

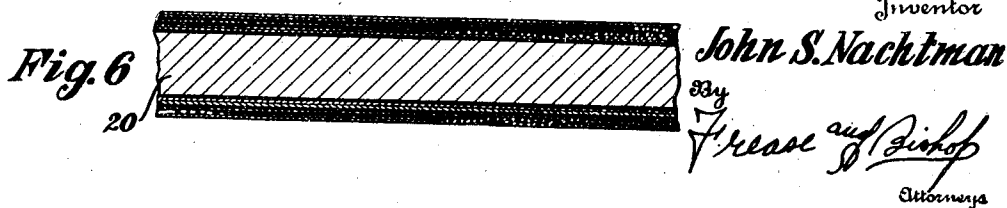
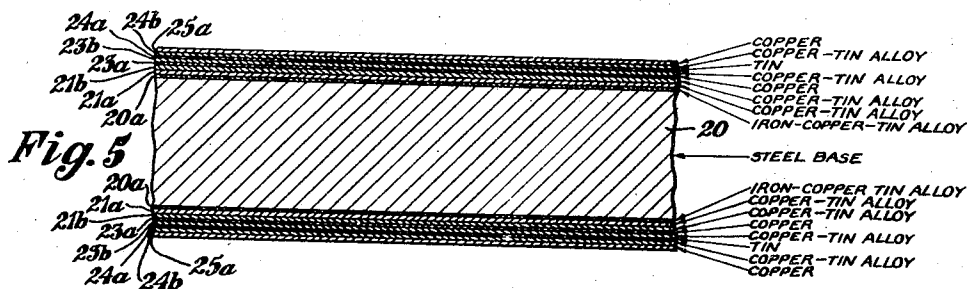
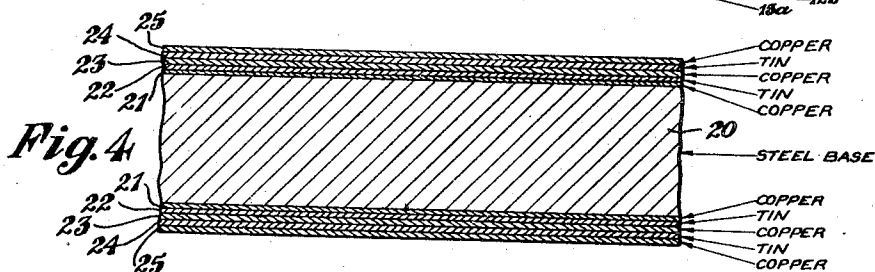
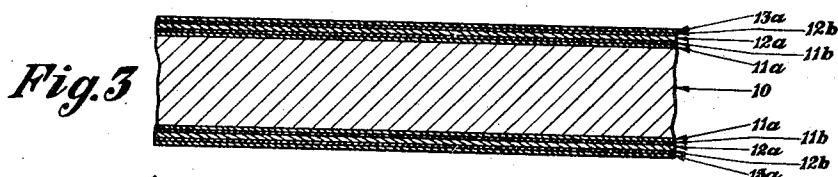
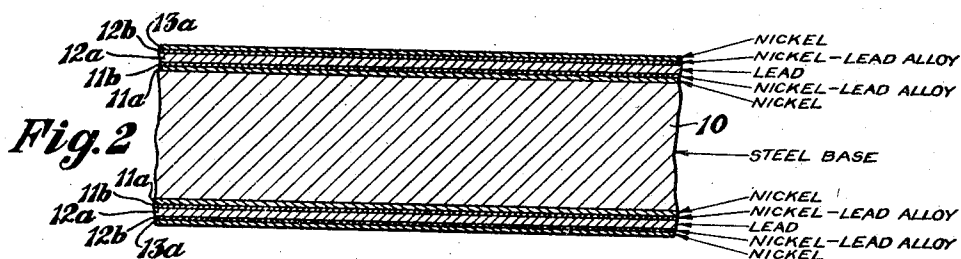
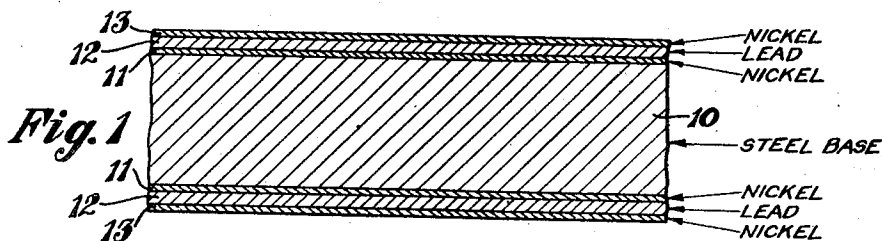
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ELECTROLYTIC DEPOSITION OF RUSTPROOF COATINGS

