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METHOD OF PORCELAIN ENAMELING FERROUS METAL AND PRODUCT

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This invention relates to the surface treatment of metals. More particularly, it relates to the surface treatment of ferrous base metals such as steel for porcelainizing.

In the art of porcelainizing a metal such as steel, the metal is normally formed into the desired ultimate shape and then cleaned with an alkali cleaner or other suitable cleaner to remove dirt, oil, etc. The cleaned metal part is rinsed and then heated in a furnace at a temperature of from about 1100 to 1250° F. for several (about 5) minutes to oxidize the surface of the metal and to remove adsorbed gases such as hydrogen, carbon monoxide, etc. The steel is then pickled in acid to remove the scale and oxidized layer, rinsed, plated with nickel such as by dipping in a nickel reducing or displacement bath, coated with a porcelain frit and finally fired at elevated temperatures to fuse the frit. This process in which the metal is heated at elevated temperatures, pickled in acid, and dipped in a nickel bath has heretofore been deemed necessary in the one-coat method of porcelainizing. However, the process is an exacting one since it is not applicable to all steels. The steels used must be of high quality. If the steel is of a different quality or slightly different composition, variations in the treating steps and baths must be undertaken to obtain satisfactory results. Many steels cannot normally be used as the porcelain coating exhibits pitting and poor adhesion unless careful adjustments in treating steps are made. Accordingly, it would be highly desirable to provide a porcelainizing process which would be applicable to a variety of different steels and which does not require critical control of the various treating baths, and, therefore, it is a primary object of the invention to afford a method for porcelainizing metal including a surface pretreatment step which avoids the difficulties alluded to hereinabove.

It is another object of this invention to provide a novel process for porcelainizing ferrous and other metals.

Still another object is to provide a porcelainized metal article.

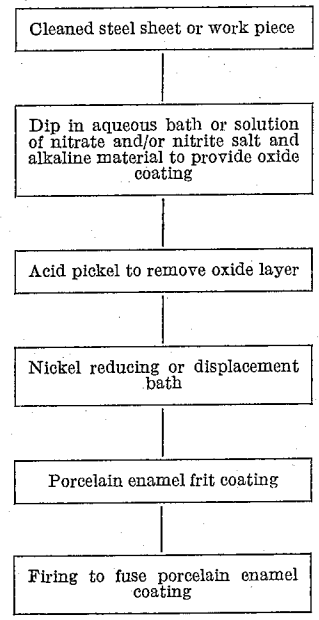
A further object is to provide a porcelainized ferrous metal article such as a steel article which has been specially treated prior to porcelainizing.

These and other objects and advantages of the present invention will become more apparent to those skilled in the art from the following detailed description and examples.

According to the present invention, it has been found that the treatment of clean ferrous base materials such as iron or steel in an aqueous alkaline nitrate and/or nitrite salt bath or solution will provide an oxide coating on the surface of the metal which can be easily removed or essentially entirely removed by the acid pickle prior to porcelainizing. It is highly useful in the method whereby only a single porcelain enamel or frit coating is applied. The present process avoids the necessity of using high temperatuers and the equipment and fuel associated therewith, uses fewer loadings and unloadings, eliminates the possibility of the slowly dissolving anneal scale being carried over into the nickel reduction baths to effect spontaneous deposition, and permits the use of a wide variety of steels of different composition and previous heat and working treatments. Moreover, by the process of the present invention, the surface of the metal where

covered with frit is completely porcelainized even including crevices and corners.

A simplified flow diagram of the method is as follows:



The process is useful on cold or hot rolled steel sheet, as well as on formed pieces and the like. Moreover, the porcelain coating obtained is not only as good as present coatings, but also exhibits improvement in bond strengths. For best results, it is preferred that the alkaline nitrate and/or nitrite oxidizing dip should be preceded by a dip or treatment in an aqueous bath or solution of an organic or inorganic acid, particularly where scale and rust are present, to provide a smooth, uniform and reactive finish for the oxidizing (nitrate and/or nitrite) bath.

The aqueous alkaline nitrate and/or nitrite salt bath can include any appreciably water soluble inorganic alkaline nitrate and/or nitrite salt such as ammonium nitrate, ammonium nitrite, potassium nitrate, potassium nitrite, sodium nitrate, sodium nitrite, rubidium nitrate, cesium nitrate, cesium nitrite, and the like and mixtures thereof. It is preferred to employ the nitrates of sodium and potassium. The alkaline material used with the nitrate or nitrite salt can be any appreciably water soluble alkaline material compatible with the nitrate and/or nitrite salt such as ammonium hydroxide, tetramethyl ammonium hydroxide, the alkali metal hydroxides, and mixtures thereof and others. Of these it is preferred to use the alkali metal hydroxides such as NaOH, KOH, RbOH and CsOH.

