Oct. 2, 1951 A. E. CHESTER ET AL 2,569,453

VITREOUS ENAMEL BASE STOCK, VITREOUS ENAMELED ARTICLES AND METHOD

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Fig. 1.

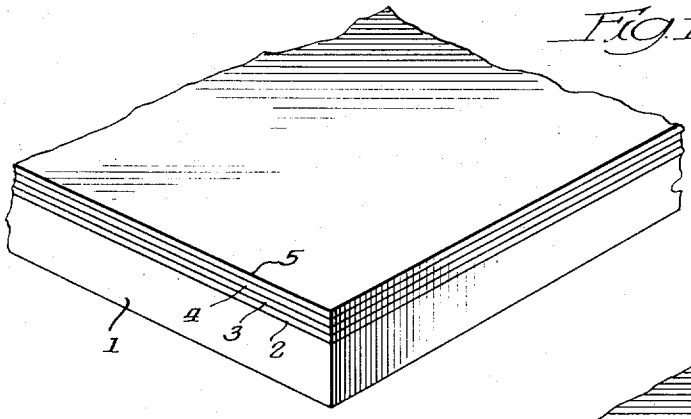


Fig. 2.

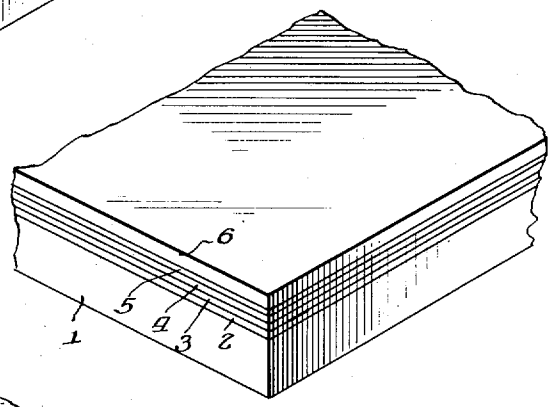


Fig. 3.

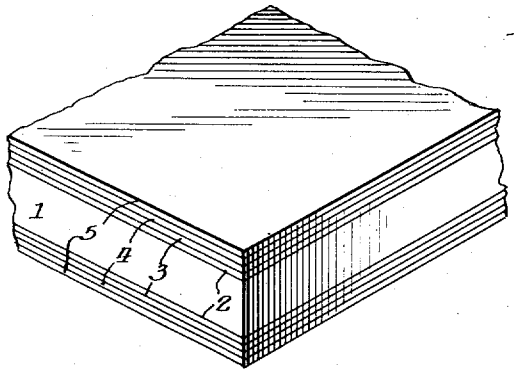
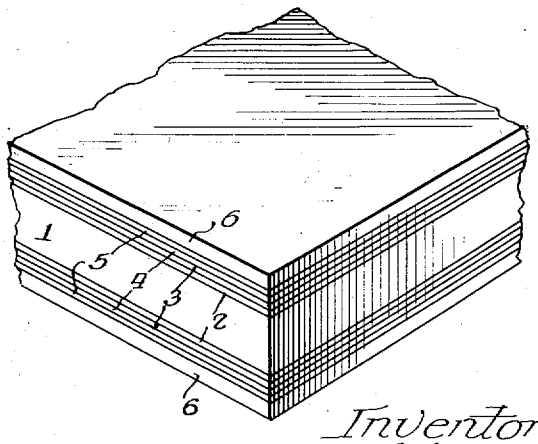


Fig. 4



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VITREOUS ENAMEL BASE STOCK, VITREOUS ENAMELED ARTICLES AND METHOD

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12 Claims. (Cl. 148—6.17)

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This invention relates to vitreous enameling, more particularly to a new and improved base stock for vitreous enamels, and to a new and improved method of controlling the adherence of vitreous enamels to ferrous metals.