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ELECTROLYTIC DEPOSITION OF RUST-
PROOF COATINGS

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3 Claims. (Cl. 204—37)

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The invention relates to the manufacture of steel strip, sheet, stripsheets or wire. More particularly, the invention relates to the provision of rust-proof coatings upon steel strip, stripsheet or wire products, any of which products are further characterized by their ability to withstand severe deep drawing, stamping, or forming operations; and this application is a companion case to my copending application Serial No. 420,247, filed November 24, 1941, and my copending application Serial No. 311,930, filed December 30, 1939.

Steel strip and the like has been plated with nickel or chrome or copper, or other materials in order to make the material rust-resistant when used for a variety of purposes; such as in the manufacture of hardware or automobile parts, or other parts exposed to the atmosphere or to corrosive liquids. Articles have also been provided with rust-proof coatings by electroplating one or more metals on the articles and subsequently subjecting the same to heat treating operations to completely alloy coating layers with each other and with the base metal so that coatings such as brass, bronze and the like are formed.

In each of the above instances in prior practice, relatively large amounts of the coating materials are used, or are required in order to obtain the required rust-resistance in the finished product; and most if not all of the coating metals normally used are, under existing conditions, required for defense purposes, so that the amounts of the same available for normal use is drastically limited.

It is a fundamental object of the present invention to provide methods of making new and improved types of coatings for steel products, which coatings are considerably more rust-resistant than the present available types of coatings, if the same amount of coating material is used; or which coatings have rust-resistance equal to present types of coatings while using, say not more than one-half the amount of coating material at present used, in order to create a substantial savings in vital materials now needed for defense purposes.

A further object of the present invention is to provide a method of making rust-proof coated steel products by electroplating alternate coating layers of different metals on a steel base, heat

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treating the coating layers to form relatively thin alloy layers between the coating layers, and then subjecting the heat treated coated product to a cold working operation to complete the manufacture of the rust-proof coated product.

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 alloy layers between the electroplated coating layers and a bright surface.

The present invention contemplates the use of at least two different coating metals, which are heated to below but not over 1150° F. In any case the heat treatment is carried out at a low enough temperature or for only such time that the characteristics including grain size, of the base stock are not appreciably affected; such heat treatment being only for the purpose of partially alloying the coating layers together to form relatively thin alloy layers between the coating layers.

Furthermore, the present invention contemplates the use of at least three different coating layers of at least two different metals. In certain cases where one of the coating metals has a melting point below 1150° F. the coating of the lower melting point metal may be advantageously located between two layers or coatings of the higher melting point metal; and in other cases, two layers of lower melting point metal may enclose one layer of higher melting point metal, if desired.

Thus, the heat treatment of the coating layers to perform the partial alloying will not affect or disturb the characteristics of the base material and accordingly annealed or normalized steel and the like may be utilized as the base material which may be subsequently cold rolled after the heat treating operation for producing the desired characteristics in the finished product.

And finally, it is an object of the present invention to provide a new method of making 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 accu-

rately 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 materials 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 steel strip 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 through 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 soft annealed or normalized 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 .001" 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 .014" is then heat treated at a temperature of from 570° F. to 590° F. for approximately one and one-half hours 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 10 still has a thickness of .010" thick, on top of which on each side is a layer of .0004" of nickel 11a, then a layer on each side of .0002" of nickel-lead alloy 11b, followed by a layer on each side of .0008" of lead 12a, followed by a layer on each side of .0002" of nickel-lead alloy 12b, and followed by a top layer on each side of .0004" 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 layers between the layers of plated metals, does not affect the soft annealed or normalized steel base; but that the cold rolling operation imparts a cold rolled finish to the product and cold rolled characteristics to the base, so that the finished product has the usual characteristics of cold rolled strip steel.

