METHOD OF ELECTROLYTIC TINNING SHEET STEEL

12 Claims, 1 Drawing Fig.

ABSTRACT: A method of electrolytic tinning sheet steel in which a sheet of steel is subjected to degreasing in an alkaline bath, pickling in an acid bath in which the sheet steel is polarized as the cathode, preliminary coating with metal, tinning in an acid bath and treating to obtain the fusion and cooling of the tin deposited on the sheet. The method makes it possible to produce tinplate that has a layer of FeSn₂ which is continuous by virtue of very dense seeding and which thus has improved corrosion resistance.
The present invention relates to a method of electrolytically tin-plating sheet steel, whereby tin-plated sheet steel of improved corrosion resistance can be produced.

One proposed method of electrolytically tin plating comprises the steps of electrolytically degreasing the sheet steel in an alkaline bath; rinsing the sheet material in water and then electrolytically pickling it in an acid bath, first cathodically and then anodically; rinsing the sheet material in water again and then subjecting the scaled and soaked material to preliminary tinning in an alkaline bath; rinsing the pretinned sheet and then putting it into an acid-tinning bath; and finally subjecting the tinned sheet to treatment for fusing and cooling the deposited tin.

This proposed method necessitates careful rinsing between pickling, pretinning and rinsing, not only to avoid neutralizing one bath by carry over from another, but also to avoid the precipitation of tin compounds in the acid-tinning bath, these tin compounds arising from alkaline stannates carried by the sheet when it leaves the pretinning section. This method also entails modifying the existing tinning installation by the provision of extra vats for the alkaline pretinning, which makes the conversion of existing plant costly.

It is known that the corrosion resistance of tin plate depends mainly on the continuity of the layer of crystalline FeSn$_x$Al$_{1-x}$ formed between the steel sheet and the coating of tin during the fusion of the deposited tin. This continuity of the crystalline layer depends on the surface condition of the steel/tin interface, this surface condition determining the density and growth of the FeSn$_x$Al$_{1-x}$grains.

The present invention at least partially eliminates the drawbacks mentioned above, one object thereof being to provide a method of electrolytic tinning whereby a sheet of steel is subjected to degreasing in an alkaline bath; pickling in an acid bath; in-situ coating of steel is polarized as the cathode, preliminary coating with metal, tinning in an acid bath and treating to obtain the fusion and cooling of the tin on the sheet. This method makes it possible to produce tinplate that has a layer of FeSn$_x$ which is continuous by virtue of dense sealing and which thus has improved corrosion resistance, while enabling certain steps in the process to be simplified.

A method of electrolytic tinning in accordance with the invention is characterized by the fact that the metallic precoating of the sheet material is carried out in the form of an acid pickling bath containing bivalent metal ions, the concentration of which is low in relation to that of hydrogen ions.

Hence, the previously degreased sheeting, when rendered cathodic in relation to two parallel counterelectrodes of which it constitutes the plane of symmetry, becomes the seat of abundant evolution of hydrogen and a slight adherent deposit of metal. The hydrogen liberated reduces the oxides and mechanically removes impurities from the surface of the sheeting, while the slight deposit of metal preserves it from any subsequent contamination.

Since the electrodeposition pickling bath is substituted directly for the conventional pickling bath, the operations of pickling and precoating can take place in one and the same working vat. However, the electrodeposition pickling may be preceded by conventional pickling when the strip is particularly heavily oxidized.

By means of the invention, an extremely thin initial coating of adherent metal can be deposited in the pickling bath on the steel sheet as soon as this is clean. This coating or deposit then protects the steel/tin interface from any contamination likely to occur between emergence from the electrodeposition pickling bath and entry into the first tinning bath proper. Despite the abundant evolution of hydrogen, the slight deposit of metal resulting from the electrodeposition pickling is not spongy, as might have been expected, but adherent and uniform.

