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ELIMINATION OF ENAMEL FISHSCALING IN IRON AND STEEL SHEETS

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This invention has to do with treatments for ferrous metallic sheets which will result in a product with a slight degree of porosity. This application is a continuation-in-part of the copending case in the name of the same inventor, entitled, Elimination of Fishscaling in Iron and Steel Sheets, filed March 29, 1962, as Serial No. 183,405, now abandoned.

A primary object of the invention is the provision of a simple and inexpensive treatment for ferrous sheets to be used in vitreous enameling, which sheets will be devoid of fishscaling. The invention is not limited to this field of utility, as a material having a slightly porous surface finds use in other fields, such as providing an improved base for the reception of metallic coatings. However, the following description will be directed to the production of articles which are to be coated with a single fired vitreous enamel.

Where a product is to be made with a first fired coating which is followed by another separately fired coating, it is generally possible not only to secure adequate adhesion by proper choice of the composition of the first fired coating, but also to produce a more acceptable product because many of the defects which may be encountered in the first coating are either masked by the second coating or are alleviated by fusion when the second coating is fired.

However, the present invention is useful in the field of products receiving more than one separately fired coating of vitreous enamel, since a product in which the first coat is without defects is a superior product, and also since fishscaling may occur even in a second coating. On the other hand, the production of single fired white or light colored enamel articles involves the necessary solution of three problems:

(1) The fired coating of enamel must have satisfactory adhesion to the base metal,

(2) The phenomenon of "primary boiling" must be obviated, and

(3) The phenomenon of fishscaling must also be prevented from occurring.

The first of these problems is generally adequately handled by careful techniques, by roughening the surfaces of the stock, and by proper selection of the formula for the frit which is to be fired to form the vitreous enamel layer.

The primary boiling of an enamel coating has been traced to carbon at the surfaces of the metal; and it is possible either to "fix" the carbon by the use of alloying ingredients, or to reduce the carbon on or in the surfaces of the stock by a decarburization treatment. Treatments which will provide a concurrent solution of problems 1 and 2 have been developed, and reference may be made to U.S. Patent No. 2,755,210, issued July 17, 1956, in the names of Sutphen et al.

The third problem manifests itself in the tendency of a coating of vitreous enamel to form "fishscales." As the vitreous material cools, it becomes friable and will tend to spall out and expose the base metal in small half-moon areas resembling fish scales. It is difficult if not impossible to predict the fishscaling tendencies of any given enameling stock, and since any fishscaling will ruin the ultimate product, it is vital to take steps to eliminate any fishscaling tendencies the stock may have.

Fishscaling is promoted in areas where the adherence of the enamel has been damaged by metal finishing operations such as grinding, or by scratches. Fishscaling generally occurs upon the initial cooling of the enamel coating, but in some instances its appearance may be delayed for a number of hours or days.

Basically, however, the phenomenon of fishscaling appears to be due to some characteristic of the metal base itself, and primarily to its surface condition. Beall et al. in U.S. Patent No. 2,878,151, issued March 17, 1959, found that fishscaling could be alleviated by a procedure which involved the formation of massive carbides in hot rolled stock, followed by cold reduction to elongate and fragment the massive carbides, presumably leaving the stock in a porous condition, after which the fragmented carbide inclusions were largely or completely removed by decarburization. According to one theory, the pores or voids in the stock provide a reservoir for hydrogen, which prevents fishscaling. The elimination of fishscaling by this method involves extra steps in a routing for enameling stock.

It is a primary object of this invention to provide a ferrous stock which has numerous small voids adjacent the surface.

It is an object of this invention to provide a way of eliminating enamel fishscaling which does not necessarily add extra steps to a normal routing.

It is an object of this invention to provide for the elimination of enamel fishscaling in a new, simple and inexpensive way.

It is an object of the invention to provide a treatment for the elimination of enamel fishscaling which does not interfere with the concurrent or simultaneous practice of other steps for the solution of others of the problems set forth above.

It is an object of the invention to provide a new and improved type of enameling stock devoid of the fishscaling difficulty, and more narrowly to provide a stock which is eminently suitable for the formation of single-fired white or light colored enameled products.

