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METHOD OF ENAMELING MILD STEEL

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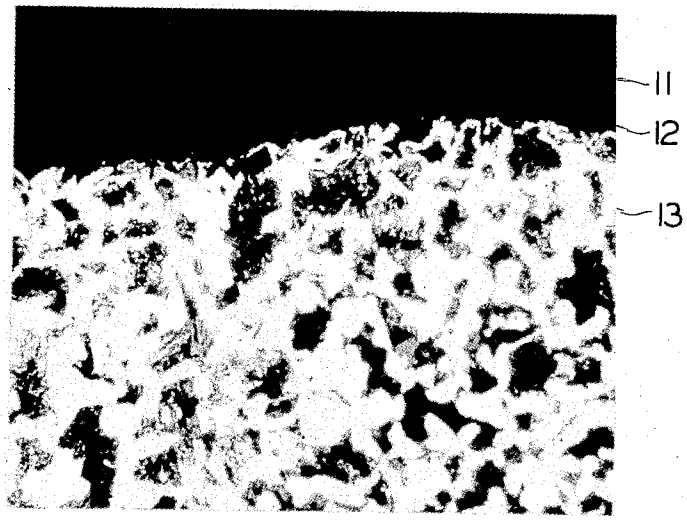


Fig. 1

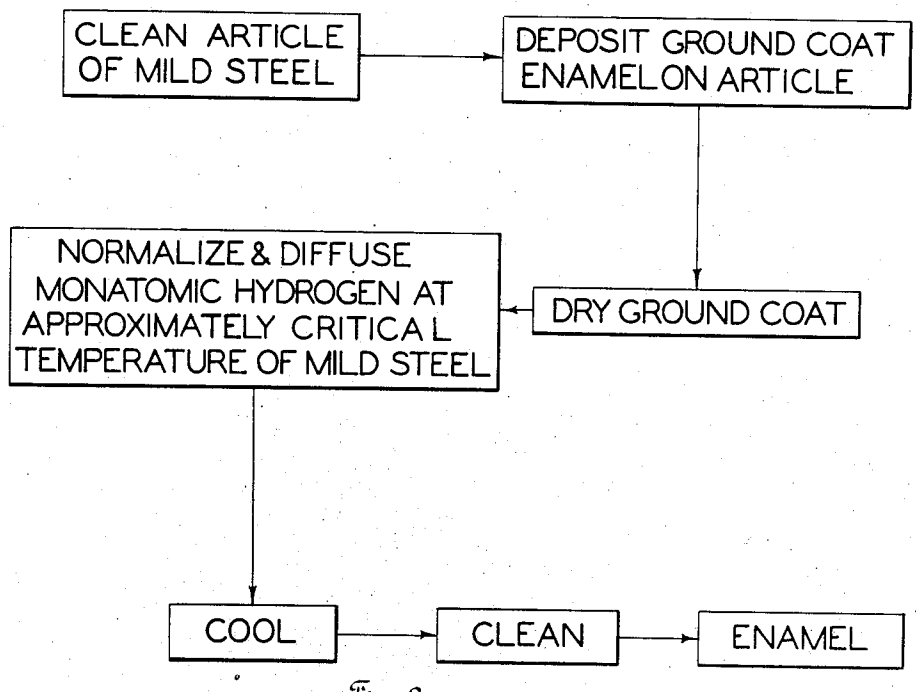


Fig. 2

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METHOD OF ENAMELING MILD STEEL

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The present invention relates to the art of coating ferrous materials, more particularly to a method of enameling mild steels of the type having a carbon content in the range of from essentially zero up to about 0.45%, and to the coated articles of manufacture resulting therefrom.

