Dec. 22, 1959 G. A. MOLLER 2,918,388

METHOD AND MEANS OF COATING METALS

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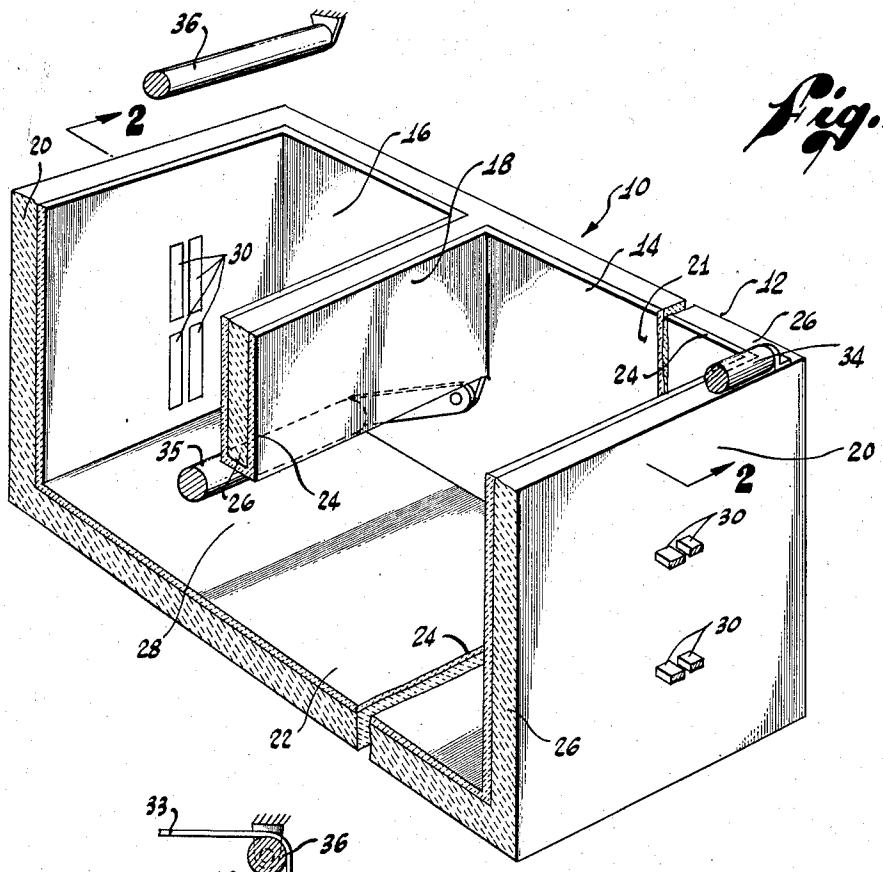

Fig. 1

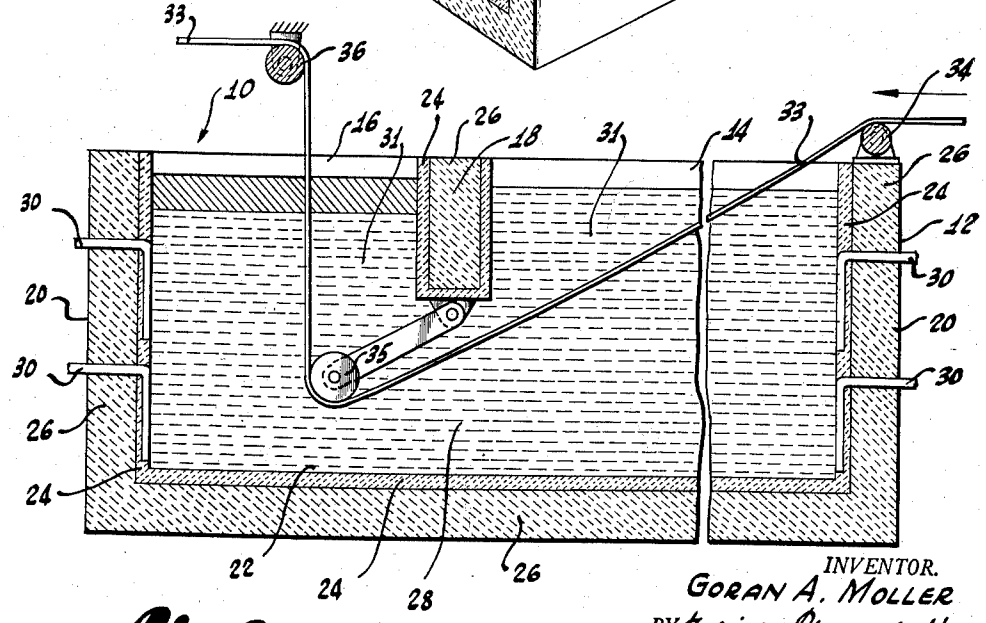

Fig. 2

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METHOD AND MEANS OF COATING METALS

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10 Claims. (Cl. 117—51)

This invention relates generally to the coating of metals and relates particularly to improvements in an apparatus and process for the coating of metals.

