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METAL COATING PROCESS

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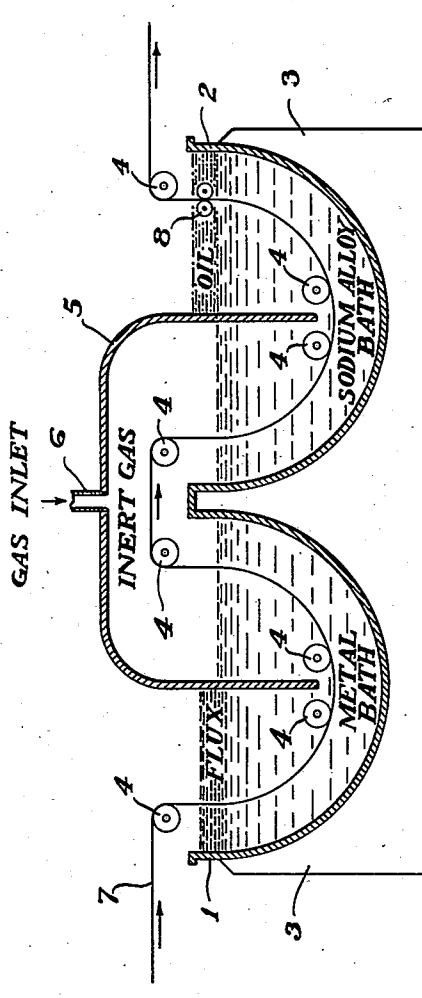


Fig. 1.

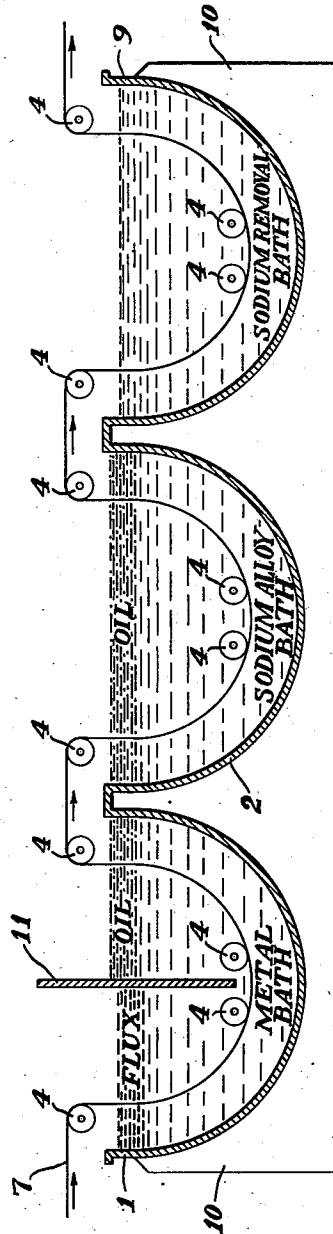


Fig. 2.

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## UNITED STATES PATENT OFFICE

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## METAL COATING PROCESS

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This invention relates to the formation of metal coating on metal bases and more particularly to fused metal coatings on metal bases.

In coating metals by methods where the metal is dipped into a molten bath of a fusible metal such as tin, zinc or lead, it has been found that the addition of sodium to the coating metal has a number of valuable advantages. For example, in U. S. Patent 1,994,276 it is disclosed that the addition of up to 2% of sodium in a fused tin coating results in a superior tin alloy coating on the steel. Likewise it has been found that the addition of up to 2% of sodium to a zinc coating produces a zinc sodium alloy coating which is more resistant to corrosion than a pure zinc coating. Aside from these particular advantages, it is generally advantageous to add a small amount of the sodium in coating a metal base with tin, zinc and lead by immersing the metal base in a molten bath of the metal. The sodium increases the adherence of the fused metal to the base and generally produces a smoother coating, freer from pin-holes.