Further features will become apparent from the following description of various ways of putting the invention into practice from the accompanying drawings, in which:

FIG. 1 is a micrograph of the alloy coating of tinplate obtained by the conventional method;

FIG. 2 is a micrograph of the alloy coating on tinplate obtained by a method in accordance with the invention, employing a stage of tinning and pickling in an acid medium;

FIG. 3 is a micrograph of the alloy coating on tinplate obtained by a method in accordance with the invention, employing a stage of cathode nickel plating and pickling in an acid medium; and

FIG. 4 is a micrograph of the alloy coating on tinplate obtained by a method in accordance with the invention, employing a stage of cathode tinning, nickel plating and pickling in an acid medium.

All these micrographs are enlarged 16,000 times.

A method of electrolytic tinning in accordance with the invention should preferably comprise the following steps:

A steel strip or sheet is first subjected to conventional degreasing; then, after drying and rinsing in water, the degreased sheet is put into an acid electrodeposition pickling bath consisting of an aqueous solution of acid containing bivalent metal ions (tin or nickel, alone or mixed, these metals preferably being used in the form of bivalent ions). The sheet is polarized as the cathode, the anode consisting of a material possessing good resistance to anodic dissolution.

Having undergone the treatment of electrodeposition pickling (pickling and precoating with metal), the sheet is dried and rinsed in water before being put into the tinning bath or baths, in which it receives an additional coating of tin by conventional electrodeposition. The tinned sheet is then subjected to a treatment for fusing the tin coating in the usual way, for example, Joule effect, induction, radiation and so forth, and is then cooled with water. This procedure is economical and does not necessitate technical alterations to existing plant, the electrodeposition pickling taking place in the section provided for the conventional pickling. When the constituents of the electrodeposition pickling baths are chemically compatible with those of the tinning bath that follows the electrodeposition pickling, the rinsing stage between the electrodeposition pickling and the conventional tinning can be reduced to the strict minimum or even dispensed with altogether.

The electrodeposition pickling bath may have an acidity of 10 to 200 gram equivalents of sulfuric acid per liter of bath.

This means that the electrodeposition pickling bath may be made with sulfuric acid or some acid other than sulfuric or from a mixture of acids from which sulfuric acid may be absent.

The content of bivalent metal or metals in the electrodeposition pickling bath may range from 0.1 to 300 grams per liter of bath. Within the limits just quoted, however, it is important not to associate any random concentration of acid with any random concentration of metal. To obtain effective electrodeposition pickling leaving an adherent homogeneous deposit of metal, it is important that the concentration of hydrogen ions should be high-enough, in relation to the concentration of metal ions, to ensure that the cathode current output in deposited metal is low, being less than 50 percent and preferably between 5 percent and 25 percent.

There is thus always an abundant evolution of hydrogen on the cathode-polarized sheet metal, and this evolution contributes essentially to the elimination of oxides on the faces of the sheeting.

In this method, the metal coating forms on the steel sheet or strip as soon as the steel has been stripped by reduction. There is therefore no risk of oxidation of the sheet, which, once it emerges from the electrodeposition pickling bath, can no longer oxidize during the subsequent rinsing in an atmospheric medium, because it is already protected by a very thin coating of metal.

To illustrate the present invention, tinning pickling, nickel-plating pickling and tinning and nickel-plating pickling are described hereunder in greater detail. No limitation on the scope of the invention is implied by these examples.
The tinning pickling bath is an acid bath made with sulfuric acid, for example, containing stannous salts. The tin content of such a bath may vary between 0.3 and 1.5 g. per liter of bath and the content of sulfuric acid between 15 and 100 g. per liter of bath, without the results varying appreciably. These figures naturally do not represent a limitation.

To effect an appreciable slowing down of oxidation of the stannous ions to stannic ions and of the ferrous ions to ferric ions (the iron coming mainly from the reduction of the iron oxides on the sheet), it is preferable to use a bath made with acids belonging to the phenolsulfonic acid family, such as, for example, phenolsulfonic or cresolsulfonic acid, or from a mixture of sulfuric and phenolsulfonic acids. In that case, the tin deposits will be still more adherent than in a sulfuric medium alone. The contents of stannous tin and acid given for the sulfuric bath are equally applicable to baths modified with phenolsulfonic acids, the acidity then being expressed in gram equivalents of sulfuric acid per liter of bath. The anodes employed are acid proof, being made of graphite, for example, or of stainless steel or an iron-silicon alloy containing 13 percent or more of silicon.