It has long been recognized in the art of vitreous enameling that it would be desirable to apply a single coat of vitreous enamel to a ferrous metal sheet and thereby eliminate the necessity for a "ground" or "grip" coat of vitreous enamel. It has also been recognized in the art that it would be desirable to provide a ferrous metal base sheet to which low firing and high firing enamels would adhere and which would also have nonwarping properties and other desirable characteristics. Despite this recognition, the problem of providing a ferrous metal base sheet of the character described has not heretofore been solved in a satisfactory manner. Even the special low carbon enamel irons which have been proven to be the best from the standpoint of less warping with high firing titanium oxide vitreous enamels must have a ground coat of a vitreous enamel prior to the finish coat of vitreous enamel in order to secure proper adherence and to avoid such defects as black specking.

One of the objects of the present invention is to provide a new and improved ferrous metal base sheet to which a finish coat of vitreous enamel, either high firing or low firing, may be applied directly without first applying a ground coat.

A further object of the invention is to provide a new and improved method of controlling the adherence of vitreous enamels to ferrous metal base stocks.

A still further object of the invention is to produce a satisfactory vitreous enamelled article from various types of vitreous enamels in white and pastel colors with but one coat of enamel. Other objects will appear hereinafter.

In accomplishing these objects in accordance with this invention it has been found that a new and improved ferrous metal base sheet for vitreous enamels may be prepared by a process involving (1) surface etching the ferrous metal base stock, preferably with a fine grained etch, in a sulfuric acid bath which preferably also contains an oxidizing agent to accelerate the pickling action and an inhibitor to prevent the formation of iron compounds; (2) applying to the etched surface of said base stock, preferably after rinsing but before drying, a bath containing P_2O_5 in chemically combined form and a reducing sulfur compound capable of liberating free sulfur;

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(3) applying to the resultant surface of said base stock, preferably after rinsing or drying, a coating of antimony; and (4) applying to the antimony coating, preferably after rinsing with water or drying, a coating of nickel.

In order to accomplish the purpose of the invention and to provide a ferrous metal base stock which can be employed for a one-coat vitreous enamel of either a high firing or low firing type, it is important to use a ferrous metal, such as ingot iron or other ferrous metal, wherein the maximum carbon content does not exceed 0.05% carbon and which is essentially free from elements other than iron except for small quantities of manganese and possibly minute quantities of sulfur and phosphorus. The low carbon content is desirable because the probability of warpage after firing with high firing enamels, i. e., enamels fired at temperatures above about 1500 degrees F., increases as the carbon content exceeds 0.05%. If the probability of warpage is not too serious the manganese content may be as high as 0.30%. The sulfur and phosphorus contents should be as low as possible. The chemistry of the ferrous metal base stock, therefore, may be essentially the same as that of what is known in the trade as "enamel iron." A typical analysis as given in "Metals Handbook of American Society for Metals," 1948 edition, page 357, is: .03 carbon, .05 manganese, .010 phosphorus, .025 sulphur, the remainder being iron.

Especially good results have been obtained in the practice of the present invention with ferrous metal base sheets consisting essentially of iron containing .02 to .03 carbon and .04 to .05 manganese, and with ferrous metal base sheets containing .02 to .04 carbon and .12 to .15 manganese. The gauge of the sheets may vary over a wide range as, for example, from 4 to 31 gauge, depending upon the use which is to be made of the finished vitreous enamelled article.

In the accompanying drawings

Figure 1 represents in perspective a sheet of ferrous metal base stock which has been subjected on one side only to the four-phase treatment outlined above;

Figure 2 illustrates the ferrous metal base stock of Figure 1 with a coating of vitreous enamel thereon; and

Figures 3 and 4 illustrate a ferrous metal base stock corresponding respectively to that shown in Figures 1 and 2 but treated on both sides.

In the practice of the invention especially good results have been obtained by etching the ferrous metal base stock in the first step with a

sulfuric acid pickling solution of about 4% to 8% by weight H_2SO_4 concentration, preferably around 6% H_2SO_4, together with auxiliary ingredients. Among the auxiliary ingredients which are desirably employed for the purpose of the invention are one or more oxidizing compounds of metals above ferrous iron in the electrochemical series. Excellent results have been obtained by adding manganese dioxide to the first pickling bath. Other compounds which may be employed are manganese nitrate, lithium nitrate, potassium nitrate and/or sodium nitrate. Ferrous sulfate is preferably added to the first pickling bath in order to condition the bath. The ferrous sulfate however, tends to build up in the bath as successive quantities of material are passed through or immersed in the bath. As the ferrous sulfate of the bath increases, however, the rate of activation of the ferrous base metal by the etching bath becomes slower and it is preferred for the purpose of this invention to maintain a ferrous sulfate concentration not greater than about 2 pounds $FeSO_4.7H_2O$ per gallon of the etching bath. The initial ferrous sulfate concentration is preferably about 17.5 grams per gallon of bath.