As of the time of the present invention, industry generally was confronted with the enigmatic situation that materials which were easily coated with vitreous enamels did not always meet structural specifications whereas the materials which did meet structural specifications were not easily coated with vitreous enamels. As one example, irons containing a high percentage of carbon have heretofore required that very particular enamels be used in only certain specific processes requiring extraordinarily close control if a good enamel-to-metal bond is to be perfected. Practically all of the enamels which have been found suitable, i.e., possess the necessary mechanical, electrical and thermal properties, for the manufacture of commutator V-rings, rectifier bushings and like parts call for extremely low carbon steels in which the carbon content does not exceed 0.04%. Because of these manufacturing limitations imposed by the lack of a better method of enameling, industry was compelled to use low carbon iron and special grades of steel in their manufacture of the aforementioned parts. Industry was then further handicapped by the lack of a ready supply of these special steels in any quantity, shape or form. For example, one such special type of enameled steel is only available in large slabs or billets so that parts made from this stock require a large amount of machine work and are therefore extremely costly. Even with all these precautions, the finished pieces frequently revealed defects due to inclusions, tubes and segregations and had to be scrapped.

For the past fifteen years many attempts have been made to substitute steels having a carbon content of from 0.010% to 0.25% and higher (these steels being able to meet higher strength requirements) for the very low carbon steels which had been required for high strength enameled fabrication. As a result of these efforts, the best method devised of those known prior to the present invention could only utilize steels having 0.16% carbon. That method consisted of analyzing the material to be enameled for its carbon content. Since 0.16% carbon was the maximum percentage allowable, articles containing more than this amount simply could not be utilized if successful enameling was to be attained. An article consisting of material which meets the carbon requirement was then normalized in a controlled atmosphere at 1600° F. for from fifteen to thirty minutes, according to the weight of the article. The article was then air cooled, sandblasted and enameled according to its specifications. This method provided an enameled article in which fish scaling occurred frequently as much as seventy-two hours or even longer after its completion. When fish scaling occurred, the articles had to be sandblasted and reworked until a true bond was attained. In some cases the work

piece had to be rejected completely. The net result of this method was that labor charges were prohibitive and many costly delays in meeting schedule dates were created.

Another prior art method incorporated an oxidizing atmosphere into the normalizing step with a resultant disadvantage that the steel became oxidized and pitted from steam and other constituents of the atmosphere as they came in contact with the heated steel.

The problem facing the present inventor at the time of her invention was therefore to create a method which would allow for an easy, efficient and inexpensive enameling of mild steels containing up to 0.45% carbon, which would consistently provide a quality bond between the enamel and the steel, and which would further significantly reduce rejections because of fish scaling, copper heading and other deleterious phenomena prevalent in the high strength enameled articles produced by the methods of the prior art.

Accordingly, the primary object of the present invention is to provide an improved method for enameling mild steel which overcomes the aforementioned deficiencies of the prior art methods.

Another object of the present invention is to provide a method for enameling mild steel which enables heating the steel to high temperatures without inducing injurious effects from oxidation.

Another object of the present invention is to provide a method for enameling heavy gauge (>¼") mild steel having a carbon content as high as 0.45% which causes substantially all of the undissolved diatomic hydrogen to be removed from within the steel and prevented from rediffusing into the steel.

Another object of the present invention is to provide a method for enameling mild steels in which substantially all of the undissolved monatomic hydrogen contained in the steel is diffused to the atmosphere to form diatomic hydrogen and other hydrogen compounds by holding the steel for an extended period of time at a temperature approaching its critical point.

Another object of the present invention is to provide a method of enameling mild steels which causes a vitreous sheath to be formed about the steel to prevent the entry of deleterious gases into the steel.

A still further object of the present invention is provision of an improved method for enameling mild steel which provides a cost reduction per unit produced of substantially two-thirds of the cost required for the production of each unit by the methods known heretofore.

These and still further objects are fulfilled by the present invention in a manner which shall become apparent from a reading of the following detailed description in conjunction with the accompanying drawing in which:

Fig. 1 is a photomicrograph at 1000× of a cross section of an enameled article prepared by the method of the present invention showing, inter alia, the bond resulting between the enamel coat and the mild steel (having a carbon content of 0.44%) with picral as an etchant; and

Fig. 2 is a schematic flow sheet indicating a sequence of steps to be followed in practicing one embodiment of the method of the present invention.