Generally speaking, this invention constitutes an improvement over the process and apparatus disclosed in my United States Patent No. 2,315,725, entitled "Process for Metallization, Especially Aluminization of Iron Articles," and is a continuation-in-part of my co-pending application, Serial No. 252,267, filed October 20, 1951, now abandoned.

In the utilization of my process described in the above-identified patent, which has numerous highly advantageous aspects, it is nevertheless sometimes found that the alloy interface between the coating metal and the base metal is very brittle. This brittleness is found to be caused by an excessive reaction between the coating metal and the base metal.

If the interfacial alloy formed is thick with respect to the thickness of the product, the entire product may be made brittle. Thus, for example, in ordinarily ductile steel strip that has been coated by the Moller process, it is sometimes found that the coating metal has alloyed with the base steel substantially throughout the diameter of the strip.

Reaction between iron and molten aluminum proceeds as soon as the two metals come in contact. The shorter the time they are in contact, the thinner will be the intermetallic layer and the smaller its effect on the ductility of the coating.

Bearing in mind the foregoing facts, it is a major object of the present invention to provide a method and means of coating metals whereby the interface formed between the coating metal and base metal is minimized.

It is another object of the present invention to provide means and a method for the coating of metals wherein the coated article produced has low brittleness and high ductility, and the coating metal is effectively bonded to the base metal.

Still another object of the present invention is to provide a means and a method for the coating of metals wherein the coating metal-base metal interface formed is sufficiently thin to render the coated product of a highly ductile nature.

Yet another object of the present invention is to provide a continuous process for the coating of metals in which the time of alloying action between the base metal and the coating metal is minimized.

It is a further object of the present invention to provide an apparatus wherein the time of contact between the base metal and the coating metal is greatly reduced.

It is still another object of the present invention to provide means and a method in which the continuous coating of metals can be conducted more rapidly.

These and other objects and advantages of the present invention will become apparent from the following description and the accompanying drawings, in which:

Figure 1 is a foreshortened perspective view of the apparatus of the present invention, one wall of the apparatus being removed to reveal the interior thereof; and

Figure 2 is a view in cross-section taken along the line 2—2 of the apparatus of Figure 1, the interior thereof containing various materials.

Generally, my improved process and apparatus for the coating of metals makes use of the discovery that the period within which the coating metal and the base metal react at high temperatures largely determines the extent of the alloying action therebetween, which, in turn, mainly determines the brittleness of the resulting coating product.

The process, illustrated in my above-identified patent, employs a single compartment salt bath furnace in which a pretreating salt bath is placed and heated to a molten state. The coating metal completely overlies the surface of the salt bath and is maintained in a molten state by heat transmitted to it by conduction from the molten salt.

When the base metal (the metal to be coated) is immersed in the lower salt bath layer through the molten coating layer, some localized wetting of the base metal by the coating metal occurs. The coating metal and base metal thus prematurely react to form an alloy, the alloying reaction continuing throughout the entire time that the base metal is submerged within, and heated by, the molten salt bath—preferably to a temperature above that of the melting point of the coating metal.

The extended period of alloying action caused by the pre-wetting of the base metal by the coating metal may result in the production of a relatively thick alloy coating metal-base metal interface, particularly in thin pieces of material, such as wire, strip, or sheet.

Referring now to the drawings, the furnace **10** comprises a tank-like, preferably rectangular, crucible or pot **12** divided by a partition wall **18** into pretreating and coating sections or compartments **14** and **16**, respectively. The crucible **12** is provided with a pair of end walls **20**, a pair of side walls **21** (one of which has been removed in Figure 1 to reveal the interior of the furnace **10**), and a floor **22**.

The end and side walls **20**, **21**, respectively, the floor **22**, and the partition wall **18** of the crucible **12** are made of suitable refractory materials capable of withstanding the corrosive action of chemical salts at high temperatures for long periods of time. For example, the walls **18**, **20** and **21**, and floor **22** of the furnace **10** may be composed of a dense, high alumina-containing refractory inner liner **24** affixed to a layer of standard, high temperature, suitably reinforced, refractory brick **26**.

The partition wall **18** is preferably affixed normal to the side walls **21** of the crucible **12**, is spaced from the end walls **20** and terminates above the floor **22**, forming an interconnecting passage **28** to enable the metal to be coated to pass thereunder. It is generally desirable to position the partition wall **18** so that the pretreating section **14** of the crucible **12** has a considerably greater length than the coating section **16**.

