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VITREOUS ENAMELING PROCESSES AND PRODUCTS

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

One of the principal problems in the art of vitreous enamelling is to secure proper adherence between the vitreous enamel coating and the base stock to which the enamel is applied without the use of a "ground" or grip coat of vitreous enamel containing cobalt, manganese and usually nickel. It has been recognized that it would be desirable to employ as the enamel base stock ordinary mild carbon steels (also called "low-alloy" or "mild alloy" steels) containing the usual percentages of carbon, as found, for example, in SAE 1010 steels, SAE 1020 steels, SAE 1030 steels, cold rolled commercial quality sheets and cold rolled drawing quality sheets. (See A. I. S. I. Steel Products Manual, section 11, October 1948 issue, pages 34 and 36.) Thus, SAE 1010 steel, as defined by Metals Handbook, 1948 edition, published by the American Society for Metals, page 307, has an average carbon content between 0.08% and 0.13% by weight; SAE 1020 steel has an average carbon content between 0.18 and 0.23% by weight; SAE 1030 has an average carbon content from 0.28 to 0.34% by weight. The attempts which have been made heretofore to use such mild carbon steels as a vitreous enamel base stock have met with little success due to warpage and distortion of the object being enamelled. Warping and distortion have been accelerated, moreover, because of the necessity of applying more than one coat of enamel in order to secure adherence.

Many efforts have been made both by enamellers and steel manufacturers to overcome the handicap of using a ground coat of vitreous enamel followed by a second or even a third coat of enamel. Special steels have been specifically produced and designed for enamel purposes. The most satisfactory vitreous enamel base stocks have been specially prepared from low carbon steels (containing say, 0.01% to 0.02% by weight of carbon) which are more expensive than many of the ordinary steels.

In my copending applications Serial No. 609,759 filed August 9, 1945, now Patent No. 2,510,071, issued June 6, 1950, Serial No. 676,853 filed June 14, 1946, now abandoned, Serial No. 680,835 filed July 1, 1946, now abandoned and Serial No. 753,805 filed June 10, 1947, now abandoned the latter being a continuation as to common subject matter of my copending application Serial No. 689,524 filed August 9, 1946, now

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abandoned I have disclosed various methods of controlling the adherence of vitreous enamels to ferrous metals by processes which involve the treatment of the ferrous metal base stock in several stages with certain chemical treating agents. The exact nature of the chemical reactions that take place during these treatments is not fully known, but, in general, the methods which I have employed involve: (1) surface etching of the ferrous metal base stock in the presence of certain types of chemical agents, and (2) applying to the etched surface of said base stock, preferably after rinsing but before drying, a layer of a metal, or a compound of a metal reducible to the metal, which is reducing with respect to ferrous iron under the vitreous enamel firing conditions (and hence is below ferrous iron in the electrochemical series) and does not flash off or volatilize rapidly at vitreous enamelling temperatures.

One of the objects of the present invention is to provide improvements in the aforementioned methods which contribute to new and improved overall results.

Another object of this invention is to provide a new and improved vitreous enamel base stock.

A further object 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 enamel article in white and pastel colors with but one coat of enamel.

Another object is to provide a simple relatively inexpensive method of treating ordinary mild carbon steel to increase the adherence of vitreous enamels thereto. Other objects will appear hereinafter.

In accordance with the invention it has been found that new and improved results are obtained in processes of the character described by the employment of certain procedures and one or more addition agents as follows:

1. The addition of a substance having an electrode potential above ferrous iron in the electromotive force series to a surface etching bath in the treatment of ferrous metals followed by the application of a coating of a metal which is below ferrous iron in the electrochemical series, preferably nickel, cobalt or alloys of nickel and cobalt.