The method of the present invention provides a desirable procedure for enameling any mild steel stock containing from zero to as high as 0.45% carbon and has been particularly useful in enameling heavy gauge slabs of three-quarter inches on up, excellent results being obtained even when two inch slabs made up the work material.

According to the present invention, the part to be enameled is first cleaned in any suitable manner such as

by sandblasting or pickling. When the part is clean, a heavy (from 0.02 to 0.03 inch) coat of porous, vitreous enamel is deposited on the cleaned surfaces in any suitable manner such as dipping, slushing or spraying. When the enamel coat is applied, the piece is next introduced to a suitable drier, such as under infrared light, which, operating preferably between 150° F. to 400° F., removes excessive water from the slip. The length of time required to dry the slip is more or less a subjective determination and reflects the thickness of the enamel coat, the size and shape of the article, the temperature of the drier and other like factors. It has been found that when the drier operates at a temperature over 200° F., most conventionally sized articles will be properly dried in from twenty to about forty-five minutes.

The piece with its dried coat of enamel is next fired to about 1600° F. in a suitable furnace. This heat treatment, variously referred to as normalizing (when steel is heated above its critical point and air cooled), annealing (when steel is heated above its critical point and furnace cooled), or commercial annealing (when steel is heated to just below its critical point and air cooled), has heretofore performed the dual functions of stress relieving the metal article and maturing the enamel coat.

The present invention incorporates a third function to the heat treatment which provides an important aspect of the present invention. By extending the duration of the firing time beyond that of the normal practice for a total period of at least three times the normal firing time, the present invention effectively expatriates substantially all excess hydrogen, i.e., the hydrogen which is not in solution, from the steel.

There is reason to believe that the excessive defects which have prevailed heretofore in enameled articles of mild steel, and rendered them unsalable, such defects being fish scale and pin point breaking due to unmatured bubbles, are for the most part caused by pressure set up along the skin surface, i.e., that bonding surface between the enamel and the steel, by entrapped hydrogen.

The prior art attempted to avoid some of the deleterious effects of the entrapped hydrogen by using only those steels for enameling which contained extremely low carbon. The procedure possessed drawbacks among which was that the low carbon metals had very low strength characteristics and were unsuitable for many manufactured structures. It therefore became clear that if enameled articles possessing desirable strength characteristics were to be manufactured, the problem of overcoming the defects resulting from entrapped hydrogen must be solved. As an answer to the problem, the present invention provides a method by which the enamel defects caused by entrapped hydrogen are eliminated and enameled articles containing carbon as high as 0.45% and possessing desirable high strength characteristics can be successfully manufactured.

Though the exact theory as to why the improved results which are realized by the present invention has not been fully developed, it is believed that as steel is heated to a temperature approximating its critical temperature, i.e., the temperature at which ferrite and pearlite transform to austenite, atoms of the monatomic hydrogen contained in the steel but which are not dissolved in the steel diffuse to the surface of the steel from whence they pass through theh porous enamel coat to the atmosphere. When the atoms of monatomic hydrogen reach the atmosphere, they may join with other atoms of monatomic hydrogen to form molecules of diatomic hydrogen or they unite with atoms of other elements to form hydrogen compounds.

As each atom of monatomic hydrogen diffuses from the surface of the article to the atomosphere, another atom of the diffusing monatomic hydrogen replaces it on the surface of the article in a process of evacuation and replacement which continues until substantially all undissolved monatomic hydrogen has been removed from the steel.

A second form of undissolved hydrogen in the steel is occluded diatomic hydrogen. It presents an additional problem since while monatomic hydrogen will diffuse through iron at a low temperature, occluded diatomic hydrogen will not. This problem is solved by heating the article to approximately the critical temperature of mild steel, since in heating the metal to this temperature, the temperature of disassociation of diatomic hydrogen gas in the presence of iron, observed to be approximately 1450° F., is reached and exceeded whereupon the occluded diatomic hydrogen breaks down into monatomic hydrogen according to the equation:

$$H_2 \xrightarrow[Fe]{\Delta} 2H$$

As monatomic hydrogen, this hydrogen experiences no difficulty in diffusing to the surface of the steel and to the atmosphere in the same manner as the aforedescribed undissolved monatomic hydrogen initially present in the steel.

