March 17, 1959 F. W. BEALL ET AL 2,878,151

METHOD FOR PRODUCING SINGLE-FIRE ENAMELING STOCK DEVOID OF FISH-SCALING AND PRODUCT THEREOF

Filed Nov. 19, 1954

FIG. 1.

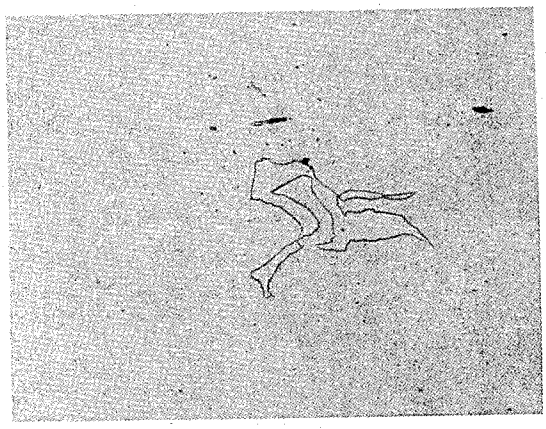


FIG. 2.

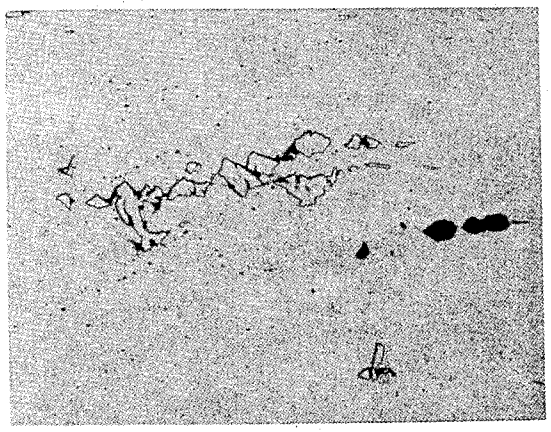
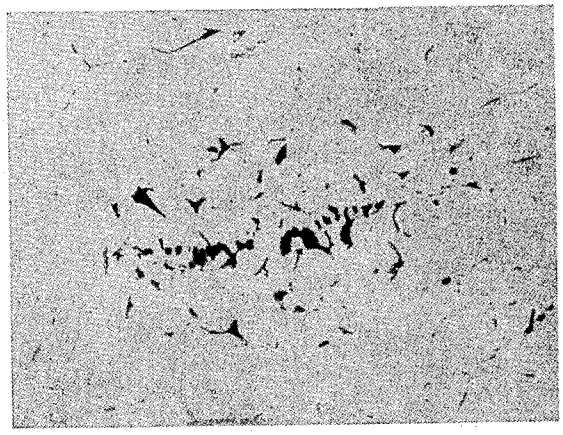


FIG. 3.



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METHOD FOR PRODUCING SINGLE-FIRE ENAMELING STOCK DEVOID OF FISH-SCALING AND PRODUCT THEREOF

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Application November 19, 1954, Serial No. 469,876

16 Claims. (Cl. 148—12)

In recent years a great deal of work has been done directed toward the provision of a ferrous sheet stock for vitreous enameling, which stock would be capable of accepting in a satisfactory manner a single-fired coating of vitreous enamel, particularly those which are white or light in color. It has been found that the provision of a successful enameling stock of this character involves the simultaneous solution of a plurality of problems.

First, it was realized that the stock would have to be one which does not give rise to the phenomenon of primary boiling. The initial firing of a coating of vitreous enamel on iron or steel sheet stock is likely to produce a vitreous surface characterized by pits, blow holes, craters, bubbles, and oxide spots. If a second coating of enamel is applied in a second firing operation, these initial defects will disappear or be masked, and a satisfactory vitreous surface will be obtained unless secondary boiling or reboiling occurs. But it will be clear that primary boiling precludes the formation of a satisfactory vitreous enamel coating produced in a single-firing operation, especially where the enamel is white or light in color.

