

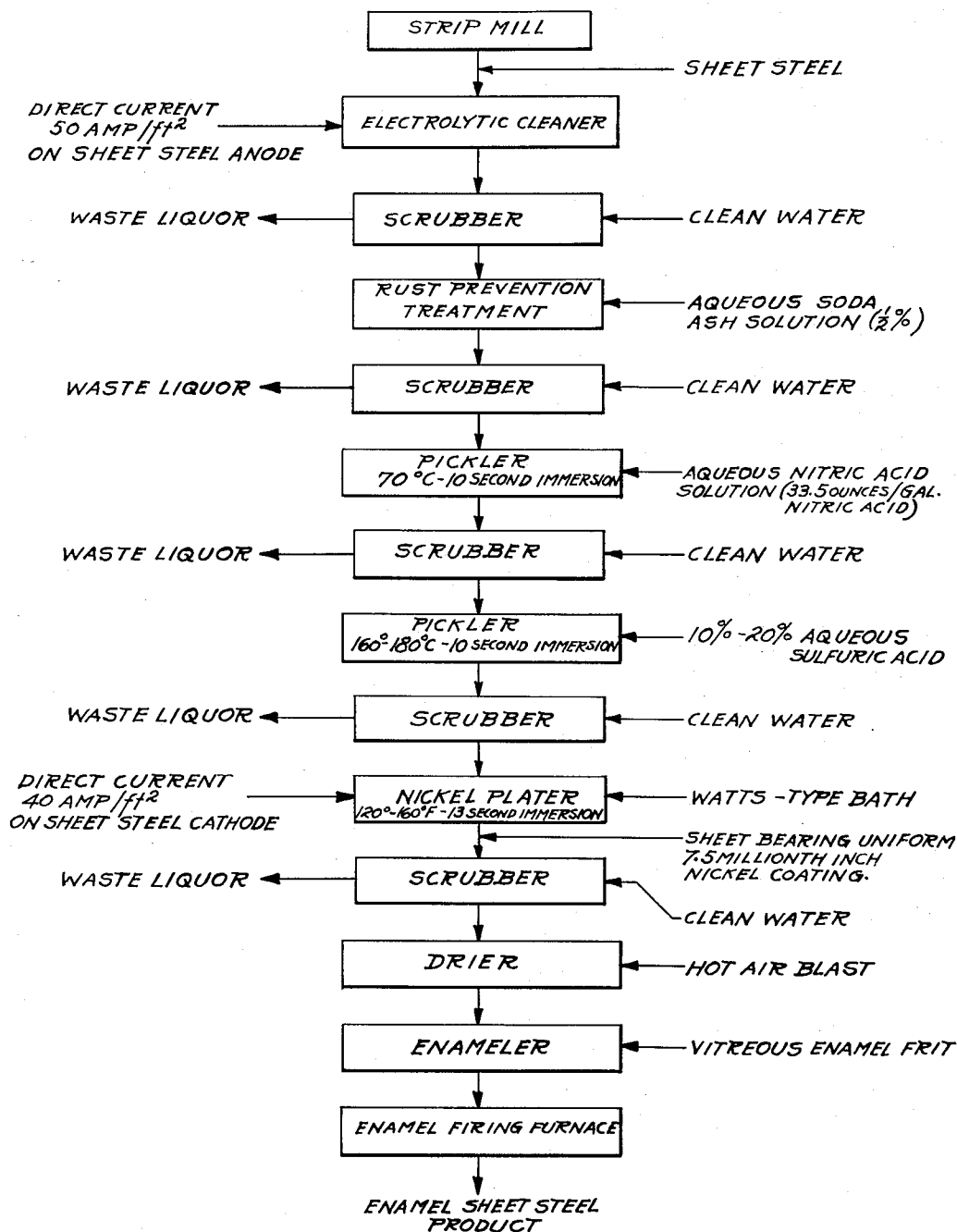
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I. P. WHITEHOUSE ET AL

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PROCESS OF ENAMELING STEEL

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INVENTORS
IRVING P. WHITEHOUSE,
FRED E. KENDALL &
BY PAUL GOLAR.