The application of sodium alloy fused coatings to steel, copper, nickel or other relatively high melting metal base involves certain difficulties caused by the rapid tendency of sodium to oxidize at the temperatures required for the coating process. Thus when sodium is added to a molten tin or zinc bath the surface of the bath must be protected from the air; otherwise the sodium in the bath will rapidly oxidize. Such baths normally are operated covered with a floating layer of a fused salt flux, for example zinc chloride, ammonium chloride, or mixtures of these and the like. It is necessary when applying fused metal coatings to treat the metal to be coated with a suitable flux, in order to obtain an adherent metal coat. The use of such flux also is required in order to obtain a satisfactory coating when the metal coating bath contains sodium. In coating steel or other base metal with a fused tin coating it is common practice to maintain a vegetable oil such as palm oil on the surface of the molten tin at the point where the coated metal base is removed from the bath. The function of the oil is to protect the tin from oxidation and to smooth out the coating. The loss of sodium in a fused metal bath used to coat a base metal is caused primarily by the reaction of the sodium with the flux material and with any vegetable oil which may be used to cover the bath. These materials react very rapidly with the sodium and when they are used over a sodium alloy bath it is practically impossible to maintain in the bath a desired so-

dium concentration within the range of from a fraction of 1% up to around 10%.

An object of the present invention is to provide an improved method for coating a ferrous metal such as iron, steel or other suitable metal base with a coating of a fusible metal such as tin, zinc, lead, tin-lead alloy and the like. A further object is to provide a method for coating such base metals with alloys of sodium and the above mentioned fusible metals. Another object is to provide a suitable method for coating metal bases with sodium alloys under controlled conditions of sodium content of the coating bath and of the coating applied and in such manner as to avoid excessive loss of sodium. Other objects will be apparent from the following description of my invention.

The above objects may be attained in accordance with my invention by immersing a metal base coated with a fusible metal into a molten bath composed of the coating metal together with a small amount of sodium, at a temperature above the melting point of the coating metal. For example, I may obtain a coating of sodium-tin alloy by immersing a tin coated base into molten tin to which has been added a small amount of sodium. I have found that within a period of about not more than one or two minutes the metal coating on the base article will acquire a sodium content substantially equal to that of the bath. An appreciable amount of sodium will enter the coating within a period of 10 to 30 seconds. Thus I may maintain in the tin-sodium alloy bath an amount of sodium greater than that required in the final coating and attain the desired result within a period of 10 to 30 seconds. The metal base when removed from the tin-sodium alloy bath will be found to be uniformly coated with an adherent, smooth, high quality coating of tin-sodium alloy. In such operations, the sodium alloy bath is protected from oxidation by the air by a suitable covering of a fluid material which is substantially unreactive chemically towards sodium in the sodium alloy bath. Such fluid protective material may be a liquid, for example a high boiling liquid hydrocarbon which is substantially inert to sodium or, by means of suitable apparatus, I may utilize a substantially inert gas such as nitrogen, hydrogen, carbon monoxide, methane, or the like in place of the liquid hydrocarbon or in conjunction therewith.

In applying this method it is not essential that the previously coated metal introduced into the sodium alloy bath be coated by a hot dip process. For example, I may coat an iron or steel sheet

with tin or zinc by an electroplating process and immerse such coated sheet into a fused sodium alloy of tin or zinc, respectively. In any case it is necessary that the temperature of the sodium alloy bath be not lower than the melting point of the metal coating on the metal base introduced into the bath. Preferably, the temperature will be from 10 to 50° above that melting point.