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, are accomplied by that procedure and in that article of which exemplary embodiments will now be set forth.

It has been discovered that a ferrous enameling stock which will be devoid of the fishscaling tendency can be attained in a single heat treatment by a control of the atmosphere of the furnace, and in particular by successive stages therein which are most conveniently called "nitriding" and "denitriding." Without intent to be bound by theory, it is believed that the basic result of the process steps hereinafter outlined is the provision of porosity adjacent the surface of the sheet stock, which porosity is of such character and extent as to be effective in the prevention of fishscaling.

There has hitherto been a practice of nitriding steel alloy articles to impart surface hardness to them. The alloys of which such articles are made usually contain about 1% aluminum, with or without chomium, molybdenum and other strong nitride formers; and articles produced from such alloys have hitherto been subjected to a heat treatment between about 950° F. and 1050° F. for about 48 hours in an atmosphere of ammonia for the purpose of producing on their surfaces a very hard "case" which will resist wear, the case usually having a thickness ranging from between .010" and .020". Also it has been suggested that steel stocks or articles be treated for the adsorption of minute quantities of nitrogen for special purposes.

The art has realized in theory at least that nitrogen could be removed from iron and steel stocks, as for

example, when it is desired to soften a case-hardened alloy article for further machining, as taught for example, in U.S. Patent No. 1,864,083.

However, prior art procedures such as those outlined above are not effective for the purposes of this invention and have not been attempted for the uses of this invention. There has been no recognition in the art or literature of the basic phenomena upon which the present invention is based.

In the practice of this invention, special alloys are not employed, but instead, ordinary irons or mild steels such as those hitherto in use for enameling purposes. Since the elimination of fishscaling is not here dependent upon the formation, fragmentation and subsequent removal of massive carbides, it is not necessary that the starting material have a relatively high carbon content. However, a stock may be used having a carbon content of the order of that of the auto body sheet stock of commerce which is about .03% to .08%, especially since decarburization may be practiced as later described.

The principles of the present invention are applicable to stocks which are either hot rolled or cold rolled, or reduced to gauge by a combination of hot rolling and cold rolling. The metal may be refined in any suitable way and by the use of any suitable melting and refining furnace including the open hearth, the electric furnace, or vessels in which the molten metal is blown with oxygen. In carefully controlled open hearth practice, a carbon content as low as about .025% is readily attained. With the exception of enough manganese to prevent hot shortness, as known in the art, alloying ingredients are not used. Any quantities of phosphorus, sulfur, silicon, nickel, molybdenum, copper or other alloying ingredients present or preferably within the range of ordinary impurities incident to the steel making process.

In view of the composition of the iron or steel in the practice of this invention, it will be evident that nitrides formed during the nitriding step hereinafter outlined will be essentially nitrides of iron. It is necessary that such nitrides be formed in sufficient quantity to effect a permanent distortion of the iron lattice at the surface of the sheet stock. Upon the subsequent decomposition of some or all of the nitride content and the removal of the evolved nitrogen, the surface of the stock will be left in the desired porous condition.

As distinguished from conventional nitriding treatments, the first stage of the heat treatment of this invention will be carried on within a temperature range of about 1200° F. to about 1500° F. (preferably in a range of about 1300° F. to about 1400° F.), for a period of about one hour in an atmosphere consisting of or containing ammonia. While in a furnace in which the stock can be handled in a single layer in the presence of streaming gas, and where times may be extended as desired, a relatively small percentage of ammonia in the annealing atmosphere may be used, such conditions are obtainable primarily in the laboratory. It has been ascertained that with rates of flow such as can be obtained in commercial furnaces, the desired effect can be produced within 15 minutes at the temperatures set forth by the use of an atmosphere consisting of ammonia. Where the atmosphere contained only about 50% ammonia, a treatment of 60 minutes was required at temperature. Where the atmosphere contained only 25% ammonia, a treatment at temperature for 120 minutes appeared to be marginal where the final effect was the elimination of fishscaling. It should be understood that the quantity of ammonia required for a given amount of nitriding is to all intents and purposes constant; but if any given heat treatment the flow rate of the atmosphere for a given quantity of base metal is increased, the percentage of ammonia in the atmosphere may be reduced.