Sodium bisulfate is preferably employed in the first bath for its buffering action and to assist in obtaining a cleaner sheet.

It has been found that the sulfuric acid pickle alone without any auxiliary ingredients will not give the desired result due to the formation of spots or black specks after the vitreous enamel coat has been applied to the base sheet. The presence of nickel and cobalt in the first pickling bath tends to aggravate black specking and therefore should be avoided. For the same reason it is desirable that the first pickling bath be essentially free from chlorides such as would be produced, for example, by adding hydrochloric acid to the pickling bath. The black specking seems to be due in part at least to the formation of iron salts or other impurities. The black specking difficulty is overcome in the practice of the invention by adding to the first pickling or surface etching bath a salt of an alkali metal or an alkaline earth metal salt or a titanium salt. The best results have been obtained with strontium salts, as, for example, strontium carbonate. Other specific illustrations of salts that have been employed effectively are lithium carbonate (Li_2CO_3), lithium phosphate ($Li_3PO_4.\frac{1}{2}H_2O$) and titanyl sulfate ($Ti_2(SO_4)_3.8H_2O$).

The temperature and time of treatment in the first bath will vary depending upon the gauge and other physical characteristics of the ferrous metal being etched but in general the temperature of the etching bath will vary within the range of 140 degrees F. to 185 degrees F. and the time of treatment will vary within a range of 12 to 25 minutes. For a 20-gauge enamel iron sheet the optimum temperature is around 155 degrees F. to 160 degrees F. for 15 minutes in the first bath. For heavier sheets the temperature and time of treatment may be more and for lighter sheets the temperature and time of treatment may be less.

It is preferable to effect the treatment in the first surface etching bath under a foam blanket which can be obtained in a well known manner by adding a small amount of a foaming agent to the bath.

After the surface etching in the first bath it is preferable to rinse the ferrous metal sheet or other article to avoid carry-over of the bath and

to prevent formation of iron salts. The rinsing may be effected at ordinary temperatures of say 60 degrees F. to 75 degrees F. with tap water which is preferably maintained slightly acid, that is, around a pH of 3 to 3.5 by the addition of small amounts, usually 0.5% to 1% by weight, of sulfuric acid. The acid addition tends to prevent the formation of iron salts.

In what has been described as the second phase of the invention the ferrous metal sheet or other article which has been surface etched in the first phase is further treated in a bath which has an additional etching action on the sheet and provides a coating of what may be described as an oxidation promoting agent. Both sulfur and phosphorus appear to be effective for the purpose of the invention. The presence of sulfur in particular seems to be essential in order to secure the desired adherence of the subsequently applied vitreous enamel. Attempts to use other oxidizing agents such as sodium chlorate have proved to be ineffective.

Sulfur is supplied to the ferrous base metal in the second phase of the invention by adding to the etching bath employed for the treatment of the ferrous metal a sulfur compound which decomposes to liberate free sulfur. The sulfur is thereby formed in a nascent state as colloidal sulfur. Among the compounds which have been found to be effective are sodium hydrosulfite and sodium thiosulfate. Other sulfur compounds such as the polysulfides may be used. The hydrosulfites and the thiosulfates both have reducing actions in an acid bath but whether or not a reduction occurs does not appear to be important for the purpose of the invention.

By employing phosphoric acid in the second etching bath and adding a sulfur-liberating compound thereto, it is possible to produce a sheet containing both phosphorus and sulfur. Addition agents which inhibit the formation of iron salts such as those described with respect to the first phase of the invention should also preferably be employed in the second phase of the invention.

The temperature of the treatment in the second phase of the invention may vary within the range of 140 degrees F. to 185 degrees F., as in the first phase.

The time of treatment in the second phase of the invention may vary, depending upon the desired phosphate coating on the sheet, and is preferably within the range of 5 to 25 minutes.

