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PORCELAIN ENAMEL ARTICLE AND METHOD
OF PRODUCING SAMEBenjamin J. Sweo, Lakewood, Ohio, assignor to
Ferro Corporation, Cleveland, Ohio, a corpora-
tion of OhioNo Drawing. Application November 6, 1951,
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6 Claims. (Cl. 117-53)

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The present invention is a continuation-in-part of my co-pending invention bearing Serial Number 139,963 filed January 21, 1950, entitled "Porcelain Enamel Article and Method of Producing Same", now abandoned.

This invention relates, as indicated, to porcelain enameling and has more particular reference to an enameling procedure and articles produced therefrom characterized by the direct application to a steel surface of porcelain enamel of the type ordinarily referred to as cover coat porcelain enamel in that it does not contain any substantial amounts of those materials, such as oxides of cobalt and nickel for example, which have heretofore been deemed necessary in order to insure satisfactory adherence between the enamel and the steel.

As indicated above, the prior art practice of insuring adequate adherence between enamel and steel has been to use adherence-promoting oxides. These are, however, usually dark in color so that if the finished product is to be white, or of a light shade it has been necessary to apply a cover coat of such light enamel. Various methods have been used in an endeavor to improve the adherence of cover coat enamels to steel. One of such methods has been by the use of steels of special compositions. Another has been by the use of a so-called "nickel flash" step by which a predetermined amount of nickel is deposited on the surface by galvanic action.

The use of special steels is undesirable for many reasons, the principal one being cost.

The use of the galvanic process for the deposition of nickel onto the steel surface to promote adherence between the enamel and the steel has been only partially successful. By the use of the "nickel flash" method the adherence of the enamel to the steel has been improved. However, that method leads to inconsistent results in that the nickel deposits on various steels from a conventional bath varies in character and amount. Thus while the "nickel flash" formation method has been used for the purposes of improving the bond between the enamel and the steel, that improvement has never been great enough to make possible the omission from the enamels of at least certain amounts of adherence-promoting oxides so that in most cases the industry has continued to use the two-coat process when producing light colored work, a first or ground coat—of dark colored enamel and a second coat of the desired light color.

It is the principal object of my invention to provide a porcelain enameled article and a meth-

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od of producing the same characterized by the direct application to the work piece of enamels which do not require the use of a ground coat or the presence therein of any substantial amounts of adherence-promoting oxides and the like.

It is a further object of my invention to provide porcelain enameled articles which are superior from the standpoint of surface characteristics and appearance with respect to any which have been capable of production by any known prior art methods. Other objects of my invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

Broadly stated, this invention comprises the method of porcelain enamelling a steel work piece which comprises cleaning and roughening the surface of the work piece so as to produce a surface condition characterized by deep sharp edged pits therein characteristic of the surface resulting from pickling with an aqueous solution of nitric acid, immersing said roughened steel work piece in an aqueous solution of a nickel salt, said solution containing a reducing agent selected from the class consisting of hypophosphorous acid and those salts thereof, the cationic portion of which is above tin in the electromotive series whereby when the steel work piece is immersed in said solution the nickel salt is reduced and nickel deposited on the work piece without ion exchange between the work piece and the solution, maintaining the work piece in said solution until there has been deposited on the roughened surface thereof from about .04 to about .25 grams per square foot of nickel coating thereon, washing and drying the work piece, then applying directly on the thus nickel-coated roughened surface of the work piece a cover coat porcelain enamel which is substantially free of adherence promoting oxides, and then firing such enamel thereon.

It will be observed from the foregoing broad statement of my invention that the method which comprises such invention for the production of articles which are likewise new, in that they have never been made heretofore, may be divided into three principal steps which for

convenience in the further description of my invention will be treated in the order in which they are usually performed.