Previous work has traced the primary boiling tendency to carbon, which may be present in the stock as massive carbides adjacent its surface or as exposed carbon or carbides on the surface resulting from carburizing atmospheres, cooling too slowly from an anneal, or as the result of a pickling operation. Decomposable chemical deposits left by pickling, nickel-flashing or other treatments likewise appear to have a deleterious effect on the enameled surface.

It is possible to "fix" the carbon in a ferrous enameling stock by the use of alloying ingredients such as titanium, but this is not only expensive but necessitates the production of a killed steel. It has been found that primary boiling can be obviated by subjecting the ferrous enameling stock to a decarburizing treatment which effectively reduces the carbon content, and renders it innocuous. In this fashion, an enameling stock may be made from rimmed steel which will not produce boiling in an initial firing operation.

The problem of adhesion of the vitreous enamel coating is a particularly difficult one in the formation of single-fired coatings of white or light colored vitreous enameled products. Where a plurality of coatings are to be applied in separate firing operations, it is conventional practice to use a frit or enamel material for the first coat which has highly developed adhesive characteristics, such as a blue cobalt coat. The blue coat is then covered and masked by one or more separately fired coatings of white or light colored enamel. It is possible, as taught in Patent No. 2,602,758, issued July 8, 1952, to apply a plurality of thin coatings of different kinds of frit to be fused in a single-firing operation, and to employ as the coating lying next the iron a layer of frit having relatively higher adhesion to the iron. It is not always desirable to do this, and a satisfactory solution of the adhesion problem normally requires some treatment of the surface of the enameling stock prior to the imposition of any frit. Moreover, it is frequently desirable to produce a single-fired coating of white or light colored vitreous enamel without the use of any layer of darker colored frit.

Various adhesion promoting treatments may be practiced on the enameling stock, including a roughening of the surface of the stock by mechanical means or by etching, or the imposition of a thin layer on the surface of the stock of an adhesion promoting metal such as nickel, cobalt, or the like, or a combination of these treatments. A peculiarly effective procedure is one outlined in the copending application of Fred G. Sutphen et al., Serial No. 101,464, filed June 25, 1949, now abandoned, entitled Method of Treating Iron or Mild Steel to Promote the Adherence of Porcelain Enamel, and Stock So Produced, now Patent 2,755,210, issued July 17, 1956, on a continuation-in-part application Serial No. 532,986, filed September 7, 1955. Here the ferrous enameling stock is provided with a thin coating of nickel, after which the stock is oxidized in a controlled fashion and then pickled to the extent of removng the scale or oxide. This produces a highly irregular, strongly undercut surface characterized by projecting non-rectilinear tentacles. It has been found that such a surface produces adequate adhesion of any fired-on coating including white or light colored vitreous enamel.

The solution of the problems of primary boiling and adhesion in rimming steel enameling stock has not, however, hitherto led to the production of a wholly satisfactory material. It has been noted that single-fired enamel coatings on such stock are particularly susceptible to a phenomenon known as fish-scaling, particularly in areas where the adherence has been damaged by metal finishing operations such as grinding, or by scratches. The surface of the vitreous enamel coating forms small blisters, and in most instances the vitreous material contained in these blisters spalls out and exposes the base metal in half moon areas resembling fish scales, ruining the appearance of the product.

It is an object of the present invention to provide a ferrous enameling stock which may be depended upon to be devoid of the tendency to produce fish-scaling in vitreous enamel coatings, even those having relatively poor adherence. While the utility of such a product lies primarily in the field of single-fired white or light colored enameled products, it has utility with other cover or finish enamel coatings, particularly those which do not contain adherence promoting oxides, such as the oxides of nickel, cobalt, antimony, and molybdenum.

It is an object of the invention to provide a rimmed steel enameling stock devoid of the tendency to produce fish-scaling.

It is an object of the invention to produce a ferrous enameling stock having characteristics embracing a simultaneous solution of the problems of adhesion and fish-scaling.

It is an object of the invention to provide an enameling stock having characteristics affording a simultaneous solution of the problems of primary boiling, adhesion, and fish-scaling in the production of white or light colored, single-fired vitreous enamel coatings, or other vitreous enamel cover coats devoid of adherence promoting oxides.