The relative amounts of nitrate and/or nitrite salt and alkali material employed in the bath will vary from about 0.35 to 0.85 mole of inorganic nitrate and/or nitrite salt to from 0.80 to 1.7 moles of the alkaline material.

Water is used in an amount sufficient to dissolve the nitrate and/or nitrite salt and alkaline material to provide a liquid bath having a concentration of these reagents sufficient to oxidize the surface of the metal. Even very minor amounts of the nitrate and/or nitrite salt and alkaline material in a large volume of water will provide satisfactory results although a longer treating time may be required. Much larger amounts of the nitrate and/or nitrite salt and alkaline material can be used up to a concentration in the water below that concentration at which these reagents would tend to salt out. In general, the inorganic nitrate and/or nitrite salt and alkaline material are used in a total amount of from about 10 to 80% by

weight (solids) of the aqueous bath while it is preferred to have a concentration in the aqueous bath from about 35 to 60% total solids weight of nitrate and/or nitrite salt and alkaline material. The bath is operable over a fairly wide range and can be replenished from time to time as needed with fresh nitrate and/or nitrite salt and alkaline material. The bath should be operated at a temperature below the boiling point of the solution and, generally, from about 25 to 90° C. The metal is dipped in the bath for a period of time as necessary to provide an oxidized surface and which will depend on various factors such as the condition of the metal, concentration of the alkaline material and nitrate and/or nitrite salt, temperature, etc. In general, a dipping time of from about 2 to 20 minutes will be saisfactory. Minor amounts of detergents or wetting agents, salts, such as NaCl, and other additives may be added to the alkaline nitrate and/or nitrite salt bath although it is preferred to operate only with an aqueous solution of the nitrate and/or nitrite salt and the alkaline material.

After dipping in the alkaline nitrate and/or nitrite salt bath the product should desirably be rinsed, preferably with hot water, and may be dried. It has a surface finish which varies in color (yellow, rust, green, red, dark blue or bluish black) depending on the concentration of ingredients in the bath and the bath temperature and immersion time. This surface finish readily dissolves in an acid solution, such as phosphoric acid solution.

As noted above, it is best to employ an aqueous acid dip prior to the alkaline nitrate and/or nitrite salt dip to remove surface scale and the like and to activate the surface of the metal for subsequent oxidation. Such bath permits the obtainment of consistently good results and more latitude in the other steps of the precess. Useful acids to employ are nitric acid, sulfamic acid, and mixtures of chromic acid and sulfamic acid, mixtures of chromic acid and sulfuric acid, and mixtures of chromic acid and phosphoric acid and the like. It is preferred to use nitric acid. The concentration of the acid in the aqueous bath can vary from about 1 to 20% by weight on the bath, although it is preferred to use from about 8 to 15% by weight on the bath. The bath can be replenished with fresh acid from time to time before it is necessary to be discarded due to increasing concentration of iron salts or treated to remove the same. This bath can tolerate an iron build-up of up to at least about 10% before it is necessary to remove the iron salts. An example of suitable nitric acid dip to employ is disclosed in U.S. Patent No. 2,837,443 to Zander, dated June 3, 1958.

This acid bath can be warmed although it can be used cold or at room temperature. It is only necessary to dip the steel or other ferrous metal in this acid bath for a short time, usually from a few seconds to several minutes. For example, from about ¼ to 3 minutes, preferably from about ½ to 2 minutes, has been found adequate.

After treating the metal in this acid bath, the metal should desirably be rinsed before dipping in the alkaline nitrate and/or nitrite bath.

After the alkaline nitrate and/or nitrite dip, the oxidized steel is dipped in an aqueous acid bath, preferably an aqueous phosphoric acid bath, to pickle it and remove the oxidized surface. This bath should contain from about 10 to 25% by volume of phosphoric acid. The time of dipping in the aqueous phosphoric acid bath can vary from about 3 to 15 minutes or more at a temperature of from about 100 to 150° F. When using the present aqueous nitrate and/or nitrite salt bath in place of the heating step of the prior art, it has been observed that the life of this phosphoric acid pickle bath is increased by about 33⅓%.