2. The employment of an intermediate treatment after the surface etching stage but before the application of the coating of a metal which is below ferrous iron in the electrochemical series thereby to establish a deposition pattern on the

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ferrous base metal surface. This intermediate treatment is preferably accomplished by the use of a bath containing dilute sulfuric acid and a small amount of a sulfate of the metal to be deposited or of a metal which is higher in the electrochemical series than the metal to be deposited. For example, if the metal to be deposited in the third stage were nickel or an alloy of cobalt and nickel, the intermediate bath might consist essentially of a dilute (.05 to .3% by weight) solution of sulfuric acid together with nickel sulfate (1 to 28 grams per liter) and/or cobalt sulfate (chemically equivalent amounts to nickel sulfate). The resultant process, therefore, is necessarily a three-stage process.

3. The maintenance of a ferrous sulfate concentration in the plating bath within predetermined limits, preferably not higher than 10 grams per liter.

4. The maintenance of higher concentrations of ferrous sulfate by employing in the plating bath a chemical which sequesters ferrous sulfate or inhibits its precipitation from solution. Citric acid is preferably employed for this purpose although formic acid and other substances capable of functioning in a similar manner may also be used.

5. The use of a metal which does not deposit on the ferrous iron but serves as a driver electromotive force to cause ion interchange between the iron and other metals. For example, in the surface etching bath where the manganese has been added as manganese dioxide, it actually exists in solution as manganese sulfate. The ferrous ion is oxidized to the ferric ion. Zinc in the form of its sulfate in this bath has a high over potential and acts as a driver electromotive force for ion interchange between the iron and the manganese. Again in the plating bath where, for example, nickel is to be plated, the zinc acts as a catalyst because it has a higher over-voltage than nickel in relation to iron. In a similar manner cadmium, aluminum and/or magnesium in the form of their soluble salts, may be employed in place of zinc. The quantities used are preferably 0.1 to 1 gram per liter of zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) or the chemically equivalent amount of the other metal salts mentioned.

6. The employment of a pH between 5 and 5.5 in the surface etching bath.

7. The employment of a pH either between 1.8 and 3.5 or between 4.5 and 5.5 in a nickel plating bath, or in a plating bath where an alloy of cobalt and nickel are plated.

8. The deposition of a nickel-cobalt alloy by over-voltage in the presence of a cathode depolarizer.

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 SAE 1010 and SAE 1020 cold reduced steel of varying gauges (18, 20, 24 and 26 gauge) are etched in a bath composed of the following ingredients:

35 grams ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)
6 grams zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)
0.8 gram manganese dioxide
9.2 grams sodium bisulfate ($\text{NaHSO}_4 \cdot \text{H}_2\text{O}$)
35 cc. commercial sulfuric acid 66° Bé.
1 gram isopropyl-naphthalene sodium sulfonate (Santomerse No. 1)
made up to 2 gallons with water.

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The steel sheets are immersed in the bath at temperatures of 130 degrees F. to 170 degrees F., preferably at 150 degrees F. to 155 degrees F.

The treatment in this first bath is preferably carried out for about 15 minutes. Although the time of treatment may vary over a wider range, it is preferably within the range of 12 to 25 minutes.

The treated sheets are withdrawn from the first bath and immersed in a second bath containing .05% to .3% by weight of sulfuric acid in water and a small amount of nickel sulfate, preferably about 1 gram to 28 grams of nickel sulfate per liter of solution. The temperature is preferably 60 degrees F. to 100 degrees F. Instead of nickel sulfate, chemically equivalent amounts of cobalt sulfate may be used.

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

170 grams nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)
40 grams nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)
17 grams boric acid (H_3BO_3)
3.8 grams citric acid
7.0 grams zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)
0.8 gram isopropyl-naphthalene sodium sulfonate (Aerosol OS)
made up to 2 gallons with water.

The pH of this bath is maintained around 1.8 to 3.5, preferably around 2.5 to 3.5. The steel sheets are immersed in this bath for periods within the range from 5 to 15 minutes. The temperature of this bath is preferably within the range of 180 degrees F. to 200 degrees F. They are then removed from the bath, rinsed, scrubbed with water and dried, and are ready to be sprayed with suitable vitreous enamel compositions, dried and fired. It is preferable to employ vitreous enamel compositions which can be fired at temperatures not higher than about 1500 degrees F.