These and other objects of the invention, which will be set forth hereinafter or will be apparent to one skilled in the art upon reading these specifications, we accomplish by those procedures, and in those stocks and enameled articles of which we shall now describe exemplary embodiments. In the accompanying drawings, the various figures (hereinafter more fully described) are photomicrographs showing carbide distribution in the ferrous material at various stages of manufacture.

It will be understood that, in the formation of iron or

mild steel sheets the general practice involves the formation of ingots which, after treatment in the soaking pits, are slabbed. The slabs are heated and are reduced on a continuous hot mill to an intermediate gauge, the material being coiled. At this stage it is convenient to refer to the material as "thin bar."

The thin bar, after pickling, will ordinarily be cold rolled to gauge on a tandem or continuous cold rolling mill.

We have found that steel sheet stock will not produce the phenomenon of fish-scaling providing (*a*) the stock initially contains at least about .020% carbon (preferably, .025% to .08% carbon, although higher values may be used), (*b*) providing that at the conclusion of the hot rolling the ferrous material is cooled from a temperature above about 1300° F. at such a relatively slow rate (about 50° to 100° F. per hour) that massive carbides are formed therein, and (*c*) providing the material is then cold rolled with at least about 25% reduction. We have also found that this freedom from fish-scaling persists through subsequent normalizing or other heat treatments necessary to develop suitable physical properties.

As indicated, the slow cooling through the carbon precipitation temperature range just below the A_1 point results in the formation of massive carbides as illustrated in Fig. 1 hereof. If the slow cooling is not practiced, the carbides form small particles randomly distributed throughout the material. Irrespective of after treatments such as cold rolling and normalizing or box annealing following the cold rolling, these small, randomly distributed carbide particles will not be materially altered in form, and enameling stocks made from such materials usually exhibit the phenomenon of fish-scaling.

When, however, massive carbides are formed as described, and the material is then cold reduced, the massive carbides, being brittle, are fragmented and strung out by the cold reduction, with the simultaneous formation of minute voids in the base metal. This is illustrated in the photomicrograph Fig. 2.

Fig. 3 is illustrative of the condition of carbide distribution in the cold rolled material when it has been subsequently normalized to gain desired mechanical properties. The normalizing treatment has resulted in the fragmented carbides forming flowered pearlite. The microscopic voids or discontinuities remain in the former carbide pattern. It may be noted that Figs. 1, 2 and 3 are photomicrographs at 500 diameters, the material having been subjected to a Picral etch.

We do not wish to be bound by theory, but it is our belief that the formation of massive carbides and the fragmentation thereof by cold rolling results in the formation of a material characterized by extremely minute voids in the form of cracks or fissures throughout its thickness as well as at its surface. We believe that gaseous elements which might otherwise produce fish-scaling are absorbed in these cracks or fissures, although the cracks may also serve the purpose of relieving stresses built up during enameling. To produce our effect, the material must initially contain sufficient carbon as set forth above, and then it must be treated to produce the massive carbides following which these must be fragmented as described to produce the necessary voids. The non-fish-scaling characteristics of our materials are not destroyed by decarburization following the fragmentation resulting from the cold rolling. Thus, it is not the presence of carbon in the final material which produces the effect, but rather presumably a condition of the steel obtained by fragmenting massive carbides. The effect will not be obtained if the material is thoroughly decarburized prior to cold rolling. We prefer to decarburize it at a later stage.

In forming our materials, ingot iron (commercially pure iron) cannot be employed because this material as produced will have definitely less than .02% carbon, which is insufficient to produce our result.

A rimmed steel or iron such as has hitherto been employed in the manufacture of enameling stock can, with the exercise of special care, be used in the practice of our invention. An exemplary sheet analysis for a conventional enameling stock metal is:

Carbon	.02%.
Manganese	.05%.
Phosphorus	Trace.
Sulfur	.035% maximum.
Iron	Balance, except for normal impurities.

But it will be noted that the carbon content in this exemplary analysis is at the extreme low end of our range, and precautions would have to be taken uniformly to attain our result. Further, the amount of manganese in this stock is low, and ordinarily we prefer a higher manganese content so that the material will not be red hot and can be rolled hot enough to coil at a temperature above 1300° F.