CLEANING AND ROUGHENING THE METAL

The steel surface to which the porcelain enamel is to be eventually applied when practicing my invention needs to have two primary characteristics. First, it must be relatively clean, that is free from all foreign materials such as dirt, grease and the usual coat of metallic oxide. Second, the surface of the steel must be reasonably rough for best adherence of the porcelain enamel. This preparation of the steel surface may be accomplished by chemical means or by mechanical means or by a combination of the two. If it is desirable to effect the preparation of the surface by chemical means only, this can be accomplished conveniently by the use of pickling baths which leave a relatively rough surface. The pickling baths which are available for this purposes are, for example those employing nitric acid and combinations of nitric acid with other acids and baths which are primarily sulphuric acid baths, but which also contain nitric acid or other oxidizing agents. This type of bath has two principal characteristics. First the bath is extremely vigorous in its action so that the required pickling time is relatively short and second, this type of bath produces a surface which may be identified, for convenience, as a deeply etched surface, in that it contains pits which are relatively deep with the crests between such pits relatively sharp. Because of this peculiar type of surface just described which is produced by pickling baths of the type just described they are preferred for use in my process since it has been found that adherence between the enamel and the steel is greatest when the steel surface is thus preliminarily prepared.

Instead of utilizing baths of the character referred to above satisfactory results may be obtained by utilizing pickling baths in which the principal components are salts which are readily reduced in the presence of iron, for example, trivalent iron salts such as ferric chloride. Since the ferric chloride pickling process wherein the effective components of the bath are continuously regenerated by the introduction of chlorine thereto are well-known in the pickling art, it is believed unnecessary to further describe such process at this point.

All of the various pickling processes referred to above are capable of producing the roughened surface on the work which is characterized by deep sharp-edged pits therein. This type of surface preferably is produced by means of a pickling solution which is an aqueous solution of nitric acid containing about one part of concentrated nitric acid to each four parts of water. When using such a bath, a satisfactory surface will usually be produced in about one minute at room temperature. As the temperature increases the time is accordingly reduced. Typical examples of sulphuric acid baths containing oxidizing agents which are effective to produce a surface characterized by deep sharp-edged pits therein are as follows:

	Percentage
H ₂ SO ₄	7
Sodium chlorate	3
Water	90
H ₂ SO ₄	6
HNO ₃	3
Water	91

The length of time during which the work piece must be immersed in baths of the type represented by the last two examples above will depend not only on the temperature of the bath, but also on the relative concentrations of sulfuric acid and oxidizing agent. The sodium chlorate bath given above will usually produce a satisfactory surface, when operated at 160° F. temperature, for 3 minutes. The sulfuric acid bath utilizing nitric acid as the oxidizing agent as given above when operated at 140° F. temperature will produce a satisfactory result in about 3 minutes.

Instead of chemically preparing the surface of the steel in the manner just described satisfactory results may be secured by a simple sand blasting operation which is effective to not only remove the foreign material and oxides from the sheet, but also leave the sheet reasonably rough for the reception of the nickel deposit. It is within the contemplation of my invention to combine chemical and physical means for the preparation of the sheet and in this the sand blasting operation which is described may be preceded or followed by a second step and when the pickling step is the last to be employed then it should preferably be of the type which will produce the deeply etched surface of the character previously described.

NICKEL DEPOSITIONS

The "nickel flash" method previously referred to, i. e. the process for the deposition of nickel which depends upon galvanic action by the work piece and the bath has not been satisfactory for use in my process. It is believed that one reason why deposition of the nickel by galvanic action does not give satisfactory results is not only the inconsistency of that process and the variations in the deposits resulting therefrom, but also the nature of character of the nickel deposit resulting from such process. Since the very nature of the process is galvanic, this requires that there be a certain area of the steel surface always exposed to the action of the bath if the galvanic process is to proceed. The nickel layer thus laid down by the galvanic process is not what may be termed a uniform or substantially continuous layer of nickel. Instead it is a coating of nickel which is interrupted by areas wherein the base metal is exposed or only superficially coated.

It has been established that porcelain enamel deposited over a thick layer of pure nickel has very poor adherence to such nickel. It will be concluded therefore that for proper adherence by the enamel to the work piece there must be a certain amount of iron in combination or elemental form available in the bonded area. I have found that the iron thus available on a surface coated with nickel by the galvanic method is too great for best results and it is believed that this accounts for the poor bond which is secured between the base metal and the enamel if only galvanically deposited nickel is used and if there are no adherence-promoting oxides present in the porcelain enamel.

