MANUFACTURE OF RUSTPROOF ELECTROLYTIC COATINGS FOR METAL STOCK

Filed Nov. 24, 1941

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Inventor

John S. Nachtmann

Attorney
MANNUFACTURE OF RUSTPROOF ELECTROLYTIC COATINGS FOR METAL STOCK

John S. Nachtman, Youngstown, Ohio

Application November 24, 1941 Serial No. 428,247

3 Claims. (Cl. 294—37)

1. The present invention comprehends that the heat treating and cold working operations may be divided into alternate steps, repeatedly carried out, if desired.

A further object of the present invention is to provide methods of making rust-proofed or rust-resistant coated steel products having relatively thin coating layers and a bright surface.

The present invention contemplates the use of at least two different coating metals, which must be heated to between 1100° F. to 1800° F. for partially alloying the same together to form the relatively thin alloy layers between the coating layers.

Furthermore, the present invention contemplates the use of at least three different coating layers of two different metals, with the coating of the lower melting point metal located between two layers or coatings of the higher melting point metal in event that one of the coating metals has a melting point below 1100° F.

Thus, the heat treatment of the coating layers to perform the partial alloying may also be utilized to normalize or anneal the base material and accordingly it is unnecessary to anneal the base material prior to the commencement of the improved rust-proofing operations; and hard or unannealed strip-sheet or wire products may be utilized as the base material.

And finally, it is an object of the present invention to provide a new method of making new rust-proof coated steel products, by which the characteristics of the resultant finished product may be accurately controlled, and by which the amounts of coating metals used may be accurately controlled so as to conserve vital raw materials.

These and other objects and advantages may be obtained by the methods, steps, combinations and controls herein described in detail and claimed, and by the examples hereinafter specifically set forth, reference being had to the accompanying drawings in which

Figure 1 illustrates diagrammatically in cross section a steel strip upon which alternate layers of coating metals have been plated;

Fig. 2 illustrates diagrammatically in cross section the plated strip of Fig. 1 after heat treatment;

Fig. 3 illustrates diagrammatically the plated heat treated strip of Fig. 1 after it has been cold rolled;

Fig. 4 illustrates diagrammatically in cross section a strip steel upon which more layers of different metals have been plated on each side;
Fig. 5 illustrates diagrammatically the material of Fig. 4 after heat treatment; and Fig. 6 illustrates diagrammatically the material of Fig. 5 after cold rolling. Similar numerals refer to similar parts throughout the various figures of the drawings.

The invention is further illustrated by the following examples:

**Example I**

As a first example of the manner in which the new method may be carried out in providing a rust-proof coating composed of alternate layers of nickel and lead with thin layers of nickel-lead alloy between the nickel and lead layers, the hard unannealed steel strip, say .010" thick indicated at 10 in Fig. 1 is electroplated on each side with a layer of .0005" of nickel 11, followed by an electroplated layer on each side of .0001" of lead 12, followed by an electroplated layer on each side of .0005" of nickel 13.

The strip which will then have a total thickness of approximately .0122" is then heat treated at a temperature of from 1100° to 1800° F. for approximately one-half an hour in the presence of a neutral or reducing gas to form very thin layers of nickel-lead alloy between adjacent layers of nickel and lead.

The material after such heat treatment is illustrated diagrammatically in Fig. 2, in which the steel base 16 still has a thickness of approximately .010" thick, on top of which on each side is a minute layer or thickness of iron-nickel alloy so infinitesimal that it is not shown, followed by a layer on each side of .00046" of nickel 14, then a layer on each side of .00008" nickel-lead alloy 15b, followed by a layer on each side of .00009" of lead 14a, followed by a layer on each side of .00008" of nickel-lead alloy 12b, and followed by a top layer on each side of .00046" of nickel 13a.

The strip illustrated in Fig. 2 is then cold rolled to a finished gauge having a thickness of say .010" thick, as illustrated in Fig. 3, during which cold rolling step the steel base and the alternating single metal and thin alloy metal coatings are each reduced in thickness.

It is of course understood that the heat treatment to form the thin hair-like alloy between the layers of plated metals anneals the steel base so that the finished cold rolled stock is not only coated with a rust-proof coating, but also has the usual characteristics of cold rolled strip steel.

It is understood in connection with the Example I that additional alternate layers of lead and nickel may be plated before the heat treating and cold rolling operations; that electroplated layers of other thicknesses may be used if desired, as for instance by providing more, thinner layers; and that the heat of heat treatment may be reduced somewhat or increased somewhat in order to reduce or increase the thickness of the alloy layers between the plated metal layers.