The quantity of phosphorus on the sheet after the second phase of the invention is subject to variation but is preferably within the range of .0005 to 0.03 gram per square foot of surface, calculated as P_2O_5.

After the second phase of the invention the ferrous metal base sheet or other article may be dried directly or may be rinsed with cold water and is then ready for the third phase of the invention.

In the third phase of the invention the etched surface of the ferrous metal is sealed with a thin coating of antimony. This may be accomplished either by plating the antimony with applied electromotive force or by plating it by over-voltage out of a suitable bath. An antimony bath which is essentially antimony potassium tartrate is preferable for the purpose of the invention. A reducing agent, preferably a thiosulfate, may be employed as an optional ingredient in the antimony bath. The antimony coating in conjunction with the subsequently applied nickel coating improves the adherence of the vitreous enamel sheet even

when the second phase of the invention is omitted. The thickness of the antimony coating may vary but is preferably within the range from 5 to 50 millionths inch.

After the third phase of the invention the resultant product may be dried directly or rinsed with water and is then ready for the application of a thin plate of nickel. The nickel is preferably applied by an over-voltage from an alkaline bath of nickel salts but may be applied by electrodeposition using applied electromotive force either in the form of direct current or alternating current superimposed on direct current.

The amount of nickel applied to the surface of the ferrous metal base stock is subject to variation but is preferably within the range of 7 to 20 millionths inch thickness. After the nickel coat has been applied over the antimony coat the sheet may be dried and is then ready for vitreous enameling with either low firing or high firing types of vitreous enamels. Excellent results have been obtained in the application to this type of sheet of a single coat of a high firing titanium oxide enamel which is fired at 1480 degrees F. to 1540 degrees F.

The invention will be illustrated, but is not limited by the following examples in which the quantities are stated in parts by weight unless otherwise indicated.

Example I

Sheets of iron in the form of racks consisting of 6 sheets each of a 20-gauge thickness and 3'' x 6'' dimensions are etched in a bath composed of the following ingredients:

280 cc. sulfuric acid (concentration sufficient to give 6% H_2SO_4 by weight of bath)
35 grams ferrous sulfate ($FeSO_4.7H_2O$)
10 grams sodium bisulfate ($NaHSO_4.H_2O$)
2 grams lithium phosphate ($Li_3PO_4.\frac{1}{2}H_2O$)
1 gram manganese dioxide
0.5 gram isopropylnaphthalene sodium sulfonate (Santomerse No. 1)

made up to 2 gallons with water.

The sheets are immersed in the bath at temperatures of 155 degrees F. to 160 degrees F. for 15 minutes.

The treated sheets are withdrawn from the bath and immersed in a second bath containing 0.5% to 1% of sulfuric acid in water at a temperature of 60 degrees F. to 75 degrees F.

The metal sheets are taken from the second bath and immersed in a third bath having the following composition:

200 cc. of 72% phosphoric acid (H_3PO_4)
2 grams lithium phosphate ($Li_3PO_4.\frac{1}{2}H_2O$)
1.14 grams sodium hydrosulfite ($Na_2S_2O_4$)

made up to 2 gallons with water.

The sheets are immersed in this bath at a temperature of 155 degrees F. to 160 degrees F. for 15 minutes. They are then removed from the bath and rinsed with cold water at a temperature of 60 degrees F. to 75 degrees F.

The treated sheets are then immersed in a bath composed of the following ingredients:

76 grams tartar emetic [$K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$]
152 grams sodium thiosulfate ($Na_2S_2O_3.5H_2O$)

made up to 2 gallons with water.

The pH of this bath is held around 5.5 to 5.7 and the sheets are immersed for a period of time from ½ minute to 15 minutes.

The antimony plated sheets are rinsed with water at 60 degrees F. to 75 degrees F. and are immersed in an alkaline nickel plating bath having the following composition:

228 grams nickel chloride ($NiCl_2.6H_2O$)
15.2 grams sodium hypophosphite ($NaH_2PO_2.H_2O$)
380 grams ammonium chloride
760 grams sodium citrate ($C_6H_5O_7Na_3.2H_2O$)

made up to 2 gallons with water and to a pH of 8 to 10 with dilute ammonium hydroxide.