It will be noted that the times involved preclude the use of an open or continuous heat treatment. Heat treatments in tightly wound coils or stacked sheets are not fully reliable since the furnace gases are likely not to have free access to the surfaces of the stock whether or not an annealing separator is used.

The best method presently available for the practice of the heat treatment is loose coil annealing. In coiling the stock, a strand is wound into the coil between convolutions. In some instances the strand will then be removed, leaving the coil convolutions in a separated condition. In an alternative and preferred procedure, a metal, wire-like separating strand may be wound into the coil and left between the convolutions during the annealing operation. The strand will be so configured as not only to separate the convolutions of the coil, but to provide adequate space for gas movement past the separating strand. A loose coil formed in either of these ways may be annealed in a muffle-type furnace, where the coil will normally be supported on end upon a foraminous means through which the furnace gases can pass. Some muffle furnaces are provided with a positive device for circulating the furnace atmosphere and directing it through the coil between the convolutions. Means are provided for the introduction and withdrawal of the atmosphere, and for changing the atmosphere within the muffle during the operation thereof.

The treatment of the stock in the way set forth will result in the formation of a "case" which can be seen under a microscope. However, unlike the case formed in conventional nitriding operations, the thickness of the surface skin in the practice of this invention is preferably very much less, namely, of the order of .001" to .002". It will be understood that satisfactory results can be attained with thicker cases, such for example as cases measuring .003" to .005", but this is unnecessary in most instances.

As previously indicated, nitriding steels, as hitherto known in the art, contain alloying substances, and the hardened surface or case consists of a tempered martensitic structure containing a fine dispersion of alloy nitrides. The stock employed in the practice of this invention is a low carbon rimmed steel which does not contain substantial proportions of nitride-forming alloying elements; and the case formed in the first step of the heat treatment of this invention consists primarily of iron nitrides. The case will contain substantially all of the nitrogen which has been absorbed during the first stage of the heat treatment since the times involved are not long enough to permit extensive diffusion. Thus the thickness of the case can be taken as an index of the extent of the nitriding.

It is difficult otherwise to indicate the extent of the nitriding required. The elimination of fishscaling can, however, be accomplished by treating the stock as above set forth and with the formation of a case varying from about .001" to .002" in thickness. The gauge of the stock itself has an unexplained effect upon the requirements for the elimination of fishscaling, heavier gauges being advantageously treated for the production of heavier cases. The case thickness preferably varies directly with the stock thickness. But within the range of the limits of case thickness set forth, fishscaling may be dependably prevented over the entire gamut of gauges normally used for ferrous sheet stock intended for vitreous enameling, and extending at least from about 12-gauge to about 26-gauge.

Where, during the first or nitriding step of the heat treatment, the atmosphere does not consist entirely of ammonia, it is preferable that the remainder of the atmosphere be hydrogen. Other non-oxidizing gases may be employed, such as cracked ammonia, argon, DX gas and similar mixtures; but it will generally be desirable to avoid a gas which has a carburizing effect at the temperatures involved.

Decarburization may be desired, and a low surface carbon content is of value in preventing primary boiling. Decarburization may be done in known ways at any

point in the processing of the stock, but is preferably accomplished during the first, second or both stages of the heat treatment described herein (at the temperatures and within the times set forth) by using a wet atmosphere, i.e. by so treating the ammonia or mixture of ammonia and other gases that the atmosphere will have a dew point of about 125°±25° F. By "decarburization" in the sense of this application is meant a reduction of the carbon content at least at the surfaces of the stock to such a value that primary boiling will not occur upon the application of a single fired coat of vitreous enamel. This is not necessarily a matter of total carbon content of the stock, since rimmed steels may often be enameled successfully when the carbon content of the actual surfaces is low, even though the stock as a whole may analyze .05% total carbon or more.