**Example II**

As a second example of the manner in which the new method may be carried out in providing a rust-proof coating composed of alternate layers of chromium and zinc with thin layers of chromium-zinc alloy between the chromium and zinc layers, a hard unannealed steel strip, say .010" thick is electroplated on each side with a layer of .0005" of chromium, followed by an electroplated layer on each side of .0001" of zinc, followed by an electroplated layer on each side of .0005" of chromium.

The strip which will then have a total thickness of approximately .0122" is then heat treated at a temperature of from 1100° F. to 1800° F. for approximately two to three hours in the presence of a neutral or reducing gas to form very thin layers of chromium-zinc alloy between adjacent layers of chromium and zinc.

The resultant heat treated material then has a steel base of a thickness approximating .010" thick, on top of which on each side is a trame of iron-chromium alloy of infinitesimal thickness, followed by a layer on each side of .00046" of chromium, then a layer on each side of .00008" of chromium-zinc alloy, followed by a layer on each side of .00009" of zinc, followed by a layer on each side of .00008" of chromium-zinc alloy, followed by a top layer on each side of .00046" of chromium.

The strip is then subjected to a light cold rolling or skin passing operation to improve its surface lustre.

Although Figs. 1, 2 and 3 are particularly noted and referred to in connection with Example I, the same figures diagrammatically represent the same process carried out with different materials as described in Example II.

**Example III**

As a third example of the manner in which the new method may be carried out in providing a rust-proof coating composed of alternate layers of copper and nickel with thin layers of copper-nickel alloy between the copper and nickel layers, a hard unannealed steel strip say .010" thick indicated at 20 in Fig. 4 is electroplated on each side with a layer of .00033" of copper 21, followed by an electroplated layer on each side of .0005" of nickel 22, followed by an electroplated layer on each side of .00033" of copper 23, followed by an electroplated layer on each side of .0005" of nickel 24, followed by an electroplated layer on each side of .00033" of copper 25.

The strip will then have a total thickness of approximately .01385", and is then heat treated in a temperature of from 1100° to 1800° F., preferably within the range of 1100° to 1400° F. for approximately one hour in the presence of a neutral or reducing gas to form very thin layers of copper-nickel alloy between adjacent layers of copper and nickel.

The material after such heat treatment is illustrated diagrammatically in Fig. 5 in which the steel base 26 still has a thickness of approximate .010" thick, on top of which on each side is a layer of .00015" of iron-copper alloy 26a, followed by a layer on each side of .00008" of copper 21a, followed by a layer on each side of .0002" of copper-nickel alloy 21b, followed by a layer on each side of .00003" of nickel 22a, followed by a layer on each side of .00008" of copper 23, followed by a layer on each side of .0002" of copper-nickel alloy 24, followed by a layer on each side of .00003" of copper 25a, followed by a layer on each side of .00003" of copper 25a, followed by a layer on each side of .00002" of copper-nickel alloy 24b, and followed by a top layer on each side of .00003" of copper 25a.

The strip illustrated in Fig. 5 is then cold rolled to approximately 50% reduction to have a finished gauge of a thickness of approximately .010", as illustrated in Fig. 6, during which cold rolling step the steel base on the alternating metal and al-
loy metal coatings are each reduced in thickness.

**Example IV**

As the next example of the manner in which the new method may be carried out in providing a rust-proof coating composed of alternate layers of copper and tin with thin layers of copper-tin alloy between the copper and tin layers, a hard unannealed steel strip say .010 thickness is electroplated on each side with a layer of .00006" of copper followed by an electroplated layer on each side of .00004" of tin, followed by an electroplated layer on each side of .00005" of copper, followed by an electroplated layer on each side of .00005" of tin, followed by an electroplated layer on each side of .00005" of copper.

The strip will then have a total thickness of approximately .01220" and is then heat treated for approximately five minutes in the presence of a neutral or reducing gas at a temperature from 1100° to 1300° F. to form very thin layers of copper-tin alloy between adjacent layers of copper and tin.

The metal after such heat treatment comprises the steel base still having a thickness approaching .010 thickness on top of which on each side is a layer of .000016" of iron-copper-tin alloy, followed by a layer on each side of .00004" of copper-tin alloy of approximately 50 per cent copper and 50 per cent tin, followed by a layer on each side of .00004" of copper-tin alloy rich in copper, followed by a layer on each side of .00001" of copper, followed by a layer on each side of .00004" of copper-tin alloy, followed by a layer on each side of .00001" of tin, followed by a layer on each side of .00004" of copper-tin alloy, and followed by a top layer on each side of .00003" of copper.