Rickey & Watts
ATTORNEYS

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PROCESS OF ENAMELING STEEL

Irving P. Whitehouse, Cleveland, Fred E. Kendall, Chagrin Falls, and Paul Golar, South Euclid, Ohio, assignors to Republic Steel Corporation, Cleveland, Ohio, a corporation of New Jersey

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The present invention relates generally to the protective coating art and is more particularly concerned with a novel method of producing tenaciously adhering, uniform and continuous vitreous enamel coatings on ferrous metal surfaces.

In accordance with the best commercial practice prior to this invention, porcelain enameling of hot or cold rolled ferrous metal articles, such as steel sheets and strips, involved as an essential operation the provision of bonding or ground coats of enamel. Ground coat enamels contain one or more adherence-promoting materials selected from the group comprising the oxides of antimony, molybdenum, cobalt, nickel and manganese, and they are typically but not invariably of dark color and are completely opaque. Thus, if an enamel finish of light or different color is required, a second enamel coat, known in the art as a "finish" coat, must be applied. In cases where a white finish is to be produced two such finish coats are usually required. In any event, however, the additional enamel coats are produced separately and at substantial expense. Consequently, there have been numerous determined efforts made by others to bond finish coat enamels containing no appreciable quantity of dark-colored, adherence-promoting oxide directly to ferrous metal surfaces. To the best of our knowledge, however, these efforts have all been commercially unsuccessful in that enamel coats produced were unsatisfactory because of inconsistent bonding to the metal surfaces and because the surfaces of these coats were often blistered or otherwise defective.

By virtue of our present invention, it is now for the first time commercially possible to produce a tenaciously adhering, uniform and continuous finish enamel coating on a ferrous metal surface produced by either hot or cold rolling, without first providing a ground coat of any type on said surfaces. Furthermore, this invention enables the employment of enamels which are substantially free from adherence-promoting oxides in manufacture of articles bearing only a single enamel coat.

Our invention is predicated upon our discovery that by treating the surface of a hot or cold rolled ferrous metal article in such a manner as to remove a very thin portion of said article without, however, excessively pitting the article, and by applying to the resulting surface a coat of nickel or other equivalent non-ferrous metal of certain critical thickness, consistently good bonding of enamel to the article may be accomplished without a preliminary ground coat and without employing any adhesive-promoting oxide as a constituent of the enamel slip. The application of the enamel coat follows the formation of the nickel coating on the surface of the article specially prepared in accordance with a process subsequently to be described. Normally, the nickel coating is applied to the article as soon as practicable after preparation of the surface by removal of the said thin portion. Also, the enamel coating is preferably applied to the nickel coat on the article as soon as practicable after the formation of that nickel coat to assure good bonding of the enamel.

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However, if it is not convenient to apply the enamel coating until some substantially later time, such as a month or more, and the article is not to be kept in a clean and dry location, the nickel coat may be oiled before the article is put away in storage. Prior to the application of the enamel to a nickel surface thus protected, the oil is entirely removed in any convenient manner so that a tenaciously adhering enamel coat can be produced quickly on the article.

As a result of this discovery, we have hypothesized the existence on rolled or otherwise worked ferrous metal articles of a skin or a surface condition of only a few molecules thickness which interferes with the adherence or anchoring of enamel coatings. According to our theory, prior ground coats have the ability to adhere to metal articles covered by this skin because they contain substantial proportions of adhesive-promoting oxides, and therefore offer good foundations for enamel finish coatings.

