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PREPARING METAL FOR ENAMELING

George W. McGohan, Middletown, Ohio, assign-
or to The American Rolling Mill Company,
Middletown, Ohio, a corporation of Ohio

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6 Claims. (Cl. 148—7)

This is a continuation of my application of the same title, Serial No. 675,645, filed June 13, 1933.

My invention relates to providing an initial coating of metallic substance, comprising an adhesion promoting metal, preferably nickel, on iron and steel, and more particularly on sheet metal, so as to prepare it for enameling as with vitreous enamel.

Among other things, my invention provides a method of forming in the surface elements of a sheet or other piece of metal an extremely small thickness of coating which greatly assists in promoting adhesion of a subsequently applied coating of vitreous enamel. My method has the advantage of being subject to accurate control, and is admirably adapted to use at the rolling mill where the iron or steel sheets are prepared.

Sheets which are very low in carbon are recognized as the best for vitreous enameling, and while my method can be applied to steel of higher carbon content, the very low carbon is the best. Also, although my coating is productive of a most excellent bond of a first coat of enamel even on a cold rolled high finish sheet, still if applied to a sheet which has been sand blasted or is roughened in some other way, it will be easier to build up a first coat of desired thickness thereon prior to firing (of enamel).

While my method can be divided into parts so that the final step may be carried out at the plant of the enameler, yet, one of the desirable features of my invention is that it is excellently adapted to being performed entirely at the rolling mill plant, since the surface effect is not interfered with by the pickling applied by the enameler for cleaning his metal prior to applying the first coat of enamel.

My method has the further advantage of permitting the formation of the desired surface coating at various stages in the process of manufacturing the sheets themselves. Thus it is possible to form the surface on sheet bars, or the more modern thin bar or rough plate, used as starting pieces in hot or cold reduction processes. Much handling can be saved in this way; and I have found that the surface effect will persist through the subsequent reductions, giving ultimately sheets which may be pickled and handled in the usual way. I am able thus to allocate the coating operation to any convenient point in the processing sequence, and in particular to arrange to employ such heating step or steps as form a part of the reduction process.

One principle on which my invention is based is my discovery that if a piece of iron or steel

is coated with a solution of a nickel salt, or the salt of some other metal which promotes adhesion in vitreous enameling, and heated high enough to convert the coating to a layer of the metal itself, or at least to a decomposable form which will yield the metal itself, in subsequent processing steps it will yield an adherent and fixed coating which is believed to be formed of the adhesion promoting metal alloyed with the base metal. Another principle on which my invention is based is my discovery that my coating of nickel alloy or the like is persistent through the ordinary reduction processes.

I shall first describe my invention as a treatment applied to finished sheets, taking up hereinafter the other aspects of my invention.

Thus, I may take an iron sheet and dip it in a solution of about 3 to 5% nickel sulphate, and then dry the sheet and raise it to a temperature of around 700° Fahr. or greater, with the result of forming on the sheet a very thin coating of nickel, nickel iron alloy or at least of some nickel compound.

By subsequently pickling the sheet in a sulphuric acid pickling bath of usual iron and steel pickling concentration, I find that the nickel iron alloy is unaffected and/or any decomposable nickel compound is reduced, and/or, if reduction has already taken place, other undesirable reaction products are removed, as will hereinafter be explained.

I have produced my product by dipping sheets in a 5% solution of nickel sulphate, then drying and heating at around 1150° Fahr. I have also attained the desired results by normalizing at 1800° Fahr. after dipping but without necessity of drying, since the sheets are normalized individually and dry in the furnace. A neutral or slightly reducing atmosphere seems to be desirable during the heating, and a highly oxidizing flame is to be avoided, for reasons hereinafter made clear.

In my process I prefer to avoid plating out of any nickel from my original solution, because then I do not have to keep adding nickel salt to keep up the desired concentration, and all deposited films of the nickel salt are substantially uniform. Moreover, a coating formed in my procedure differs in important respects from a plated coating of nickel, electrically or chemically deposited.

I may apply the sulphate solution to a hot-rolled sheet prior to pickling and only pickle the product once after the annealing. The thin scale does not seem to interfere with the treatment re-

sulting in the formation of metallic nickel alloy on the surface of the sheet. I prefer, however, to pickle and remove the scale by washing the bars or other material from which the sheets are rolled and then proceed to the dipping in nickel sulphate solution prior to final rolling.

