United States Patent Office

2,837,443

Patented June 3, 1958

2,837,443

METHOD OF PORCELAIN ENAMELING

Jason M. Zander, Chicago, Ill., assignor, by mesne assignments, to The Eagle-Picher Company, Cincinnati, Ohio, a corporation of Ohio

No Drawing. Application July 26, 1954
Serial No. 445,887

10 Claims. (Cl. 117—53)

This invention relates to the treatment of ferrous metal surfaces, and more particularly, to the treatment of such ferrous metal surfaces so as to effectively carry out porcelain enameling thereon.

Although there are a vast number of suggestions in the art concerning procedures which may be used to activate or prepare a suitable ferrous metal surface to receive a protective coating such as a porcelain enamel coating, each of these suggested procedures leaves something to be desired. In the industry, a number of different processes are used with each one ordinarily being suitable, or reasonably suitable, for only one type of enamel coating or only one type of metal surface. In general, certain types of enamel such as the titania-opacified enamels must be applied over a "ground coat" of enamel, or such titania-opacified enamels may be applied only to certain types of metal coverings which have been given certain pretreatments. The double coating of enamel ordinarily required for titania-opacified or similar enamel coatings is, of course, less effective for a number of reasons which include the additional thickness of the overall enamel coating. The less thickness of a single enamel coating affords much greater resistance to mechanical damage, etc.; but heretofore the art was unable to devise a method for applying a single "cover coating" of titania-opacified porcelain enamel to most metal surfaces. Certain high grade and expensive steel surfaces can be prepared by conventional cleaning and pickling procedures so as to obtain an acceptable bond between a single cover coating of titania-opacified porcelain enamel and the metal surface. The instant invention provides the advantage that it not only improves the bond between titania-opacified porcelain enamel and the presently used high quality steels, but it also permits the use of a single cover coating of titania-opacified porcelain enamel on the commercially available low carbon steels, sometimes referred to as cold-rolled or enameling iron stocks, which heretofore could not be prepared so as to form a commercially acceptable bond with the titania-opacified porcelain enamel.

The instant invention provides the unique sequence of cleaning, etching, pickling, etc. steps which, in the particular sequence to be described herein, result in a unique activation of the ferrous metal surface. The instant invention thus permits, by virtue of the peculiar activation of such ferrous metal surfaces, the use of commercial grade cold-rolled steel and the like industrially available ferrous metals in a field of porcelain enameling heretofore not available to these metals. This field is the so-called "direct on" or single coating porcelain enameling procedure wherein titania-opacified porcelain enamel may be applied directly to the activated metal surface as a single porcelain enamel coating; and preliminary sub-coats or bonding coats are not required in order to obtain adequate adherence between the titania-opacified porcelain enamel coating and the metal itself.

It is, therefore, an important object of the instant invention to provide an improved ferrous metal treating process and an improved porcelain enameling process embodying the ferrous metal treating process.

It is a further object of the instant invention to provide an improved sequence of metal treating steps which effects superior cleaning of a ferrous metal surface, plus uniform activation thereof to receive an adherent coating, such uniform activation including uniform etching as well as uniform nickel flash deposition.

Yet another object of the instant invention is to provide an improved method of porcelain enameling a ferrous metal surface, that comprises the steps of alkaline cleansing, nitric acid treatment, sulfuric acid-hydrogen sulfide treatment, occluded hydrogen gas removal treatment, alkaline cyanide treatment, nickel flash treatment, and finally the application of the porcelain enamel coating.

Other and further objects, features and advantages of the instant invention will become apparent to those skilled in the art from the following detailed disclosure thereof describing particularly preferred embodiments of the instant invention.

The instant invention consists in a method of treating a ferrous metal article surface, that comprises subjecting the surface to an alkaline cleanser solution followed by rinsing to remove surface contaminants and residual cleanser; subjecting the surface to aqueous nitric acid solution followed by rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to an aqueous sulfuric acid-hydrogen sulfide pickling solution followed by cold and hot water rinsing to etch the surface and remove occluded hydrogen, rust, scale and residual oxides from the nitric acid treatment; subjecting the surface to aqueous alkaline cyanide solution followed by rinsing to remove substantially all ferrous oxidation products; subjecting the surface to aqueous nickel salt solution followed by rinsing to deposit a nickel flash on the surface by electromotive displacement; and neutralizing residual acid on the surface followed by drying the surface.

The ferrous metal surface thus treated is ready to receive a "direct on" single cover coating of titania-opacified porcelain enamel, which is applied directly to the treated metal surface without the necessity for further preliminary steps.