In order to provide a lower ratio of iron to nickel on the surface of the steel work piece and to bring such ratio into the range wherein greatest adherence between the enamel and the work piece is secured, it is essential that the nickel coating deposit be substantially uniform while at the same time permitting the occurrence of at least a minor amount of iron, in free or combined form, at the bond. The process of depositing nickel by means of an electrolytic bath

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will produce a substantially continuous layer of nickel but such process is unsatisfactory for a number of reasons. First it can be used successfully only on simple shapes such as flat sheets because if the article treated has any substantial contour deviating from a flat plane there will be sufficient variation in the thickness of the nickel deposited on the various areas of the article to produce best results. Since the nature of the nickel deposit, i. e. its thickness and character are quite critical, when the article is contoured the thickness of the coat on the high points, for example, will be sufficiently different from the thickness of the coat on the low points for example, so that if the coating at one place is adjusted to the narrower range for best results, the coating on the other area will be outside of such range. Thus the process of depositing the nickel electrolytically can be used satisfactorily only on flat surfaces such as unfabricated steel sheets and strips and even on such surfaces the character of the deposit laid down by the electrolytic method is sufficiently different from the character of the deposits laid down by a chemical reduction method that it is not possible to secure the high order of adherence with the electrolytic process as it is with the process wherein the nickel is laid down by chemical reduction.

When flat steel sheets are prepared by the electrolytic process and they are then subsequently formed into the various shapes required by the enameling industry, such forming, especially if it is accomplished with any burnishing, grinding or welding steps will either sufficiently disrupt the layer of deposited nickel or destroy it entirely so that the resultant work piece is defective because of unsatisfactory adherence in the area where these operations have been performed.

Accordingly my invention comprises the coating of the work piece with nickel which is deposited thereon from a bath wherein the nickel is generated by chemical reduction and without ion exchange between the work and bath.

As previously indicated, the amount of nickel deposited is critical for best results. There is one feature, however, which has an influence on the amount of nickel which will produce optimum results and that is the roughness characteristic of the steel sheet. It will be found that as the roughness or etched characteristics of the sheet vary the amount of nickel to be deposited will vary also. As indicated above, preferred results are secured when the surface preparation of the work leaves it in a deeply etched condition. On this type of surface the amount of nickel to be deposited for best results will be found to lie between about 0.04 and about 0.250 grams of nickel per sq. ft. of surface area. A coating of approximately 0.150 to 0.1750 grams of nickel per sq. ft. of surface area will generally be the preferred range. The baths which may be used for the chemical reduction of nickel and its deposition onto the work are described in the literature, for example U. S. Patent No. 2,532,283. These baths may be either alkaline or acid. The alkaline baths are described in Journal of Research—National Bureau of Standards, July 1946. A typical example of an alkaline bath which may be used in carrying out my invention is as follows:

Example I

Nickel chloride	g./liter	30
Sodium hypophosphite	do	10
Ammonium chloride	do	50
Sodium citrate	do	100
Ammonium hydroxide to a pH of 8 to 10		

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The alkaline baths have one drawback in that they are, under certain circumstances, inconvenient and uneconomical because at elevated temperatures there is a rapid loss of ammonium and the bath gives off copious fumes. The acid type baths which may be used in this step of my process are described in Journal of Research—National Bureau of Standards, November 1947. A representative example of an acid bath is as follows:

Example II

Nickel chloride	g./liter	30
Sodium hypophosphite	do	10
Sodium acetate	do	10
pH		4 to 6

Since the acid baths generally operate with a very low loss of constituents by vaporization this type of bath is somewhat more controllable than the alkaline type baths described above.

While the foregoing examples of plating baths show the use of sodium hypophosphite as the reducing agent I have successfully used various other hypophosphite salts and hypophosphorus acid, however, since the sodium salt is the cheapest and most readily obtainable I prefer the use of sodium hypophosphite.

Instead of employing sodium hypophosphite as the reducing agent in the nickel plating baths I may use instead hypophosphorus acid and the salts thereof, the cationic portion of which is above tin in the electromotive series. The expression just used in the identification of the cationic portion of the salt is intended to include not only the metals, but also the ammonium radicle which can be said to have a chemical action similar to the alkali metals. While all salts formed of cations which are above tin in the electromotive series are of utility, they are by no means of equal commercial value. The alkali metals and the alkaline earth metals are very much preferred for use. While cadmium, zinc and chromium occur in the electromotive series above tin and are useful, the hypophosphite salts thereof are not as active reducing agents as hypophosphorus acid and the alkali and alkaline earth and ammonium salts thereof which have been indicated as preferred. It has been found that the cadmium, zinc and chromium hypophosphites are so slow in their action that they do not lend themselves readily to continuous commercial operations where time is always a factor.