The present invention is not limited, as regards the tinning pickling bath, to the acid or acid mixture solutions quoted as examples. It should be emphasized that the use of other acids, alone or in the form of mixtures, mineral or organic, comes within the scope of the invention.

The stannous ions are introduced into the tinning pickling bath in the form of stannous salts, such as stannous sulfates or else by the dissolution of one or more soluble tin anodes placed among the acid proof anodes, or again in the form of used or excess tinning bath containing stannous ions. This last method is particularly advantageous on grounds of economy, acid-tinning baths tending to become rich in stannous ions. This procedure also enables the acidity of the tinning pickling bath to be kept constant. The introduction of fresh stannous ions to the bath is carried out, of course, as the stannous ions in the bath are consumed by the deposition of tin and in such a way that the concentration of stannous ions remains within a definite range, for the baths mentioned above, for example, within the range of 0.3 to 1.5 g. per liter of bath.

The time taken by the sheet metal to pass through the tinning pickling bath may amount to up to 3 seconds. The current-density values vary, being 10 and 60 A./sq.dm., and the bath temperature lies between 20°C. and 50°C.

Tests of the A.T.C. (Alloy Tin Couple) type made with sheets of tinplate manufactured in accordance with the invention have given values of between 0.5 and 0.12 μ a./sq.cm.

The values obtained by tests of I.S.T. (Iron Solution Test) type, though usually below 20 g. of iron, have shown considerable improvement.

The adhesion of solder to tinplate prepared by a method in accordance with the invention is in general improved on average by 15 to 25 percent in relation to adhesion to tinplate obtained by traditional methods.

In general, tinplate manufactured in accordance with the invention has a better surface shine than tinplate obtained without tinning pickling.

The A.T.C. test consists in determining in microamperes per square centimeter the electric current arising in a cell consisting of an electrode of pure tin and a specimen of tinplate from which the coating of tin has been dissolved and of which the FeS₈₅₅₅₅ alloy coating has remained adhered to the steel sheet. The two electrodes are immersed on short circuit in deaerated grapefruit juice at a temperature of 26°C. The short-circuit current is measured after a 20-hour output of the cell. It is considered that the sheet of tinplate has good corrosion resistance when this current is less than 0.12 A./sq.cm. and very good resistance if it is less than 0.085 A./sq.cm.

The I.S.T.-type test consists in measuring in micrograms the total quantity of dissolved iron derived from a specimen of tinplate having a cross-sectional area of 20.25 sq.cm. (2-inch diameter disc), immersed for 2 hours in a substantially normal sulfuric acid solution at a temperature of 27°C. It is considered that, for good corrosion resistance, this quantity of dissolved iron should be less than 20 μg.

By way of example, the following compositions will be discussed for an acid tinning pickling for use in a method in accordance with the invention, along with the results obtained.

### Example 1

The tinning pickling bath contained 100 g. of sulfuric acid and 1.5 g. of tin per liter of bath, the tin being introduced into the bath in the form of stannous sulfate. The bath temperature was 40°C., the current density was 17 A./sq.dm., the duration of treatment was 2 seconds and the mass of the tin deposit obtained by the pickling operation was 0.7 g./sq.m.

The mass deposited per unit surface area is the sum of the masses deposited on each side of this unit surface area. This method of calculation is usual in the tinplate industry. The actual mass deposited per face of unit surface area is thus one-half of that given.

In accordance with the invention, the degreased and rinsed sheeting was passed to the tinning pickling section. On emerging from the tinning pickling, it underwent further tinning, to bring the total amount of tin deposited up to 16.8 g./sq.m.

The coating of tin was then fused by Joule effect and dipped into water.

### Example 1-2

The tinning pickling bath contained 50 g. of sulfuric acid, 0.7 g. of phenolsulfonic acid and 0.4 g. of stannous tin per liter of bath, the last two constituents having been added to the bath in the form of used tinning bath. The bath temperature was 35°C. The current density was 15 A./sq.dm. The duration of treatment was 2.5 seconds. The mass of the tin deposited here was 0.6 g./sq.m.

The sheet was subjected to the same series of operations as in example 1.

