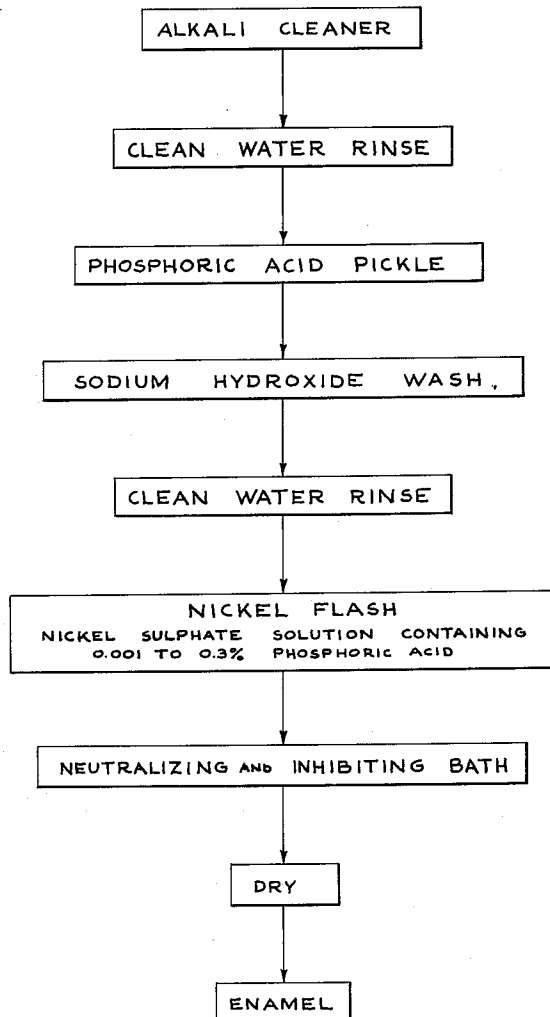


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ONE COAT ENAMEL PROCESS
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INVENTORS

EVAN M. OLIVER,
HARLAN P. TRIPP,
LYNN E. FUSSELL &
FRANK L. MICHAEL

BY

Walter E. Fule

THEIR ATTORNEY

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ONE COAT ENAMEL PROCESS

Evan M. Oliver, Harlan P. Tripp, Lynn E. Fussell, and Frank L. Michael, all of Louisville, Ky., assignors to General Electric Company, a corporation of New York

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The present invention relates to a one-coat enameling process and is more particularly concerned with an improved process for providing ordinary, low carbon sheet steel with a finish coat of vitreous enamel applied directly thereto without the application of a ground coat of enamel.

In accordance with the usual commercial practice, the porcelain enameling of sheet steel products involves first the application and firing of a ground coat of enamel followed by the application and firing of a finish enamel coat. The principal functions of the ground coat are to provide good adherence between the enamel layer and the base metal and to prevent the finish enamel coat from becoming contaminated by fusible color-forming components of the base metal produced during firing of the finish coat. Because of the added cost of the ground coat and for various other reasons, numerous efforts have been made to eliminate the ground coat and apply the finish enamel coat directly to ordinary, low carbon sheet steel. Substantially all of the proposed processes have been completely unsuccessful or of only limited commercial success. Some were too costly as compared with the two coat system. In others, involving various cleaning, pickling or coating treatments of the steel, the bond between the metal surface and the enamel coat was poor or there were defects in the enamel such as the development of pits or black specks in the fired enamel surface.

In the light of the work leading to the present invention, it now appears that prior efforts along these lines have not been completely satisfactory from a commercial standpoint because many of the attempts to solve the one-coat enamel problem have been based on the assumption that the key to the solution would be found in the provision of a particular treatment of the sheet steel regardless of the manner in which the steel had been previously processed or was to be processed for the application of the finish enamel coat. In other words, it was assumed that a particular pickle or etching treatment or the application of a particular coating to the steel would solve both the bonding and enamel appearance problems. The present invention is based primarily on the discovery that for the satisfactory preparation of the steel for application of a one-coat enamel, it is necessary to subject the steel to a series of treatments which, to a substantial extent, are interdependent. More specifically, it has been discovered that a completely satisfactory one-coat enameled product can be obtained by subjecting an alkali-cleaned low carbon steel surface to a sequence of operations including a controlled etching in a phosphoric acid bath having a controlled iron ion content, the immediate rinsing of the pickled or etched product in a mild alkaline solution for the removal of all of the phosphate coating and phosphoric acid residue, the application of a galvanically deposited nickel layer of controlled thickness employing a nickel flash bath containing a controlled phosphate ion content, followed by a final neutralizer or inhibiting wash using a weak solution of an