The following is a list of examples of additional nickel plating baths employing hypophosphites other than the preferred sodium hypophosphite used in examples I and II.

Example III

Nickel chloride	g./liter	30
Potassium hypophosphite	do	9.8
Sodium acetate	do	10
pH		4 to 6

Example IV

Nickel chloride	g./liter	30
Calcium hypophosphite	do	15.6
Sodium acetate	do	10
pH		4 to 6

Example V

Nickel chloride	g./liter	30
Ammonium hypophosphite	do	7.8
Sodium acetate	do	10
pH		4 to 6

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Example VI

Nickel chloride	g./liter	30
Magnesium hypophosphite	do	24.6
Sodium acetate	do	10
pH		4 to 6

Example VII

Nickel chloride	g./liter	30
Hypophosphorus acid (30%)	ml./liter	17.8
Sodium acetate	g./liter	10
pH		4 to 6

Example VIII

Nickel chloride	g./liter	30
Manganous hypophosphite	do	9.6
Sodium acetate	do	10
pH		4 to 6

Example IX

Nickel chloride	g./liter	30
Ferrous hypophosphite	do	8.8
Sodium acetate	do	10
pH		4 to 6

Example X

Nickel chloride	g./liter	30
Aluminum hypophosphite	do	7
Sodium acetate	do	10
pH		4 to 6

Example XI

Nickel chloride	g./liter	30
Nickel hypophosphite	do	14
Sodium acetate	do	10
pH		4 to 6

Example XII

Nickel chloride	g./liter	30
Cobalt hypophosphite	do	8.9
Sodium acetate	do	10
pH		4 to 6

Example XIII

Nickel chloride	g./liter	30
Zinc hypophosphite	do	9.2
Sodium acetate	do	10
pH		4 to 6

In carrying out the nickel deposition step the previously treated sheet as prepared by step 1 of my improved process is immersed in the bath for a length of time on the order to about one minute at about 70° C., i. e., for a period of time depending on temperature and other conditions such as the condition of the bath in order to lay down a deposit of nickel within the ranges specified above. After the work is removed from the nickel bath it is washed, preferably in warm water, preparatory to receiving the application of porcelain enamel which occurs in the third step of my process. The application of the porcelain enamel comprises the third step of my process and should be performed within a reasonable time after the completion of the nickel deposition, in order to have a clean surface onto which to apply the porcelain enamel. It should be noted that the surface of the nickel will not change substantially from the condition in which it was, immediately after the nickel was laid down.

THE ENAMEL STEP

This third step of my process is substantially conventional porcelain enameling practice such as would be followed in the application of cover coats to work pieces previously provided with

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an adherent ground coat. As previously indicated, the porcelain enamel which may be used in this step may be any conventional sheet steel cover coat porcelain enamel need not contain any substantial amount of adherence-promoting oxides which characterize ground coat porcelain enamels. An example of a cover coat porcelain enamel which has produced porcelain enamel sheet steel articles in carrying out my process, with desirable characteristics superior to those of any porcelain enamelled steel sheet ever made regardless of the process or type of porcelain enamel, is as follows:

Dehydrated Borax	lbs.	159
Feldspar	do	143
Sodium nitrate	do	364
Cryolite	do	195
Zinc oxide	do	96
Boric acid	do	345
Powdered quartz	do	1204
Titanium dioxide	do	294

The foregoing enamel fires out on 20 gauge steel in about 3½ minutes at about 1480° F. It will be found that when carrying out my process and utilizing conventional sheet steel cover coat porcelain enamels, of which there are many variations available, best results will be secured if the porcelain enamel is fired slightly harder than the conditions under which it would be fired as applied over a ground coat. Thus, the porcelain enamel given above which would normally be fired over a ground coat for 3½ minutes at 1480° F. gives unexpected superior results when fired out at about 1520° F. for the same length of time.