The nickel is plated onto the antimony coating of the ferrous metal base sheet by over-voltage at a temperature of 190 degrees F. to 200 degrees F. for periods varying from 1 minute to 15 minutes.

In preparing the foregoing bath the nickel chloride and ammonium chloride are mixed together and purified by the addition of 10 cc. of hydrogen peroxide at a temperature of 160 degrees F. The hydrogen peroxide oxidizes any iron present and the iron precipitates when the pH is raised to 8 to 10 by the addition of the ammonium hydroxide. Dilute ammonium hydroxide is employed because concentrated ammonium hydroxide will precipitate nickel. The sodium hypophosphite in this bath acts as a reducing agent and the quantity thereof may vary within the range of 0.5 gram to 15 grams per liter of bath.

The resultant ferrous metal base stock when coated with a vitreous enamel and fired yields an excellent vitreous enamel coated sheet. For example, a high firing titanium oxide enamel (Chicago vitreous enamel CV–1452) was applied to sheets prepared as above described and fired at 1520 degrees F. for 3 to 4 minutes. The resultant sheet showed excellent adherence and freedom from black specking.

Example II

The invention is carried out as described in Example I except that a phosphoric acid bath containing sodium hydrosulfite is replaced by a phosphoric acid bath containing sodium thiosulfate and having the following composition:

200 cc. of 72% phosphoric acid (H_3PO_4)
1.14 grams sodium thiosulfate ($Na_2S_2O_3.5H_2O$)
2.0 grams lithium phosphate ($Li_3PO_4.\frac{1}{2}H_2O$)

made up to 2 gallons with water.

An analysis of the sheet after various time intervals in the foregoing bath showed the following P_2O_5 content on the surface:

Time in Bath	P_2O_5 oz. per Sq. Ft. Surface	P_2O_5 Grams per Sq. Ft. Surface
5 Minutes	.0000210	.000588
10 Minutes	.0000217	.000616
15 Minutes	.0000403	.001141

Example III

The process is carried out as described in Example I except that the sodium thiosulfate is omitted in the antimony potassium tartrate bath (tartar emetic bath). Good results are obtained but not quite as good as those obtained with the sodium thiosulfate.

Example IV

The invention is carried out as described in Example I using sodium hydrosulfite instead of sodium thiosulfate in the antimony plating bath in the same proportions with substantially the same results.

Example V

The invention is carried out as described in Example I using a nickel bath of the following composition instead of the alkaline nickel bath described in Example I:

2272 grams nickel sulfate ($NiSO_4.6H_2O$)
454 grams nickel chloride ($NiCl_2$)
114 grams citric acid

made up to 2 gallons with water.

This bath is purified in a manner similar to the alkaline bath by mixing the nickel sulfate and nickel chloride with water at a temperature of 160 degrees F., bringing the pH to 6, adding hydrogen peroxide and filtering. The citric acid is added to the filtrate and the pH is brought to 2.5 by adding nickel carbonate.

Nickel is plated out of the bath onto the ferrous metal base stock at a temperature of 140 degrees F. to 160 degrees F. at 40 amperes per square foot current density. Various thicknesses of the nickel are plated by setting the rheostat at 10 amperes and varying the plating time over a period of 5 to 50 seconds.

The citric acid in this bath functions primarily as a buffer. Tartaric acid may be used instead of citric acid but is not as effective. Likewise other buffers, such as boric acid, are not as effective as citric acid.

It will be understood that variations may be made in the exact procedure and proportions described above provided they do not depart from the invention. If the baths are to be used over and over again the ingredients thereof must be replenished from time to time. For example, in the phosphoric acid bath described in Example I the sodium thiosulfate may be replenished by adding .57 gram of sodium thiosulfate for each rack of six sheets 3'' x 6''. Those skilled in the art can readily determine by simple tests what additions are necessary to replenish a given bath for treating ferrous metal base stock.

Referring to the drawings and the foregoing examples it will be seen that in Figure 1 the ferrous metal base stock comprises a sheet 1 having a surface etch shown as a layer 2 which corresponds to the first phase treatment, a phosphorus and sulfur containing coating 3 corresponding to the second phase treatment, an antimony coating 4 corresponding to the third phase treatment and a nickel coating 5 corresponding to the fourth phase treatment.