It is understood in connection with Example I that additional alternate layers of lead and nickel may be plated before the heat treating and cold

rolling operations; that electro-plated layers of other thicknesses may be used if desired, as for instance by providing more thinner layers; and that the time 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 tin and nickel with thin layers of nickel-tin alloy between the tin and nickel layers, soft annealed or normalized steel strip, say .010" thick is electroplated on each side with a layer of .0005" of tin, followed by an electroplated layer on each side of .001" of nickel, followed by an electroplated layer on each side of .0005" of tin. The strip which will then have a total thickness of approximately .014" is then heat treated at a temperature of from 390° F. to 410° F. for approximately one hour in the presence of a neutral or reducing gas to form very thin layers of nickel-tin alloy between adjacent layers of tin and nickel.

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 trace of iron-tin alloy of infinitesimal thickness, followed by a layer on each side of .00045" of tin, then a layer on each side of .0001" of nickel-tin alloy, followed by a layer on each side of .0009" of nickel, followed by a layer on each side of .0001" of nickel-tin alloy, followed by a top layer on each side of .00045" of tin.

The strip is then subjected to a light cold rolling or skin passing operation to improve its surface lustre and to provide the desired gauge of material.

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 chromium and zinc with thin layers of chromium-zinc alloy between the chromium and zinc layers, a soft annealed or normalized 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 .001" 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 .014" is then heat treated at a temperature of about 700° F. for approximately five 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 layer of .0004" of chromium, then a layer on each side of .0002" of chromium-zinc alloy, followed by a layer on each side of .0008" of zinc, followed by a layer on each side of .0002" of chromium-zinc alloy, followed by a top layer on each side of .0004" of chromium.

The strip is then subjected to a light cold roll-

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ing 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 III.

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 soft annealed or normalized steel strip say .010" thick indicated at 20 in Fig. 4 is electroplated on each side with a layer of .00036" of copper 21, followed by an electroplated layer on each side of .0004" of tin 22, followed by an electroplated layer on each side of .0005" of copper 23, followed by an electroplated layer on each side of .0005" of tin 24, followed by an electroplated layer on each side of .0005" of copper 25.

The strip will then have a total thickness of approximately .01452" and is then heat treated at a temperature of about 405° F. for approximately one hour in the presence of a neutral or reducing gas to form very thin layers of copper-tin alloy between adjacent layers of copper and tin.

The material after such heat treatment is illustrated diagrammatically in Fig. 5 in which the steel base 20 still has a thickness of approximately .010" thick, on top of which on each side is a layer of .00016" of iron-copper-tin alloy 20a, followed by a layer on each side of .0004" of copper-tin alloy 21a of approximately 50 per cent copper and 50 per cent tin, followed by a layer on each side of .0004" of copper-tin alloy 21b rich in copper, followed by a layer on each side of .0001" of copper 23a, followed by a layer on each side of .0004" of copper-tin alloy 23b, followed by a layer on each side of .0001" of tin 24a, followed by a layer on each side of .0004" of copper-tin alloy 24b, and followed by a top layer on each side of .0003" of copper 25a.

The strip illustrated in Fig. 5 is then cold rolled lightly to improve the surface lustre as illustrated in Fig. 6.

Example V

As a 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 lead and tin with thin layers of tin-lead alloy between the lead and tin layers, a soft annealed or normalized steel strip say .010" thick, is electroplated on each side with a layer of .0005" of lead, followed by an electroplated layer on each side of .001" of tin, followed by an electroplated layer on each side of .0005" of lead.

The strip which will then have a total thickness of approximately .014" is then heat treated at a temperature of from 330° F. to 345° F. for approximately two hours in the presence of a neutral or reducing gas to form very thin layers of tin-lead alloy between adjacent layers of lead and tin.

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 layer of .0003" of lead, followed by a layer on each side of .0004" of tin-lead alloy, followed by a layer on each side of .0006" of tin, then a layer

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on each side of .0004" of tin-lead alloy, followed by a top layer on each side of .0003" of lead.

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 V.

As a variation upon Example V, the plating sequence may be tin-lead-tin instead of lead-tin-lead; in which case the first layer of tin alloys with the steel base to a slight extent, making the tin layer next to the base slightly thinner.