The phosphoric acid pickled metal article is then preferably rinsed and dipped in a nickel bath, such as nickel reducing or displacement bath, to deposit from about 0.02 to 0.25 gram per sq. ft. of nickel on the metal. For best results, the amount of nickel deposited should be from about 0.07 to 0.10 gram per sq. ft. Nickel reducing baths are well known to the art. They generally comprise an aqueous solution of nickel salts, preferably nickel sulfate, an alkali hypophosphite such as sodium hypophosphite and an alkali acetate, for example sodium acetate at a pH of about 5.2 to 5.9. The metal article is dipped or placed in this bath for several minutes at a temperature above room temperature, for example from about 80 to 200° F. Examples of such baths are shown in U.S. Patent No. 2,695,249 to Sweo et al., dated November 23, 1954, and entitled "Porcelain Enamel Article and Method of Making Same," and references cited therein. See, also, U.S. Patent No. 2,581,310 to Sweo, dated January 1, 1952, and entitled "Porcelain Enamel Article and Method of Producing Same," and references cited therein.

The nickel coated sheet is then preferably rinsed and dried and coated with a porcelain enamel, frit or similar composition wet or dry, by electrostatic coating methods, by dipping, spraying or by other means and then fused at a high temperature generally below that at which distortion of the metal might occur, for example, not above about 1450° F. Fusible inorganic porcelain compositions and the like to use include glazes, glasses, enamels, frits and the like and can comprise feldspar, lime and quartz; borax, feldspar, quartz and cryolite; and other materials well known to the art for this purpose. They may be suitably pigmented as known to the art. Examples of some useful types to employ are disclosed in the aforementioned U.S. patents and in U.S. Patent No. 2,671,029 to Moss, dated March 2, 1954, and entitled "Porcelain Enameling."

While this process is particularly effective in the one-coat method of porcelainizing, it will be useful in other methods of porcelainizing where a ground coat(s) is applied before the finish coat or coats, or where one or more poreclain, glass, ceramic or similar inorganic coatings are applied.

The metal treated can be steel, iron and their alloys or other ferrous base metals in the form of strip, sheet and the like or in definite pieces or objects such as those obtained after forming or other metal working steps. The steel is preferably a low carbon steel and can be cold or hot rolled. It is preferred to use those steels which have not been aluminum killed since they tend to develop fish scaling, and to use steel rather than enameling iron also to avoid the possibility of obtaining fish scales.

Prior to treatment according to this invention the metal should be cleaned of dirt, oil and other extraneous matter by treatment with an alkaline cleaner, detergent or other cleaning material. The rinsing steps should preferably be conducted with de-ionized water or water free or substantially free of ions, such as chloride ions, to avoid the possibility of blistering.

The following examples will serve to illustrate the invention with more particularity to those skilled in the art:

Example I

Low carbon steel plates were cleaned with an alkali cleaner, rinsed and placed in an aqueous bath containing 6 lbs. of a mixture (50–50 by weight) of sodium hydroxide and sodium nitrate per gallon of water. The steel pieces were left in the bath for ten minutes at a temperature of 70° C. and then rinsed. The plates were next placed in a phosphoric (H_3PO_4) acid bath containing about 16% by volume of phosphoric acid for about 8 minutes to pickle the plates. The oxide coating dissolved quickly in the phosphoric acid pickle bath. The pickled plates were then removed from the phosphoric acid bath, rinsed and placed in an aqueous nickel reducing solution containing 3.9 oz./gal. of nickel sulphate, 0.8 oz./gal. of sodium acetate and 28 grams per gallon of sodium hypophosphite at a temperature of about 90° F. for 3.5 to 4.5 minutes to deposit about 0.08 g./ft.^{2} of nickel on the plates. After the nickel was deposited on the sheets, they were rinsed and dried in an oven. The dried sheets were then

coated with a porcelain enamel frit and fired at a temperature of about 1400° F. to fuse the porcelain and provide a porcelain enamel surface. The resulting articles were examined and were in many cases free of pinholes. The coatings were generally smooth and adherent to the metal base.

Example II

The method of this example is the same as that of Example I, above, except that prior to dipping the steel plates in the aqueous sodium hydroxide-sodium nitrate bath, they were dipped in a cold aqueous solution containing about 10% by weight of nitric acid for from 30 seconds to 2 minutes and then rinsed. The porcelain coated plates obtained by this method were free of pinholes and other surface defects and the surfaces were entirely smooth and adherent.

The products of the present invention can be used in the manufacture of cooking wear; wash basins; cabinets, walls and floors of refrigerators; sinks; chemical reactors; washing machine tubs; and wherever a porcelainized surface is desired.

It will be understood that the above description is by way of illustration rather than limitation and that, in accordance with the provisions of the patent statutes, variations modifications of the specific methods and articles disclosed herein may be made without departing from the spirit of the invention.