The following is a representative series of steps which may be followed in the process of producing a porcelain enamelled sheet steel article when utilizing my invention.

The steel sheet, which may be conventional cold rolled steel as produced in large quantities in this country and of appropriate gauge on the order of 18 or 20 gauge, is first cut to size and formed to the desired contour of the finished article. The blank thus produced is then cleaned of adhering dirt and grease by the use of a conventional alkaline cleaning bath after which the work piece is thoroughly rinsed.

If the work piece carries any rust on its surface which was not removed during the alkaline cleaning step, such rust should be removed and this can be accomplished by immersing the work piece in a sulfuric acid bath consisting of about a 6 to 7% aqueous solution of concentrated sulfuric acid, such bath being maintained at a temperature of about 140 to 150° F. The work piece is kept in this sulfuric acid for a length of time sufficient to remove the rust. Since this bath does not contain any oxidizing agent, it will not have any particular effect in producing the necessary roughened surface on the steel required as a preliminary to the application of the nickel. If the work piece does not carry any rust, this sulfuric acid pickle step may be omitted. If it is necessary to use this sulfuric acid bath then the work piece, after being taken from such bath, should be thoroughly rinsed before it is subjected to the roughening step.

The thus preliminarily cleaned work piece (which need not be dried) is then subjected to the required roughening action which can be accomplished as indicated by immersing the work in a 10% aqueous solution of nitric acid at room temperature for a period of about one minute.

After the work is removed from the nitric acid bath it should be washed with water and then immediately dipped several times in a 6 to 7% aqueous solution of concentrated sulfuric acid at a temperature of about 140 to 150° F. to remove from the surface any salts which may have been formed thereon by the reaction of the nitric acid with the work. The work is then again washed with water.

The thus roughened work piece (which need not be dried) is then immersed in any of the nickel baths referred to above under such conditions of time and temperature as to deposit thereon an amount of nickel within the limits stated. As an indication of the time and temperature conditions of this step it will be noted that when employing an acid bath as per Example II, with the bath maintained at about 70° C., the time of immersion will be on the order of about one minute to lay down the desired amount of nickel.

After the work is removed from the nickel plating bath it is then washed again and preferably dried before the application of the porcelain enamel thereto.

The porcelain enamel used may be any of the sheet steel cover coat porcelain enamels available, a representative formula of which has been given above. As is well-known, this enamel is initially prepared in the form of a frit and a suspension thereof is then made by milling the frit in a ball mill along with suitable mill additions. The mill additions employed will depend upon the particular enamel selected for use and the other desired properties of the ultimate slip, all of which is conventional in porcelain enameling practice.

The enamel is applied as by dipping or spraying directly onto the nickel coated work piece and after being initially dried as is conventional in enamelling practice, is then fired under conditions which, as explained above, are the best conditions at which the particular porcelain enamel matures. The firing temperature as indicated will be in the neighborhood of 1400 to 1500° F. and the firing time on the order of from 2 to 5 minutes.

As a striking example of the unexpected results which can be secured by the use of my process, a sample of ordinary cold rolled steel, which up to the time of my invention was considered to be practically unusable for direct cover coat application, was pickled at room temperature in a nitric acid bath comprising one volume of nitric acid to four volumes of water; pickling time one minute. The sheet was then rinsed in warm water and immersed in the chemical acid reduction nickel bath, the analysis of which has been given above, at a temperature of 70° C. for one minute. The sheet was then rinsed again in warm water and dried. By chemical analysis the sheet was found to carry a coating of .163 grams of nickel per sq. ft. of surface area.

The coated sheet, which is described, was then sprayed with a cover coat enamel having an analysis substantially like that given above at a weight of about 20-30 grams (dry components) per sq. ft. of surface area and fired at about 1520° F. for about 3½ minutes. The finished fired sheet had an extremely smooth texture, no surface pits or copperheads and had superior glass-metal adherence when tested by the conventional impact test used to determine adherence. In another test on the same base equally satisfactory results were re-cured by the

same procedure excepting that the pickling step was performed in a 7% sulphuric acid bath containing from 1 to 3% sodium chlorate with the pickling performed at a temperature of 160° F. The process comprising my invention may be used to advantage, for example, in enameling shops and when used makes possible the fabricating of the desired work pieces from untreated cold rolled steel which is one of the lowest cost forms of sheet steel available today. After the article has been completely fabricated, i. e., all welding, burnishing or like steps completed, the article is then subjected to the steps outlined and the described process will produce a finished article in which the superior surface coating is uniform throughout.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