It has been further observed that even though the solubility of hydrogen in iron substantially increases at the temperature of disassociation of diatomic hydrogen (e.g., going from 6.2 to 9.8 cc. per 100 gms. of pure iron), this increase absorbs a relatively small percentage of the total hydrogen disassociated and the major portion is expelled to the atmosphere. Thus while the quantity of monatomic hydrogen in solution in the iron is increased, the total hydrogen situated in the iron is drastically reduced. And it is that portion of the total hydrogen which is not in solution which is believed to be the cause of the defects heretofore prevalent in enameled articles of mild steel.

It is understood that the aforedescribed theory is an attempt to analyze the mechanics of the present invention to explain the improved results realized therefrom by a theory which is not fully developed. Consequently, the present invention is not intended to be limited thereby.

During the heating step of the present invention, the vitreous coat of enamel becomes fluid and matures to provide a viscous glassy coating or sheath on the steel article. This sheath successfully isolates the hydrogen gas which has diffused to or is present in the atmosphere from the hot steel surface and thus prevents the hydrogen from contacting the hot steel surface. Were the sheath not present, the diatomic hydrogen, upon contacting the hot steel surface, would redisassociate into monatomic hydrogen which could then reenter the steel and refill the occlusions from which the occluded diatomic hydrogen gas had been evacuated. If this were to occur, the purpose of the heat treatment would be frustrated and its improvement of the steel for enameling substantially nullified.

The viscous sheath further prevents the disassociation of steam which may be present into oxygen and monatomic hydrogen by also isolating the hot steel from the steam.

The rate of diffusion of monatomic hydrogen gas, which is substantially increased by the heating step, is believed in part attributable to the increased mobility of the hydrogen because of the heat and in part attributable to the increased mobility of the iron atoms in the steel. Similar increase in diffusion rate is observed for other dissolved gases which exert deleterious effects upon the enamel.

According to the aforedescribed prior art heat treatment processes some undissolved hydrogen may be dispelled from the steel. However, the amount dispelled is not sufficient to prevent the formation of pockets of diatomic hydrogen gas between the enamel coating and the steel since the duration of the heat treating was based upon and limited to the physical transformation of the metal and the maturation of the enamel coating. When these conditions were fulfilled, the cooling cycle was begun. Thus the cooling cycle is commenced before any appreciable amount of hydrogen is evacuated from the

steel and while large amounts of undissolved monatomic hydrogen and occluded diatomic hydrogen are still in the steel. Upon cooling, the rate of diffusion of the monatomic hydrogen and the mobility of the iron atoms which obstruct the diffusion of the gas, greatly decreases so that hydrogen is not effectively removed from the steel during cooling. The net effect of treating steels by the prior art methods is to provide steels which retain a deleterious quantity of hydrogen which prevents the achievement of proper bonds between the steel and its enamel coat. Perhaps an explanation of the prior art deficiency is its failure to grasp the concept of hydrogen removal which the present invention successfully utilized to achieve its improved results.

The present invention incorporates the discovery that when the heating of an enamel coated steel article is significantly extended most of the undissolved monatomic hydrogen and substantially all of the occluded diatomic hydrogen originally in the steel is diffused from within the steel to its surface through the fluidized enamel coat, and to the atmosphere. It has further been ascertained that the length of time necessary to properly expunge the hydrogen from the steel is related to the length of time required to effect the physical transformation of the enamel coat, i.e., its maturation or vitrification. It is observed that the prolonged heating period should extend at least three times the time required to effect the aforesaid maturation of the enamel, and preferably for a period extending approximately five times that time which is known to the art as "normal firing time."