EXAMPLE II

Steel sheets (22 gauge) were treated on a large scale as described in Example I using a Mesta pickler. The raw steel was loaded and then immersed in the successive baths. Each bath consisted of 4000 gallons of solution made up in the same relative proportions given in Example I. After the treatment in the third bath, the steel was unloaded, scrubbed, dried and stacked.

In order to compensate for losses of the chemical addition agents of the bath due to their adherence or reaction with the metal and drag-out losses, additional quantities were added by increments to the first bath at the rate of 0.8 pound to 1.74 pounds per ton of steel produced of a composition made by fusing together:

7.5 parts $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
1.0 part MnO_2
11.5 parts $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$

A 0.3% sulfuric acid solution was added to the second bath continuously together with 3.75 pounds of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ per ton of steel sheet. This second bath was allowed to run over continuously at the rate of 750 gallons per hour. Instead of the nickel sulfate, cobalt sulfate was also used.

In the third bath, additional zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) was added in increments at the rate of .44 to .51 pound per ton of steel produced. The citric acid content was maintained at about 1 gram per liter. Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) was added at the rate of .17 to .51 pound per ton

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of steel produced. Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) was added at the rate of 8.3 to 9.9 pounds per ton of steel produced. Boric acid was added at the rate of .11 pound to .4 pound per ton of steel produced. Aerosol OS was added at the rate of .033 to .042 pound per ton of steel produced.

The ferrous sulfate will tend to build up in the first and third baths. In the first bath, a small amount of ferrous sulfate is desirable but more than 2 pounds per gallon interferes with the activity of the bath. If the amount of ferrous iron becomes too high in the third bath, a spongy deposit of iron is formed on the sheet which interferes with the bonding power of the subsequently applied vitreous enamel. The citric acid permits the operation of this bath over a longer period of time by preventing the precipitation of ferrous sulfate. Where no citric acid was used, the practical limit of ferrous iron concentration was 10 grams per liter, while with the employment of citric acid, this limit may be increased to 30 grams per liter or even higher in some cases to 45 grams per liter, but care must be exercised to insure that the concentration is below the point at which a spongy deposit of iron occurs.

The surface tension of the third bath is preferably maintained at 30 drops per minute or greater as measured on a Stalagmometer.

The pH of this bath may be around 2.0 to 2.5 but may vary over a wider range of 1.8 to 3.5. At a pH around 4.0 there is a very sharp drop in nickel deposition. At a pH of 4.5 to 5.5, however, excellent results are obtained with proper buffers.

The quantity of citric acid employed should not be any more than is employed to keep the iron in solution or to prevent precipitation of the ferrous sulfate in the above mentioned operating range. One gram of citric acid per liter of solution will usually be sufficient. Too much citric acid interferes with nickel deposition where the nickel is being deposited by over-voltage as in the present case. Formic acid and other substances which have a sequestering or an inhibiting effect on the precipitation of ferrous sulfate may be employed instead of the citric acid.

By a procedure of the type described in this example, the steel is given a surface etch and manganese salts are deposited thereon and sealed with a nickel plate of approximately 0.01174 to 0.01267 ounce per square foot. The thickness of this nickel plate in terms of millionths of an inch is of the order of 8.0 to 8.6. The sheet containing the nickel coating has a bright metallic finish. The nickel coating may be removed readily with nitric acid solution and after this has been stripped, the sheet exhibits a dark grain etch.

EXAMPLE III

Ferrous sulfate is added to the first or surface etching bath 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 content of the bath increases, 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 two pounds of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per gallon in the etching bath. The following example illustrates the manner in which the ferrous sulfate concentration increases.

In an etching bath such as described in Example I, the concentration of ferrous sulfate to begin with was 17.5 grams per gallon. Four

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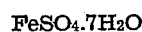
thousand gallons of this bath was used as an immersion bath at 15 minute intervals for successive racks of 18 gauge SAE 1010 deep drawing ferrous base stock consisting of 66 sheets size 36" by 86" per rack.