Ordinarily, auto body sheet may have an exemplary analysis as follows:

Carbon	.05 to .08%.
Manganese	.25 to .60%.
Phosphorus	Nil.
Sulfur	.035% maximum.
Copper	.15% maximum.
Iron	Balance.

It will be noted that auto body sheet stock of this analysis contains a greater amount of carbon, and in this respect is preferable to conventional enameling stock. At the same time, however, it contains so much manganese that sagging is likely to be encountered when the stock is fired for enameling purposes.

As a consequence, the best practice of our invention is accomplished with a stock of intermediate analysis. The time when the carbon content is important in our process is during the slow cooling following the hot rolling and during the subsequent cold rolling. We prefer to have at the conclusion of the hot rolling procedure a ferrous product which analyzes as follows:

	Percent
Carbon	.025 to .08
Manganese	0.8 to .15

The phosphorus, sulfur and copper may be the same as in the analysis above, although ordinarily it is well to diminish the surfur content. The manganese may under some circumstances be increased to about .2%, but to avoid any possibility of sagging, we prefer to keep it within the range above noted.

When a carbon content below the preferred minimum of .025% and approaching .020% is used, the complete absence of fish-scaling becomes more dependent upon the use of effective adherence promoting means, upon taking care to cool the hot rolled coils slowly through the carbon precipitation range, as well as upon avoiding enamel over-firing. Carbon contents above .08% and even as high as .15% may be used successfully; but when the material is to be decarburized at a later stage, a longer decarburizing time will be required.

In general, we prefer rimmed steels because of their relative freedom from lines, seams, and other surface defects frequently encountered in killed materials. Such defects are difficult to cover with single coats of enamel. However, our invention is equally applicable to killed materials and they are preferred for certain drawing applications, particularly where strain aging would be encountered.

The hot rolling may be carried on in any way desired, and the practice of our process is not dependent on the use of the continuous hot mill, although the greater part of hot rolled materials are today produced on such mills. We ordinarily hot roll our stock to a thickness of about

.080 to .150 in., in view of the fact that subsequent cold rolling can readily be employed to carry the stock down to the desired finished gauges. The specific hot rolled gauge is not a limitation on the invention.

At the conclusion of the hot rolling, the cooled product may, if desired, be heated to a temperature above the A_1 point and then cooled slowly at a rate of about 50° to 100° F. per hour while within the temperature range of 1200° to 900° F. This can be done in various ways, as by annealing in a box, or by heating sheets or coils in a muffle furnace preferably in a protective atmosphere, so that the small precipitated carbides can go into solution and then cooling them in air or under a cover at the desired rate to precipitate carbon in the form of massive carbides. When cold material is reheated for our purpose, it will be well to heat it to a temperature around 1350° to 1500° F. in order to make sure that all parts of it reach a temperature above the A_1 point (usually lying in the range of 1300° to 1310° F.). A slower cooling than that specified above may be practiced if desired, but it will be found well to avoid both excessive temperatures and time at temperature as well as excessively slow rates of cooling, since these tend toward excessive grain growth and decarburization.

A separate heat treatment is a matter of some expense, and this expense may be largely or entirely avoided by a very much simpler procedure carried on in connection with continuous hot rolling. As is well known, in such a rolling operation the slab is treated in a plurality of stands of hot mills forming a tandem train, and the greatly elongated thin bar is coiled at the end of the train. The finishing temperature can be controlled by controlling such factors as speed, specific reduction per pass, and the extent of water cooling applied. We have found that the growth of massive carbides can be insured in our materials by coiling them at the end of the hot mill train at a temperature above the A_1 point. Depending upon circumstances, cooling the coil in air will frequently result in the desired cooling rate. However, without departing from the spirit of our invention, we may place the hot coil in a box or cover to delay the cooling. We avoid forming the coil at too high a coiling temperature to eliminate excessive grain growth; and ordinarily the temperature at which our material is coiled following its issuance from the hot mill is not allowed to exceed about 1400° F. It is important that the material cools at a rate of 50° to 100° per hour between 1200° and 900° F. An average rate of around 75° per hour over this temperature range is easily attained commercially and has given excellent results. Similarly, the material may be cut into sheets as it leaves the hot mill and piled for slow cooling.

