oxide coating should be from about 0.05 to about 0.4 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 molybdenum oxide. Similarly, in the case where nickel or cobalt oxide is also used, it appears that sufficient nickel oxide or cobalt oxide should be present to yield from about 0.05 to about 0.2 gram of nickel or cobalt per square foot of surface in order to realize the enhanced benefits attributable to the combined metals but above this level no appreciable improvement is noted. In the case of the combination of molybdenum and nickel oxides, the relative amounts of the two oxides may vary but we have obtained best results when the total contained nickel and molybdenum is from about 0.1 to about 0.4 gram per square foot of surface. Within this range, the relative proportions may vary considerably but generally we prefer to use a minimum of 0.05 gram per square foot of each metal. For example, good results are obtained with amounts of from about 0.05 gram per square foot of each metal up to about 0.2 gram per square foot of each, but equally good results are also obtained using about 0.05 gram per square foot of one of the metals with from about 0.05 to about 0.35 gram per square foot of the other metal. And, sufficient oxide of titanium, antimony, or tungsten should be present to yield, upon reduction thereof by reaction with metallic iron, from about 0.2 to about 0.8 gram of titanium antimony, or tungsten per square foot of the supporting base surface. In the present invention, very good enamel adherence is possible when using the minimal amount of adherence metals specified.

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.

When the oxide coating is applied as a suspension or dispersion containing starch as a suspending agent, it is preferred to heat or bake the coating to polymerize the starch before heating to the elevated temperature required for reduction of the oxide by interaction with the metallic iron. Thus, heating for a few minutes at a temperature between 150° F. and 300° F. polymerizes the starch and forms a firmly adherent coating of the oxide on the base before reduction thereof to the metal state and diffusion into the base.

Following the co-deposition of the organic iron salt and the adherence-promoting metal oxide or the in situ formation of the metal oxide, the co-deposited base coating is heated to an elevated temperature for a sufficient time to initiate decomposition of the organic iron compound to yield free iron. Thus, decomposition of the organic iron salts takes place at a temperature between about 1100° F. to 1200° F., and the reduction-diffusion reaction which is initiated continues as the temperature is raised. Broadly, the temperature range in the reduction-diffusion heating step is from about 1150° F. to about 2000° F. dependent upon the nature of the base and the time of treatment. For example, in the case of enameling iron it is preferred to use a relatively high temperature which may be from about 1400° F. to about 2000° F. and it will usually be most economical to conduct the heating step in a continuous manner, such as in a continuous normalizer so that the heating time is short, e.g. from about 1 to about 5 minutes. On the other hand, in the case of a mild steel base (0.05 to 0.10% carbon) the heating step can be conducted at a relatively lower temperature, e.g. from about 1150° F. to about 1300° F., and for a much longer period of time on the order of 3 to 12 hours. In the case of the latter procedure, it will be found that a batch type box annealing operation is the most economical technique. Thus, it will be understood that as far as enamel adherence is concerned, the time and temperature of the heating step of the invention are correlative factors so that for any given type of iron or steel base substantially equivalent results may be obtained at conditions of high temperature short time or low temperature long time.

While it is possible to carry out the heating and reducing steps in a variety of treating atmospheres, the heating of the oxide coating should be carried out in an atmosphere substantially non-oxidizing to iron, and preferably in an oxygen-free atmosphere, 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 con-

ventional nickel strike or flash before application of the enamel coat.

In order to illustrate some of the features of the present invention, but not by way of limitation, the following specific embodiments are presented:

Example I

An oil-free cold reduced test strip consisting of enameling iron having the following composition on a weight basis: .035% C, .07% Mn, .007% P, .029% S, .08% Cu, is coated wtih an aqueous starch suspension containing about 25 grams cornstarch per liter and having the hereinafter specified amount of nickel oxide dispersed therethrough and ferric oxalate dissolved therein. After allowing the excess suspension to drain from the strip, the strip is dried in an oven between 160° F. and 300° F. for about 10 minutes. Thereafter, the strip is subjected to the decomposition, reduction, and diffusion heat treatment for 5 minutes in a reducing atmosphere containing 5% hydrogen at a temperature of about 1850° F., whereupon the oxalate is decomposed to give free metallic iron which in turn reacts with the nickel oxide to yield reduced metallic nickel. Any nickel oxide remaining unreduced can react with the iron in the test strip to yield reduced metallic nickel. The reduced metallic nickel diffuses into the base metal test strip.