We have further hypothesized, as a result of our discovery, that with the skin removed and with the article bearing the nickel coating, the iron underlying this coating and exposed through numerous small openings in the coating is oxidized to a small but adequate extent during firing of the enamel slip to provide a secure bonding medium for the resulting enamel coat. In other words, in accordance with this invention the adherence-promoting oxides commonly employed in enamels are eliminated as ingredients of the enamel slip. The amount of nickel or other equivalent non-ferrous metal required to assure secure bonding in accordance with this invention is relatively small compared to the requirements in accordance with prior art for two principal reasons. In the first place, the interfering skin is eliminated in accordance with our discovery, and secondly, the nickel or other equivalent non-ferrous metal is concentrated at the critical location to accomplish its desired results instead of being distributed more or less uniformly throughout the enamel slip as it is applied to the article before firing is begun. Consequently, the amount of iron oxide associated with the final enamel coat, according to this invention, is so small that no undesirable color effects are produced thereby and the necessity for a ground coat is eliminated. Small amounts of oxides of other metals, such as the nickel of the nickel coating and elements alloyed with the iron of the article, may also be formed during firing and may assist in bonding the enamel coat, but in no case will these impart undesirable color effects to the enamel coat when the enamelling operation is carried out in accordance with the preferred practice of this invention.

Thus far we have not been able thoroughly and conclusively to demonstrate the existence of this skin or of the bonding effect of metal oxides formed in situ during firing, but we offer these theories as a possible explanation of the remarkable results obtained in accordance with this invention. We do not, however, intend that these theories shall constitute in any respect a limitation upon our invention or the appended claims.

Briefly stated, our invention comprises the steps of uniformly removing the skin of a ferrous metal piece and thereby producing a surface on the article substantially free from gas-retaining recesses, non-galvanically applying to the thus prepared piece a coating of nickel ranging in thickness between about two and about ten millionths of an inch, applying porcelain enamel slip directly to the resulting nickel coated piece, and firing the slip to produce a hard enamel coating tenaciously adhering to the surface of said piece. By the term "non-galvanically" as used herein and in the appended claims, we mean and include only the electroplating or electrodeposi-

tion method and the chemical reduction method of depositing nickel on a prepared ferrous metal piece.

Removal of the skin from a ferrous metal surface to be enameled in accordance with this invention may be accomplished by chemical, electrochemical or physical methods, or by any suitable combination of these methods but we prefer to employ the chemical method because it is rapid, inexpensive, and more readily controlled than either of the other methods. Regardless of which method is employed, however, care should be exercised to prevent irregular removal of the skin and excessive pitting or etching of the metal surface to be enameled because such a surface will permit entrapment of gases when the enamel is applied, causing blisters to form in the resulting enamel coat during the firing period. Also, whatever method is employed, the weight of metal removed from the piece should amount to at least about 0.01 gram per square inch of surface, which represents a thickness of metal between about 7 and about 8 one hundred thousandths of an inch. Of course, a substantially greater portion of the metal piece may be removed chemically, electrochemically or mechanically to produce a suitable surface for enameling, provided excessive pitting or etching, as just mentioned, is avoided.

Prior to the removal of the skin, the surface of the metal piece should be cleaned of grease and adhering foreign matter by any suitable means such as alkaline reagents, electrolytic methods, and organic solvents; and this cleaning should be sufficiently complete that the metal surface displays no water breaks.

In general, any solution of ferrous metal pickling acid or salt may be employed to remove the skin from a ferrous metal piece in accordance with this invention. By way of example, we have found the following acid solution of an oxidizing salt to produce satisfactory surfaces within 1 to 2 minutes immersion time when the solution temperature is between about 100° F. and 110° F.

	Grams per liter
Ammonium persulfate -----	200
Sulfuric acid -----	184

We prefer, however, to use solutions of sulfuric, hydrochloric, phosphoric, acetic or nitric acid, and we have a particular preference for nitric acid solutions in connection with continuous line commercial operation wherein production is at a high rate. A 25% by weight solution of nitric acid at room temperature, we have found, is generally equivalent as an etchant to the foregoing oxidizing salt solution but acts much faster to effectively remove all the interfering skin from a ferrous metal surface in approximately five seconds. This rate, however, may be increased or decreased by varying the concentration and/or the temperature of the acid, as those skilled in the art will understand. If any of the other acids or salts are employed, the time required for such removal will be substantially greater, assuming a constant temperature. Nitric acid has the further advantage over some of the others of not causing any hydrogen embrittlement of the articles.