Example VI

Annealed or normalized steel strip of say .010" thick is electroplated with .0005" on each side of an alloy of nickel-iron of the approximate composition of 60% nickel and 40% iron from an electroplating bath containing salts of both nickel and iron in the desired concentration. Upon the nickel-iron alloy layers there is then electroplated on each side a layer of zinc .001" thick, followed by another electroplated layer on each side of .0005" thick of nickel-iron alloy of the approximate composition of 60% nickel and 40% iron.

The strip, which will then have a total thickness of approximately .014", is then heat treated at a temperature of from 600° F. to 700° F. for approximately six hours in the presence of a neutral or reducing gas to form very thin layers of an alloy of zinc-nickel-iron of undetermined thickness between the electroplated layers of nickel-iron alloy and zinc.

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 alloy without an intermediate layer of a pure metal.

Furthermore, the heat treatment in each instance which acts to form the thin hair-like layers between the layers of plated metals, does not disturb the soft annealed or normalized condition of the steel base, so that the material after heat treatment is in proper condition for subsequent cold rolling operations.

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 coating layers may be of two or more metals plated in one or more sets of alternate layers, and any of the metals may be plated next to the base if desired. For instance, the plating sequence may be tin-nickel-tin, tin-nickel-tin-nickel, nickel-tin-nickel, etc.

The thickness of any electroplated layer in any instance may be as thin as .000005" 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-oxi-

izing or reducing atmosphere, for example an atmosphere of hydrogen or carbon monoxide, or nitrogen, or hydrocarbon vapor, or a mixture of any two or more or all of such gases. The heat treatment is carried out at the desired temperature at or below 1150° F. in the case of pot or batch type heating in coils, or at or below 1800° F. in the case of continuous heat treatment of moving strip 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 solutions of the metals of the alloy as one or more of the coating layers, using one or more pure metals for other layers; and the subsequent heat treatment will form alloys of different composition between the plated layers. This is to say that there is at least one heat treating operation with the formation of at least two thin layers of alloy between the electroplated layers, with or without a subsequent cold rolling operation, as desired.

Although one heat treating 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 rolling.

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, and prevents "stretcher strains" in the coated metal. The cold working operation also evens up 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 materials, in conjunction with the cold working operation after heat treatment.

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.

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.

Uses for the products produced by the improved method include materials for the automotive industry, materials for bearings, electric equipment and in other fields where a good rust-re-

sisting coating with a minimum amount of coating metal is desired.

The coating may be layers of the following metals in any combination, with thin alloy layers produced between the layers of pure metal: tin, lead, zinc, nickel, chromium, and copper, cadmium, antimony, bismuth and silver.

Although in each of the above examples, strip steel having a thickness of .010" is indicated as being the base metal, strip steel up to .180" 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 .00025".

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. When ever the word "strips" or the words "strips and the like" are used therein, the same are intended to include products such as strips, stripsheets, 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 and the appended claims, 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 comprising electroplating on 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, silver and alloys thereof, one of said metals being between two layers of the other metal, then heat treating the base stock in a non-oxidizing atmosphere at a temperature below the annealing temperature of the base stock and below the melting point of the lower melting point metal, the time and temperature of heat treatment being sufficient to form two thin partial alloy layers of adjacent plated metals of substantial thickness but no greater than .0005" between said adjacent plated metals.

2. A method of making steel strip and the like comprising electroplating on 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, silver and alloys thereof, one of said metals being between two layers of the other metal, then heat treating the base stock in a non-oxidizing atmosphere at a temperature not exceeding 1150° F. below the annealing temperature of the base stock, the time and temperature of heat treatment being sufficient to form two thin partial alloy layers of adjacent plated metals of substantial thickness but no greater than .0005" between said adjacent plated metals.

3. A method of making steel strip and the like comprising electroplating on 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, silver and alloys thereof, the lower melting point metal being between two layers of the other metal, then heat treating the base stock in a non-oxidizing atmosphere at a temperature not exceeding 1150° F. below the annealing temperature

of the base stock and below the melting point of the lower melting point metal, the time and temperature of heat treatment being sufficient to form two thin hair-like layers of partial alloys of adjacent plated metals of substantial thickness but no greater than .0005" between said adjacent plated metals.

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