For example, a coating furnace has been built having the following inner dimensions: 30 feet in length, 2 feet in depth, and 2 feet in width. The pretreating section of this furnace is approximately 28.5 feet long, 2 feet wide, and 2 feet deep, the coating section being 1 foot in length, and equal to the width and depth of the furnace. The partition wall, approximately 0.5 foot in length, separates the two sections.

If the coating section of the furnace is further reduced, as is preferable in some instances, for example, to a length of 6 inches, the pretreating section is increased in length of 29 feet, the pretreating section thus 58 times the length and volume of the coating section.

The crucible 12 is heated electrically by spaced heating electrodes 30 embedded preferably in the lower portion of each of the end walls 20.

The interior of the crucible 12 contains a bath of molten salts 31 which completely covers the electrodes 30 in both sections 14 and 16, and is a means of transferring heat from the electrodes 30 to a material that is placed in the interior of the furnace 10. The coating section 16 also contains a molten coating layer 32 which rests upon the salt layer 31 and is in direct contact therewith. The salt bath 31 and the coating metal 32 are an integral part of the furnace 10, since these molten materials are replenished as needed, and the level of the materials is essentially constant.

The salt bath 31 is preferably composed of the chloride, bromide, and fluoride salts, especially those of the alkali and alkaline earth groups. Also, aluminum fluoride and cryolite (NA_3AlF_6) are especially advantageous.

The precise combination of salts used in the salt bath 31 is determined primarily by the composition and density of the coating metal and also by the composition and physical condition of the base metal to be coated. For example, if a pure aluminum metal is the coating material, the temperature at which it must be maintained is its melting point, 1218° F. The pretreating salt bath 31 must therefore comprise a combination of salts that is stable above 1218° F. On the other hand, if an aluminum alloy is to be used as the coating material, the temperature of the salt bath need not be maintained as high as with the pure aluminum, since the melting point of the aluminum alloys is generally lower than that of pure aluminum. Hence, a factor in the determination of the composition of the salt bath is the composition of the coating metal.

Generally, if the metal to be coated has a large amount of oxides on its surface, it is advisable to include in the salt bath composition a greater amount of fluorides than would ordinarily be present for the purpose of dissolving aluminum oxides, the fluorides having also a greater tendency to dissolve the metal surface oxides. The amount of fluorides added thus varies from 0.0% to 20% of the total weight of the salt, although it is generally advantageous to employ from 0.1% to 10% of the fluoride salts. Hence, the condition of the base metal is a factor entering into the determination of the salt bath composition.

The composition of the salt bath is also determined, in part, by the density of the coating metal. It is generally desirable to support the coating metal directly on the salt bath, and therefore the composition of the salt bath is such as to have a density that will support a coating layer 32.

Bearing in mind all these factors, a salt bath composition that has been employed with excellent results in the coating of metals with various lightweight metals including pure aluminum or its alloys, at molten salt bath temperatures ranging between 1000° F. and 1650° F. is the following:

I. 70–75% barium chloride, by weight
20–25% sodium chloride, by weight
0.1–10% sodium fluoride, by weight

II. 70–75% calcium bromide, by weight
20–25% sodium chloride, by weight
0.1–10% sodium aluminum fluoride, by weight

III. 70–75% potassium iodide, by weight
20–25% sodium chloride, by weight
0.1–10% aluminum fluoride, by weight

IV. 70–75% barium bromide, by weight
20–25% strontium chloride, by weight
0.1–10% sodium fluoride, by weight.

Composition I is presently preferred because of the relative cheapness of the chlorides.

The metal material to be coated, for example, wire or metal sheet 33, is first immersed in the pretreating section 14, thence passed beneath the partition wall 18 and upwardly through the coating section 16. The preferred conveying mechanism for this purpose consists of a guide roller 34 rotatably mounted onto the end wall 20 of the pretreatment compartment 14, a submerged guide roller 35 pivotally mounted to the baffle 18 in the coating section 16, and a third roller 36 spaced tangentially above the submerged guide roller, and rotatably mounted preferably substantially above the furnace 10, to allow cooling of the coated material to occur before the metal 33 is bent. The pivotal mounting of the submerged guide roller 35 allows it to be taken out for inspection, and for other purposes, through the salt layer 31 in the pretreating section 14, thus eliminating the need for its withdrawal through the molten aluminum 32. A series of such withdrawals through the molten aluminum results in a high degree of attack on the roller material which is generally made of steel.

The rollers 34, 35, and 36 are preferably of equal length, parallel to each other, and have the ends thereof terminating in the same vertical plane.

The relative arrangement of the pretreating rollers 34, 35 is such that the metal 33 to be coated follows an approximately diagonal path upon passing downwardly through the furnace 10. Further, the tangential arrangement of the submerged and coating rollers 35, 36 is such that the path along which the metal 33 passes upwardly in the coating section 16 is substantially normal to the plane of the coating layer 32, the metal thus following the shortest possible path through the coating material.