As was mentioned previously, certain premium steels, which are grades of steel that have been formulated or processed under special circumstances so as to permit the direct application of cover coat enamels, are available for this specific purpose. Such premium steels are not identical in their behavior, however, and a specific pickling or etching process is ordinarily proposed for each of such premium steels. The non-premium grades, which include enameling irons and cold rolled steel have heretofore been used only with two-coat enameling systems. The instant invention, however, provides a method for treating enameling irons and cold rolled non-pre-

mium grades of steel so as to permit the use of only a single cover coat enamel; and the instant invention also provides a treatment for premium steels which effects an improvement in the bond between such premium steels and single cover coat enamels, although such improvement is less noticeable than that obtained in connection with the non-premium ferrous metals. Non-premium grades of steel are presumed to have a low impurity content of approximately the following compositions:

	Enameling Iron, percent	Cold Rolled (Mild Steel), percent
Carbon	.03	.09
Manganese	.05	.40
Phosphorus	.004	.008
Sulphur	.025	.025
Silicon	Trace	.005

The non-premium grades of steel suitable for enameling purposes produced by various mills do not possess the same chemical characteristics with respect to rate of acid attack. It cannot be definitely stated whether or not these differences in chemical activity result from variations in processing or variations in composition. In the instant invention, however, these differences in chemical behavior of non-premium grades of steel produced by various mills are substantially equalized by the chemical treatment here given. Also, certain differences in the premium grades of steel are also substantially equalized by the instant chemical treatment, although these differences are less apparent, as previously mentioned.

In order to demonstrate the instant invention, pieces of enameling iron and cold-rolled steel having the compositions above indicated are processed in accordance with the following schedule:

Step No.	Type of Bath Cleaner	Bath Operating Details
1	Aqueous alkaline cleaner	Material: Commercial alkali cleaner (Na_3PO_4, Na_2CO_3, NaOH, soaps, wetting agents and detergents). Concentration: 6–8 oz. per gallon—2% Na_2O. Temperature: Boiling. Immersion: 10–15 minutes.
2	do	Same as above.
3	Running Water Rinse	Temperature: Warm.
4	do	Temperature: Cold.
5	Aqueous Nitric Acid	Concentration: 8–15%. Temperature: 80°–10° F. Immersion: ½–1 minute. 10% ferric nitrate maximum impurity content.
6	Running Water Rinse	Temperature: Cold.
7	Aqueous Sulphuric Acid/ Iron Sulphide.	Concentration: 6.5–8.0% sulphuric acid, 4–8 grams iron sulphide per gal. of acid solution. Temperature: 180°±5° F. Immersion: 4–5 minutes. 12% ferrous sulphate maximum impurity content.
8	Running Water Rinse	Temperature: Cold.
9	do	Temperature: 170°±10° F. Immersion: 2–3 minutes.
10	do	Temperature: Cold.
11	Aqueous Sodium Cyanide	Concentration: 1.0–.25 oz. per gal. Temperature: 120°±10° F. Immersion: 2–3 minutes.
12	Running Water Rinse	Temperature: Cold.
13	Aqueous Nickel Sulphate	Concentration: 1.75–.25 oz. per gallon. Temperature: 170°±5° F. pH: 3.5–.3. Immersion: 4–5 minutes. Weight of Nickel Deposit: .07±.02 gm. per sq. ft. cold rolled; .09±.03 gm. per sq. ft. enameling iron.
14	Running Water Rinse	Temperature: Cold.
15	Aqueous Neutralizer	Concentration: Soda Ash .16 oz. per gal. Borax .05 oz. per gal. Na_2O: .075–.025%. Temperature: 165°±10° F. Immersion: 2–3 minutes.
16	Dryer	Temperature: 325°±25° F.

In addition to the described factors involved in each step of the process, the time of transfer involved in moving ware from bath to bath plays an important part in the success of the operation. A transfer time of not more than 15 seconds is preferred to minimize atmospheric oxidation of the metal surface. Excessive oxidation can be the source of various types of enamel defects.

A unique feature of the instant invention resides in the fact that both cold rolled steel and enameling iron are subjected to substantially identical operating conditions in order to adequately prepare these materials to receive the one coat titania-opacified enamel. In this way, articles containing both types of ferrous metal or containing premium steels also may be given this treatment so that all of the ferrous surfaces thereof will be ready to receive the enamel coat.

The enamel coat is applied in a conventional manner (without the necessity for applying a sub-coat) to the surfaces of the articles treated in accordance with the foregoing Schedule A.

The following formula is typical of the conventional type of titania-opacified cover coat enamel melted oxide frit composition and mill addition utilized in conjunction with the instant one-coat process. The materials shown in the mill formula are milled to a fineness, such that a .5 to 1.0 percent will remain on a 200 mesh screen, and applied by spraying or dipping at a dried application weight of approximately 35–40 grams per sq. ft.