The heat treated material is then cold rolled lightly to improve the surface lustre.

In each of the above examples it is to be understood that more layers of the indicated metals may be plated if desired; and that if one or more of the layers is made relatively thinner than another layer of the same material as in Example IV, there may be succeeding layers of different alloys without an intermediate layer of a pure metal.

Furthermore, the heat treatment in each instance acts not only to form the thin hair-like alloy layers between the layers of plated metals, but also to normalize or anneal the hard unannealed steel base so that to render the same in proper condition for the subsequent cold rolling operation.

In carrying out the method described in the above examples, the electroplating baths may be of the standard types well known to the art. Since the procedures for electroplating the metals mentioned herein are well known, these procedures and the preparation of the base metal are not described herein. It is sufficient to say that the strip steel stock is to be properly cleaned and etched when necessary prior to electroplating; and that any of the well known plating solutions are to be employed for electroplating the layers of metals.

The thickness of any electroplated layer in any instance may be as thin as .00005" and may be anywhere between such thickness and .005" thick. The heat treatment is carried out in each instance in a suitable furnace having a non-oxidizing or reducing atmosphere, for example, an atmosphere of hydrogen, or carbon monoxide, or nitrogen, or a hydrocarbon vapor, or a mixture of any two or more of all of such gases. The heat treatment is carried out at the desired temperature in the range between 1100° and 1800° F. for a suitable length of time to give the desired diffusion or alloying between the coated layers, thus forming a thin alloy metal band between adjacent layers of metals, and leaving a portion of some or all of the plated layers unalloyed.

In any event, the heat treatment is such that the alloy layers may range anywhere from a minute thickness or trace up to a thickness of .0005". In some instances, as stated, there may be a difference in thickness of the various coating layers, as plated, and two or more of the layers may completely alloy one with the other, at the time and temperature utilized for heat treatment, while others of the coating layers are only partially alloyed and thin hair-like alloy layers are formed between them.

It is furthermore understood that in some instances, alloys may be plated directly from an electroplating bath containing salts of the metals of the alloy as one or more of the coating layers, using other pure metals for other layers and the subsequent heat treatment will form alloys between the plated layers. This is to say that there is at least one heat treatment operation followed by at least one cold rolling operation, with at least two thin layers of alloy formed between the electroplated layers.

Although one heat treatment operation and one cold rolling operation has been indicated, these steps may be multiplied if desired to include additional alternate steps of heat treatment and cold working.

The cold working or rolling or drawing operations on the sheet, strip or wire base, having electroplated heat treated coatings thereon, refines the grain size of the base metal and of the metal in the coating layers, because the same may have become large due to the heat treatment; and prevents "stretcher strains" in the coated metal. The cold working operation also everts and reduces the coating thickness and produces a product suitable for deep drawing and forming operations. The cold working operation also reduces the porosity of the coated metals on the product.

The product thus produced has the properties of being rust-resistant and also has a good surface lustre; and has low coating porosity, the porosity being greatly reduced by the formation of the thin alloy layers between the layers of pure electroplated metals, in conjunction with the cold working operation after heat treatment.

If desired, when producing a coating having alloy layers of alloying metals, such as are used in making a stainless alloy layer, or all of the iron to be incorporated may be plated next to the base. This procedure prevents the migration of elements, such as carbon, from the base into the electroplated layers during heat treatment; and the first coating of electrolytic iron also provides a good surface for the deposition of other plated layers and permits a tight bond of the coating layers to the base metal.

In the product produced by the new method, a great reduction in the amount of coating metals necessary is obtained; that is to say, much thinner layers are used in making a product of rust-resistance equal to similar products made in accordance with present practice. For example, parts are plated with copper, nickel and chromium for use in the automotive industry and in
In this instance, the coating metals are electroplated without any subsequent heat treatment and rolling. Under the present invention heat treatment and rolling is carried out after plating, followed by subsequent forming operations to make such automotive parts; and much smaller amounts and much thinner layers of the coating metals may be used for equal rust resistance.

Another advantageous feature of the heat treating operation is that all trapped gases which may be in the electroplated metals following the electroplating operation are driven out during the heat treatment.

Other uses for the products produced by the improved method are materials for bearings, electrical equipment, and in other fields where a good rust-resisting coating with a minimum amount of coating metal is desired.

