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PROCESS OF PREPARING A FERROUS SURFACE FOR ONE-FIRE PORCELAIN ENAMELING

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This invention relates to the art of porcelain enameling, and in particular to the coating of iron and steel articles with a finish layer of porcelain enamel applied directly thereto without the prior firing of a ground or sub-coat as required in previous enameling practice.

In the past there has been no commercially successful technique for fusing a single finish coat of enameling frit directly to an ordinary ferrous metal surface to form a smooth, uniform enamel finish. Heretofore it has been necessary to fuse a so-called ground coat to the metal, followed by application and then fusion of a finish layer of glass over the ground coat, particularly in order to obtain the freedom from blemishes and the good adhesion which is necessary in the production of porcelain enameled sheets and stampings suitable for the commercial trade.

Although numerous attempts have been made to provide a so-called "one-fire" process, that is, a method of applying a single finish coat of enamel directly to a conventional iron or steel enameling stock, none of these attempts have been successful, inasmuch as bubbles, pits or specks develop almost inevitably in the surface of the single coat of enamel, marring its uniformity and texture, or the adhesion of the enamel to the metal is imperfect and the enamel is therefore more prone to chipping. Certain relatively expensive enameling metals have been developed which do take one-fire enamel finishes, but the cost of these has prevented their extensive use.

Thus, the standard practice in the industry has been to first apply a ground coat, usually dark in color, before applying a finish coat of enamel, either white or tinted, to the metal surface. The ground coat has good adhesion to the metal and provides an enamel surface to which the gloss top coat readily bonds with consistently good results. However, the double handling and double firing procedure obviously increases production costs to an undesirably high degree.

Enamelware is usually fabricated from low carbon steel sheets produced in rolling mills or from so-called enameling iron. At present the usual procedure is to prepare the metal surface for enameling by pickling it in acid to remove rust, weld scale and dirt and to activate or condition it for subsequent deposition of a ground coat of enamel. The acid employed in this pickling operation is usually hot sulfuric or cold hydrochloric acid.

The enameling surface thus prepared is then dipped or sprayed with a first coat of enameling slip, after which the slip is dried and fired, whereby the ground coat frit in the slip fuses and bonds to the metal. A finish coat of enamel is then applied to complete the operation. The pickling steps have as their objective the removal of metallic scale, oxide or rust as well as dirt, oil or other foreign matter. In addition, the pickling operation etches the surface to increase the adherence and the uniformity of the enamel coating thereon. It is well known that the bond between the enamel and the base is largely dependent on the proper conditioning, i.e., "roughening" or "activation," of the metal surface. In general, the surface must be sufficiently rough to promote good adherence, but not so rough that the enamel cannot form a smooth outer surface upon firing.

We have discovered a novel process of preparing the

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surface of irons and steels suitable for conventional two coat enameling, by the practice of which it is possible to fuse a single finish coat of enamel directly to the metal to furnish a highly bonded, chip-resistant porcelain enamel finish which is devoid of pits or specks, whereby a commercially acceptable finished product can be produced at low cost. Otherwise expressed, in accordance with the present invention, a unique etching and pickling process so prepares and conditions the ferrous metal surface that a single coating of a conventional porcelain enamel composition may be applied and fused onto the metal surface as a finish coat, no preliminary ground or sub-coat being required to obtain proper bonding of the finish coat to the metal.

More specifically, this one-fire process of enameling iron comprises a pickling and etching technique which includes closely controlled treatments of the enameling stock in solutions of ferric sulfate and sulfuric acid, whereby scale and rust are effectively removed and a sharp, fine grained, uniformly etched metal surface is obtained which provides excellent bonding reception to a finish coat of enamel.

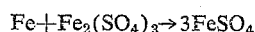
Ferric sulfate exerts an extremely rapid etching action on enameling iron and thereby presents difficulties in maintaining uniform process conditions for the large scale production of enameled articles. As compared, for example, to sulfuric acid, ferric sulfate may quickly cause severe pitting and for that reason, its use does not in general produce a surface which is suitable for subsequent enameling. Moreover, although the ability of ferric sulfate to attack iron has been known, the vigor of its attack and the difficulties of controlling the reaction rate, plus the fact that it does not effectively remove rust or scale, no doubt explains the reason that it has never found usage in the porcelain enameling field.