I therefore particularly point out and distinctly claim as my invention:

1. In the method of porcelain enamelling a cleaned and roughened steel work piece surface having deep sharp edged pits therein, the steps comprising immersing said roughened steel work piece in an aqueous solution of a nickel salt, said solution containing a reducing agent selected from the class consisting of hypophosphorous acid and salts thereof in which the cationic portion is above tin in the electromotive series, whereby when the steel work piece is immersed in said solution the nickel salt is reduced and nickel deposited on the work piece without ion exchange between the work piece and the solution, maintaining the work piece in said solution until there has been deposited on the roughened surface thereof from about .04 to about .25 grams per square foot of nickel coating thereon, washing and drying the work piece, then applying directly on the thus nickel-coated roughened surface of the work piece a cover coat porcelain enamel which is substantially free of adherence promoting oxides, and then firing such enamel thereon.

2. In the method of porcelain enamelling a cleaned and roughened steel work piece surface having deep sharp edged pits therein, the steps comprising immersing said roughened steel work piece in an aqueous solution of a nickel salt, said solution containing as a reducing agent an alkali metal hypophosphite, whereby when the steel work piece is immersed in said solution the nickel salt is reduced and nickel deposited on the work piece without ion exchange between the work piece and the solution, maintaining the work piece in said solution until there has been deposited on the roughened surface thereof from about .04 to about .25 grams per square foot of nickel coating thereon, washing and drying the work piece, then applying directly on the thus nickel-coated roughened surface of the work piece a cover coat porcelain enamel which is substantially free of adherence promoting oxides, and then firing such enamel thereon.

3. In the method of porcelain enamelling a cleaned and roughened steel work piece surface having deep sharp edged pits therein, the steps comprising immersing said roughened steel work piece in an aqueous solution of a nickel salt, said solution containing as a reducing agent an alkaline earth metal hypophosphite, whereby when the steel work piece is immersed in said solution the nickel salt is reduced and nickel deposited

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on the work piece without ion exchange between the work piece and the solution, maintaining the work piece in said solution until there has been deposited on the roughened surface thereof from about .04 to about .25 grams per square foot of nickel coating thereon, washing and drying the work piece, then applying directly on the thus nickel-coated roughened surface of the work piece a cover coat porcelain enamel which is substantially free of adherence promoting oxides, and then firing such enamel thereon.

4. In the method of porcelain enamelling a cleaned and roughened steel work piece surface having deep sharp edged pits therein, the steps comprising immersing said roughened steel work piece in an aqueous solution of a nickel salt, said solution containing as a reducing agent hypophosphorous acid, whereby when the steel work piece is immersed in said solution the nickel salt is reduced and nickel deposited on the work piece without ion exchange between the work piece and the solution, maintaining the work piece in said solution until there has been deposited on the roughened surface thereof from about .04 to about .25 grams per square foot of nickel coating thereon, washing and drying the work piece, then applying directly on the thus nickel-coated roughened surface of the work piece a cover coat porcelain enamel which is substantially free of adherence promoting oxides, and then firing such enamel thereon.

5. The method of porcelain enamelling a steel work piece which comprises cleaning and roughening the surface of the work piece so as to produce deep sharp edged pits therein by means

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of an aqueous solution of nitric acid, immersing said roughened steel work piece in an aqueous solution of a nickel salt, said solution containing as a reducing agent sodium hypophosphite, whereby when the steel work piece is immersed in said solution the nickel salt is reduced and nickel deposited on the work piece without ion exchange between the work piece and the solution, maintaining the work piece in said solution until there has been deposited on the roughened surface thereof from about .04 to about .25 grams per square foot of nickel coating thereon, washing and drying the work piece, then applying directly on the thus nickel-coated roughened surface of the work piece a cover coat porcelain enamel which is substantially free of adherence promoting oxides, and then firing such enamel thereon.

6. As a new article of manufacture, a porcelain enamelled steel article produced by the process of claim 1.

BENJAMIN J. SWEO.

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