The test strips thus treated are enameled by applying a white cover coat enamel by spraying and firing for approximately 5 minutes at about 1500° F. The enamel frit applied has 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
LiO_2	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	3400.00
Clay	84.5
Sodium nitrite	4.25
Sodium aluminate	8.5
Bentonite	17.00
Potassium carbonate	8.5
Gum tragacanth	2.1
Water	1300.00

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

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 results obtained when the specified amounts of nickel and iron are co-deposited in the foregoing manner as nickel oxide and ferrix oxalate, respectively, are shown in the following Table I:

TABLE I

Coating		Ratio, Ni/Fe	Atmosphere during test	Adherence Rating
Equiv. wt. of Ni, as Nickel oxide (gm./ft.²)	Equiv. wt. of Fe, as Ferricoxalate (gm./ft.²)			
0.043	0.054	[1] 0.8	5% H_2+N_2	Good to Excellent.
0.091	0.082	[1] 1.1	100% N_2	Excellent.
0.089	0.079	[1] 1.1	5% H_2+N_2	Good to Excellent.
0.108	0.098	[2] 1.1	100% N_2	Excellent.
0.112	0.101	[2] 1.1	5% H_2+N_2	Good.
0.097	0.123	[3] 0.8	5% H_2+N_2	Excellent.

[1] Panels with coating baked/at 300° F. for 10 mins. before reduction.
[2] Panels with coating baked at 160° F. for 10 mins. before reduction.
[3] Panels scaled at 1 g. Fe_3O_4 per sq. ft. in pretreatment before reduction.

As a standard of comparison, several tests were made following the above-mentioned procedure but omitting from the base coating the iron oxalate. The results obtained are shown in the following Table II:

TABLE II

Coating—Equiv. wt. of Ni, (gm./ft.²):	Adherence rating
0.05	Poor.
0.10	Fair.
0.15	Good.
0.20	Excellent.

It will be apparent from Tables I and II, that where 0.05 gram per square foot of nickel alone is used, the adherence rating was poor, whereas, with approximately the same amount of nickel in the presence of about 0.05 gram iron per square foot, the adherence rating is "good to excellent." Also, with nickel alone, it required approximately 0.20 gram of nickel per square foot to attain a rating of excellent, whereas with the present practice using iron oxalate in combination with the nickel oxide, an adherence rating of excellent is obtained with nickel present in amounts of from about 0.04 to about 0.1 grams per square foot. And, when ferric oxalate by itself was used in a starch suspension and treated in precisely the above manner, poor adherence of the enamel coat was obtained.

Others may practice the invention in any of the numerous ways which are suggested to one skilled in the art, by this disclosure, and all such practice of invention are considered to be a part hereof which fall within the scope of the appended claims.

I claim:

1. In a process for preparing a ferrous metal base for receiving a vitreous enamel coating which includes the steps of providing on the surface of the metal base a coating of a ferrous metal vitreous enamel adherence-promoting metal oxide, and heating the coated base in an atmosphere non-oxidizing to iron to a temperature effecting reduction of the oxide and diffusion of the reduced metal into the base; the improvement comprising: providing on the surface of a metal base an intimate mixture of a ferrous metal vitreous enamel adherence-promoting metal oxide and a compound of iron which on thermo decomposition forms free metallic iron and volatile decomposition products and heating the said mixture until metallic iron is formed by thermo decomposition of the said iron compound and said iron reacts with the adherence promoting oxide to reduce said oxide and form ferrous oxide and said ferrous oxide and reduced oxide diffuse into the metal base.