Having thus described my invention, I claim:

1. The method which comprises treating a cleaned ferrous base metal with an aqueous solution containing dissolved therein an appreciably water soluble inorganic salt selected from the group consisting of inorganic nitrate and nitrite salts and an appreciably water soluble alkaline material compatible with said salt, the relative amounts of said salt and said material being from about 0.35 to 0.85 mole of said salt to from 0.80 to 1.7 moles of said material and the total amount of said salt and said material in said solution, the time and temperature being sufficient to oxidize the surface of said metal, pickling said metal with an acid solution, depositing elemental nickel on said pickled metal from a nickel solution, applying a porcelain composition to the nickel surface on said metal and fusing the same.

2. The method according to claim 1 which comprises, prior to treating said base metal in said aqueous solution of said salt and alkaline material to oxidize the same, treating said base metal with an aqueous solution containing from about 1 to 20% by weight of a mixture of chromic acid and sulfuric acid to provide the surface of said base metal with a smooth, uniform and reactive finish.

3. The method according to claim 1 which comprises, prior to treating said base metal in said aqueous solution of said salt and alkaline material to oxidize the same, treating said base metal with an aqueous solution containing from about 1 to 20% by weight of a mixture of chromic acid and phosphoric acid to provide the surface of said base metal with a smooth, uniform and reactive finish.

4. The method according to claim 1 which comprises, prior to treating said metal in said aqueous solution of said salt and alkaline material to oxidize the same, treating said base metal with an aqueous solution containing from about 1 to 20% by weight of a mixture of chromic acid and sulfamic acid to provide the surface of said metal with a smooth, uniform and reactive finish.

5. The method according to claim 1 which comprises, prior to treating said metal in said aqueous solution of said salt and said alkaline material to oxidize the same, treating said base metal with an aqueous solution containing from about 1 to 20% by weight of sulfamic acid to provide the surface of said metal with a smooth, uniform and reactive finish.

6. The product produced by the method of claim 1.

7. The method which comprises treating a cleaned ferrous base metal with an aqueous solution containing dissolved therein an inorganic salt selected from the group consisting of inorganic nitrate and nitrite salts and an alkaline material selected from the group consisting of sodium, potassium, rubidium and cesium hydroxides, the relative amounts of said salt and said material being from about 0.35 to 0.85 mole of said salt to from 0.80 to 1.7 moles of said material and the total weight of said nitrate salt and said alkaline material being from about 10 to 80% by weight of the solution, for a period of time and at a temperature sufficient to oxidize the surface of said metal, rinsing said oxidized metal, pickling said oxidized rinsed metal in a dilute phosphoric acid solution, rinsing said pickled metal, depositing elemental nickel on said pickled rinsed metal from a nickel solution, rinsing and drying said nickel containing metal, applying a porcelain enamel composition to the nickel surface on said metal and fusing the same.

8. The method which comprises treating a cleaned ferrous base metal with an aqueous solution containing dissolved therein an inorganic nitrate salt selected from the group consisting of ammonium, potassium, sodium, lithium, and cesium nitrates and an alkaline material selected from the group consisting of sodium, potassium, rubidium and cesium hydroxides, the relative amounts of said salt and said alkaline material being from about 0.35 to 0.85 mole of said salt to from 0.80 to 1.7 moles of said material and the total weight of said nitrate salt and said alkaline material being from about 35 to 60% by weight of the solution, for a period of from about 2 to 20 minutes at a temperature of from about 25 to 90° C. to oxidize the surface of said metal, rinsing said oxidized metal, pickling said rinsed metal in a dilute phosphoric acid solution containing from about 10 to 25% by volume of phosphoric acid at a temperature of from about 100 to 150° F., rinsing said pickled metal, depositing elemental nickel on said pickled metal from a reducible nickel salt solution, rinsing and drying said nickel containing metal, applying a porcelain frit to the nickel surface on said metal and fusing the same.

9. The method which comprises treating a cleaned low carbon steel in an aqueous solution containing dissolved therein sodium nitrate and sodium hydroxide, the relative amounts of said nitrate and said hydroxide being from about 0.35 to 0.85 mole of said nitrate to from 0.80 to 1.7 moles of said hydroxide and the total weight of said sodium nitrate and said sodium hydroxide being from about 35 to 60% by weight of the solution, for a period of from about 2 to 20 minutes at a temperature of from about 25 to 90° C. to oxidize the surface of said steel, rinsing said oxidized steel, pickling said rinsed steel in a dilute phosphoric acid solution containing from about 10 to 25% by volume of phosphoric acid at a temperature of from about 100 to 150° F., rinsing said pickled steel, depositing elemental nickel on said pickled steel from a reducible nickel salt solution, rinsing and drying said nickel containing steel, applying a porcelain enamel frit to the nickel surface on said steel and fusing the same.

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