The next stage of the heat treatment is denitriding and is accomplished by heating the previously nitrided stock in a non-oxidizing gas which is devoid of ammonia or which is characterized by a partial pressure of nitrogen lower than the partial pressure of nitrogen in the steel itself. Again, the gaseous atmosphere is preferably hydrogen, although other non-oxidizing gases may be employed. It will be understood that diatomic nitrogen does not nitride the stock and may be contained as a diluent in the denitriding atmosphere. Ammonia, however, is a strong nitriding gas; and must be kept out of the denitriding atmosphere to as great an extent as possible. The hydrogen contained in the atmosphere will tend to combine with monatomic nitrogen from the stock to produce ammonia. Thus the movement of the denitriding atmosphere over the surfaces of the stock must be rapid enough to keep the quantity of ammonia very low; and the statement above concerning the partial pressure of nitrogen should be understood in this context.

Where the heat treatment is being conducted with the material in open coil form in a muffle furnace, as above described, the ammonia bearing atmosphere present in the muffle during the first stage will be swept out of it and replaced by the fresh gas which is substantially devoid of ammonia. The same temperature range given above for the nitriding stage can be employed during denitriding. While high temperatures may be used for the treatments of this invention, the A_3 critical temperature may be considered a maximum for the retention of optimum drawing properties.

To obtain the results of this invention, the denitriding should result in the decomposition of the greater part of the nitrides of iron present in the stock as the result of the first stage treatment. Some residue of nitrogen or nitrides in the stock is tolerable; but it has been ascertained that substantial quantities of nitrogen or nitrides in the stock will produce primary boiling. In this respect nitrides appear to act similarly to carbon and carbides. In other words, the product of this invention will preferably be free of any substantial quantity either of carbon or nitrogen after full treatment; and hence it will be free of the tendency toward primary boiling. But the treatment outlined herein, unlike a bare decarburization, is also effective in eliminating the tendency toward fishscaling.

The length of time required for denitriding is found to be substantially the same as that for nitriding at the same temperatures. The degree of nitriding will depend both upon the quantity of ammonia in the atmosphere and the time of treatment at temperature, i.e. the time duration of that phase of the heat treatment during which the ammonia content is maintained in the atmosphere. Similarly in the denitriding phase, the time duration of the treatment in a hydrogen bearing gas devoid of ammonia will vary with the extent of the nitriding, and the temperature. In general, for a heat treatment of minimum time duration, the quantity of ammonia for nitriding within the range given may vary inversely to the temperature,

while the denitriding time will also vary inversely to the temperature within the temperature range set forth.

It is likely that the degree of nitrogen pickup necessary will vary somewhat depending upon the fishscaling tendencies of the different stocks. It has been found that .12% nitrogen will be adequate to prevent difficulties in most common materials in the form of 20-gauge sheet stock. The density of iron is 7.87 grams per cubic centimeter as against densities of 6.34 and 6.57 respectively for the iron nitrides Fe_2N and Fe_4N. The density of a sample such as the 20-gauge sample referred to was measured before and after treatment. Comparing the product before nitriding with the product after nitriding (with a nitrogen pickup of .12%) and denitriding indicated a reduction in density amounting to .019 gram per cubic centimeter. This reinforces the theory that as a nitride particle forms in the iron, an expansion occurs producing a plastic deformation of the iron lattice surrounding the particle. When the particle is subsequently wholly or partially reduced to metallic iron during the denitriding step, the deformed lattice does not contract, and a void is produced. The voids are believed to be predominantly intergranular. They are frequently visible under the microscope, but this is not always so.

The tendency toward fishscaling will be found to be different in different sheet stocks having the same or approximately the same formulae. Consequently, the minimum change in density to eliminate fishscaling can be expected to vary. However, uniformly satisfactory results may be expected on enameling stocks treated within the limits above set forth, which is to say, nitrided in an atmosphere containing from about 50% to 100% ammonia at temperatures from about 1200° F. to 1500° F. for times varying from about 60 minutes to about 15 minutes (the time varying inversely to the percentage of ammonia in the atmosphere) and then denitrided at the same temperatures in a non-ammonia-bearing gas for substantially the same lengths of time, in open coil form in a muffle with normal gas flows of, say, 1800 c.f./hr. Higher rates of gas flow will permit either a reduction in treatment time or a reduction in the percentage of ammonia in the gas.