The cold rolling may be carried on in any way desired, in any number of passes, and on any suitable cold rolling apparatus, inclusive of tandem stands of cold mills operating as a continuous train, reversing cold mills with coilers at each side, and the like. It is only necessary that the initial cold rolling produce a reduction of at least about 25% and preferably about 50% before any annealing is practiced. At about 25% reduction, the tendency to fish-scale is noticeably reduced, while above 40% it is usually completely absent. We prefer around 50% to assure regular and complete attainment of our result and because it is a commercially convenient amount of cold reduction on most production equipment. Higher reductions without intervening annealing are permissible.

A normalizing or box anneal will follow the cold rolling treatment to improve mechanical properties, and is frequently the final step in producing the enameling stock. In our process, these heat treatments will produce the flowered pearlite or cementite from the fragmented carbides if the material has not previously been decarburized. The voids produced by cold rolling remain unaffected. A normalizing treatment fits the enameling stock for drawing and forming, while a box anneal will produce a somewhat softer result, frequently desired for more severe deep drawing. For some applications adequate formability will result from a brief open anneal below the A_1 point.

The procedures outlined above serve to produce an enameling stock which is not subject to the defect of fish-scaling. Additional treatments may be combined with those hereinabove outlined. As has been indicated, a decarburizing treatment may be practiced, and is preferably a brief continuous heat treatment at a temperature from substantially 1250° to 1650° F. in an atmosphere oxidizing to carbon but not oxidizing to iron, and containing from about 2% to about 30% of water vapor by volume. Various atmospheres may be employed, including hydrogen, mixtures of hydrogen and other gases which are either inert or non-oxidizing, and non-carburizing to iron at the temperatures involved. Cracked ammonia is an exemplary source of a hydrogen bearing atmosphere. A treatment of finished gauge strip or sheets as described will serve to reduce the average carbon of the stock to a value not greater than substantially .010%, and will produce a stock which will not cause boiling upon the initial firing of a porcelain enamel coating.

It is not to be understood that such decarburized material is necessarily of uniform carbon content throughout, and there is some indication that the surface carbon is frequently higher than the average of the cross section. It may be that the decarburization process puts this surface carbon in a harmless form with respect to the formation of pits or black specks. While the phenomenon is not completely understood, we have found that when enameling with a single white coat, boiling is avoided when the concentration of carbon through the thickness of the sheet is reduced to an average concentration not greater than .010%.

In the practice of our invention, the decarburizing treatment must not precede the initial cold rolling which produces at least a 25% reduction in the metal. It may be practiced at any subsequent stage.

An adhesion promoting metal may be imposed on the stock at any stage. It is possible, though not necessarily desirable, to impose an adhesion promoting metal on the surfaces of the thin bar, the metal persisting through subsequent cold reductions, or it may be applied to the surface of the material at its final gauge. An adhesion promoting metal such as nickel may be applied in any of three ways, as (*a*) by electroplating, (*b*) by chemical substitution in a bath of a salt of the metal, or (*c*) by coating the ferrous body with a salt of the adhesion promoting metal, and then subjecting the product to heat under reducing conditions so as to reduce elemental metal from its salt.

Mechanical roughening and chemical etching may be practiced at any stage subsequent to the completion of the cold rolling.

As indicated above, an especially advantageous treatment for adhesion is set forth in the said copending application, Serial No. 101,464. The teachings of that application are here referred to for the details of the process. In general, the procedure involves (*a*) coating the surfaces of the ferrous metal sheet stock or article with a thin layer of nickel, (*b*) scaling or oxidizing the nickel treated stock by heating it preferably to above about 1650° F. in an atmosphere which is oxidizing and preferably non-carburizing to iron. This appears to alloy at least a part of the nickel with the iron, producing a peculiar surface oxide such that (*c*) when the scaled stock is acid pickled for the removal of the oxide, a rough, undercut surface having non-rectilinear tentacles is produced.