It has been further determined that the heating step may be performed in an oxidizing atmosphere which further entraps the hydrogen by the formation of hydrogen compounds.

When the heating step is completed, the article is then cooled by any suitable manner, such as by air, which will not affect the physical characteristics of the metal resulting from heat treatment.

During cooling, the vitreous enamel hardens into a vitreous coating from the viscous fluid state in which it existed during the heating step while the hydrogen was being evolved from the steel. This coating, both while viscous and hardened, forms a protective sheath about the steel article which prevents the entry of hydrogen and other gases into the steel and effectively isolates the steel from the atmosphere surrounding the enamel. When the article has been completely cooled, e.g., to room temperature, a firm enamel sheath is uniformly and firmly bonded to the metal. The cooled article is further characterized by a greatly reduced hydrogen content as the undissolved occluded hydrogen atoms have been dispersed to the atmosphere. Consequently the bonding surface or skin surface of the article of the present method, which when prepared by prior art methods contained pockets of entrapped gases, such as hydrogen, which resulted in enamel coatings characterized by fish scaling and bubble bursting, is substantially hydrogen free.

When the fired part has been cooled by a suitable method, the resulting cooled low hydrogen enamel sheathed article is then cleaned by a suitable method such as sandblasting, dipping in molten caustic, or other suitable means and the article is ready to be enameled according to the specifications the final article shall meet. Because of the improvement provided by the method of this invention, the mild steel articles can now be enameled with porcelain enamels and the like and a good bond achieved because the skin surface is rendered free of gas in a manner which does not cause scale or pitting.

An enameled article prepared by the method of the present invention and subsequently coated with a porcelain enamel is shown in Fig. 1 in which the enamel is identified by the reference numeral 11, the bonding surface by 12, and the steel by 13.

As previously stated, it has been determined that at least three times the normal firing time is the desired minimum time for holding the article at a temperature approximating the critical point of the steel base. There appears to be no maximum time for holding the piece at heat since pieces have been held as long as twenty-one times their normal firing time without adversely affecting the properties of the final article. It should be added however that beyond a certain point, i.e., when all removable gases have been removed, no further gas removal will be effected and that heating beyond this point, while not injurious to the article, is a great waste of fuel and unnecessarily increases costs.

The term "firing time" is herein used as a conventional term of the enameling art and it is dependent, inter alia, upon the weight and shape of the article to be enameled since the surface of the steel article must be heated to the maturing temperature of the enamel before maturation of the enamel will be effected.

The temperature recitation of 1600° F. contained in this disclosure is cited as illustrative of a temperature just below the lower critical temperature of mild steel being enameled and will subject to variations depending upon the actual steel chosen for enameling.

The term "transformation" as herein used is likewise a term of the art although it is technically somewhat of a misnomer. The effect of heating on the steel is primarily one of spheroidizing rather than one of transformation and usually only about one-tenth of the alloy becomes austenitic. The important effect of the heating is that the graphite contained in the steel converts from plate to spherular form thus enhancing the plastic flow of the metal and reducing its brittleness.

The enamels herein described are those heretofore well known for coating articles of the type herein identified, the spirit of the present invention being a novel method of preparing mild steel articles, i.e., steel articles having up to about 0.45% carbon, for coating with a vitreous enamel which provides between the article and a subsequently deposited vitreous coating, an interfacial tenacity heretofore unknown in this art.

To aid in a fuller appreciation of the present invention, the following are examples of frit compositions (molten basis) of the type consisting essentially of feldspar, borax and quartz which have firing temperatures in the preferred range of 1450–1600° F., and which assume a relatively porous condition in the molten state. All of the examples represent compositions which are suitable for obtaining the improved results of this invention and may be used in the practice thereof.