It will be clear that the heating step is an essential part of the process, for the purpose of decomposing the nickel salt. Not only would a coating of nickel salt as such, i. e., without the heating step, be lacking in ultimate adhesion, but it would be highly undesirable in the enameling step because of the setting-up effect of the nickel salt upon the enamel itself. When the pieces are heated in an atmosphere which is not highly oxidizing, and particularly in neutral or reducing atmospheres, a relatively strongly adherent coating is produced. I do not desire to be bound by theory; but I am led by my results to believe that unless the atmosphere of the furnace is extremely oxidizing, a chemical reaction occurs between a nickel compound at some stage and the iron itself, involving a reduction of one or more nickel compounds to metallic nickel, which alloys or otherwise is joined to the surface of the iron. I have reason to believe therefore, that a thin nickel iron alloy layer is formed at the surface, together with the production of considerable quantities of iron oxide and iron sulphide, instead of a nickel oxide layer. This conclusion appears to be supported by the following experimental evidence: A thin oxide layer formed by heating the treated iron piece to scaling temperature, as may be done during heating for rolling, or during annealing, appears to consist essentially entirely of iron oxide with very little, if any, nickel oxide. Too, it is impossible by scrubbing or the like to remove any appreciable proportions of the nickel. Sand-blasting of the sheet surface fails to remove the nickel, while grinding with abrasion wheels does remove it. While I therefore believe that a true nickel-iron alloy is produced, yet where I use the term "alloy" I desire to be understood as referring to the result produced by following my process, irrespective of the correctness of the theoretical explanation which I have advanced.

An ultimate pickling step is of importance, not only to possibly effect the reduction of any nickel compounds which persist but also to remove the iron sulphide produced as I have indicated above, and to clean the sheet. It is to be noted, however, that this pickling need not immediately follow the heat treatment, but may be any pickling which is incident to the process of producing sheets at the rolling mill, or may even be, as I have indicated above, the usual pickling applied to the sheets by the enameler.

I have discovered as indicated, that coatings of nickel or the like may be produced on pieces for rolling, such as sheet bars, rough plate or thin bars, by the steps of coating with the salt of the coating metal, followed by a heat treatment, with or without a pickling, and that such coatings will be persistent throughout subsequent sheet reducing operations.

For example, in following a hot reduction method, thin bars, produced as usual on the roughing mill, are preferably pickled to obtain a clean surface which will be easily wet. The pickled thin bars are then wetted with a nickel solution, preferably by running them between rag rolls soaked with the solution, whereupon they may or may not be dried. They are then heated for hot reduction of thickness in the usual manner and are processed according to the ordinary

methods used for producing sheets by the hot reduction method. Since the production of the thin bar on the roughing mill and the following pickling operation are usual practices, the application of the nickel solution to the bar is the only additional operation necessary to produce nickel treated sheets. The drying and formation of the nickel alloy in the upper surface elements of the thin bar may be accomplished by the usual pre-heating for hot rolling, and involves no extra operation. The coating machine may conveniently be located in the production line. Ordinarily, finished sheets will be given an annealing. It has been pointed out above that in so far as a heat treatment results in scaling, the scale will be found to consist almost entirely of iron. Consequently, the usual annealing treatment is not destructive of my coating. The annealing is usually followed by a pickling, and the effects of this pickling have been outlined above.

In the exemplary cold reduction method, pickled thin bars are coated as described, and then are heated in a furnace at approximately 1000 to 1500° Fahr., which forms the nickel alloy on the surface of the bars. The bars are afterward cooled and reduced to sheets by cold rolling methods as usually practiced in the art. In this exemplary process the heating of the thin bars is, of course, an extra operation, but is necessary for reasons which will be clear from the foregoing explanation. The heating at approximately 1000 to 1500° Fahr. forms a thin gray-blue oxide on the sheets, which is very tightly adhering. The heating forms the nickel alloy in the surface elements of the sheet or bar so that it is not removed during the cold reduction. The scale which I have just described, does not appear to have any detrimental effect upon the rolls in the cold mills, and it has the advantage of providing an ultimate pickled sheet the surfaces of which are alloyed with nickel and are also slightly roughened. This likewise promotes adhesion of the enamel.

It has been found by experience that the optimum concentration of nickel sulphate is approximately 55 to 60 grams of nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) per 100 cc. of solution, applied to rolling pieces of twice the final thickness.

It will be understood, in these specifications, where I employ such terms as nickel coating, decomposable substance, oxide layer, nickel-iron alloy, etc., that I do not use these expressions in a limiting sense, but desire them to be understood, in the light of the explanations which I have given hereinabove, as referring to such coatings as produce the surface effect resulting from the teachings set forth in these specifications.

The nickel-iron alloy is in a very thin layer. My work would indicate that if less than .02 gram of nickel per square foot of surface of finished sheet is deposited, the best adhesion is not obtained. The desirable thickness of nickel deposit according to my investigation is between .03 and .10 gram per square foot of surface as determined by chemical analysis. It can be regulated by controlling the concentration of nickel sulphate solution in which the sheet is initially dipped. A suitable dried film of nickel sulphate weighing from .14 gram per square foot to .46 gram per square foot of surface, will serve the purpose; but my invention is not limited by these figures. I have, for example, secured excellent results by treating thin bar with the concentration of nickel solution given above, so as to produce a bar having .07 to .10 gram of metallic

nickel per square foot of bar surface, by analysis. This will give from .03 to .05 gram of metallic nickel per square foot of sheet surface on the finished sheets, after rolling, with an average of 50% reduction of the bar. By the term "sheet surface" is meant a thickness in the order of .0002 to .0005 inch thick.

So far as I have been able to determine, any type of annealing of the metal sheet will serve as the heat treatment necessary to decompose the salt originally deposited on the sheet.

A cobalt flashing can be applied by following my method, also other salts than the sulphate salt of adhesion promoting metals can be used but I preferably employ nickel sulphate because it is quite inexpensive.

It is practical, instead of giving a pickle to the heat-treated product directly, to ship the product with the resulting film upon it, and have the enameler pickle it.

The product in sheet form may be shipped to the enameler and by him formed into shape, followed by the usual pickling and cleaning methods, without interfering with the effectiveness of the coating.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent, is:—

1. A process of preparing iron or steel for vitreous enameling which consists in coating the metal with a heat decomposable salt of an adherence enhancing metal, heating the metal to decompose the salt and form a thin coating of the adherence enhancing metal alloyed with the iron or steel and acid treating the product, said metal being nickel.

2. A process for the purpose described which comprises coating iron or steel pieces with a sulphate salt of an adhesion promoting metal for enameling work, decomposing said salt on the surface of said pieces by a heat treatment whereby in part at least, an alloy of iron and the adhesion promoting metal is produced, together

with a compound of iron and sulphur, and afterward pickling said pieces sufficiently at least to decompose said compound of iron and sulphur.

3. A process of preparing iron or steel for vitreous enameling, which comprises dipping iron or steel pieces in a water solution of a heat decomposable salt of an adherence enhancing metal chosen from a group consisting of cobalt and nickel, and drying and heating the metal to decompose the salt and form a thin coating of the adherence enhancing metal alloyed with the iron or steel, afterward acid treating said pieces.

4. A process of preparing iron or steel for vitreous enameling which comprises coating iron or steel pieces with a water solution of a sulphate salt of an adherence enhancing metal chosen from a group consisting of cobalt and nickel, drying and heating the metal to decompose the salt and to form a thin coating of the adherence enhancing metal alloyed with the iron or steel, the concentration of the solution being such as to result in a final coating after full treatment of more than .02 gram and less than around .14 gram of the adherence enhancing metal per square foot of the surface of the pieces, and afterward acid treating the pieces.

5. A process as claimed in claim 3 including also the step of reducing said pieces by rolling after the formation of the alloyed coating thereon.

6. A process for the purpose described which comprises coating iron or steel pieces with a sulphate salt of an adhesion promoting metal for enameling work, decomposing said salt on the surface of said pieces by a heat treatment whereby in part at least, an alloy of iron and the adhesion promoting metal is produced, together with a compound of iron and sulphur, afterward reducing said pieces by rolling and finally pickling said pieces sufficiently at least to decompose said compound of iron and sulphur.

GEORGE W. MCGOHAN.