The scaling operation just referred to may be combined with a normalizing treatment, since both may be carried on as open or continuous heat treatments. By a normalizing treatment, we mean as understood in the art, heat-

ing the stock to a temperature above the A_3 point followed by a rapid cooling. A normalizing treatment may be combined with a decarburizing treatment by dividing a continuous furnace so as to permit the maintenance of different temperatures and different atmospheres in the divided parts. It will be noted that decarburization is preferably carried on at a temperature below that of normalizing. It is sometimes desirable to normalize in a non-oxidizing atmosphere to avoid the necessity of subsequent pickling.

A box annealing treatment may be carried on at varying temperatures, normally above 1200° F. but extending up to around 2000° F. if desired. The material may be treated in coils or in stacks of sheets in a box in which a non-oxidizing atmosphere is preferably maintained.

Various routings may be practiced within the scope of our invention. Thus, the following steps will produce a non-fish-scaling enameling stock:

Hot roll,
Hot coil, or anneal with slow cooling,
Pickle,
Cold roll at least 25% and preferably at least 50% without intermediate annealing,
Normalize,
Pickle.

As a variant of this procedure, an open anneal below the A_3 point or a decarburizing anneal or a box anneal may be substituted for the normalizing, or a box anneal may be used in addition to either an open anneal or a normalize for optimum drawing properties. The final pickling may be eliminated if a suitable protective atmosphere is used.

Routings incorporating decarburization and the preferred adhesion promoting treatment may take the following forms:

1.

Hot roll,
Hot coil or anneal with slow cooling,
Pickle,
Cold roll at least 25% and preferably at least 50% without intervening annealing,
Coat with nickel,
Normalize in a scaling atmosphere,
Pickle,
Decarburize.

2.

Hot roll,
Hot coil or anneal with slow cooling,
Pickle,
Cold roll at least 25% and preferably at least 50% without intervening annealing,
Normalize,
Pickle,
Coat with nickel,
Decarburize.
Scale anneal,
Pickle.

3.

Hot roll,
Hot coil or anneal with slow cooling,
Pickle,
Cold roll at least 25% and preferably at least 50% without intervening annealing,
Coat with nickel,
Decarburize.
Normalize in a sufficiently oxidizing atmosphere to produce the desired scale,
Pickle.

It may be stated that in carrying out the preferred surface treatment for adhesion, the amount of nickel deposited should be from substantially .02 to .2 gram per square foot, from .05 to .10 gram per square foot being preferred. Suitable oxidizing conditions for scaling are more difficult to define since these will vary with temperature, time and the nature of the atmosphere. However, the conditions employed should be no less oxidizing than an atmosphere of burned natural gas containing 11% combustibles based on dry gas analysis and having a dew point of 150° F., and the oxidation produced should not be substantially less than that produced in such an atmosphere in a furnace at temperatures of substantially 1400° to 2000° F. for a treatment time of substantially 2 to 5 minutes.

Modifications may be made in our invention without departing from the spirit of it. Having thus described our invention in certain exemplary embodiments, what we claim as new and desire to secure by Letters Patent is:

1. In a process of producing a ferrous enameling stock free from a tendency to produce fish-scaling in a fired-on coating of vitreous enamel, the steps of hot rolling to an intermediate gauge a ferrous enameling stock containing in the hot rolled condition at least substantially .02% carbon, causing said carbon in said stock to form massive carbides by slowing cooling said stock from a temperature above its A_1 point at a rate not more rapid than substantially 50° to 100° F. per hour while said stock contains at least substantially .02% carbon, cold rolling the stock containing the said massive carbides by a reduction of at least about 25% without intervening annealing, whereby to elongate and fragment and massive carbides, and subjecting the so-treated stock to a heat treatment.

2. The process claimed in claim 1, wherein the hot rolled stock is rapidly reheated to a temperature above its A_1 point and is then promptly cooled at a rate of not more than substantially 50° to 100° F. per hour.

3. The process claimed in claim 1, wherein the hot rolled stock is produced on a continuous hot mill, and wherein the stock is caused to issue from the said mill and is coiled while at a temperature of at least about 1300° F., whereby cooling of said stock is retarded so as to produce the said massive carbides.