Melted oxide enamel frit composition:

Na_2O	8.58
Al_2O_5	1.62
SiO_2	45.80
B_2O_3	13.65
K_2O	7.10
ZnO	2.00
P_2O_5	1.00
F	3.00
TiO_2	18.50

Mill addition composition:

Enamel frit	pounds	100.0
Enamelers' clay	do	4.0
Potassium carbonate	do	.5
Sodium nitrite	do	.25
Water	do	38.0

The enameling iron, cold rolled steel, and premium steel articles thus treated and enameled are found to have a uniquely superior bond between the enamel coating and the metal surface and these enamel coatings are found to be free from defects on each of these metal articles.

Referring again to Schedule A, it will be noted that steps 1 through 4 involve first hot alkaline cleaning in a conventional manner in step 1 using commercially available alkali cleansers. Such cleansers ordinarily contain one or more strongly alkaline chemicals as well as various detersive additives and the like; but the treatment of metals in an alkaline cleansing bath is considered to be a conventional cleansing step for the removal of various surface contaminants such as oils which may be applied to the metal surfaces during working of the metal. In the instant process, it is particularly important that this alkaline cleansing step be carried out as an initial step in the process immediately prior to the successive nitric and sulfuric acid treatments. Also, it has been found to be important to use successive alkaline cleansing solution treatments, for the reason that the initial failure of these alkaline cleansing solutions is not too readily detected, particularly because of the presence of the removed contaminants in the solution. Accordingly, the first cleansing step involves the removal of the bulk of such contaminants and the first bath retains such contaminants therein, whereas the second bath is substantially free therefrom and by using the second bath it is possible to insure complete alkaline cleansing. Defective

alkaline cleansing may not be readily detected and certain unseen defects resulting from incomplete cleansing would not be detectable until perhaps the final enameling step. Hot and cold rinsing have also been found to be preferred in this particular sequence of steps (i. e., steps 1 through 4) in order to effectively remove all of the various ingredients in the cleaner solution. Also, the sequence of first hot (i. e., 90 to 150° F.) and then cold (i. e., the temperature in the water mains which is a little below room temperature) rinsing effects the removal of materials more readily removed by hot water than by cold, and vice versa, while at the same time reducing the temperature of the metal parts thus rinsed so as to avoid any problems in temperature control in the subsequently used nitric acid bath.

In general, the activity of alkaline cleansing solutions is measured on the basis of the Na_2O content or concentration (although it is appreciated that the activity of such solutions is also affected by the presence of various detersive agents, wetting agents, etc. therein). The instant alkaline solutions should have an Na_2O content of at least about 1% and not more than about 3% for the dipping times set forth in the instant Schedule A. Preferably, the Na_2O concentration is about 2%. It will be appreciated, however, that variations in the length of dip as well as the Na_2O concentrations may be made in order to substantially duplicate the alkaline cleansing here obtained; but the instant concentrations and dip times are established as part of a commercially practicable schedule.

With respect to steps 5 and 6, it will be noted that the metal surfaces are exposed to strong aqueous nitric acid at relatively low temperatures, i. e., from about 60° F. (which is about as low a temperature as is ordinarily available in a water source without refrigeration) to about 95 or 100° F. (which is about the maximum practical temperature because of the increased activity of the solution and the relatively short dipping time permitted) and preferably the bath temperature is about room temperature (i. e., 70 to 90° F.). The immersion time in the bath is correlated with the temperature and is maintained at a practical minimum of about ½ to 1 minute. The nitric acid concentration ranges from a minimum of about 8% to a maximum of about 15%. Concentrations above this may be used and below also, without departing from the inventive concept here involved; but these concentrations have been found to be most satisfactory. Concentrations below about 8% will not always provide the necessary chemical attack on the metal surface, particularly because of the accumulation of a ferric nitrate concentration in the solution. The ferric nitrate concentration in the solution should not be permitted to rise above about 10%; and the solution should be repeatedly changed in order to avoid going above this ferric nitrate concentration. The rinsing step 6 is important, of course, more for the removal of ferric nitrate contaminant than for any other reason, because the next bath (step 7) is also an acid bath. However, there is a critically important feature of the instant invention here which involves the use, first, of nitric acid to impart substantially uniform chemical activity to the surface and, secondly, of sulfuric acid-hydrogen sulfide to uniformly etch the chemically active surface thus provided. The use of nitric acid and sulfuric acid-hydrogen sulfide in combination in the same bath will not accomplish this result, nor will the use of sulfuric acid-hydrogen sulfide first followed by nitric acid. For this reason, steps 5 and 7 are distinct and separate steps with the rinsing step 6 therebetween and the sequence of steps 5, 6 and 7 is critical.