2. A ferrous metal base having a coating produced according to the process of claim 1.

3. A process as in claim 1, wherein the compound of iron is an organic iron salt.

4. A process as in claim 3, wherein the organic salt

of iron is selected from the group consisting of iron oxalate, iron tartrate and iron formate.

5. A process of preparing an iron-containing metal base for receiving a vitreous enamel coating which comprises providing on the surface of an iron-containing metal base a coating of a mixture of a ferrous metal vitreous enamel adherence-promoting metal oxide and an iron compound which on heating decomposes to form free iron and volatile non-oxidizing decomposition products, heating the said coated base in an atmosphere non-oxidizing to iron at a temperature at which the said iron compound decomposes to form free iron which reacts with the said oxide to effect reduction of the oxide to the reduced metal and formation of ferrous oxide, the said reduced metal being diffused into the metal base and the ferrous oxide being dispersed throughout the base coat and dissolved in the metal base.

6. A process as in claim 5, wherein the coated base is heated at a temperature above about 1150° F. and not substantially above about 2000° F.

7. A process as in claim 5, wherein the iron salt is an organic iron salt selected from the group consisting of iron oxalate, iron tartrate, and iron formate.

8. A process of preparing an iron-containing metal base for receiving an adherent surface coating of a vitreous enamel which comprises applying to the surface of an iron-containing metal base a base coating of an intimate mixture of nickel oxide and ferric oxalate, heating the said coated base in an atmosphere non-oxidizing to iron to a temperature between about 1150° F. and 2000° F., whereupon the said ferric oxalate decomposes to form free iron which reacts with at least a portion of the nickel oxide to form reduced metallic nickel and ferrous oxide, the said reduced nickel being diffused into the metal base and the ferrous oxide being dispersed throughout the base coat and dissolved in the metal base.

9. A process as in claim 8, wherein the nickel oxide and the ferric oxalate are present on an equivalent weight basis in a ratio of about 1 to 1.

10. A process as in claim 8, wherein the nickel oxide is present in an amount sufficient to provide an equivalent weight of between about .04 and .12 gram nickel per square foot, and the ferric oxalate is present in an amount sufficient to provide an equivalent weight of between about .04 and .12 gram iron per square foot.

11. A process of preparing an iron-containing metal base for receiving an adherent surface coating of a vitreous enamel which comprises applying to the surface of an iron-containing metal base a base coating of an intimate mixture of molybdenum trioxide and ferric oxalate, heating the said coated base in an atmosphere non-oxidizing to iron to a temperature between about 1150° F. and 2000° F., whereupon the said ferric oxalate decomposes to form free iron which reacts with at least a portion of the molybdenum oxide to form reduced molybdenum and ferrous oxide, the said reduced molybdenum being diffused into the metal base and the ferrous oxide being dispersed throughout the base coat and dissolved in the metal base.

12. A process of preparing an iron-containing metal base for receiving an adherent surface coating of a vitreous enamel which comprises applying to the surface of an iron-containing metal base a base coating of an intimate mixture of cobalt oxide and ferric oxalate, heating the said coated base in an atmosphere non-oxidizing to iron to a temperature between about 1150° F. and 2000° F., whereupon the said ferric oxalate decomposes to form free iron which reacts with at least a portion of the cobalt oxide to form reduced cobalt and ferrous oxide, the said reduced cobalt being diffused into the metal base and the ferrous oxide being dispersed throughout the base coat and dissolved in the metal base.

13. A process for enameling a ferrous metal 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 a ferrous metal vitreous enamel adherence-promoting metal oxide admixed with an iron compound which on thermal decomposition produces free metallic iron and volatile decomposition products, heating the said coated base in an atmosphere non-oxidizing to iron at a temperature at which the said iron compound decomposes to metallic iron and reduction of the said metal oxide by reaction with free metallic iron takes place, 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.

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