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inhibitor such as tetrasodium pyrophosphate. It has also been found that in subjecting the steel surface to the pickle, neutralizing, plating and inhibitor treatments, best results are obtained if at least this portion of the entire process is carried out in such a way that the steel surface is maintained continuously wet as the steel passes from one treating step to another. Following the inhibitor and neutralizing step subsequent to the nickel flash treatment, the ware is dried, coated with a finish enamel coat and fired.

For a better understanding of the invention reference may also be had to the flow sheet drawing accompanying and forming part of this specification.

In the preferred practice of the present invention there is employed a steel sheet or strip of low-carbon steel or enameling iron stock having a low-carbon content in the neighborhood of 0.10 percent or at least not exceeding about 0.25 percent carbon which has been shaped into the form of the desired finished article. The article is first subjected to the action of an alkali cleaning bath, either spray or immersion, for the purpose of removing the dirt, grease, oil or drawing compounds present on the surface of such formed products. A suitable alkali cleaning bath is one containing from about $\frac{1}{16}$ to 6 ounces per gallon of sodium phosphate and operating at a temperature from 170 to 210 degrees. Suitable wetting agents can be used in conjunction with the sodium phosphate to improve efficiency. Following removal of the article from the alkali cleaning bath, it is rinsed at least once with clean water to remove all traces of the alkali cleaner. Thereafter and without drying of the cleaned surface, the article is pickled with a spray or immersion solution of phosphoric acid held at a temperature of from about 130 to 180 degrees F. and containing from about 10 to 30 percent by weight of phosphoric acid. The composition of this pickling bath is regulated so that it will contain from 0.01 to 1.0 percent ferrous ions and 0.05 to 3.0 percent ferric ions. The article is subjected to the action of this pickling solution until the total amount of iron removed from the steel surface is between 1.5 and 3.0 grams per square foot of exposed surface. The rate of etching is controlled by the acid concentration and by the ferrous and ferric iron content of the solution and by temperature. The action of the phosphoric acid on the iron produces ferrous ions. These become oxidized by the action of the spray and deliberate mixing of air with the pickling solution to form ferric ions. The surface layer of the iron article is then removed largely by the ferric ions which in turn produces additional ferrous ions. Thus by controlling this cycle of reactions and particularly the ferric ion concentration, the rate of removal of iron from the surface can also be controlled and it has been found that best results are obtained by operating within the limits described hereinbefore. While the ferric ion concentration is obtained by oxidation, the ferrous ion concentration is kept within limits by circulation of the pickling solution through an ion exchange unit designed to remove the excess ferrous ions. The ion exchange equipment containing a cation exchange resin removes ferrous ions from the solution thereby limiting the amount of ferrous iron available for conversion to ferric iron. The use of a suitable commercial cation resin in the ion exchanger substitutes hydrogen ions for the ferrous ions and returns to the tank a pickling solution which is practically free from ferrous ions.

Following the etching treatment in the phosphoric acid bath, the article is rinsed with clean water to remove excess acid carried from the bath and the surfaces thereof are then thoroughly flushed with an alkaline solution containing up to about 1 percent by weight of soda ash or caustic soda to remove any phosphate coating de-

veloped in the pickling stage. Further rinsing with clean water removes residual alkali from the ware in order to prevent alkali carry-over into the next step of the process.