As will be brought out throughout this specification, the particular sequence of steps here involved is of great importance. Even the rinsing steps in the particular manner here outlined make an important contribution to the success of the instant operation. In preparation for the

nitric and sulfuric acid-hydrogen sulfide treatments, it is important to absolutely clean without etching the metal surface and this is done by the alkaline cleanser and subsequent rinsing operations. Next follows the nitric acid treatment which, in turn, is followed by the sulfuric acid-hydrogen sulfide treatment so as to obtain not only the type but the level of metal surface roughening by acid etching that is necessary for a satisfactory bond and fired enamel texture development.

It is recognized that nitric acid or sulfuric acid-hydrogen sulfide solutions have been employed for etching purposes previously. Nitric acid alone can be utilized for roughening sheet steel surfaces. In the instant process, however, the function of the nitric acid (correlated with the subsequent sulfuric acid function) is unique.

There are broad variations in the chemical behavior with respect to acid etching not only among the various grades of steel but even among steel products of the same grade produced by different mills or produced using different heating schedules in the same mill. These differences in chemical activity of steel stocks make it impossible to consistently secure reasonably uniform metal surface roughening of the type required for direct cover coat enamel application, using the pickling procedures heretofore employed, or using a single etching solution. It has been found that nitric acid in the instant process is unique in that it functions not only as an excellent metal surface etchant, but it also has the property of activating less chemically active steel surfaces or portions of these surfaces so that they are more susceptible to the subsequent attack of the sulfuric acid-hydrogen sulfide solution. Nitric acid, as used in the instant process, is unique in that it is capable of imparting substantially uniform chemical activity to the ferrous metal surfaces treated thereby. This uniform chemical activity is uniform with respect to the manner in which the metal surface responds to the subsequent sulfuric acid-hydrogen sulfide treatment. In this respect, the concentrations, temperatures and immersion times for steps 5 and 7 are of very real significance in correlating these two steps. Appreciable departures from the scheduled conditions for step 5 would perhaps not render the instant process inoperative, but would require corresponding changes in step 7, as those skilled in the art will readily appreciate.

After the metal surface has been rinsed with cold water in step 6 to reduce surface oxidation and remove both nitric acid and ferric nitrate salts, the metal surface is subjected to the strong aqueous sulfuric acid solution (with the slight amount of iron sulfide additive) so as to complete the pickling etch and to remove any adherent rust or sweat scale, and to remove chemically the residual oxide coating produced by the nitric acid pickle. The iron sulfide additive in the source of the evolved hydrogen sulfide gas which is so essential to the process in question. The latter is produced by the reaction between the hot sulfuric acid and iron sulfide addition. In step 7, a hot aqueous sulfuric acid and hydrogen sulfide is used, at temperatures which should be at least about 160° F. and are preferably 175 to 185° F. Temperatures above about 185° F. up to as much as 200° F. may be used, of course, but the immersion time will have to be reduced correspondingly in order to avoid overpickling. In general, the temperatures used may range from about 160° F. to about 200° F. and the immersion times may range from a practical minimum of about 1 minute to a practical maximum of about 5 or 6 minutes, the immersion time being correlated with the temperature in order to obtain the desired etch. Preferably, the bath temperature is maintained below 185° F. because of the volatile components in the solution. Sulfuric acid itself gives off fumes to some extent and the present sulfuric acid solution contains a small amount of hydrogen sulfide which is generated by the presence of the iron sulfide. In addition to the temperature and immersion time, the

concentration of sulfuric acid must be considered in controlling the etch. Preferably, the concentration of sulfuric acid is within the range of about 6% to about 8%. Unless otherwise indicated in this specification, percent means percent by weight. The sulfuric acid concentration may be lower than the range indicated, but this requires additional immersion time and it may be higher than the range indicated, which will again require correlation of the temperature and immersion time in order to obtain the desired etch. The concentrations, temperatures and immersion times here indicated are correlated within rather narrow ranges so as to give the best results in carrying out the instant process.

Another important feature of the aqueous sulfuric acid pickling solution is the incorporation therein of a small amount of iron sulfide additive. In general, the iron sulfide additive will serve to maintain a hydrogen sulfide gas concentration in the solution of at least about 0.1%. Since concentrations appreciably above this will not ordinarily be retained in this solution at the operating conditions here used, the increased hydrogen sulfide gas concentrations usually desirable for assisting in the proper functioning of the sulfuric acid pickling solution are obtained more or less temporarily by repeated additions of iron sulfide. As each "basket" of metal articles is to be dipped into the sulfuric acid solution, a small amount of iron sulfide is added to this solution. The amount added is preferably about 4 to about 8 grams per gallon of solution. This will free nascent hydrogen sulfide so that the hydrogen sulfide concentration in the solution may temporarily rise to as much as about 1%. In general, the use of a small iron sulfide addition to a sulfuric acid pickling solution to produce nascent hydrogen sulfide to assist in the pickling is known; but the results obtained in the practice of the instant invention reside in a correlation between the nitric acid treatment and the sulfuric acid treatment, in the sequence and using the conditions here specified.