Figure 2 illustrates the ferrous metal base stock shown in Figure 1 after the application of a vitreous enamel coat 6.

In Figures 3 and 4 the coatings on the ferrous metal base stocks correspond to those in Figures 1 and 2 and are given like numerals except that the coatings are on both sides of the sheet.

It is believed that the invention provides for the first time a new and improved type of ferrous metal base stock which is satisfactory for the application of a single finish coat of either a high firing or low firing vitreous enamel without the necessity for a ground coat. The invention also provides ferrous metal base stocks characterized by improved adherence to vitreous enamels. Additionally the invention provides ferrous metal base stocks which may be enamelled directly with white or pastel shades of vitreous enamels without black streaking. The vitreous enamelled base stocks and the vitreous enamelled articles provided in accordance with the invention are also essentially free from warpage and other undesirable characteristics.

The invention makes it possible for the enameler to employ any of the commercially available vitreous enamel frits without a special knowledge as to the exact nature of the frit and without applying a ground coat to the base coat.

The invention is hereby claimed as follows:

1. In a method of preparing low carbon ferrous metals for vitreous enameling, the steps which consist essentially in acid pickling said ferrous metal in a sulfuric acid bath, depositing on the pickled surface a coating of a phosphate and elemental sulfur, sealing said deposited coating with a thin coating of antimony and sealing said coating of antimony with a thin coating of nickel.

2. A method of controlling the adherence of vitreous enamels to low carbon ferrous metals in a sulfuric acid bath which comprises essentially acid pickling said ferrous metal, depositing on the pickled surface a coating of a phosphate and elemental sulfur, sealing said deposited coating with a thin coating of antimony, sealing said coating of antimony with a thin coating of nickel and firing a vitreous enamel over said nickel coating.

3. In a method of preparing ferrous metals for vitreous enameling, the steps which comprise essentially acid pickling in a sulfuric acid bath a ferrous metal having an average carbon content not greater than about 0.05% by weight, an average manganese content not greater than 0.30% by weight, an average phosphorus content not greater than about 0.010% by weight, an average sulfur content not greater than about 0.025% by weight and the remainder being essentially iron, depositing on the pickled surface a coating of a phosphate and elemental sulfur, sealing said deposited coating with a thin coating of antimony and sealing said coating of antimony with a thin coating of nickel.

4. A method of controlling the adherence of vitreous enamels to ferrous metals which comprises essentially acid pickling in a sulfuric acid bath said ferrous metal having an average carbon content not greater than about 0.05% by weight, an average manganese content not greater than 0.30% by weight, an average phosphorus content not greater than about 0.010% by weight, an average sulfur content not greater than about 0.025% by weight and the remainder being essentially iron, depositing on the pickled surface a coating of a phosphate and elemental sulfur, sealing said deposited coating with a thin coating of antimony, sealing said coating of antimony with a thin coating of nickel and firing a vitreous enamel over said nickel coating.

5. In a method of preparing a low carbon ferrous metal for vitreous enameling, the steps which comprise essentially pickling a ferrous metal in a sulfuric acid pickling bath containing 4% to 8% by weight sulfuric acid, a quantity of an oxidizing compound of manganese effective to accelerate the rate of pickling and a quantity of an inhibitor for the formation of black specks in the enamelled product, rinsing the resultant pickled ferrous metal in a slightly acid bath, treating the pickled surface of the ferrous metal with a phosphoric acid etching bath containing an inhibitor for the formation of black specks in the enamelled product and a compound which decomposes to liberate elemental sulfur in said bath to form a ferrous metal having an etched surface with a coating of phosphate and elemental sulfur thereon, sealing said coating with a thin plated coating of

antimony and sealing said antimony coating with a thin plated coating of nickel.