One preferred method of practicing my invention is illustrated by Fig. 1 of the appended drawing. In the apparatus of Fig. 1, two hemispherical vessels 1 and 2 containing fused coating metal are set in a furnace setting 3 which is illustrated diagrammatically. The vessels are heated by means not shown in the drawing. Associated with the vessels are guide rolls 4 for guiding a flexible metal strip through the apparatus. Vessel 1 is partly filled with a fused coating metal, for example molten tin, while vessel 2 is partly filled with a fused sodium alloy, for example a tin-sodium alloy containing around 1% by weight of sodium. The hood 5 is arranged to dip into both vessels 1 and 2 and is sealed around the edges of the vessels by means not shown so as to form a substantially air-tight gas chamber. The vertical portions of hood 5 serve to form partitions dividing the upper portion of each vessel into two halves. In vessel 1 on the outside of hood 5 a layer of suitable flux, for example fused zinc chloride, is placed to float on the surface of the molten tin. In vessel 2 on the outside of hood 5 a layer of oil which is inert to sodium floats on the surface of the sodium alloy bath. The chamber inside of hood 5 is maintained filled with inert gas preferably at a pressure just slightly in excess of one atmosphere. The pressure is applied by introducing the inert gas such as nitrogen through the inlet 6.

In operating the above described apparatus a continuous strip or sheet of metal, for example a steel strip, is first passed through suitable pickling and cleaning operations of conventional type not illustrated in the drawing and preferably also dried. The cleaned steel strip 7 is then passed continuously first through the flux overlying the fused metal in vessel 1, then under the partition formed by hood 5 and out of vessel 1 into the atmosphere of inert gas, thence down into the sodium alloy bath in vessel 2 and out of vessel 2 through the layer of oil. Guide rolls 4 serve to guide the metal through the apparatus in the manner indicated. The strip emerging from vessel 1 is coated with a coating of fused tin which may be more or less irregular. If desired, smoothing rolls may be situated above the metal bath to smooth out the coating on the strip leaving vessel 1 but ordinarily this will not be necessary. During its passage through the inert atmosphere in hood 5 the speed of the metal strip usually will be such that it will not be cooled sufficiently to solidify the fused coating thereon. As the coated strip passes through the sodium alloy bath it acquires a sodium alloy coating. The sodium content of that coating will depend upon the concentration of sodium in the alloy bath and the speed of the steel strip through the bath. It is feasible, by employing a sufficiently high concentration of sodium in the alloy bath in the range of, for example, 1 to 10%, to pass the steel strip through the alloy bath so that it is in the bath for a period of not more than 30 to 60 seconds, and thereby obtain a desired sodium concentration in the coating. As the steel strip passes out of the sodium alloy bath it may, if desired, be passed through a pair of smoothing

rolls 8 which are shown diagrammatically in the drawing. The inert gas in hood 5 and the oil on the surface of the sodium alloy bath serve to prevent the oxidation of the sodium by the action of the air. Hence, substantially the only loss of sodium from the alloy bath is due to the sodium which is alloyed with the coating metal in the coated material leaving vessel 2. If desired after cooling to solidify the coating on the strip leaving vessel 2, the coated strip may be subjected to any desired conventional finishing operations such as polishing, oiling or the like.

In some cases it is desired to produce a metal coated article which has the desirable physical characteristics of an article coated by means of a molten metal containing sodium but which coating actually contains no sodium. I have discovered that this result may be accomplished by treating the sodium alloy coated base with a reagent reactive to sodium at a temperature above the melting point of the fused alloy coating. Reagents suitable for this purpose will be apparent to chemists and need not be cataloged completely in this description. I prefer to use for this purpose fused chlorides or mixtures of them, for example for removing sodium from a tin-sodium alloy coating I prefer to use a fused mixture of stannous chloride and ammonium chloride. Fused zinc chloride or fused zinc chloride mixed with ammonium chloride also is very satisfactory for removing sodium from a sodium-tin alloy coating, as well as from a sodium-zinc alloy coating.