As has been mentioned, the instant process is unique in that it provides for uniformity in type and depth of etch by the use in succession of the nitric acid treatment first and then the sulfuric acid-hydrogen sulfide treatment, under the conditions here specified. The etching of metal surfaces is carried out so as to prepare these surfaces for a number of subsequent treatments, one of which is enameling, but others include coating with paints, varnishes, metal (electroplated) surfaces, etc. It will thus be seen that, although the instant invention provides a sequence of process steps that are uniquely suitable for the porcelain enameling art, the uniform etch here obtained on ferrous metal surfaces may be advantageously used in other arts.

Following the sulfuric acid-hydrogen sulfide treatment of step 7 are three rinsing steps. Step 8 is a cold rinse which is employed immediately after the sulfuric acid-hydrogen sulfide treatment so as to minimize oxidation and to remove products of chemical decomposition, including ferrous sulfate as well as the sulfuric acid. It should also be mentioned that the ferrous sulfate concentration in the sulfuric acid pickling solution should not be permitted to rise above about 12% under the conditions here prescribed; but there will always be an appreciable amount of ferrous sulfate present in the solution and this material plus the sulfuric acid should be removed immediately after the completion of the sulfuric acid-hydrogen sulfide etch of step 7. The cold water rinse of step 8 accomplishes such removal using cold water to minimize oxidation (which would be catalyzed by the presence of sulfuric acid); and the cold water rinse of step 8 is followed by a hot water rinse in step 9. The purpose of the hot water rinse (at temperatures from about 150 to 200° F., and preferably 160–180° F. for 1–5 minutes, and preferably 2–3 minutes) is to remove occluded hydrogen which has been formed during step 7, and perhaps step 5 also. The removal of occluded hydrogen is particularly important, since it may cause the formation of delayed "fish scale" on enameling. Apparently any occluded hydrogen which may be formed during step 5 and retained on the metal surface does not appreciably affect the uniformity of chemical activity of the surface which is obtained through step 5; and it is thus possible to effect the complete removal of all occluded hydrogen as late as step 9, without having any other difficulties.

The hot water rinse of step 9 is followed by a cold water rinse in step 10 which is carried out for the purpose of making additionally certain that all contaminants have been rinsed from the surface of the metal and further for the purpose of reducing the temperature of the metal in preparation for step 11. This feature is important, because the cyanide solution of step 11 tends to decompose when heated above about 130° F. For this reason, the cold water rinse of step 10 is carried out so as to reduce the metal temperature substantially below 130° F.

The aqueous alkaline cyanide solution treatment is carried out for the purpose of further conditioning and activating the etched metal surface so that it will be more receptive, and more uniformly receptive, to subsequent coating operations. In particular, the aqueous alkaline cyanide solution treatment in the sequence herein set forth assists materially in perfecting the instant porcelain enameling operation. In the instant procedure, a particularly important function of the alkaline cyanide solution is to remove substantially all ferrous oxidation products from the surface of the metal. The removal of such oxidation products is particularly important with respect to the procurement of a satisfactory fired enamel texture in the final step.

Although other alkaline cyanides (and particularly the alkali metal cyanides such as potassium cyanide) may be used in the practice of the instant invention, sodium cyanide is preferred and it is preferably used in dilute concentrations ranging from at least about ¼ oz. to about 2 oz. per gallon, and preferably ¾ to 1¼ oz. per gallon. In general, the use of aqueous alkaline cyanide baths for the treatment of metals is not new; but in the instant process, under the conditions here prescribed, the aqueous alkaline cyanide bath is used in a particular sequence so as to obtain a superior result. Preferably, the bath temperature is at least about 100 or 110° F. and not in excess of about 130° F. (above which decomposition is noticeable). The immersion time is preferably about 1–3 minutes, but longer immersion times may be used at lower temperatures. As indicated, the purpose in this particular sequence of steps for the use of the cyanide solution is the removal of substantially all ferrous oxidation products from the metal surface, and the conditions involved in the use of the instant alkaline cyanide solution should be such that this purpose is accomplished.

The aqueous alkaline cyanide treatment of step 11 is followed by a cold water rinse in step 12 which is carried out for the purpose of removing any adhering iron salts as well as the cyanide in the solution. In particular, it is important to remove the cyanide from the surface, because the carry-over of even small amounts of cyanide produces a marked effect upon the pH in the subsequently used nickel solution of step 13.

After the rinsing step 12, the metal surface is subjected to an aqueous nickel salt solution (having an acid pH) in order to deposit a nickel "flash" or extremely thin coating on the surface by electromotive displacement. The deposition of a nickel flash on steel surfaces by the use of such aqueous nickel salt solutions is, in general, understood; but the deposition of the nickel flash in the practice of the instant invention is accomplished more advantageously and in a generally more uniform manner, because of the particular steps, and the particular sequence of steps, which are carried out prior to the nickel salt treatment.