### Example 1-3

The tinning pickling bath contained 53 g. of phenolsulfonic acid (equivalent to 15 g. of sulfuric acid) and 0.6 g. of stannous tin per liter of bath. The stannous ions were introduced into the bath in the form of excess tinning electrolyte. The bath temperature was 60°C. The current density was 16 A./sq.dm. The time taken by the degreased sheeting to pass through the bath was 1.8 seconds. The sheeting emerging from this bath was lightly tinned (0.8 g. of tin per sq.m.).
The sheeting was subject to the same series of operations as in example 1.

<table>
<thead>
<tr>
<th>Tests on the same steel sheeting</th>
<th>I.S.T. µG. Fe</th>
<th>A.T.C. µA./sq.cm.</th>
<th>Solder adhesion kg./cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>With tinning pickling</td>
<td>4</td>
<td>0.65</td>
<td>11</td>
</tr>
<tr>
<td>Without tinning pickling</td>
<td>11</td>
<td>0.32</td>
<td>9</td>
</tr>
</tbody>
</table>

It should be noted that in the three foregoing examples, the shine on the tinplate obtained with tinning pickling was clearly better than that of tinplate obtained without tinning pickling.

In FIGS. 1 and 2, the micrographs (enlarged sixteen thousand times) show the appearance of the crystalline FeSn₅ layer on one and the same kind of steel, according to whether or not the tinning pickling here proposed is used.

FIG. 1 shows the appearance of the alloy layer of the tin plate obtained with conventional cadmium pickling, while FIG. 2 shows the appearance of the alloy layer of tinplate obtained with tinning cadmium acid pickling. The distribution of alloy tin in FIG. 1 is 2.5 g./sq.m. and that in FIG. 2 is 1.9 g./sq.m.

The operations of degreasing, tinning after pickling, fusion and cooling were identical in both cases. The two drawings clearly show that the tinplate obtained by a method in accordance with the invention has, in general, the advantage, over tinplate of traditional type, of having a distinctly higher grain density. This results in an alloy layer of more compact structure and hence in an appreciably better A.T.C. test value, which is changed from 0.32 µa./sq.cm. (tinplate obtained by conventional method) to 0.08 µa./sq.cm. (tinplate obtained by a method in accordance with the invention).

II - NICKEL-PLATING PICKLING

Example II-1

The electrodeposition pickling bath contained 15 g of sulfuric acid and 1 g. of nickel in sulfate form per liter of bath. The bath temperature was 60° C., the current density 14 a./sq.dm. and the duration of treatment 2 seconds. The mass of the nickel deposited during the electrodeposition pickling was 0.1 g./sq.m.

The operating sequence was the same as in example 1-1 above, the sole difference being that the tinning pickling was replaced by nickel-plating pickling.

<table>
<thead>
<tr>
<th>Tests on the same steel sheeting</th>
<th>I.S.T. µG. Fe</th>
<th>A.T.C. µA./sq.cm.</th>
<th>Solder adhesion kg./cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>With nickel-plating pickling</td>
<td>8</td>
<td>0.10</td>
<td>9</td>
</tr>
<tr>
<td>Without nickel-plating pickling</td>
<td>14</td>
<td>0.37</td>
<td>7.5</td>
</tr>
</tbody>
</table>

The improvement in surface shine obtained on tinplate by nickel-plating pickling was less marked than with tinning pickling. The appearance of the alloy coating on the tinplate obtained by this application of the invention is shown in FIG. 3. The proportion of alloy tin in FIG. 3 is 1.8 g./sq.m. and the A.T.C. value 0.10 µa./sq.cm.

III - TINNING AND NICKEL-PLATING PICKLING

Example III-1

The electrodeposition pickling bath contained 15 g. of sulfuric acid, 1 g. of nickel in sulfate form (NiSO₄, 7H₂O) and 0.5 g. of stannous tin in the form of used or excess acid tinning bath per liter of bath. The bath temperature was 60° C., the current density 14 a./sq.dm. and the duration of treatment 2 seconds. The mass of the metal electrodeposited during pickling was 0.2 g. of tin and 0.02 of nickel per sq.m.