Upon removal of the metal from the nitric acid solution it is preferably dipped into 10% sulfuric acid solution having a temperature of about 180° F. in order to remove oxides formed on the metal as a result of the oxidizing action of the nitric acid, and is then water rinsed to remove adhering sulfuric acid. It will be understood, of course, that any other suitable pickling solution may be employed in place of sulfuric acid and that the temperature of sulfuric acid of other equivalent solution may be varied widely without material effect upon the quality of the final articles.

The thus prepared article is next treated as promptly as convenient, and preferably immediately, to produce on the surface, substantially free from gas-retaining recesses, a non-ferrous metal coating of critical thickness between about two and ten-millionths of an inch. This coating

may desirably be of nickel, cobalt, antimony or molybdenum, these being the metals whose oxides are believed to promote adherence of enamel coats to iron or steel articles. Other metals may also or alternatively be used for this coating purpose providing they have suitable stability characteristics and physical properties. Thus the alkali metals, for instance, would be entirely unsatisfactory for this purpose because of their extremely reactive natures. Beyond this some metals may be excluded as a practical matter because of the difficulty of commercially applying coatings of them to base articles of iron or steel. A nickel coating may, however, be readily applied by either of the usual electroplating or chemical reduction methods. In the preferred practice of this invention we apply the nickel coating to the skinned ferrous metal article surface by the electroplating method through the use of a typical Watts-type bath, but it will be understood that any suitable nickel electrolyte bath may be employed for this purpose. As indicated above, though, the galvanic, that is the chemical substitution method is not contemplated by the invention. Where the article to be nickel plated and subsequently enamelled is in the form of a sheet and its entire flat surface is to be treated, this electroplating method is particularly advantageous, being easily controlled, inexpensive in the coatings used and absolutely consistent and reliable in producing uniform coatings.

Where the article is of some other shape not so adaptable to the electrodeposition method, or where the article has been put through a metal finishing operation, the chemical reduction method may advantageously be employed to apply the nickel coating to the article. This chemical reduction method may be carried out as described in detail in the Journal of Research National Bureau of Standards, issues of July, 1946 and November, 1947.

The appended claims, as indicated above, include both the electroplating method and the chemical reduction method of depositing nickel or equivalent on the prepared surface of an article to be enameled and these claims exclude the galvanic or chemical substitution method of accomplishing such metal deposition. Thus, as used in these claims, it will be understood that the expression "chemically but non-galvanically" includes both the chemical reduction and the electroplating methods and excludes the chemical substitution or galvanic method, and this expression also excludes all physical deposition methods such as those involving molten metal spraying or dipping.

Regardless of which of these two methods is employed, we prefer not to work the base article substantially after the coating of nickel has been laid down upon it. Certain kinds of working, such as bonding or drawing may be carried out on a nickel coated article without adversely affecting said coating or the enamel coat subsequently applied thereto, but metal finishing operations tending to remove or destroy the nickel coat should be avoided wherever possible. If working must be carried out at a later time, as for instance where the article must be subjected to a final deep drawing step just before enameling, the nickel coating should be in the heavier end of the critical thickness range. For the sake of economy where such subsequent working operations are not to be carried out, we recommend the establishment of coatings in approximately the middle portion of the said thickness range. It is, however, interesting in this connection to note that unless the ferrous metal surface to be enameled is prepared in accordance with this invention and the skin is removed as described, the application of a nickel film is of little assistance in the production of a satisfactory enamel coat regardless of how thin or thick this film may be or how nearly perfect it is.

For making the nickel coating by the chemical reduction method we prefer the acid-type baths as set forth in the November 1947 Journal of Research identified above

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because these baths are not subject to material change in composition through volatilizing effects in use and they are therefore more readily used than the alkaline baths which include ammonia. A typical acid-type bath which may be used to obtain the results of this invention has the following composition:

	Grams per liter
Nickel chloride	30
Sodium hypophosphite	10
Sodium acetate	10

pH 4 to 6.