The present invention is predicated on the discovery and determination that enameling iron initially etched with ferric sulfate under controlled conditions possesses superior surface receptivity for fused porcelain enamel frit, and that the application and fusion of a ground coat as heretofore required can be eliminated without sacrifice in quality of the bond of the glass to the metal and without sacrifice of the surface qualities of smoothness, uniformity and freedom from blemishes. For this purpose and result it is requisite that the pH of the ferric sulfate solution be carefully controlled during the etching treatment. The invention is further predicated on the discovery that the attack of ferric sulfate solution on the enameling stock may be controlled by oxidizing ferrous sulfate to ferric sulfate as the former compound forms during etching, to replenish the diminishing supply of the latter, and that by controlling the concentration of ferrous sulfate so that it is maintained within certain limits, a reliable and effective one-fire process of porcelain enameling is achieved.

The present process may best be explained by reference to the various chemical reactions which take place when a ferrous metal is treated with ferric sulfate.

Ferric sulfate attacks iron to produce ferrous sulfate by chemical combination of iron atoms with sulfate groups.

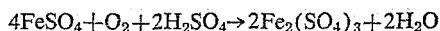
Thus,



It is apparent that the treatment of iron with a fixed amount of the ferric compound of itself brings about a gradual and continuing conversion of that compound to its ferrous state.

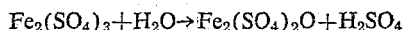
Ferrous sulfate, in contrast to ferric sulfate, does not etch iron. Moreover, its concentration in solution with the latter must be kept below a certain maximum for suitable metal surface conditioning to occur. According to the present invention, the concentration of ferrous sulfate in the treating solution is stabilized during proc-

essing by oxidizing ferrous ions to reconstitute ferric sulfate and thereby constantly maintain the concentration of that compound within proper limits. Thus,



In the preferred embodiment of the invention, this is accomplished by using hydrogen peroxide as the oxidizing agent, but the use of other oxidizers is contemplated.

Ferric sulfate tends to precipitate out of the solution as the basic ferric sulfate. The precipitation apparently results from hydrolysis at the preferred operating temperature at which the solution is maintained during processing:



We have found that such precipitation can be controlled without adversely affecting the pickling process by maintaining the acidity of the solution at proper pH through the addition of sulfuric acid in admeasured amount.

The removal of iron by the action of ferric sulfate, producing ferrous sulfate, and the oxidation of the resulting ferrous iron to ferric iron, brings about a gradual increase in the ferric sulfate content of the solution. Regulation of concentration of the ferric salt within specified limits is effected simply by adding water to the bath.

Thus, the present invention at once provides the desired process whereby iron may be conditioned to receive a one-fire enamel finish, and a process for continuously regulating the principal treating bath during the surface conditioning operation.

We have further discovered that the process best prepares the iron surface for a subsequent one-fire enamel finish when certain further conditions are established and maintained. In particular, we have found that the ferric sulfate solution should preferably be maintained at a ferric sulfate concentration which is between approximately 3.0 and 6.0 weight percent. The weight percent of ferrous sulfate in the processing solution should preferably be no greater than approximately 1.5. Furthermore, the solution should be maintained at a pH in the range approximately 1.1 to 1.4 for best results.

To facilitate understanding of the invention reference may also be had to the flow sheet accompanying this specification.

Following is an example of the preparation of iron in accordance with a preferred embodiment of this invention.

Example 1

(1) The ferrous surface to be porcelain enameled is first subjected to an alkali cleaning step to remove oils, dirt and grease from the metal surface, as is conventional. The cleaner, for example, may comprise an aqueous solution of alkali resinates or sodium orthosilicate. The iron is immersed in a tank containing approximately five ounces of the cleaner per gallon of water for a period up to about ten minutes at boiling temperature.