6. A method of controlling the adherence of vitreous enamels to low carbon ferrous metals which consists essentially in pickling a ferrous metal in a sulfuric acid pickling bath containing 4% to 8% by weight sulfuric acid, a quantity of an oxidizing compound of manganese effective to accelerate the rate of pickling and a quantity of an inhibitor for the formation of black specks in the enamelled products rinsing the resultant pickled ferrous metal in a slightly acid bath, treating the pickled surface of the ferrous metal with a phosphoric acid etching bath containing an inhibitor for the formation of black specks in the enamelled product and a compound which decomposes to liberate elemental sulfur in said bath to form a ferrous metal having an etched surface with a coating of phosphate and elemental sulfur thereon, sealing said coating with a thin plated coating of antimony, sealing said antimony coating with a thin plated coating of nickel and firing a vitreous enamel over said nickel coating.

7. In a method of preparing a ferrous metal for vitreous enameling, the steps which comprise essentially acid pickling a ferrous metal having an average carbon content not greater than about 0.05% by weight, an average manganese content not greater than 0.30% by weight, an average phosphorus content not greater than about 0.010% by weight, an average sulfur content not greater than about 0.025% by weight and the remainder being essentially iron in a sulfuric acid bath containing 4% to 8% by weight sulfuric acid, a quantity of ferrous sulfate between 17.5 grams and two pounds per gallon of bath, a quantity of manganese dioxide, and a quantity of lithium phosphate, rinsing said pickled ferrous metal with a solution of 0.05% to 1% sulfuric acid, treating the pickled surface with a bath of dilute phosphoric acid containing lithium phosphate and a quantity of an inorganic reducing sulfur compound decomposable in the bath to deposit elemental sulfur, sealing the resultant coated surface of the ferrous metal with a thin coating of antimony in the presence of a reducing inorganic sulfur compound which decomposes to liberate elemental sulfur and sealing the antimony coating with a thin coating of nickel.

8. A method of controlling the adherence of vitreous enamels to ferrous metals which consists essentially in acid pickling a ferrous metal having an average carbon content not greater than about 0.05% by weight, an average manganese content not greater than 0.30% by weight, an average phosphorus content not greater than about 0.010% by weight, an average sulfur content not greater than about 0.025% by weight and the remainder being essentially iron in a sulfuric acid bath containing 4% to 8% by weight sulfuric acid, a quantity of ferrous sulfate between 17.5 grams and two pounds per gallon of bath, a quantity of manganese dioxide, and a quantity of lithium phosphate, rinsing said pickled ferrous metal with a solution of 0.05% to 1% sulfuric acid, treating the pickled surface with a bath of dilute phosphoric acid containing lithium phosphate and a quantity of an inorganic reducing sulfur compound decomposable in the bath to deposit elemental sulfur, sealing the resultant coated surface of the ferrous metal with a thin coating of antimony in the presence of a reducing inorganic sulfur compound which decomposes to liberate elemental sulfur, sealing the antimony coating with a thin coating of nickel and firing a vitreous enamel over said nickel coating.

9. A vitreous enamel base stock consisting essentially of a sulfuric acid pickled low carbon ferrous metal having on the pickled surface thereof a coating of phosphate and elemental sulfur, a thin coating of antimony over the phosphate and sulfur coating and a thin coating of nickel over the antimony coating.

10. A vitreous enamel base stock consisting essentially of a sulfuric acid pickled ferrous metal sheet having an average carbon content not greater than 0.05% by weight, an average manganese content not greater than 0.30% by weight, an average phosphorus content not greater than 0.010% by weight, an average sulfur content not greater than 0.025% by weight and the remainder being essentially iron, a coating of phosphate and elemental sulfur on the pickled surface of said sheet, a thin coating of antimony over said phosphate and said sulfur coating and a thin coating of nickel over said antimony coating.

11. A vitreous enamelled article obtained by firing a vitreous enamel on a low carbon ferrous metal which has been acid pickled in a sulfuric acid bath and has had a coating of phosphate and sulfur deposited on the acid pickled surface and sealed with successive coatings of antimony and nickel.

12. A vitreous enamelled article obtained by firing a vitreous enamel on a ferrous metal having an average carbon content not greater than 0.05% by weight, an average manganese content not greater than 0.30% by weight, an average phosphorus content not greater than 0.010% by weight, an average sulfur content not greater than 0.025% by weight and the remainder being essentially iron, which has been acid pickled in a sulfuric acid bath and has had a coating of phosphate and sulfur deposited on the acid pickled surface and sealed with successive coatings of antimony and nickel.

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