An alkaline-type bath suitable for use in this invention in the establishment of the critical thickness of nickel coating has the following composition:

	Grams per liter
Nickel chloride	30
Sodium hypophosphite	10
Ammonia chloride	50
Sodium citrate	100

Ammonia hydroxide pH 8 to 10.

Hypophosphites of the other alkali metals, potassium and lithium, and of ammonium may be used instead of or with sodium hypophosphite or with each other.

In using either of these types of chemical reduction baths the freshly skinned object is immersed in the bath so that its skinned area is in contact therewith and the object is maintained thus long enough for a nickel film of desired thickness to be established thereon. Normally, a period of one minute would be sufficient to produce a nickel film of about five-millionths inch thickness when the temperature of the bath and the object surface are about 70° C. Inasmuch as the time and temperature both affect the rate of deposition of nickel from these baths, these factors may be varied. Also, the concentration of the bath constituents may be varied with resultant effect upon the rate of deposition. Consequently, these various factors may be manipulated as desired to suit the convenience of the operator with assurance that uniform nickel coatings will be produced consistently through any standardized procedure.

Following the application of the nickel coat, the piece is preferably rinsed with cold and then hot water, and then allowed to dry. The piece is then ready to receive the enamel coating which may be applied to any time thereafter. However, to protect the article over a protracted period of storage or transit, we oil the thus prepared surface, and when the enamel coating is to be applied, we cleanse the surface of oil in an electrolytic alkaline cleaner and then acid rinse and dry it.

If the skin is removed electrolytically, an electrically conductive electrolyte of any reasonable concentration and temperature may be employed such as an aqueous sulfuric acid solution, for instance, the work being the anode in an electric circuit including the solution. The skin may be removed in this manner in a matter of two or three minutes, the rate of such removal depending upon the temperature, current density and concentration of the conducting electrolyte. The conductive electrolytes are not critical as to type and any of those used in commercial electrolytic operations of generally similar purpose and description may be substituted for the sulfuric acid solution. In this operation care should be exercised to obtain substantial etching of the metal surface but without pitting of the surface. Such surface irregularities, as above mentioned, are conducive to the production of undesirable blistered enamel coats due to the entrapment of gases below the enamel surface when fired.

The mechanical methods of skin removal presently appear to be the least desirable from the standpoint of commercial operation, but we contemplate the employment of such means for removal of the skin in accordance with this invention. Sand or vapor blasting, grinding and filing are the mechanical methods which now appear to offer the best commercial possibilities. Care, of course,

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must be exercised to prevent skin removal in a manner which will result in a relatively rough surface that will offer refuge for gases below the surface of the enamel coating.

A finishing operation which will produce a surface which is neither too rough nor too smooth may be employed in the production of consistently tenacious, continuous uniform enamel coats. Such an operation may be accomplished mechanically, chemically or electrochemically, as those skilled in the art will readily understand, but will, in any event according to our theory, result in the removal from the metal surface of selected grains of ferrite so that said surface will comprise substantially only resistant ferrite grains.

The porcelain enamel slip is applied directly to the nickel-coated surfaces generally in the same manner as the slips of cover coats of enamel are applied to metal articles upon which adherent ground coats have been provided. Any of the so-called conventional sheet steel porcelain enamels are generally suitable and useful in accordance with this invention, but those enamels which are regarded as finish coat or cover coat enamels and which contain substantially no adherence-promoting oxides are of special utility in the present method as indicated above. Depending upon the type of enamel employed, the firing temperatures and the length of the firing periods necessary to assure production of a uniform enamel coat of good surface and secure bond to the base articles will vary. Thus, we contemplate the employment of a wide variety of time and temperature circumstances in our enamel firing operations because of the wide range of enamel compositions which may be successfully employed in this invention.