It will be seen that a complete denitriding may not in all instances be necessary for the formation of the desired voids, depending upon the extent of the original nitriding. For example, a 20-gauge material produced in accordance with this invention, and which exhibited no fishscaling when coated with a vitreous enamel frit and fired for 5 minutes at 1600° F. was, upon analysis, found to contain .066% nitrogen. However, iron nitrides, when present in sufficient quantity, are likely to cause primary boiling, as has been pointed out. Consequently, a reasonably thorough denitriding is prefrred; and the time of the denitriding stage may be prolonged to whatever extent is required to produce a stock which is not only non-fishscaling, but free of primary boiling also.

Adjustments may be made in time, temperature, atmosphere and rate of circulation as may be found desirable, and these are comprised within the intended practice of the invention. But while it would be possible to effect a given degree of nitriding in an atmosphere containing much less than the stated minimum of ammonia, this would take so long a time as to diminish seriously the commercial practicability of the process. In general, the process as herein taught can be carried on in a loose coil muffle with a total holding time at temperature of about two hours. Both the nitriding and the denitriding steps together can be accomplished within the time required for an adequate decarburization which might be six to ten hours in commercial practice. Where other annealing equipment, or a separate furnace for each stage, is used, the times can be varied, or the two stages can be separated in point of time with intervening cooling of the material.

The invention finds its greatest utility in the treatment of sheet stock made from rimmed iron or mild steel of

the composition set forth above. The ferrous metal is cast into ingots which may be bloomed into sheet bars and hot rolled to gauge in ways known in the art, or hot rolled to an intermediate gauge with or without cooling and reheating of the metal at slab thicknesses. It is possible to apply the invention to killed steels, but the nitriding treatment may have to be longer or more intensive in order to nitride the metallic aluminum in the steel before the formation of the described case.

Several exemplary routings are listed below for the production of enameling stock.

EXEMPLARY ROUTINGS

(1) Hot roll to final gauge	(3) Hot roll
Normalize	Pickle
Pickle	Cold roll
Nitride	Nitride
Denitride	Denitride
(2) Hot roll to final gauge	(4) Hot roll
Pickle	Pickle
Nitride	Cold roll
Denitride	Normalize
	Pickle
	Nitride
	Denitride

Decarburization may be practiced, if desired, at any suitable point in the routing, including the nitriding and denitriding stages of the heat treatment.

The routings set forth above are relatively simple routings and, as will be evident, are intended for a procedure in which the material is either hot rolled or cold rolled to a final gauge. The routings may be modified in various ways.

Irrespective of the manner in which the material is carried down to final gauge, various treatments for special purposes may be practiced. For example, some enameling stocks must be normalized, and a normalizing treatment may be included in the routing. As set forth in the Sutphen et al. patent noted above, the surfaces of the stock subsequent to the noted heat treatment may be coated with nickel, then heat treated in an oxidizing atmosphere to produce a scale, and then either pickled or annealed in a reducing atmosphere. In any instance where it is found desirable, a temper rolling involving a slight reduction may be added at the end of the routing without destroying the porosity. The effect of the porosity is not destroyed by the forming or drawing procedures to which enameling stocks are ordinarily subjected.

Example

The material used in this test was ordinary, low-carbon rimmed steel of 20-gauge. The stock had been reduced to gauge by the conventional combination of hot rolling and cold rolling, and it was annealed in a 50 pound charge in a simulated open coil furnace with a total gas flow of 2.7 c.f./hr. The annealing was done at 1300° F. in a gas consisting of 40% hydrogen, 60% nitrogen, and a water content sufficient to give a dew point of 120° F. The material annealed in this manner is representative of a full scale commercial anneal, and was found to be decarburized. However, when the material was coated with vitreous enamel in a single firing, severe fishscaling occurred.