One specific method of thus obtaining a sodium-free metal coating is shown by way of example as illustrated by Fig. 2 of the drawing. In Fig. 2 a vessel 1 for the coating metal and a vessel 2 for the sodium alloy are associated with a vessel 9 which contains a reagent for removing the sodium from the sodium alloy coating. These three vessels may be mounted together in furnace setting 10, shown diagrammatically in the drawing, and heated by means not shown so as to maintain the temperature above the melting point of the coating to be applied. Vessel 1 is provided with partition 11 which serves to divide the upper part of vessel 1 into two portions so as to separate the flux from the oil. Steel strip 7 having previously been properly cleaned passes through the three vessels over guide rolls 4. The strip first passes through a flux and then into a molten metal in vessel 1, thence through an oil layer out of vessel 1. The layer of oil on the surface of the fused metal in vessel 1 is a hydrocarbon oil which is not reactive towards the sodium so that any oil picked up by the metal strip leaving vessel 1 will not bring a sodium reactive material into vessel 2. The sodium alloy in vessel 2 is covered with oil which is not reactive to sodium and the metal strip passes through this oil layer both entering and leaving the bath. The metal strip leaving vessel 2 is coated with a sodium alloy. It then passes through vessel 9 wherein the reagent such as fused tin chloride, ammonium chloride mixture or the like rapidly reacts with the sodium so that the strip leaving vessel 9 is coated with a substantially sodium-free metal. I have found that the reaction between the sodium and a suitable reagent, such as fused tin chloride, zinc chloride and the like, to completely remove sodium is substantially as rapid as the introduction of sodium into the metal coating which occurs in vessel 2. Accordingly, a rate which is suitable for passing a metal strip through

one of the three operations illustrated in Fig. 2 will be suitable for all three operations.

Fig. 2 also illustrates a method whereby the sodium alloy is protected from the atmosphere by means only of a liquid hydrocarbon, no inert gas being used. If desired, the arrangement shown in Fig. 1 could be adapted to the process described in Fig. 2 in order to maintain an inert gas atmosphere over one side of the sodium alloy bath in vessel 2 and over one side of the metal coating bath in vessel 1.

My invention is further illustrated by the following examples:

#### Example I

Strips of 22 gage commercial tin plate were immersed in a sodium-tin alloy bath under a mineral oil ("WIROLE E" at a temperature of 240° C. and after 45 seconds were removed and allowed to cool. The strips were then analyzed for their sodium content.

Tin-sodium bath at start-----	0.680% Na
Tin-sodium bath at end-----	0.667% Na
Sodium content of the tin which	
coated the strips-----	0.529% Na

#### Example II

Strips of 22 gage sheet iron were pickled and tinned in pure tin using the usual  $\text{ZnCl}_2$ - $\text{NH}_4\text{Cl}$  flux. These strips were removed from the tin bath and allowed to cool. They were then introduced into a tin-sodium alloy bath at 250° C. held under "Wirole E." No flux was used. The strips were then removed and cooled. The tin-sodium alloy bath contained 0.88% sodium and the amount of sodium in the resulting tin-sodium alloy coating was approximately 0.08%.

Another experiment was performed as above but using a tin-sodium alloy bath containing 0.172% of sodium, and operating at a temperature of 270° C. In this case the resulting sodium-tin coating contained 0.065% Na.

#### Example III

A bath of 2% of Na in zinc was prepared and held in a nitrogen atmosphere at a temperature of 575° C. Strips of standard 22 gage galvanized iron were dipped in this sodium-zinc bath for 30 seconds and then removed and let cool in air until the coating had solidified.

The pieces of coated material were then analyzed for their sodium content and it was found that the zinc in the coating contained 0.182% sodium.

#### Example IV

Strips of sheet iron were pickled in hydrochloric acid until free from mill scale and were immersed in aterne bath containing 40% tin and 60% lead at a temperature of 260° C. Theterne bath was covered with the usual zinc chloride-ammonium chloride flux. A good adherent coating ofterne metal was obtained.

The previously preparedterne plated strips were then immersed in aterne bath made by adding 0.607% sodium to a composition of 40% tin and 60% lead. The metal bath was held at 270° C. and the strips were immersed therein for 45 seconds. Upon removal of the strips they were analyzed for sodium and the metal coating was found to contain 0.102% of sodium.

#### Example V

A bath was prepared by melting 150 gm. of stannous chloride,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , and adding 150

gm. of ammonium chloride. The bath was heated to 270° C.