The process of this invention is applicable generally to ferrous metal bodies, but has particular utility in connection with iron and steels in which the carbon content is less than about 0.30%. Enamel coats of good bond and surface characteristics are, however, obtainable by this invention where the base articles are either of commercially pure iron, or steel of carbon content between about 0.01% and 0.30%. Steels of higher carbon content as well as malleable, white and gray cast irons may nevertheless be used as base articles in accordance with this invention with consistently satisfactory enamel coats resulting, providing that the graphite particles in the surface portions of these articles are not too large to interfere with the bonding of the nickel coat to the base body. The ferrous metals used in the present processes may contain minor amounts of alloying elements such as manganese, titanium, nickel, copper, molybdenum, and the like, without materially impairing their ability to receive and tenaciously retain the nickel bonding coat and the enamel cover coats applied directly thereto. The present method, however, is especially suitable for use with cold rolled steel of less than about 0.30% carbon content, which is known in the trade as commercial quality plain carbon steel and may suitably be in the form of sheets or strips, although bars and other shapes may also be employed.

The following example of this invention, as it may be practiced on a large scale commercially in connection with a continuous strip mill and as it is illustrated in the flow sheet drawing accompanying and forming a part of this specification, is offered to explain further to those skilled in the art, the present invention and its objects and advantages.

Example

Twenty gauge sheet steel is run continuously from a strip mill into a suitable vat containing a hot alkaline electrode cleaning solution, the strip being made the anode in a direct current circuit in which the current density is maintained at about 50 amperes per square foot of strip surface immersed in said solution. The cleaner solution temperature is maintained between about 160° F. and 180° F., heat being supplied to the cleaner vessel in any suitable manner to compensate for heat loss attributable

to the continuous movement of initially relatively cool sheet into the cleaner solution. Dirt, grease and oil adhering to the sheet as it emerges from the mill is normally entirely removed by this electrolytic treatment, but the sheet is thoroughly rinsed with clean water after passing through the alkaline cleaner to assure the removal of any loose solid matter and also to free the sheet of adhering alkaline cleaner so that subsequent acid treatment of the sheet will not be impaired through the neutralizing effects of this adhering cleaner. The sheet, which is chemically clean after this rinse, is subjected to an alkaline dip to prevent rusting. The alkaline dip is a weak aqueous soda ash solution containing about 0.5% sodium carbonate. The sheet, on emerging from this dip is scrubbed once again with clean water in order to remove the thin film of soda ash adhering to its surface, and then is promptly dipped into a nitric acid pickling bath contained in a suitably shaped dipping vessel. This acid bath is maintained at a temperature of about 70° C. and contains one part by volume of 70% nitric acid (specific gravity 1.42) and three parts by volume of water.

On emerging after a ten-second immersion period from the pickling bath, the sheet is scrubbed again with clean water promptly in order to remove all traces of nitric acid and smut from the surface of the steel. The sheet is next immersed in a sulfuric acid bath to remove any oxides from the steel surface, the period of this immersion also approximating ten seconds. This pickling solution contains 10% to 20% sulfuric acid by weight and is kept at a temperature between about 160° F. and 180° F. A clean water rinse promptly follows removal of the sheet from this latter pickling bath to remove all traces of adhering sulfuric acid solution from the pickled sheet.

The sheet is next plated with nickel, the thickness of the nickel coat ranging between about two and ten millionths of an inch. This is accomplished by immersing the sheet in a Watts-type nickel plating bath having the following composition:

NiSo ₄ ·6H ₂ O.....	25 to 45 ounces per gallon.
NiCl ₂	6 to 9 ounces per gallon.
H ₃ BO ₃	4 to 6 ounces per gallon.
pH.....	3 to 5.
Temperature.....	120° to 160° F.

A thirteen second plate at a current density of 40 amperes per square foot may be employed to deposit a coat of nickel about 7.5 millionths of an inch thick from such a bath.