(2) The ware is rinsed with fresh water at a temperature of about 110°.

(3) The ware is immersed for a second period of about ten minutes in an alkali cleaning solution of approximately the same composition as in step 1 and rinsed as in step 2. This second cleaning step is undertaken as a precaution to insure that the metal surfaces are properly cleansed.

(4) The metal is then subjected to a final cold or tap water rinse during which the heat imparted to the metal during the cleaning step is dissipated.

(5) The metal is treated with a solution containing between approximately 3.0 and 6.0 weight percent of ferric sulfate, at a temperature of about 160° F. for a period of about two minutes. The solution should have a pH in the range from approximately 1.1 to 1.4 maintained as necessary by the addition of sulfuric acid to the solution. The concentration of ferrous sulfate in the bath should not exceed about 1.5 weight percent.

During this treatment, the ferrous surface is rapidly given a fine grain, uniform etch, preparatory to an acid etch as will be described.

The speed of the ferric sulfate etch treatment permits the use of automatic processing equipment, whereby the entire process is conducted on a continuous immersion or spray basis rather than in batch quantities.

The sulfate solution may be sprayed on the surface if desired, provided treatment conditions are adjusted appropriately.

(6) Following the ferric sulfate treatment, the metal is rinsed in cold running water to cleanse it of that solution.

(7) The metal is then given an acid etch with a solution which preferably comprises about seven percent by weight sulfuric acid at a temperature of about 160° F. for a period of about two to four minutes. The bath should preferably be discarded after it has reached a ferrous sulfate concentration of nine percent. It should be noted that the acid etch may precede, as well as follow, the ferric sulfate etch.

While sulfuric acid is preferred, other inorganic acids, as for example hydrochloric or phosphoric acid, may be used under suitably adjusted conditions. Strong organic acids can also be used. The use of acid etch baths by themselves is well known in the art; this invention, however, depends not on the acid etch alone, but on the combination of an acid etch with a ferric sulfate etch.

(8) The etched metal is then given a cold water wash.

(9) After the etch treatments and rinse, the enameling surface is given a nickel dip by immersion in a bath preferably containing about two ounces of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ per gallon of water. The bath should be maintained at a temperature of about 165° F. and its pH should be about 3.2. The metal is immersed in this bath for about five minutes, during which time nickel is displaced from combination with the sulfate as a light, thin flashing of nickel on the enameling surface, ferrous sulfate forming in this step of the process. The deposit should total about 0.1 gram of nickel per square foot of metal surface. The concentration of ferrous sulfate in the nickel dip solution should be preferably regulated so as not to become greater than .8 percent. The use of a light nickel flash is generally conventional for controlling the rate of oxidation of the metal surface during the firing of the enamel coating which is necessary for bond development. We have found, however, that a nickel flashing considerably heavier than is conventionally employed, one totaling about 0.1 gram of nickel per square foot of metal surface, achieves the best bond.

(10) The metal is rinsed in cold water.

(11) The metal is treated with a neutralizing solution containing for example approximately .16 ounce of soda ash and .05 ounce of Borax per gallon, and having an Na_2O concentration of about .05 weight percent. This bath should be at a temperature of 165°. The metal is immersed in this solution for between two and four minutes, whereby the various reagents which may be present in small amounts on the metal surface are neutralized.

(12) The metal is dried at about 250° F. The surface to be enameled is now clean and conditioned to be coated with a single finish coat of enamel, which may be of conventional finish coat composition and which may be applied in accordance with conventional finish coating techniques. The coating so obtained is uniform, contains no bubbles or pits, and displays good adherence to the metal surface.

It will be appreciated that not all of the steps of the foregoing example are critical or necessary elements of the invention and that latitude of treatment in the conventional processing steps is contemplated.