Another portion of the same starting material was annealed in the same apparatus in an atmosphere consisting of 50% ammonia, 20% hydrogen and 30% nitrogen for one hour. After the first hour the ammonia was eliminated from the atmosphere, and the anneal was continued until the final carbon content reached .001%. Final portions of the anneal were carried out in an atmosphere consisting of 40% hydrogen, 60% nitrogen with a water content sufficient to give a dew point of 120° F. The total annealing time was about 4 hours in this test. It had been expected after the denitriding treatment that the nitrogen level would have been lowered to the value of normal residual nitrogen, which is about .003%. In the particular test, however, the denitriding was not as efficient as had been anticipated because water seals used with the furnace had become contaminated with ammonia. The denitrided stock was found to contain a total of .012% nitrogen. Nevertheless the stock enameled well and did not fishscale or show primary boiling.

This example is given as demonstrating the efficacy of nitriding and denitriding for the elimination of fishscaling despite a somewhat higher residual nitrogen value than is usual in furnace treatments of shorter duration wherein better control of the elimination of ammonia in the denitriding atmosphere results both in a lower residual nitrogen and in a shortening of the time cycle to a value of about two hours, or less.

Modifications may be made in the invention without departing from the spirit of it. The invention having been described in various exemplary embodiments, what is claimed as new and desired to be secured by Letters Patent is:

1. In a process of producing low carbon iron or mild steel enameling stock, the steps which consist in nitriding the stock in an ammonia containing annealing atmosphere to the extent of producing on the surfaces thereof a case consisting essentially of iron and iron nitrides and having a thickness not less than substantially .001", and then denitriding the stock in a hydrogen containing annealing atmosphere substantially devoid of ammonia, including the step of effecting continuous flow of the denitriding atmosphere over the surfaces of the stock so as to substantially remove ammonia produced by nitrogen from the stock combining with hydrogen in the annealing atmosphere, whereby to produce a stock characterized by porosity, which stock is substantially devoid of vitreous enamel fishscaling tendency.

2. In a process of producing low carbon iron or mild steel enameling stock, the steps which consist in first heat treating the final gauge stock to a temperature of substantially 1200° F. to substantially 1500° F., first in an annealing atmosphere non-oxidizing to iron, and containing from substantially 50% to substantially 100% ammonia whereby to nitride the stock, and second in a hydrogen bearing annealing atmosphere substantially devoid of ammonia, including the step of maintaining the partial pressure of nitrogen in the last named atmosphere normally lower than the partial pressure of nitrogen in the stock, whereby to denitride the stock, the final product being a low carbon ferrous material devoid of primary boiling and fishscaling tendencies when coated with vitreous enamel.

3. The process claimed in claim 2 in which at least one of said atmospheres contains nitrogen in diatomic form.

4. The process claimed in claim 3 wherein the times of treatment at temperature in each of the first and second steps is about one hour.

5. The process claimed in claim 3 wherein the times of treatment at temperature in the first and second steps vary from substantially 15 minutes to substantially one hour, the quantity of ammonia in the first step varying inversely with the time at temperature.

6. The process of making ferrous sheet stock for enameling which comprises reducing a low carbon mild steel to finished sheet gauge, and subjecting the said stock in loose coil form to a heat treatment at a temperature of substantially 1300° F. to 1400° F. in an annealing atmosphere which during a first phase of the heat treatment is an atmosphere non-oxidizing to iron, containing from substantially 50% to substantially 100% ammonia and having a dew point of substantially 125°±25°, and in which a second phase of the heat treatment is a hydrogen bearing atmosphere substantially devoid of ammonia in which the partial pressure of nitrogen in the last named atmosphere is normally maintained lower than the partial pressure of nitrogen in the stock.

7. The process claimed in claim 6 wherein the said heat treatment is carried on in a muffle furnace in which the atmosphere is changed intermediate the first and second phases.

8. The process claimed in claim 7 wherein the time duration of each of the first and second heat treatments is substantially one hour.

9. The process claimed in claim 7 wherein the time duration of the first heat treatment is from substantially 15 minutes to substantially one hour, and in which the time duration of the second phase is at least 15 minutes and long enough to reduce the nitrogen content of the stock to an extent to eliminate primary boiling resulting from residual nitrogen in the stock.

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