The nickel plated steel emerging from the plating bath is promptly scrubbed with clean water to free it from adhering plating solution and then is thoroughly air-dried, suitably by means of a hot air blast. The steel is then ready for an application of enamel to its surface and this operation is carried out with a typical porcelain enamel of the following composition:

Dehydrated borax.....	Lbs. 159
Feldspar	143
Sodium nitrate.....	363
Cryolite	195
Zinc oxide.....	96
Boric acid.....	345
Powdered quartz.....	1204
Titanium oxide.....	294

This enamel is fired out at about 3½ minutes at a temperature of 1480° F.

This is a continuation-in-part of our copending application Serial No. 770,748, filed August 26, 1947, now abandoned.

Having thus described the present invention so that those skilled in the art will be able to understand and practice the same, we state that what we desire to secure by Letters Patent is defined in what is claimed.

What is claimed is:

1. The method of producing a tenaciously adhering, uniform and continuous porcelain enamel finish coat on a steel article having a carbon content between about 0.01% and about 0.30% which consists essentially of the steps of uniformly and regularly removing a surface portion of said article equivalent to at least about 0.01 gram per square inch and thereby producing a surface on the article substantially free of gas-retaining recesses due to excessive pitting, etching or roughness, chemically but non-galvanically applying to said recess-free surface a coating of non-ferrous metal selected from the group consisting of nickel, cobalt, molybdenum and antimony ranging in thickness between about two and about ten millions of an inch, applying porcelain enamel slip substantially free from adherence promoting oxides directly to the resulting coating, and firing said slip and producing said enamel finish coat.

2. The method of producing a tenaciously adhering uniform and continuous porcelain enamel finish coat on an article of commercially pure iron which consists essentially of the steps of uniformly and regularly removing a surface portion of said article equivalent to at least about 0.01 gram per square inch and thereby producing a surface on the article substantially free of gas-retaining recesses due to excessive pitting, etching or roughness, chemically but non-galvanically applying to said recess-free surface a coating of nickel ranging in thickness between about two and about ten millionths of an inch, applying porcelain enamel slip substantially free from adherence promoting oxides directly to the resulting nickel coating, and firing said slip and producing said enamel finish coat.

3. The method of producing a tenaciously adhering, uniform and continuous porcelain enamel finish coat on cold rolled sheet or strip steel having a carbon content between about 0.01% and about 0.30% which consists essentially of the steps of uniformly and regularly removing a surface portion of said article equivalent to at least about 0.01 gram per square inch and thereby producing a surface on the article substantially free of gas-retaining recesses due to excessive pitting, etching or roughness, non-galvanically applying to said recess-free surface a coating of nickel ranging in thickness between about two and about ten millionths of an inch, applying porcelain enamel slip substantially free from adherence promoting oxides directly to the resulting nickel coating, and firing said slip and producing said enamel finish coat.

4. The method of producing a tenaciously adhering, uniform and continuous porcelain enamel finish coat on a ferrous metal article having a carbon content less than about 0.30% which consists essentially of the steps of uniformly and regularly removing a surface portion of said article equivalent to at least about 0.01 gram per square inch and thereby producing a surface on the article substantially free of gas-retaining recesses due to excessive pitting, etching or roughness, electrodepositing on said recess-free surface a flash coat of nickel between about one and about ten millionths of an inch thick, directly applying porcelain enamel slip substantially free from adherence promoting oxides to the resulting nickel coating, and firing said slip and producing said enamel finish coat.

5. The method of producing a tenaciously adhering, uniform and continuous porcelain enamel finish coat on a ferrous metal article having a carbon content less than about 0.30% which consists essentially of the steps of uniformly and regularly removing a surface portion of said article equivalent to at least about 0.01 gram per square inch and thereby producing a surface on the article substantially free of gas-retaining recesses due to excessive pitting, etching or roughness, depositing a layer of nickel between about two and about ten millionths of an inch thick on said recess-free surface by the chemical reduction method, applying porcelain enamel slip

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substantially free from adherence promoting oxides directly to the resulting nickel coating, and firing said slip and producing said enamel finish coat.