4. The process claimed in claim 1, wherein the last mentioned heat treatment is a normalizing heat treatment.

5. The process claimed in claim 1, wherein the last mentioned heat treatment is a normalizing heat treatment, and wherein said stock is decarburized subsequent to cold rolling to bring its average carbon content to at most a value of about .010% whereby said stock is rendered free from primary boiling.

6. The process claimed in claim 1, wherein the last mentioned heat treatment is a normalizing heat treatment, wherein said stock is decarburized subsequent to cold rolling to bring its average carbon content to at most a value of about .010% whereby said stock is rendered free from primary boiling, and wherein the said cold reduced stock is given a surface treatment to promote the adhesion of vitreous enamel.

7. The process claimed in claim 1, wherein the hot rolled stock is produced on a continuous hot mill, wherein the stock is caused to issue from the said mill and is coiled while at a temperature of at least about 1300° F., whereby cooling of said stock is retarded so as to produce the said massive carbides, and wherein the cold reduced stock is subjected to a decarburization reducing the average carbon therein to a value at most about .010%, whereby the stock is rendered free from primary boiling.

8. The process claimed in claim 1, wherein the hot rolled stock is produced on a continuous hot mill, wherein the stock is caused to issue from the said mill and is coiled while at a temperature of at least about 1300° F., whereby cooling of said stock is retarded so as to produce the said massive carbides, wherein the cold reduced stock is subjected to a decarburization reducing the average carbon therein to a value at most about .010%, whereby

the stock is rendered free from primary boiling, and wherein said stock is subjected to a surface treatment promoting the adherence of vitreous enamel.

9. The process claimed in claim 1, wherein the hot rolled stock is produced on a continuous hot mill, wherein the stock is caused to issue from the said mill and is coiled while at a temperature of at least about 1300° F., whereby cooling of said stock is retarded so as to produce the said massive carbides, and wherein the cold reduced stock is subjected to a decarburization reducing the average carbon therein to a value at most about .010%, whereby the stock is rendered free from primary boiling, and wherein said stock is subjected to a surface treatment promoting the adherence of vitreous enamel, said surface treatment comprising the steps of imposing nickel on the surfaces of said stock, subjecting the said surfaces to a heat treatment under conditions oxidizing to iron whereby to form a scale thereon, and removing said scale by pickling.

10. A ferrous enameling sheet stock free of the tendency to fish-scale a fired-on coating of vitreous enamel, said stock having a surface condition produced by slowly cooling said stock from above its A_1 point at a time when it contains at least about .02% carbon whereby to form massive carbides therein, and by fragmenting and elongating said massive carbides by cold rolling said stock with a reduction of at least 25% without intervening annealing.

11. The product of claim 10, having in its final condition an average carbon content of at most about .010% carbon.

12. The product of claim 11, having a surface condition characterized by undercut irregularities and projecting, non-rectilinear tentacles.

13. The product of claim 10, bearing on its surface a single-fired coating of vitreous enamel.

14. The product of claim 11, bearing on its surface a single-fired coating of vitreous enamel.

15. The product of claim 12, bearing on its surface a single-fired coating of white or light colored vitreous enamel.

16. In a process of producing a ferrous enameling stock free from a tendency to produce fish-scaling in a fired-on coating of vitreous enamel, the steps of hot rolling to an intermediate gauge a ferrous enameling stock containing in the hot rolled condition substantially .025% to .08% carbon, causing the carbon in said stock to form massive carbides by slowly cooling said stock from a temperature above its A_1 point at a rate not greater than substantially 50° to 100° per hour while said stock contains at least substantially .02% carbon, cold rolling the stock containing the said massive carbides by a reduction of at least about 40% without intervening annealing, whereby to elongate and fragment said massive carbides, and subjecting the so-treated stock to a heat treatment.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,878,151 March 17, 1959

Francis W. Beall et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 19, for "hot", first occurrence, read -- short --; line 45, for

Manganese - - - - - - 0.8 to .15

read

Manganese - - - - - - .08 to .15

Signed and sealed this 14th day of July 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents