

UNITED STATES PATENT OFFICE

2,276,101

ART OF TREATING AND COATING METALS

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No Drawing. Application February 16, 1939,
Serial No. 256,724

3 Claims. (Cl. 91-70.3)

This invention relates to improvements in the art of treating and coating metals.

The principal object of this invention relates to a method for producing heavy malleable zinc coatings on iron or steel articles such as sheets, strip, rods, wire, and the like, and has special reference to the application of heavy malleable zinc coatings to light gauge sheets, to hot rolled or cold-reduced strip, and to rods and wire.

This invention also relates to the cleaning and annealing of ferrous and other metallic articles with special reference to strip, sheets, rods, and wire, prior to a zinc or other metallic coating process, where the cleaning and annealing are preferably carried out simultaneously.

A further object of this invention is the treatment of ferrous and other metallic articles, prior to the application of a non-metallic coating such as paint, lacquer, varnish, or enamel.

At the present time, so far as I am aware, there is no known commercially available process for applying heavy malleable coatings of zinc to light gauge iron or steel sheets, say sheets lighter than 24 gauge (nominal .0239 inch thickness) where said zinc coating is required to withstand deformation or fabrication. With the heavier gauge sheets, say gauge 20 (nominal thickness .0359 inch) and heavier, it is possible to sand blast, or grit blast, the sheets, so that reasonably heavy coatings may be applied thereto which will not crack or peel from the sheet under most fabricating conditions. The blasting process, however, does not allow the production of bright smooth coatings, and is not suitable, or satisfactory, for use with lighter gauge sheets. Furthermore, the annealing of iron or steel sheets by the usual process requires several days, although in some instances, a faster heating method is used, which permits the formation of a heavy scale on the sheets. After pickling to remove this heavy scale, a better adherence of the heavier coatings is obtained than when normal annealing and pickling is used. This, and other methods are only makeshifts, far from satisfactory, and have little or no value for use with light gauge sheets.

The bulk of galvanized sheets used for building purposes and for farm use, such as poultry equipment, machinery equipment, tanks, and the like, is under 24 gauge in thickness. Heretofore, it has been practically impossible to consistently coat these sheets with a heavy coating of zinc, say on the order of 1.50 ounces of zinc per square foot of sheet surface on a 28 gauge (nominal thickness .0147 inch) sheet, which would with-

stand more than the most simple fabrication or forming after coating.

I have discovered that when a sheet is immersed in a molten bath comprising borax and fluorspar, especially in the proportion of 90 percent borax and 10 percent fluorspar, (such as described in an application filed of even date herewith) kept at a suitable annealing temperature, say around 1450 degrees Fahrenheit, that not only will the scale be removed from the surface of the sheet in approximately two and one-half (2½) to three (3) minutes (or the time required for annealing) but it will also act on the surface of the sheet so that after the sheet is removed from the bath and the adhering bath material is removed from the sheet, a zinc coating applied to the sheet will firmly adhere thereto and the coated sheet may be fabricated or deformed severely without damage to the coating. The higher the temperature used the less the time required within reasonable limits for the annealing and cleaning action to take place. The borax used may be a commercial grade, and the fluorspar may be a commercial open hearth grade containing about 85 percent calcium fluoride.

Using the method described above, I have coated sheets of 28 gauge with coatings as high as 2.75 ounces of zinc per square foot of sheet surface, and said coated sheet could be bent flat upon itself without flaking or peeling of the zinc coating. I have also subjected 26 gauge (nominal thickness .0179 inch) and 28 gauge sheets, having from 2.08 to 2.66 ounces of zinc per square foot of sheet surface, to severe deep drawing operations with no damage whatever to the coating.

I have also subjected sheets of 24, 26, and 28 gauge respectively having heavy zinc coatings applied by my process, to severe deformation in roll forming machines without damage to the coating whereas 1.50 ounce coatings applied by the usual hot galvanizing process peeled badly from the sheets of the same respective gauges when subjected to the same forming operation.

It is known that molten borax will absorb iron oxide. I have found that if a ferrous sheet having iron oxide scale thereon is immersed in a bath of molten borax and held at a temperature of 1450 degrees Fahrenheit, it will take approximately twenty minutes to completely remove the scale. Furthermore, after the sheet is removed from the molten borax and the adhering borax is allowed to solidify, it is very difficult to remove the borax coating from the sheet without the aid of a solution of some kind such, for example, as hot water, or a dilute acid.

I have discovered that the use of fluorspar with the borax accelerates the action of the borax in the scale removal to such an extent that the time of action described above is reduced from approximately 20 minutes to a period not exceeding three (3) minutes. Less time is required if the sheet is heated and immersed in the molten bath while still in the heated condition. Furthermore, and what is highly important, the film of bath material which adheres to and covers the sheet upon removal therefrom can be very easily detached from the sheet by mechanical manipulation without resorting to the use of solution means of any kind. I say this is highly important because it allows the re-use of the bath material which, after removal from the sheet, can be returned directly to the bath and used over and over again, or, if desirable, the removed bath material may be remelted in a separate container and returned to the bath in a molten condition. I mean by "direct re-use" that the bath material removed from the sheet may be recovered and directly re-used without an intermediate refining operation. This re-use factor, together with the accelerated action produced by the fluorspar makes it commercially possible to use this bath material on a competitive basis with the commonly used two step cleaning and annealing methods.

It is obvious, of course, that as more and more sheets are immersed in the bath, the latter will gradually increase in iron oxide content. I have found that this is not detrimental until the amount of iron oxide reaches about 15 percent. Then, fresh borax-fluorspar material is added to the bath in order to bring this oxide content down.

I have tried various proportions of borax and fluorspar ranging from 95 percent borax and 5 percent fluorspar, to 95 percent fluorspar and 5 percent borax, but the proportion of 90 percent borax and 10 percent fluorspar seems to give the best results. Just what reaction takes place in the molten bath, and just why the fluorspar should act as an accelerator, I do not know; but I do know that the results such as are described above are readily accomplished. Furthermore, I have found that the bath is stable at the high temperatures used for annealing or heat-treating ferrous articles. I have also tried cryolite with the borax but this does not give as good results as does the fluorspar. A bath comprising 70 percent boric acid and 30 percent sodium carbonate gives good results, but I do not consider this combination as good as that of borax and fluorspar.

The molten coating bath which adheres to and covers the steel surface after removal therefrom protects the surface from further oxidation during the cooling cycle. Occasionally, it may happen that due to handling, or for some other reason, some of the hardened coating material may crack off the sheet before it has cooled below the oxidation point of the steel and so permit a part of the sheet surface to again become oxidized. I have found that in such a case, immersing the sheet for three (3) or four (4) minutes in a three (3) percent cold muriatic acid solution will completely remove the oxide without affecting the surface of the sheet so far as the adherence of the zinc coating to be applied thereafter is concerned.

Another advantage of the borax-fluorspar bath is that it lends itself for use either continuous or intermittent coating operations. This means,

for example, that strip in continuous lengths may be passed through the molten borax-fluorspar, and the bath material adhering to and covering the strip after removal from the bath allowed to cool thereon, following which, the strip passes through mechanical means, such, for example, as rollers, to break off the hardened bath material, passing the strip into a molten zinc coating bath, and cooling the coated strip, all of this being carried out as a continuous operation. The coated strip may be coiled or cut into suitable sizes and stacked. A similar process may also be used for rods and wire. In a similar manner, detached sheets may be annealed, cleaned, and coated in continuous sequence as described above, or, the sheets may be annealed, cleaned, and coated in a step by step, or intermittent process.

In the event that strip or wire, or any article lending itself to a continuous process, is being coated with zinc, said strip or wire may be first heated and while in a heated condition passed into the molten cleaning and annealing bath. After leaving the bath with the strip or wire having their respective surfaces covered with a film of bath material, the latter is allowed to cool to a temperature not below that of the subsequent zinc coating bath, removed from the strip or wire and the latter then coated with zinc in the usual manner. If desirable, the coating may then be treated by the trade name processes well known to those skilled in the art, as Galvannealed or Flame Sealed processes. Obviously modifications of the heating steps described above may be used.

I am aware that molten bath materials have been used for cleaning and annealing various articles prior to coating but, so far as I know, none of these has been used for preparing the surface of the sheet to permit the application of heavy flexible and malleable zinc coatings. Furthermore, molten baths heretofore used have had a number of disadvantages, such as the length of time required to effect the operations; the difficulty of removal of the bath material from the treated sheet; the inability to re-use the bath material repeatedly because of the necessity for dissolving the material from the ferrous surface, which necessitates the use of an intermediate recovery process; the volatility of the bath material; cost of raw materials; and the inability of the bath to act on the ferrous surface so that heavy malleable and flexible coatings of zinc may be applied thereto. All of these disadvantages have been overcome by the present invention.

It is obvious to those skilled in the art, that coatings other than zinc may be applied to the ferrous surface such, for example, as tin, aluminum or other metals, and that the annealing and cleaning may be used in conjunction with electro-plating processes, for the application of metals such as zinc, tin, copper, nickel, chromium, and the like. Furthermore, treatment in the borax-fluorspar molten bath leaves the surface of the sheets, or other ferrous metals, in excellent condition for the application of adherent coatings of paint, varnish, enamel, or lacquer, or to be otherwise decorated.

The examples and descriptions given herein are for illustrative and explanatory purposes and are not intended as limitations as to weights of coating, gauges of sheets, analyses or grades of materials used, or procedure followed.

What I claim is:

1. The method of applying coatings to metallic articles which comprises subjecting said articles

to a molten annealing and cleaning bath, removing said articles from said bath with a portion of said bath material covering said articles, allowing said covering material to solidify without reducing the temperature of the article below the temperature of a subsequent molten metallic coating bath, mechanically removing said solidified material from said articles for direct re-use of same in said annealing and cleaning bath and then coating said articles in the molten metallic coating bath.

2. The method of applying coatings to metallic articles, which comprises subjecting said articles to a molten annealing and cleaning bath comprising borax and fluorspar in the proportions, substantially 90 per cent borax and 10 per cent fluorspar, removing said articles from said bath with a portion of said bath material covering said articles, allowing said covering material to solidify without reducing the temperature of the article below the temperature of a subsequent molten metallic coating bath, me-

chanically removing said solidified material from said articles for direct re-use of same in said annealing and cleaning bath, and then coating said articles in the molten metallic coating bath.

5 3. The method of applying coatings to metallic articles, which comprises subjecting said articles to a molten annealing and cleaning bath comprising borax, fluorspar and iron oxide, replenishing the bath with borax and fluorspar as the iron oxide increases so that the proportions of iron oxide will not exceed 15 per cent of the total, removing said articles from said bath with a portion of said bath material covering said articles, allowing said covering material to solidify without reducing the temperature of the article below the temperature of a subsequent molten metallic coating bath, mechanically removing said solidified material from said articles for direct re-use of same in said annealing and cleaning bath and then coating said articles in the molten metallic coating bath.

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