The article while still wet is then provided with a nickel flash coating, the weight of this nickel flash coating ranging between 0.02 to 0.35 gram per square foot of exposed surface. This is accomplished by immersing the article in or spraying onto the surface of the article, a solution containing from about 1 to 4 ounces per gallon nickel sulphate and adjusted, by the addition of sulphuric acid and phosphoric acid, to have a pH from 2.0 to 3.5 and a phosphate (PO_4) ion content of from 0.001 to 0.03 percent by weight. This bath is preferably operated at a temperature within the range from 130 to 180 degrees F. and the ferrous iron content is maintained between 0.01 and 0.50 percent by weight.

It has been found that regulation of the nickel solution helps control fishscaling and black-specking of the enamel coat. One factor affecting these two defects has been found to be the phosphate content in the nickel solution, with the lower effective limit being about 0.001 percent PO_4 in the nickel solution. While the upper limit varies somewhat for various steels, the preferred upper limit which is satisfactory for most low carbon is about 0.005 percent by weight of PO_4 in solution.

The upper limit of phosphate content in the nickel solution is determined by the occurrence of black-specks in the enameled surface. It has been found that when the nickel solution is aerated with an air pipe and virtually all the precipitate has been removed, some black-specking will occur at .005 percent PO_4 , which is the operating top limit in production. Thus, it is believed that a certain amount of precipitate then must be present in the nickel solution to maintain the necessary balance of phosphates. As an explanation of this, it is theorized that a thin coating of phosphate from the phosphate in the nickel solution prevents hydrogen from entering the steel during the firing operation—perhaps by converting nascent hydrogen newly released by chemical reaction to molecular hydrogen, which does not dissolve in steel.

After the nickel flash, the ware is rinsed with clean water to remove the nickel solution and is then rinsed with a solution containing a suitable neutralizer such as about 0.03 percent to 0.50 percent by weight of tetrasodium pyrophosphate. This is followed by another clean water rinse after which the ware is dried and is ready for an application of enamel to its surface. This operation is carried out with a typical porcelain enamel frit such as one obtained by firing out the following composition at 1480° F.

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

Other titania containing enamels can be used in place of the one specified.

The following is a specific example of one manner in which the present invention can be carried into effect.

Example

Articles formed from low carbon sheet steel were run through a spray cleaning machine in which the parts were washed with a hot solution of sodium phosphate to remove the oils and drawing compounds adhering to the parts. The parts were then thoroughly rinsed with clean water to remove any loose matter and also to remove all traces of the alkaline cleaner so that subsequent phosphoric acid treatment of the parts would not gel residue

cleaner on the surfaces since the presence of the gelled cleaner, even in traces, will cause defects in the final enamel finish applied to the ware.

The parts were then pickled in a solution containing 20 percent phosphoric acid by weight and having a controlled ferric and ferrous iron content. The ferric ion content was maintained at about 0.4 percent by weight. Using this pickling bath maintained within the temperature range of from 130 degrees to 140 degrees F., the parts were treated until the total iron removal was within the range from 1.5 to 2.0 grams per square foot of exposed surface. The time required for this treatment was about 1¼ minutes. In this pickling bath, the control of the ferric phosphate concentration was accomplished by the use of a cation exchange unit and by adding air to the phosphoric acid solution. The cation exchange equipment through which the solution was continuously circulated removed ferrous ions from the solution thereby limiting the amount of ferrous ions available for conversion to ferric ions during the pickling operation. The ferrous ion concentration was held at about 0.15 percent by weight by this means. Conversion of the ferrous ions in the solution to the ferric ions was accomplished by continuously circulating a portion of the pickling solution through a spray nozzle positioned above the bath so that oxygen from the air become dissolved in the solution for oxidation of the ferrous ions to ferric ions. In other words the ferrous and ferric ion contents of the solution were held within limits such that neither ferrous phosphate nor ferric phosphate exceeded its respective solubility limit for the purpose of obtaining the desired etch or pickling of the steel and also to prevent deposition of either of the phosphates in the ion exchange unit.

Following the pickle, the parts were rinsed with clean water to flush off all acid carried from the bath. They were then flushed with a mildly alkaline solution containing about 1 percent by weight of sodium hydroxide to remove any traces of a phosphate coating developed in the pickling stage. A further rinse with clean water was employed to remove residual alkali from the ware in order to prevent contamination of the subsequent treating solution.