The coatings may be layers of the following metals in any combination, with thin alloy layers produced between the layers of pure metal; tin, lead, zinc, iron, nickel, chromium, copper, bismuth, antimony, cadmium and silver. The last four metals mentioned have not been indicated in any specific examples given, but they may be substituted for or utilized in connection with the metals named in the examples.

Although in each of the above examples, cold rolled strip steel having a thickness of .010" is indicated as being the base metal, strip steel up to .100" in thickness may be utilized, wire up to 3/4" in diameter may be treated in accordance with the present method, and sheets up to 1/4" in thickness may be similarly treated. The cold rolling which may be performed following heat treatment may range from 80 per cent reduction down to a cold rolling to reduce the thickness by .0025".

The term "cold rolling" when used herein and in the appended claims is intended to include a cold rolling, a cold working, a skin rolling, or a cold drawing operation. Whenever the word "strips" or the words "strips and the like" are used herein, the same are intended to include products such as strips, strip sheets, sheets or wire.

And finally, in the foregoing description certain terms have been used in the sense that they are usually used in the art, for brevity, clearness and understanding, but no unnecessary limitations are to be implied therefrom beyond the requirements of the prior art, because such words are not utilized for the purpose of limitation and are intended to be broadly construed.

I claim:
1. A method of making steel strip and the like suitable for deep-drawing, stamping and forming, comprising electroplating on cold-rolled hard unannealed steel strip base stock at least three layers of two metals selected from the group consisting of tin, lead, zinc, iron, nickel, chromium, copper, bismuth, antimony, cadmium and silver, one of said two metals having a melting point appreciably above the other and with the higher melting point metal directly on the base stock and with the lower melting point metal between two layers of the higher melting point metal, then so heat treating the base stock between 1100° F. and 1800° F. under non-oxidizing conditions as to anneal the base stock and form at least two partial alloy layers of substantial thickness but no greater than .0005" between adjacent plated metal layers, and then cold rolling the plated annealed strip.

2. A method of making steel strip and the like suitable for deep-drawing, stamping and forming, comprising electroplating on cold-rolled hard unannealed steel strip base stock at least three layers of two metals selected from the group consisting of tin, lead, zinc, iron, nickel, chromium, copper, bismuth, antimony, cadmium and silver, one of said two metals having a melting point appreciably above the other and with the higher melting point metal directly on the base stock and with the lower melting point metal between two layers of the higher melting point metal, then so heat treating the base stock under non-oxidizing conditions as to anneal the base stock and form at least two partial alloy layers of substantial thickness but no greater than .0005" between adjacent plated metal layers, and then cold rolling the plated annealed strip.

3. A method of making steel strip and the like suitable for deep-drawing, stamping and forming, comprising electroplating on cold-rolled hard unannealed steel strip base stock at least three layers of two metals selected from the group consisting of tin, lead, zinc, iron, nickel, chromium, copper, bismuth, antimony, cadmium and silver, one of said two metals having a melting point appreciably above the other and with the higher melting point metal directly on the base stock and with the lower melting point metal between two layers of the higher melting point metal, then so heat treating the base stock between 1100° F. and 1800° F. under non-oxidizing conditions as to anneal the base stock and form at least two partial alloy layers of substantial thickness but no greater than .0005" between adjacent plated metal layers, and then cold rolling the plated annealed strip.

JOHN S. NACHTMAN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,746,987</td>
<td>Bennett</td>
<td>Feb. 11, 1930</td>
</tr>
<tr>
<td>1,963,391</td>
<td>Wirshing et al.</td>
<td>June 19, 1934</td>
</tr>
<tr>
<td>2,156,262</td>
<td>Pink et al.</td>
<td>May 2, 1939</td>
</tr>
<tr>
<td>1,578,254</td>
<td>Bennett</td>
<td>Mar. 30, 1926</td>
</tr>
<tr>
<td>2,044,742</td>
<td>Armstrong et al.</td>
<td>June 16, 1936</td>
</tr>
<tr>
<td>2,219,728</td>
<td>Copson</td>
<td>Oct. 29, 1940</td>
</tr>
</tbody>
</table>

FOREIGN PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Country</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>415,037</td>
<td>Great Britain</td>
<td>Aug. 14, 1934</td>
</tr>
<tr>
<td>424,724</td>
<td>Great Britain</td>
<td>Feb. 27, 1935</td>
</tr>
</tbody>
</table>

OTHER REFERENCES