Steel strips which had previously been coated with tin-sodium alloy were dipped in this bath for 10 seconds and then removed and allowed to cool. The resulting coatings had a good appearance and when analyzed for sodium were found to be entirely free from sodium.

Sodium content of coatings at start=0.065% Na.  
Coatings after treatment with bath=0.00% Na.

Similar results were obtained at temperatures above the melting point of tin with reagents such as an ammonium chloride-zinc chloride flux, palm oil, fused caustic, and also when exposed to room air over periods of  $\frac{3}{4}$ -1 hour at a temperature above the melting point of the coating.

I claim:

1. The process for coating a metal base with an alloy of sodium and a fusible metal which has a melting point lower than that of said base which comprises first providing a metal base having a coating of said fusible metal, providing a homogeneous molten bath of an alloy of sodium and said fusible metal existing as a single liquid phase out of contact with any other liquid metal bath and having its upper surface covered with a fluid material substantially chemically inert to sodium, immersing the said coated metal base downwardly into the said alloy bath until a fused sodium alloy coating is formed on said base and then removing said base upwardly out of said alloy bath and through said fluid material covering the alloy bath.

2. The process for coating a ferrous base with an alloy of sodium and a fusible metal which has a melting point lower than that of said base which comprises first providing a ferrous base having a coating of said fusible metal, providing a homogeneous molten bath of an alloy of sodium and said fusible metal existing as a single liquid phase out of contact with any other liquid metal bath and having its upper surface covered with a fluid material substantially chemically inert to sodium, immersing the said coated ferrous base downwardly into the said alloy bath until a fused sodium alloy coating is formed on said base and then removing said base upwardly out of said alloy bath and through said fluid material covering the alloy bath.

3. The process for coating a ferrous base with an alloy of sodium and tin which comprises first providing a ferrous base having a coating of tin, providing a homogeneous molten bath of sodium-tin alloy existing as a single liquid phase out of contact with any other liquid metal bath and having its upper surface covered with a fluid material substantially chemically inert to sodium, immersing said coated ferrous base downwardly into said alloy bath until a fused sodium-tin alloy is formed on said base and then removing said base upwardly out of said alloy bath and through said fluid material covering the alloy bath.

4. The process for coating a ferrous base with an alloy of sodium and zinc which comprises first providing a ferrous base having a coating of zinc, providing a homogeneous molten bath of sodium-zinc alloy existing as a single liquid phase out of contact with any other liquid metal bath and having its upper surface covered with a fluid material substantially chemically inert to sodium, immersing said coated base downwardly into said alloy bath until a fused sodium-zinc alloy is formed on said base and then removing said base

upwardly out of said alloy bath and through said fluid material covering the alloy bath.

5. The process for coating a ferrous base with an alloy of sodium and tin which comprises first providing said base with a coating of tin, providing a homogeneous molten bath of sodium-tin alloy existing as a single liquid phase out of contact with any other liquid metal bath and having its upper surface covered with a liquid hydrocarbon substantially chemically inert to sodium, immersing the coated ferrous base downwardly into said alloy bath until a fused sodium-tin alloy is formed on said base and then removing said base upwardly out of said alloy bath and through said liquid hydrocarbon covering the alloy bath.

6. The process for coating a ferrous base with an alloy of sodium and tin which comprises first providing said base with a coating of tin, providing a homogeneous molten bath of sodium-tin alloy existing as a single liquid phase out of contact with any other liquid metal bath and having its upper surface covered with a gas substantially chemically inert to sodium, immersing said coated base downwardly into said alloy bath until a fused sodium-tin alloy is formed on said base and then removing said base upwardly out of said alloy bath and through said gas covering the alloy bath.