The specific physical or physico-chemical condition of the metal surface as achieved by this invention is not fully understood, but in any event, following the ferric sulfate and acid etching steps, the metal surface is satis-

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factorily etched for a single fire enamel finish. The ferric sulfate acts very quickly on the surface as compared with the rate of attack of the subsequent acid etch; for example, the ferric sulfate etch removes 1-2 grams of metal per square foot of etch surface, that is, 2-4 grams of metal per square foot of ware, while the acid treatment removes about one half to one gram per square foot of ware. This differential in rates may somehow account for the surface condition which the combined sulfate-acid etches provide, but the invention is not to be limited by any theory in this regard.

An important aspect of the present invention resides in the continuous regulation of the sulfate etchant so that the ferric sulfate concentration remains within the preferred limits of about 3.0 and 6.0 weight percent and so that the ferrous sulfate concentration does not exceed about 1.5 weight percent. In accordance with the preferred embodiment of the invention, these concentration limits are maintained by oxidizing ferrous sulfate which forms, as described above, as a reaction product of the attack of ferric sulfate on iron, to the ferric state. During the processing of ware, the concentration of ferric sulfate in the starting solution is diminished by its conversion into the ferrous compound, the concentration of which increases, so that the concentration of the former compound tends to drop below the preferred minimum, while the concentration of the latter tends to exceed the preferred limit. By oxidizing the ferrous salt to the ferric salt, these trends are offset so that both concentrations remain within their preferred ranges.

We prefer to oxidize the ferrous ions to the ferric state by using hydrogen peroxide as the oxidizing agent; apparently ionic oxygen is more effective for this purpose than is molecular oxygen such as is present in air or cylinder oxygen. However, oxidation may be effected by other means which do not contaminate the solution. If the concentration of ferric sulfate in the bath becomes too great, it may be diminished simply by adding water. By continuous control of the ferric sulfate solution in this manner, the process is adapted for the processing of ware on a continuous, as opposed to batch, basis. The ferric sulfate solution is controlled by standard titration and control techniques which are well known and need not be described here.

During the processing of ware in the ferric sulfate bath, the pH of the bath increases (i.e. the bath becomes less acid) with the formation of ferrous sulfate. To prevent the possible precipitation of ferric sulfate by hydrolysis as the basic sulfate, we prefer to maintain the pH of the solution in the approximate range 1.1 to 1.4. This may be simply effected, for example, by adding sulfuric acid at a rate such that the pH is continuously maintained within the desired limits.

Process conditions may be controlled by intermittent adjustment or continuous regulation, the general principles of control being the same in each instance.

While the present invention is primarily directed to a process for etching ferrous surfaces prior to the direct application of a finish coat of enamel thereon, the process is not limited to such use alone. The quality of surface preparation is such that a standard two coat enamel finish may be applied to the surface with improved results. Bonding of the enamel is obtained over a broader firing range and an excellent surface texture is provided. In each instance the invention provides a metal surface etching process which permits the successful enameling of a wide range of cold rolled and enameling iron stocks, which is suitable for continuous as well as batch processing, and which does not involve the utilization of expensive chemicals or process equipment.

Having described our invention, we claim:

1. A process for conditioning a ferrous surface for the subsequent application thereon of a one-fire porce-

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lain enamel finish, said process comprising the steps of subjecting the surface to an initial cleaning step which is effective to remove oil and dirt from it, rinsing the surface, subjecting the surface to a solution containing between about 3.0 and 6.0 weight percent of ferric sulfate at a pH between about 1.1 and 1.4 and having a ferrous sulfate concentration which is less than about 1.5 weight percent, rinsing the surface, subjecting the surface to a strong acid etchant, rinsing the surface, subjecting the surface to a solution containing nickel sulfate and thereby causing the surface to be coated with a thin nickel flashing, and rinsing and drying the surface.

2. A process for conditioning a ferrous surface for the subsequent application thereon of a one-fire porcelain enamel finish, said process comprising the steps of subjecting said surface to an initial cleaning step which is effective to remove oil and dirt from it, rinsing the surface, subjecting the surface to a solution containing between about 3.0 and 6.0 weight percent of ferric sulfate at a pH between about 1.1 and 1.4 and having a ferrous sulfate concentration which is less than about 1.5 weight percent, rinsing the surface, subjecting the surface to a solution containing about seven percent by weight of sulfuric acid, rinsing the surface, subjecting the surface to a solution containing nickel sulfate and thereby causing the surface to be coated with a thin nickel flashing, and rinsing and drying the surface.