In step 13, the nickel salts which may be used include a number of different nickel salts such as nickel sulfate and nickel chloride as well as the "double" nickel-ammonium sulfate salts, etc. In general, the use of any nickel salts other than single nickel sulfate salts would necessitate the establishment of a set of both conditions somewhat different from that herein specified in order to obtain comparable results. In the instant process, nickel sulfate is preferred. And it is used in concentrations which may range from about 1 oz. to about 3 oz. per gallon, and preferably 1½ to 2 oz. per gallon, using immersion times which may range from 2 to 7 minutes, and preferably 4 to 5 minutes. Also, the bath temperature should be maintained at at least about 150° and not more than about 200° F., and preferably about 165 to 175° F. The pH should be controlled rather carefully so as to be maintained within the range of 3 to 4, the preferred pH being within the range 3.2 to 3.8. As will be appreciated, the instant ranges for each of the various conditions here mentioned are the preferred ranges for obtaining best results in the practice of the instant invention. The purpose of the aqueous nickel salt treatment is the deposition, by electromotive displacement, of nickel onto the metal surface in amounts which may range from about .05 gram per sq. ft. to as much as about .15 gram per sq. ft. The amount of nickel deposited for a given type of ferrous metal surface may vary, since certain amounts have been found to give the best results with certain types of ferrous surfaces. For example, 0.05 to 0.09 gram per sq. ft. is preferred on the cold rolled steel surface treated in accordance with the instant process, whereas 0.06 to 0.12 gram per sq. ft. is preferred for enameling iron treated in accordance with the instant process. The concentration, temperature, immersion time and pH are thus controlled generally within the ranges herein set forth so as to obtain the desired amount of nickel deposition (which can be readily calculated through the weight increase here obtained). It has been found that the flash deposition of nickel in accordance with step 13, and in the sequence of steps herein specified, produces a distinct improvement in adherence of the subsequently applied enamel coating.

Following the nickel salt treatment of step 13, the metal surface is rinsed in cold water so as to remove any nickel salts and iron sulfate which may tend to remain on the surface.

Following the rinsing step 14, the metal surface is exposed to a neutralizing slightly alkaline bath. The principal purpose of this treatment is to remove any residual acidity which might be retained on the surface of the metal. As will be appreciated, steps 5 and 7 both employ strong acids which, for the most part, are probably removed from the metal surface by the time step 15 is reached; but even extremely minor amounts of acid adhering to the surface could accelerate oxidation. Also, the nickel salt solution is an acid solution (the pH being adjusted by the use of very slight amounts of sulfuric acid) and it is particularly important to completely neutralize any residual acid on the metal surface during step 15. In general, the neutralization step is carried out using only weakly alkaline materials which are themselves substantially non-corrosive with respect to the ferrous metal surface, or are at least ineffective in the dilute concentrations used. Very dilute solutions of sodium carbonate, caustic sodium tetraborate or mixtures of these solutions may be used, providing an alkali content of 0.05 to about 0.10% Na_2O. Extremely dilute alkaline solutions of other materials such as trisodium phosphate may also be used, but it is generally preferable to use a combination of 0.1 to 0.2 oz. (and preferably 0.16 oz.) per gallon of sodium carbonate with 0.02 to 0.1 oz. (and preferably 0.05 oz.) per gallon of borax. The neutralizing bath is preferably a hot bath having a temperature of at least about 120° F. up to 200° F., and preferably 155 to 175° F., and the immersion time may be within the range of 1 to 5 minutes, but is preferably about 2–3 minutes.

The drying step 16 involves primarily subjecting the metal surface to a temperature substantially above the boiling point of water to remove all moisture from the surface of the metal.

After the drying step, the metal surface is ready for the application of the porcelain enamel coating. The porcelain enameling procedure employed is the conventional procedure which need not be described in further detail herein. It is important to note, however, that a sub-coating is not required for the application of more difficultly bonded porcelain enamels such as the titania-opacified porcelain enamels. Titania (TiO_2) is a well known white pigment or opacifier which has a number of uses. In titania-opacified porcelain enamels, which are a well known class or group of enamels, the principal opacifying agent is titania and it is ordinarily included in the frit composition in amounts ranging from as little as 10% to as much as 25% and preferably 15–20%, the remaining constituents in the frit being "glass-forming" metal oxides primarily (with small amounts of fluorides or phosphorous oxides).

With respect to step 7, the presence of hydrogen sulfide gas in the sulfuric acid is necessary for the procurement of the degree and type of metal surface etching that is required in the process for enamel bond development and good enamel texture. Although this gas is obtained in the process through the addition of iron sulfide, it can also be produced by the direct addition of alkali thiosulfate salts to the sulfuric acid or the direct pumping in of cylinder tank hydrogen sulfide.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of the present invention.