This example showed a noteworthy improvement in the A.T.C. in relation to the examples I-land II-1, this improvement having been obtained by the addition of a little tin to the nickel-plating pickling bath. It should be noted that the improvement in surface shine thus obtained on the tinplate was as marked as with tinning pickling, as compared to that of the traditional tinplate.

The appearance of the alloy layer on tinplate obtained by this form of application of the invention is shown in FIG. 4. Here the relatively dense structure is clearly brought out. The distribution of alloy tin in FIG. 4 is 1.6 g./sq.m. and the A.T.C. value is 0.05 µa./sq.cm.

The details given above for tinning pickling, namely the bath temperature, cathode current density, duration of treatment, nature of counter-electrodes, form in which the metal ions are introduced into the bath and the protection of oxidizable metal ions against oxidation, are valid for the other electrodeposition pickling methods.

The results described above are thus obtained by the use of relatively modest means in conventional acid tinning plant, by merely modifying the composition of the bath as well as the counter-electrodes of the existing electrolytic pickling section.

A method in accordance with the invention offers the important advantage of relative simplicity over other proposed methods based on the use of baths that are chemically not very compatible with the preceding and following baths, which entails thorough drying and rinsing. Before these known methods can be put into practice, too, existing acid tinning plant requires extensive modification.

Another not inconsiderable advantage of a method in accordance with the invention is that the recovery of excess acid tinning bath liquid is permitted.

The invention is naturally not limited to the forms described, but includes all variants thereof.

Thus, one variant of the invention consists in subjecting the sheet steel, after degreasing, to conventional acid electrolytic pickling, followed by the electrodeposition pickling described above. This procedure may be found useful when the sheeting is heavily oxidized, but the preliminary pickling is not necessary in everyday practice.

We claim:

1. In a method of electrolytically tin-plating sheet steel comprising subjecting the sheet steel to the steps of:
   - anodic degreasing;
   - pickling in an acid bath; preliminary coating with a metal; acid pickling; and fusing and cooling the tin deposited on the sheet steel; the improvement comprising carrying out the preliminary coating of the sheet steel, polarized as the cathode, in an acid bath having a temperature between 20° and 80° C. containing bivalent ions of a metal selected from the group consisting of tin and nickel in an amount between 0.1 and 1.5 g. per liter of bath and an acid content between 10 and 100 grams equivalent of sulfuric acid per liter of bath, thereby removing oxides from the steel strip surfaces and simultaneously depositing a thin coating of tin or nickel on the steel, said strip being passed through said acid bath for a time of about 1 to 5 seconds, and supplying to said steel strip an electric current of about 10 to
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30a./sq.dm., thereby ensuring a cathode efficiency in deposited metal of about 5 to 25 percent.

2. A method according to claim 1, in which the metal ions contained in the acid pickling bath are stannous ions.

3. A method according to claim 2, in which the stannous ions are introduced into the acid pickling bath in the form of used or excess tinning bath.

4. A method according to claim 1, in which the metal ions contained in the acid pickling bath are bivalent nickel ions.

5. A method according to claim 1 in which the metal ions contained in the acid pickling bath are a mixture of stannous and nickel ions.

6. A method according to claim 1, in which the metal ions are introduced to the acid pickling bath in the form of bivalent salts.

7. A method in accordance with claim 1, in which an antioxidant additive is added to slow down the oxidation of the readily oxidizable metal ions in the pickling bath, which additive is compatible with the acid content in the acid pickling bath.

8. A method according to claim 1 in which the step of pickling in an acid bath is preceded by a conventional acid pickling.

9. The process of claim 1 wherein the bath contains bivalent tin and nickel ions, and includes the step of simultaneously depositing a thin coating of tin and nickel on the steel strip surfaces.

10. A method according to claim 1, in which the bivalent metal ions of tin are introduced to the acid pickling bath in the form of used or excess tinning bath.

11. A method according to claim 1, in which an antioxidant additive is added to the pickling bath to slow down the oxidation of the readily oxidizable metal ions in the pickling bath, which additive is compatible with the acid content in the acid pickling bath.

12. A method according to claim 1, in which the electrodepositing pickling step in an acid bath is preceded by a conventional acid pickling.

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