While still wet the parts were transferred to the next stage in which they were given a nickel flash coating whereby a nickel deposit of about .05 gram per square foot of exposed surface was applied. This was accomplished by spraying the parts with a solution containing from 2 to 3 ounces per gallon of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ at about 180° F. for 3 minutes. The solution contained a combination of sulphuric acid and phosphoric acid to provide a pH of 2.5. The amount of phosphoric acid used for this purpose was such that the PO_4 content of the solution was about .004 percent by weight. The ferrous ion content of the bath was maintained below about 0.3 percent.

It is believed that the presence of the phosphate ions in the nickel flash bath is essential to prevent fishscale in the final enamel coating if the finish enamel coating is one having a high fusion point as distinguished from low fusion point enamels. However, the phosphate content should be maintained below the upper limit of about 0.03 percent by weight since it has been found that a substantial increase of the phosphate ion content over this value may result in black specks in the final enamel coat. During the nickel flash operation there is also an etching action on the surface of the parts with the result that from 0.15 to 0.4 gram per square foot of iron is removed, in addition to iron replaced by nickel.

After the nickel flash, the parts were rinsed in clean water to remove the nickel solution residue and were then sprayed with a neutralizer solution containing 0.5 percent by weight of tetrasodium pyrophosphate to neutralize the surface. All traces of the neutralizing solution are thereafter removed by a clear water rinse before

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the parts are allowed to dry in preparation for the application of a one-coat enamel layer.

An important aspect of the present process resides in the fact that the parts are continuously processed through the cleaning, pickling, nickel flashing, and inhibitor steps in a wet condition as it has been found that any separation of these steps which permits drying of the parts between the various operations markedly affects the quality of the final enamel coat probably due to the fact that undesirable surface reactions can take place when the parts are dried between the steps. In some cases the drying of the parts between steps may so change the condition of the surface of the parts as to change the action of the succeeding treatments.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The method of treating a steel surface for application of a single finish coat of enamel which comprises the steps of cleaning said surface by means of an alkali cleaning solution, pickling the cleaned surface by means of a hot solution containing from 10 to 30 percent phosphoric acid and having a controlled ferrous ion content of from 0.01 to 1.0 percent by weight and a ferric ion content of from 0.05 to 3.0, to remove from the surface from 1.5 to 3.0 grams of iron per square foot of exposed surface, washing the pickled surface with a weak alkaline solution to remove therefrom phosphate coating formed during pickling of said surface, subjecting said washed surface to the action of a hot nickel sulphate solution containing from 1 to 4.0 ounces per gallon $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.001 to 0.03 percent by weight of phosphate ions until there is obtained on said surface a nickel flash coating between 0.02 and 0.35 gram per square foot of surface, rinsing the nickel coated surface with an alkaline neutralizing or inhibiting solution and then with clear water before drying said surface in preparation for the application of a one-coat porcelain enamel.

2. The method of producing a one-coat porcelain-

enameled steel article which consists essentially of the steps of cleaning the surface of said article in an aqueous alkali cleaning bath, water rinsing the article, immediately contacting the rinsed article with a pickling bath maintained at a temperature of from 130 to 180° F. and consisting essentially of an aqueous solution of phosphoric acid containing from about 10 to 30 percent phosphoric acid, a ferric ion content of 0.05 to 3.0 percent and a ferrous ion content of from 0.01 to 1.0 percent by weight to remove from 1.5 to 3 grams iron per square foot of surface, rinsing the pickled article in a weak alkaline solution to remove any phosphate coating therefrom, without drying the article applying a nickel flash coating of from 0.02 to 0.35 gram per square foot employing a nickel flash bath held at a temperature of 130 to 180° F. and containing about 1 to 4 ounces of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ per gallon and a small amount of phosphoric acid sufficient to provide from 0.001 to 0.03 percent by weight of phosphate ions in said bath, rinsing the nickel coated article in a weak aqueous solution of an alkali inhibiting material selected from the group consisting of tetrasodium pyrophosphate, sodium phosphate and sodium cyanide, drying said article, and thereafter applying a porcelain enamel slip and firing the slip to produce a one-coat enamel finish on said article.

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