I claim as my invention:

1. A method of treating a ferrous metal article surface, that comprises subjecting the surface to an alkaline cleanser solution followed by rinsing to remove surface contaminants and residual cleanser; subjecting the surface to aqueous nitric acid solution followed by rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to the aqueous sulfuric acid-hydrogen sulfide pickling solution followed by rinsing to etch the surface and remove occluded hydrogen, rust, scale and residual oxides from the nitric acid treatment; subjecting the surface to aqueous alkaline cyanide solution followed by rinsing to remove substantially all ferrous oxidation products; subjecting the surface to aqueous nickel salt solution followed by rinsing to deposit a nickel flash on the surface by electromotive displacement; neutralizing residual acid on the surface followed by drying the surface; and applying directly to the surface a titania-opacified cover coat of porcelain enamel.

2. A method of treating a steel surface, that comprises subjecting the surface to successive exposures of 10–15 minutes each to boiling 1–3% Na_2O content aqueous alkaline cleanser solution followed by hot and cold rinsing to remove surface contaminants and residual cleanser; subjecting the surface to 8–15% aqueous nitric acid solution at 70–90° F. for ½ to 1 minute followed by cold rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to 6–8% aqueous sulfuric acid solution, with 4–8 g. iron sulfide additive per gallon, at 175–185° F. for 4 to 5 minutes followed by cold, hot and then cold rinsing; subjecting the surface to ¾ to 1¼ oz. per gallon concentration of aqueous sodium cyanide solution at 110°–130° F. for 2 to 3 minutes followed by cold rinsing to remove substantially all ferrous oxidation products; subjecting the surface to 1½ to 2 oz. per gallon concentration of aqueous nickel sulfate solution at 165°–175° F. and pH 3.2–3.8 for 4 to 5 minutes followed by cold rinsing; subjecting the surface to aqueous neutralizing solution of

0.16 oz. per gallon sodium carbonate and 0.05 oz. per gallon sodium tetraborate contents at 155°–175° F. for 2 to 3 minutes to neutralize any residual acid and then drying the surface; and applying directly to the surface a titania-opacified porcelain enamel mill addition composition and firing the same to obtain an adherent porcelain enamel coating on the surface.

3. A method of treating a ferrous metal article surface, that comprises subjecting the surface to an alkaline cleanser solution followed by rinsing to remove surface contaminants and residual cleanser; subjecting the surface to 8–15% aqueous nitric acid solution at 70–90 F. for ½ to 1 minute followed by cold rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to the aqueous sulfuric acid-hydrogen sulfide pickling solution followed by rinsing to etch the surface and remove occluded hydrogen, rust, scale and residual oxides from the nitric acid treatment; subjecting the surface to aqueous alkaline cyanide solution followed by rinsing to remove substantially all ferrous oxidation products; subjecting the surface to aqueous nickel salt solution followed by rinsing to deposit a nickel flash on the surface by electromotive displacement; neutralizing residual acid on the surface followed by drying the surface; and applying directly to the surface a titania-opacified cover coat of porcelain enamel.

4. A method of treating a ferrous metal article surface, that comprises subjecting the surface to an alkaline cleanser solution followed by rinsing to remove surface contaminants and residual cleanser; subjecting the surface to 8–15% aqueous nitric acid solution at 70–90° F. for ½ to 1 minute followed by cold rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to 6–8% aqueous sulfuric acid solution, with 4–8 g. iron sulfide additive per gallon, at 175–185° F. for 4 to 5 minutes followed by cold, hot and then cold rinsing; subjecting the surface to aqueous alkaline cyanide solution followed by rinsing to remove substantially all ferrous oxidation products; subjecting the surface to aqueous nickel salt solution followed by rinsing to deposit a nickel flash on the surface by electromotive displacement; neutralizing residual acid on the surface followed by drying the surface; and applying directly to the surface a titania-opacified cover coat of porcelain enamel.

5. A method of treating a ferrous metal article surface, that comprises subjecting the surface to an alkaline cleanser solution followed by rinsing to remove surface contaminants and residual cleanser; subjecting the surface to aqueous nitric acid solution followed by rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to 6–8% aqueous sulfuric acid solution, with 4–8 g. iron sulfide additive per gallon, at 175–185° F. for 4 to 5 minutes followed by cold, hot and then cold rinsing; subjecting the surface to aqueous alkaline cyanide solution followed by rinsing to remove substantially all ferrous oxidation products; subjecting the surface to aqueous nickel salt solution followed by rinsing to deposit a nickel flash on the surface by electromotive displacement; neutralizing residual acid on the surface followed by drying the surface; and applying directly to the surface a titania-opacified cover coat of porcelain enamel.