Example 1

Component:	Percent
Potassium and sodium oxide	18.0
Boric oxide	14.1
Alumina	5.4
Silica	44.1
Calcium fluoride	6.8
Cobalt oxide	2.9
Manganese oxide	6.8
Nickel oxide	1.9

Example 2

Component:	
Potassium and sodium oxide	18.6
Boric oxide	12.7
Alumina	7.1
Silica	48.1
Calcium fluoride	8.2
Cobalt oxide	0.9
Manganese oxide	4.3

Example 3

Component:	Percent
Potassium and sodium oxide	21.6
Boric oxide	13.4
Alumina	7.2
Silica	49.9
Calcium fluoride	4.8
Cobalt oxide	0.5
Manganese oxide	0.7
Nickel oxide	0.5
Fluorine	1.4

Example 4

Component:	
Potassium and sodium oxide	20.8
Boric oxide	16.6
Alumina	6.4
Silica	50.1
Calcium fluoride	4.5
Calcium oxide	1.6

Example 5

Component:	
Potassium and sodium oxide	23.7
Boric oxide	10.3
Alumina	7.3
Silica	55.6
Cobalt oxide	0.6
Manganese oxide	2.5

Example 6

Component:	
Potassium and sodium oxide	16.3
Boric oxide	9.6
Alumina	6.5
Silica	56.4
Calcium fluoride	5.9
Cobalt oxide	0.5
Manganese oxide	4.8

Example 7

Component:	
Potassium and sodium oxide	21.2
Boric oxide	13.3
Alumina	6.9
Silica	49.6
Calcium fluoride	7.5
Cobalt oxide	0.2
Manganese oxide	1.3

Example 8

Component:	
Potassium and sodium oxide	18.5
Boric oxide	15.2
Alumina	8.8
Silica	52.1
Calcium fluoride	3.8
Cobalt oxide	0.4
Manganese oxide	1.2

Example 9

Component:	
Potassium and sodium oxide	19.4
Boric oxide	13.3
Alumina	8.0
Silica	56.6
Cobalt oxide	0.7
Manganese oxide	2.0

It is understood that the present method is not limited to commutator V-rings, but for descriptive purposes, one embodiment of the method will be discussed in relation thereto.

The V-ring, having been molded to the desired form, is sandblasted to clean its surface and prepare it for enameling. When the ring is clean, an enamel slip is deposited upon its finished surface in any suitable manner such as by spraying and the coated ring is placed into an infrared drier which, operated at over 200° F., removes the excess water from the enamel slip. This step does not involve maturation of the enamel nor does it remove any water from the clay suspension agents in the enamel. It merely removes the excessive water which has provided the vehicle for the slip solution. When it is dry, the ring is placed in a furnace operating at a temperature approximating the critical temperature of mild steel, e.g., around 1600° F.

The point of maturation of the enamel, i.e., the point at which the fluid enamel becomes vitreous, can be observed by noting the glossy sheen which appears. The length of heating time required to achieve this effect is then extended at least twice again to effectively evolve all excess monatomic hydrogen from the steel and up through the fluid enamel or approximately thirty minutes more in the case of a coated article of such material, size, shape, etc., to have a normal firing time of approximately 15 minutes. After approximately three times the time of the normal firing period, and preferably about five times the normal firing time, the ring is removed from the furnace and cooled. During the cooling step the vitreous enamel coating becomes a gloss or super cooled liquid and is securely bonded to the metal ring. When the ring has been cooled to room temperature, it is cleaned to remove the gloss coat and is then ready to be enameled to any specifications which might be prescribed.

A further advantage of the present invention can be seen when it is considered that while the total processing of a commutator ring previously required sixty-seven hours of labor, it now requires but three and one-half hours.

The method of the present invention thus provides a positive solution for the problem of overcoming the deleterious effects on enamel bonds caused by the hydrogen contained in steels by effectively removing the hydrogen from the metal through the enamel in the presence of the enamel and preventing its reentry. Not only does the method of the present invention solve this major problem which has long confronted the enameling trade, it does it in such a manner as to greatly reduce the cost of producing such items as commutator V-rings, rectifier bushings, and like articles according to its teachings by simplifying operations, permitting a wide range of materials to be available for enameling, and greatly reducing rejections due to defective enamel bonding. These and other objects recited herein for this invention are thus fulfilled by the method herein disclosed.