7. The process for coating a metal base with an alloy of sodium and a fusible metal having a melting point lower than that of said base which comprises providing a molten bath of said fusible metal having its upper surface covered in part with a molten flux layer reactive to sodium and in part with a fluid material substantially non-reactive to sodium, and a separate homogeneous molten bath of a sodium alloy of said fusible metal existing as a single liquid phase out of contact with any other liquid metal bath and having its upper surface covered with a fluid material substantially non-reactive to sodium, and passing said metal base first downwardly through said flux layer into said fusible metal bath, thence upwardly into said fluid material covering said metal bath, thence through said fluid material and downwardly into said alloy bath and thence upwardly and through said fluid material covering said alloy bath.

8. The process for coating a metal base with an alloy of sodium and tin which comprises providing a molten bath of tin having its upper surface covered in part with a molten flux layer reactive to sodium and in part with a fluid material substantially non-reactive to sodium, and a separate homogeneous molten bath of sodium-tin alloy existing as a single liquid phase out of contact with any other liquid metal bath and having its upper surface covered with a fluid material substantially non-reactive to sodium, and passing said metal base first downwardly through said flux layer into said tin bath, thence upwardly into said fluid material covering said tin bath, thence through said fluid material and downwardly into said alloy bath and thence upwardly and through said fluid material covering said alloy bath.

9. The process for coating a metal base with an alloy of sodium and tin which comprises providing a molten bath of tin having its upper surface covered in part with a molten flux layer reactive to sodium and in part with a gas substantially non-reactive to sodium, and a separate homogeneous molten bath of a sodium-tin alloy existing as a single liquid phase out of contact

with any other liquid metal bath and having its upper surface covered with a gas substantially non-reactive to sodium, and passing said metal base first downwardly through said flux layer into said tin bath, thence upwardly into said gas covering said tin bath, thence through said gas and downwardly into said alloy bath and thence upwardly and through said gas covering said alloy bath.

10. The process for coating a metal base with an alloy of sodium and zinc which comprises providing a molten bath of zinc having its upper surface covered in part with a molten flux layer reactive to sodium and in part with a gas substantially non-reactive to sodium, and a separate homogeneous molten bath of a sodium-zinc alloy existing as a single liquid phase out of contact with any other liquid metal bath and having its upper surface covered with a gas substantially non-reactive to sodium, and passing said metal base first downwardly through said flux layer into said zinc bath, thence upwardly into said gas covering said zinc bath, thence through said gas and downwardly into said alloy bath and thence upwardly and through said gas covering said alloy bath.

11. The process for coating a metal base with an alloy of sodium and a fusible metal which has a melting point lower than that of said base which comprises immersing said base previously coated with said fusible metal in a bath of a molten alloy of sodium and said fusible metal until a fused sodium alloy coating is formed on said base and removing said base from said bath, the surface of said bath being in contact with a fluid material substantially chemically inert to sodium and thereafter contacting the resulting sodium alloy coated base at a temperature above the melting point of the alloy coating with a substance reactive to sodium for such period of time that at least a portion of the sodium is removed from said alloy coating, so as to leave a coating comprising said fusible metal on said base.

12. The process for coating a ferrous base with a tin-sodium alloy which comprises passing said base through a layer of molten flux reactive to sodium into a molten tin bath, thence out of said tin bath into a gas substantially chemically inert to sodium, then passing said base substantially without cooling through a molten tin-sodium alloy bath, said alloy bath having its surface in contact with said gas and thereafter contacting the resulting tin-sodium alloy coated base at a temperature above the melting point of the alloy coating with a fused salt bath reactive to sodium for such period of time that at least a portion of the sodium is removed from said alloy coating, so as to leave a coating comprising tin.

13. The process for coating a ferrous base with a zinc-sodium alloy which comprises passing said base through a layer of molten flux reactive to sodium into a molten zinc bath, thence out of said zinc bath into a gas substantially chemically inert to sodium, then passing said base substantially without cooling through a molten zinc-sodium alloy bath, said alloy bath having its surface in contact with said gas and thereafter contacting the resulting zinc-sodium alloy coated base at a temperature above the melting point of the alloy coating with a fused salt bath reactive to sodium for such period of time that at least a portion of the sodium is removed from said alloy coating, so as to leave a coating comprising zinc.

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