6. A method of treating a ferrous metal article surface, that comprises subjecting the surface to an alkaline cleanser solution followed by rinsing to remove surface contaminants and residual cleanser; subjecting the surface to 8–15% aqueous nitric acid solution at 70–90° F. for ½ to 1 minute followed by cold rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to 6–8% aqueous sulfuric acid solution, with 4–8 g. iron sulfide additive per gallon, at 175–185° F. for 4 to 5 minutes followed by cold, hot and then cold rinsing; subjecting the surface to ¾ to 1¼ oz. per gallon concentration of aqueous sodium cyanide solution at 110°–130° F. for 2 to 3 minutes followed by cold rinsing to remove substantially all ferrous oxidation products; subjecting the surface to aqueous nickel salt solution followed by rinsing to deposit a nickel flash on the surface by electromotive displacement; and neutralizing residual acid on the surface followed by drying the surface.

7. A method of treating a ferrous metal article surface, that comprises subjecting the surface to successive exposures of 10–15 minutes each to boiling 1–3% Na_2O content aqueous alkaline cleanser solution followed by hot and cold rinsing to remove surface contaminants and residual cleanser; subjecting the surface to 8–15% aqueous nitric acid solution at 70–90° F. for ½ to 1 minute followed by cold rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to 6–8% aqueous sulfuric acid solution, with 4–8 g. iron sulfide additive per gallon, at 175–185° F. for 4 to 5 minutes followed by cold, hot and then cold rinsing; subjecting the surface to aqueous alkaline cyanide solution followed by rinsing to remove substantially all ferrous oxidation products; subjecting the surface to aqueous nickel salt solution followed by rinsing to deposit a nickel flash on the surface by electromotive displacement; and neutralizing residual acid on the surface followed by drying the surface.

8. A method of treating a ferrous metal article surface, that comprises subjecting the surface to an alkaline cleanser solution followed by rinsing to remove surface contaminants and residual cleanser; subjecting the surface to aqueous nitric acid solution followed by rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to 6–8% aqueous sulfuric acid solution, with 4–8 g. iron sulfide additive per gallon, at 175–185° F. for 4 to 5 minutes followed by cold, hot and then cold rinsing; subjecting the surface to ¾ to 1¼ oz. per gallon concentration of aqueous sodium cyanide solution at 110°–130° F. for 2 to 3 minutes followed by cold rinsing to remove substantially all ferrous oxidation products; subjecting the surface to 1½ to 2 oz. per gallon concentration of aqueous nickel sulfate solution at 165°–175° F. and pH 3.2–3.8 for 4 to 5 minutes followed by cold rinsing; neutralizing residual acid on the surface followed by drying the surface; and applying directly to the surface a titania-opacified cover coat of porcelain enamel.

9. A method of treating a ferrous metal article surface, that comprises subjecting the surface to an alkaline cleanser solution followed by rinsing to remove surface contaminants and residual cleanser; subjecting the surface to 8–15% aqueous nitric acid solution at 70–90° F. for ½ to 1 minute followed by cold rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to 6–8% aqueous sulfuric acid solution, with 4–8 g. iron sulfide additive per gallon, at 175–185° F. for 4 to 5 minutes followed by cold, hot and then cold rinsing; subjecting the surface to aqueous alkaline cyanide solution followed by rinsing to remove substantially all ferrous oxidation products; subjecting the surface to aqueous nickel salt solution followed by rinsing to deposit a nickel flash on the surface by electromotive displacement; neutralizing residual acid on the surface followed by drying the surface; and applying directly to the surface a titania-opacified cover coat of porcelain enamel.

10. A method of effecting a uniform pickling etch to an alkaline cleanser cleaned ferrous metal surface, that comprises subjecting the surface to 8–15% aqueous nitric acid solution at 70–90° F. for ½ to 1 minute followed by cold rinsing to impart substantially uniform chemical activity to the surface; subjecting the surface to 6–8% aqueous sulfuric acid solution, with 4–8 g. iron sulfide additive per gallon, at 175–185° F. for 4 to 5 minutes followed by cold, hot and then cold rinsing; and subjecting the surface to ¾ to 1¼ oz. per gallon concentration

of aqueous sodium cyanide solution at 110°–130° F. for 2 to 3 minutes followed by cold rinsing to remove substantially all ferrous oxidation products.

References Cited in the file of this patent

UNITED STATES PATENTS

2,032,256 Canfield et al. ---------- Feb. 25, 1936

2,321,656 Chester ---------- June 15, 1943
2,535,794 Hempel ---------- Dec. 26, 1950
2,570,299 Zademach ---------- Oct. 9, 1951
2,695,249 Sweo ---------- Nov. 23, 1954

OTHER REFERENCES

Hansen, A Manual of Porcelain Enameling, The Enamelist Publishing Co., 1937, pp. 82–88.