6. The method of producing a tenaciously adhering, uniform and continuous porcelain enamel finish coat on a ferrous metal article having a carbon content less than about 0.30% which consists essentially of the steps of sand blasting said article and thereby uniformly and regularly removing a surface portion of the article equivalent to at least about 0.01 gram per square inch and producing a surface on the article substantially free of gas-retaining recesses due to excessive pitting, etching or roughness, depositing a layer of nickel between about two and about ten millionths inch thick on said recess-free surface by the chemical reduction method, applying directly to the resulting nickel coating porcelain enamel slip substantially free from adherence-promoting oxides, and firing said slip and producing said enamel finish coat.

7. The method of producing a tenaciously adhering, uniform and continuous porcelain enamel finish coat on a ferrous metal article having a carbon content less than about 0.30% which consists essentially of the steps of immersing said article in an aqueous sulfuric acid solution as an anode in an electrical circuit and thereby uniformly and regularly removing a surface portion of said article equivalent to at least about 0.01 gram per square inch and producing a surface on the article substantially free of gas-retaining recesses due to excessive pitting, etching or roughness, electrodepositing on said recess-free surface a flash coat of nickel between about two and about ten millionths inch thick, applying directly to the resulting nickel coating porcelain enamel slip substantially free from adherence-promoting oxides, and firing said slip and producing said enamel finish coat.

8. The method of producing a tenaciously adhering, uniform and continuous porcelain enamel finish coat on a ferrous metal article having a carbon content less than about 0.30% which consists essentially of the steps of contacting said article with a 25% by weight aqueous nitric acid solution and thereby uniformly and regularly removing a surface portion of said article equivalent to at least about 0.01 gram per square inch and producing a surface on the article substantially free of gas-retaining recesses due to excessive pitting, etching or roughness, then promptly chemically but non-galvanically applying to said recess-free surface a coating of nickel ranging in thickness between about two and about ten millionths of an inch, then applying directly to the resulting nickel coating porcelain enamel slip substantially free from

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adherence-promoting oxides, and firing said slip and producing said enamel finish coat.

9. The method of producing a tenaciously adhering, uniform and continuous porcelain enamel finish coat on a ferrous metal article having a carbon content less than about 0.30% which consists essentially of the steps of contacting said article with a solution of ferrous metal pickling acid and thereby uniformly and regularly removing a surface portion of said article equivalent to at least about 0.01 gram per square inch and producing a surface on the article substantially free of gas-retaining recesses due to excessive pitting, etching or roughness, then promptly depositing a layer of nickel between about two and about ten millionths inch thick on said recess-free surface by the chemical reduction method, applying directly to the resulting nickel coating porcelain enamel slip substantially free from adherence promoting oxides, and firing said slip and producing said enamel finish coat.

10. The method of producing a tenaciously adhering, uniform and continuous porcelain enamel finish coat on a ferrous metal article having a carbon content less than about 0.3% which consists essentially of the steps of uniformly and regularly removing a surface portion of said article equivalent to at least about 0.01 gram per square inch and thereby producing a surface on the article substantially free of gas-retaining recesses due to excessive pitting, etching or roughness, non-galvanically applying to said recess-free surface a coating of non-ferrous metal selected from the group consisting of nickel, cobalt, molybdenum and antimony ranging in thickness between about two and about ten millionths of an inch, applying porcelain enamel slip substantially free from adherence promoting oxides directly to the resulting metal coating, and firing said slip and producing said enamel finish coat.

References Cited in the file of this patent

UNITED STATES PATENTS

2,101,950	McGohan	Dec. 14, 1937
2,127,388	Canfield et al.	Aug. 16, 1938
2,469,123	Martin	May 3, 1949
2,510,071	Chester	June 6, 1950
2,615,836	Chester	Oct. 28, 1952

OTHER REFERENCES

Transactions Electrochemical Society, "Special Volume—Modern Electroplating," 1942, pp. 260-1.