While the method has been described with relation to certain specific manufacturing operations, it is understood that the present invention is not to be so limited. Rather, such modifications and variations as may readily occur to one skilled in the art are intended to be included within the scope of the present invention, it being limited only by the scope of the appended claims.

What is claimed is:

1. A method of preparing a mild steel surface for enameling comprising the steps of: coating an article of mild steel with a ground coat of enamel; maturing the enamel by heating the coated article in an oxidizing atmosphere to a temperature approximating the critical temperature of mild steel for a period of time equal to the time required for the enamel to assume a glossy fluid condition; extending the aforementioned maturing step for a further period of time equal to at least twice the period of time required to mature said enamel; and cooling the article to transform the enamel to a hard vitreous sheath firmly bonded to the steel article.

2. A method of preparing a mild steel surface for enameling comprising the steps of: depositing a coat of a slurry containing an enamel frit of the type consisting essentially of feldspar, borax and quartz on an article of mild steel containing not more than 0.45% carbon; drying said slurry coated article at a temperature in the range of from 150° to 400° F.; firing said dried article

in an oxidizing atmosphere to a temperature of 1450°–1600° F.; holding said fired article at said temperature for a time equal to at least three times the time required to mature said enamel to a vitreous condition to effect an adherent uniform surface to surface engagement between said matured enamel and said mild steel article, said holding of said article at said temperature for said time dispelling occluded hydrogen gas from within said steel through said matured enamel into said oxidizing atmosphere; and cooling said hydrogen free coated article while said cooling enamel coat precludes the migration of said hydrogen gas from said atmosphere back into said article.

3. The improvement in the art of enameling a surface consisting of mild steel having up to 0.45 percent carbon comprising the steps of: depositing a coat of a slurry containing an enamel frit of the type consisting essentially of feldspar, borax and quartz on said surface; drying said slurry coated surface at a temperature ranging from 150° to 400° F.; firing said surface having said dry coat of enamel slurry thereon to a temperature approximating the critical temperature of the mild steel surface; heat treating said surface at said temperature for a time equal to at least three times the time required to mature said dried enamel slurry coat to a vitreous condition; cooling the vitreous coated article; and cleaning said surface to remove said cooled vitreous coat therefrom whereby said surface is ready for coating with vitreous enamel in a conventional manner.

4. The method of preparing an article of mild steel containing not more than 0.45% carbon for tenaciously adhering complete surface engagement with a coating of vitreous enamel subsequently applied thereto comprising: cleaning said article; depositing upon said clean article a heavy coating of an aqueous enamel slip containing an enameling frit consisting essentially of feldspar, borax and quartz; heating said slip coated article to a first temperature of 150–400° F. to remove excess water from said slip; heating said dried slip coated article to a second temperature of at least 1450° F. and not more than 1600° F.; holding said article at said second temperature to fire said slip and convert said frit to a molten vitreous condition for a period of time equal to at least three times the period required to convert said frit to said molten vitreous condition, while occluded hydrogen is dispelled from within said article through said molten vitreous coating; cooling said article to set said molten vitreous coating whereby the reentry of said hydrogen into said article is prevented; removing the set vitreous coating from said hydrogen free article; and cleaning said article for application of said subsequently applied coating of vitreous enamel thereto.

References Cited in the file of this patent

UNITED STATES PATENTS

2,294,760	Morris	Sept. 1, 1942
2,353,165	Kreidl et al.	July 11, 1944
2,455,331	Eckel et al.	Nov. 30, 1948
2,532,640	Pfeiffer	Dec. 5, 1950
2,603,577	Eckel	July 15, 1952
2,612,457	Davis	Sept. 30, 1952

OTHER REFERENCES

Andrews: Enamels, pp. 296–297, The Twin City Printing Co., Champaign, Ill. (1935).