After two lifts the temperature of the bath was 165 degrees F. and the bath showed an analysis of 5.5% sulfuric acid and 0.20 pound per gallon of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ which corresponds to about 90.8 grams per gallon of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Eight lifts later the temperature of the bath was still 165 degrees F. and an analysis showed 5.0% sulfuric acid by weight and 0.25 pound of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per gallon.

Four lifts later the sulfuric acid content of the bath was 5.5% by weight and the bath contained .32 pound per gallon of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

Eight lifts later the bath analysis was 5.5% sulfuric acid and .37 pound per gallon of



The pH of the bath was held between 5.0 and 5.5. The tank was finally dumped when the concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ reached 2 pounds per gallon.

Ten pounds of a make-up composition consisting of a fused mixture made by heating 7.5 parts of commercial zinc sulfate, 1.0 part of manganese dioxide and 11.5 parts of commercial sodium bisulfate was added to this bath every fifth lift.

In this process, the nickel chloride in the third bath functions to increase conductivity. The boric acid functions as a buffer to maintain the pH.

The zinc is representative of a metal which furnishes driver electromotive force for the deposition of the nickel in that it has a higher over-voltage than nickel in relation to iron. Cobalt, cadmium, aluminum and/or magnesium may be similarly employed, and inasmuch as the baths contain a sulfate anion such metals will be present as the sulfate.

EXAMPLE IV

This example illustrates the process of the invention where a nickel-cobalt alloy is plated by over-voltage in the presence of a cathode depolarizer.

Ferrous metal base sheets similar to those used in Examples I, II, and III, but in the form of test plates $1\frac{1}{2}$ " by 4" ($\frac{1}{4}$ sq. ft.) were immersed in successive baths in three stages.

The first bath had the same composition as the first bath described in Example I except that it contained 205 cc. of 60 degree Baumé commercial sulfuric acid. Fifty milligrams of ferrous sulfide were added. The ferrous sulfide decomposes, liberates hydrogen sulfide which assists in activating the sheet. Instead of ferrous sulfide, sodium polysulfide may be used. The temperature of the bath was maintained at 155 to 160 degrees F. The sheets were treated in 15 to 20 minute cycles, that is, they were immersed for that length of time.

After the treatment in the first bath each sheet was rinsed and immersed in a second bath similar to that described in Example I. The second bath may be omitted but its use represents a preferred use of the process because this bath establishes the receptivity or deposition pattern of the sheet. The surface of the sheet may be regarded as containing myriads of couples with the subsequent deposition in the third bath occurring only on those areas of the proper polarity. The same time period was employed in the second bath, that is, 15 to 20 minutes.

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The third bath consisted of the following ingredients:

- 200 grams $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
- 37.5 grams $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$
- 20 grams boric acid
- 3.8 grams citric acid
- 3.75 grams dextrose
- 25 cc. of a product made by dissolving 40 pounds of sodium hydroxide in $8\frac{1}{2}$ gallons of water, adding chromic acid (CrO_3) and then mixing with 37 gallons of 50% gluconic acid. (See my U. S. Patent 2,428,356.)
- 50 mgs. sodium bisulfite (NaHSO_3) made up to two gallons with water.

The pH of this bath was maintained at 4.9 to 5.1 and the treatment again was in a 15 to 20 minute cycle. In this bath the use of the dextrose is optional. The compound derived by the reaction of the sodium hydroxide, chromic acid and gluconic acid acts as a depolarizer. The sodium bisulfite functions as a reducing agent. This bath deposits alloys of nickel and cobalt by over-voltage onto the ferrous base stock previously treated in the first and second baths. For the purpose of this invention, excellent results have been obtained where the alloy plated consisted essentially of 90% nickel and 10% cobalt or 92.8% nickel and 7.2% cobalt.

In the foregoing examples, cold rolled commercial quality and drawing quality sheets may be used with excellent results. One such steel is specified as .08 carbon max. and .32 to .42 manganese, as described in A. I. S. I. Steel Products Manual, sec. 11, October 1948, pp. 34 and 36.