3. The process of claim 2 wherein the surface is subjected to the ferric sulfate solution at a temperature of about 160° F. for a period of about two minutes.

4. The process of claim 2 wherein the surface is subjected to the ferric sulfate solution for a period of about two minutes at a temperature of about 160° F. and wherein the surface is subjected to the sulfuric acid solution at a temperature of 160° F. for a period of about two to four minutes.

5. The process of claim 4 wherein the sulfuric acid solution has a concentration of ferrous sulfate which is less than about nine weight percent.

6. The process of claim 2 wherein the surface is caused to be coated with the nickel flashing by treating the surface with a solution containing about two ounces of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ per gallon of water at a temperature of about 165° F. and having a pH of about 3.2, for a period of about five minutes.

7. The process of claim 2 wherein said nickel flashing weighs about 0.1 gram per square foot of surface area.

8. A process for preparing a ferrous surface for the subsequent application thereto of a one-fire porcelain enamel finish in which said process includes the separate steps of subjecting the surface to an aqueous solution containing between about 3.0 and 6.0 weight percent ferric sulfate at a pH between about 1.1 and 1.4 and having a concentration of ferrous sulfate less than about 1.5 weight percent and subjecting the surface to a strong acid etchant.

9. The process of claim 8 wherein said solution is at a temperature of about 160° F. and wherein said surface is in contact with said solution for a period of about two minutes.

10. The process of claim 8 wherein the solution contains an amount of sulfuric acid such that its pH is between about 1.1 and 1.4.

11. The process of claim 8 wherein the strong acid etchant comprises a seven percent by weight solution of sulfuric acid.

12. The method of claim 8 wherein said solution contains between about 3.5 and 5.0 weight percent of ferric sulfate.

13. The method of claim 12 wherein said solution contains about .75 weight percent of ferrous sulfate.

14. In a continuous process for preparing ferrous metal surfaces for the subsequent application thereto of one-

fire porcelain enamel finishes which process includes the step of treating the surfaces with an aqueous solution of ferric sulfate, ferrous sulfate being formed in the solution as a reaction product of said treatment, the method which comprises, maintaining the pH of the solution between about 1.1 and 1.4 by adding sulfuric acid to the solution, regulating the concentration of ferric sulfate in the solution so that it stays between about 3.0 and 6.0 weight percent and simultaneously regulating the concentration of ferrous sulfate in the solution so that it does not exceed about 1.5 weight percent, by oxidizing the ferrous sulfate to ferric sulfate and adding water to said solution.

15. The method of claim 14 wherein the concentration of ferric sulfate is regulated so that it stays between about 3.5 and 5.0 weight percent.

16. The method of claim 14 wherein the concentration of ferrous sulfate is regulated so that it is about .75 weight percent.

17. The method of claim 14 wherein hydrogen peroxide is added to said solution to oxidize the ferrous sulfate to ferric sulfate.

18. A process for conditioning a ferrous surface for the subsequent application thereto of a one-fire porcelain enamel finish, said process comprising the sequential

steps of subjecting said surface to an initial cleaning step which is effective to remove oil and dirt from it, rinsing the surface in water, subjecting the surface to a solution containing between about 3.0 and 6.0 weight percent of ferric sulfate at a pH between about 1.1 and 1.4 and having a ferrous sulfate concentration which is less than about 1.5 weight percent at a temperature of about 160° F. for a period of about two minutes, rinsing the surface, subjecting the surface to a solution containing about seven percent by weight of sulfuric acid at a temperature of about 160° F. for a period of between about two and four minutes, rinsing the surface, subjecting the surface to a solution containing about two ounces of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ per gallon of water at a temperature of about 165° F. for a period of about five minutes to coat it with a thin nickel flashing, rinsing, neutralizing and drying the surface.

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