The term "mild alloy steels" as used herein is intended to cover steels having an average carbon content in excess of 0.02% and not more than 0.45%, preferably 0.07 to 0.20%, including the steels having the following specific compositions:

Compositions

C	Mn	Si	P	Ni	Cr	Cu	Mo
.09	Low	.55	.005	---	---	.45	.24
0.10	0.25	0.75	0.15	---	0.75	0.40	---
0.12	0.60	---	0.08	---	---	0.40	---
0.08	0.35	0.95	---	---	0.80	0.40	---
0.15	0.70	0.17	---	---	0.50	0.60	---
0.10	0.60	0.15	0.12	0.50	---	1.10	---
0.14	0.80	0.15	---	---	0.12	0.30	---
0.10	0.60	---	0.10	0.60	---	0.60	0.20
0.10	0.35	0.08	---	0.35	0.12	0.25	---
0.13	0.90	0.15	---	---	---	0.20	0.25
0.10	0.75	0.30	0.10	0.50	0.75	0.50	---
0.13	0.70	0.80	---	0.20	0.60	0.20	(Zr=0.12)
0.10	1.10	0.05	0.12	---	---	0.35	---
0.12	0.75	---	---	0.75	---	1.40	0.10
0.15	1.00	0.50	---	---	---	0.25	0.10
0.08	0.50	0.25	---	2.0	---	1.00	---
0.07	0.35	Trace	0.06	0.75	---	0.40	---

The employment of the various addition agents, such as the zinc sulfate to supply driver electro-motive force, the citric acid to prevent precipitation of the ferrous sulfate, the nickel chloride to increase conductivity, the buffer materials to maintain the pH and the wetting agents to reduce surface tension and to overcome gas polarization, all represent optional procedures which can be employed in conjunction with the manganese dioxide activation or with other treatments of the type described in my aforementioned copending applications. Each of these types of addition agents contributes to a very substantial improvement in the overall results.

The metal which is to be treated may be a regular cold rolled box annealed steel sheet of the type commonly referred to as autobody sheets.

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The control of the composition of the metal, the annealing of the sheet and the temper rolling, if any, will be determined from the requirements of the end use of the sheet, especially as to the amount of drawing and firing which has to be done. Temper rolling of the sheet may be performed before or after the processing herein described, whichever is more convenient in a particular plant.

As an example of a suitable vitreous enamel composition there may be mentioned a molybdenum bearing enamel which is made from the following smelter batch:

	Parts by weight
Borax—hydrous	21.3
Silica sand	31.8
Soda ash	2.9
Potassium nitrate	5.5
Sodium fluosilicate	5.3
Fluorspar	2.2
Barium carbonate	8.3
Zinc oxide	3.4
Titanium dioxide	4.5
Molybdic oxide—pure	4.0
Sodium antimonate	10.8

The finishing and pouring temperature of this batch after smelting is approximately 2100 degrees F.

For coats applied by spraying the following mill batch may be used:

Frit (parts by weight)	100
Clay (parts by frit weight)	4
Sodium nitrite (parts by frit weight)	0.5
Antimony opacifier (parts by frit weight)	4
Water (parts by frit weight)	40

This is ground or milled to a fineness of 0-25% residue on a 200 mesh screen, preferably 4-8% residue. The resultant composition is then applied at the rate of 15 to 30 grams per square foot to the base stock prepared as previously described, dried and fired at a temperature of 1350 degrees F. to 1500 degrees F.

Good results are also obtained with an enamel containing approximately 60% of a non-feldspathic glass and 40% of a feldspathic glass leadless cast iron vitreous enamel.

A typical non-feldspathic frit is made from the following ingredients:

	Parts by weight
SiO_2	10.9
ZnO	10.5
H_3BO_3	21.9
BaCO_3	35.0
Na_2SiF_6	22.6

A typical feldspathic frit is made from the following ingredients:

	Parts by weight
Feldspar	21.7
Borax	31.0
Quartz	7.0
Soda ash	2.4
Barium carbonate	8.6
Sodium nitrate	5.7
Zinc oxide	7.0
Fluorspar	7.6
Whiting	4.5
Sodium zirconium silicate	4.5

The foregoing frits are made in the usual manner by mixing, smelting, fritting and drying the compositions.

The frits are then mixed together in the 60:40 ratio and the following mill additions are made:

Frit (parts by weight) -----	100
White clay (parts by frit weight) -----	7
Color oxide or opacifier (parts by frit weight) -----	0-20
Bentonite (parts by frit weight) -----	1/8
Barium carbonate (parts by frit weight) --	1/4
Water (parts by frit weight) -----	43

The resultant composition is milled to a fineness of 1-2 grams residue on a 200 mesh screen from a 50 cc. sample and then applied to the previously prepared ferrous metal base stock, dried and fired at a temperature within the range of 1250 degrees F. to 1300 degrees F.

Excellent results were obtained on the steel sheets treated as previously described with both types of vitreous enamels mentioned.

The importance of the invention resides in the fact that it provides a very simple and economical method of increasing the adherence of vitreous enamel coatings to ferrous metal base stocks without the use of ground or grip coats of vitreous enamels containing cobalt, manganese and/or nickel. As a result, it is possible to prepare vitreous enamel coated articles containing only a single coat of the vitreous enamel possessing excellent adherence to the base stock. The simplicity of the procedures involved in securing this adherence is such that the enameler is not required to depend upon the use of a special type of base stock. The base stock used can be similar to that now employed in making automobile bodies. Another important advantage of the invention is that it can be applied in the treatment of welded shapes.

The invention is hereby claimed as follows:

1. A method of controlling the adherence of vitreous enamels to mild alloy steels which consists essentially in subjecting a mild alloy steel having a carbon content between 0.02% and 0.20% to the action of a surface etching bath comprising an acid solution of ferrous sulfate, manganese dioxide and a compound from the group consisting of the soluble salts of zinc, cadmium, aluminum and magnesium, treating the steel with a dilute substantially non-etching acid solution containing a soluble salt of a metal from the group consisting of nickel and cobalt, then electrodepositing on the steel a thin coating of a metal from the group consisting of nickel, cobalt and alloys of nickel and cobalt, and firing a vitreous enamel on the plated surface.

2. The product of the method recited in claim 1.

3. The method of controlling the adherence of vitreous enamels to mild alloy steels which con-

sists essentially in subjecting a mild alloy steel having a carbon content between 0.02% and 0.20% to the action of a surface etching bath comprising an acid solution of ferrous sulfate, manganese dioxide and a compound from the group consisting of the soluble salts of zinc, cadmium, aluminum and magnesium, treating the steel with a dilute substantially non-etching acid solution containing a soluble salt of a metal from the group consisting of nickel and cobalt, then electrodepositing on the steel a thin coating of a metal from the group consisting of nickel, cobalt and alloys of nickel and cobalt, said electrodeposition being carried out in an aqueous electrolyte containing in solution a compound from the group consisting of the soluble salts of zinc, cadmium, aluminum and magnesium, and firing a vitreous enamel on the plated surface.

4. The product of the method recited in claim 3.

5. A method of controlling the adherence of vitreous enamels to mild alloy steels which consists essentially in subjecting a mild alloy steel having a carbon content between 0.02% and 0.20% to the action of a surface etching bath comprising an acid solution of ferrous sulfate, manganese dioxide, a compound from the group consisting of the soluble salts of zinc, cadmium, aluminum and magnesium, and a buffer capable of maintaining the pH of said bath between 5 and 5.5, treating the steel with a dilute substantially non-etching acid solution containing a soluble salt of a metal from the group consisting of nickel and cobalt, then electrodepositing on the steel a thin coating of a metal from the group consisting of nickel, cobalt and alloys of nickel and cobalt, adding a buffer to the bath from which said thin coating of metal is electrodeposited capable of maintaining the pH of the plating bath between 1.8 and 3.5 and firing a vitreous enamel on the plated surface.

6. The product of the method recited in claim 5.

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