The conveying mechanism for coating individual pieces continuously may be modified to consist of an endless chain (not shown) to which the base metal may be hooked and sent downwardly through the pretreating section 14, through the interconnecting passage 28, and upwardly through the coating section 16, the arrangement of the rollers being also modified to allow for the passage of the individual pieces.

Having set forth a preferred embodiment of my coating apparatus, a preferred method of utilizing the apparatus to aluminize materials will now be described.

In this specification and in the appended claims, the term "aluminization" means a coating of a metal with aluminum or its alloys. Further, whenever the word "aluminum" is used, it is to be taken as meaning aluminum or its alloys.

The material to be coated, for example, continuous sheet metal 33 is sent over the pretreating roller 34, immersed in the salt bath pretreating section 14, thence passes downwardly beneath the partition 18 through the interconnecting passage 28, around the submerged roller 35, and thence upwardly through the coating section 16 contacting the aluminum coating layer 32 which is one to four inches in thickness, for preferably a fraction of a second, to be thereby aluminized. The aluminized material 33 is then preferably immediately quenched or greatly lowered in temperature to prevent further interreaction between the aluminum and the base metal.

The temperature range of the molten salt bath ranges from 1000° F. to 1650° F., depending on the coating metal 32 used, the degree of cleaning and deoxidation of the base metal 33 desired, and other factors. As mentioned previously, the temperature of the salt bath 31 is maintained at least equal to the melting point of the coating metal 32, so that the salt bath may maintain the coating metal in a molten state by direct conduction of heat therefrom.

The rate of passage of the base metal 33 through the molten salt bath is such as to impart to the base metal a temperature preferably at least equal to the melting point of the coating metal 32 prior to its entry into the coating metal 32. It is also particularly effective, in many instances, to impart to the base metal 33 a temperature approximately equal to the temperature of the salt bath 31 prior to its entry into the coating metal 32.

It is to be noted that the continuous metal **33** enters the salt bath **31** initially and does not first enter an aluminum layer. Thus, no reaction is initiated between the aluminum and the base metal prior to the actual coating step. The pretreated metal material, entering the aluminum coating layer **32** just prior to its exit from the furnace **10**, has an exceedingly short period of reaction according to my invention, since the aluminum-base metal alloying action can progress only in that period of time between the actual coating step which occurs as the base metal leaves the furnace **10**, and the cooling step.

An exceedingly short period of time, of the order of a fraction of a second, is sufficient to cause an effective bond to form, but positively eliminates the production of a thick, brittle interface, which would cause the entire product to be brittle. It is found that an effective bond is produced, even when the interfacial alloy is exceedingly thin—that is, on the order of molecular dimensions.

It is to be understood that the process above-described is adapted for use with coating metals other than aluminum, these other metals including those lighter than the salt bath **31**.

The speed at which continuous materials and discontinuous materials may be continuously coated is limited mainly by the fact that the base metal **33** is preferably brought to coating temperature, that is, a temperature above the melting point of the coating material **32**, before the actual coating can occur. In order to increase the speed at which metals may be coated, the pretreating section **14** is greatly elongated with respect to the coating section **16**, as previously mentioned. Thus, as the metal **33** travels through the salt bath **31** at great speed, it will nevertheless readily attain the temperature of the salt bath prior to its entry into the coating layer **32**. In this connection, it is preferable also that the base metal material **33** pass diagonally downwardly through the furnace **10**. Continuous materials have been run through the elongated furnace **10** in this manner at speeds of several hundred feet a minute without any sacrifice in the quality of the coating or the ductility of the product produced.

It is also desirable, in some instances, to pass the material to be coated vertically downwardly into the pretreating section **14**, around a submerged roller, along the floor **22** of the furnace **10**, to the coating section **16**, and thence vertically upwardly through the coating section in order to obtain a yet longer run through the furnace.

It is to be noted that, in any case, the continuous material **33** travels in one direction through the furnace **10** in order to avoid any points of tension and stress that might otherwise arise if reversals of direction of the material were provided for.

The types of metals that have been aluminized with especially excellent results include iron, nickel, cobalt, manganese, titanium and copper metals and alloys thereof. These metals fall in the transition group of elements.

While a preferred embodiment of my apparatus and method has been described, it is apparent that many changes and modifications may be made which lie within the scope of the invention. Therefore, I do not intend to be limited by what I have shown and described, but only to be limited by the appended claims.

I claim:

1. A process for continuously coating base metals with a coating metal selected from the group consisting of aluminum and aluminum alloys, which comprises the steps of: immersing the base metal to be coated in a preheating molten salt bath having a temperature of between 1000° F. and 1650° F., said base metal being immersed in said salt bath without previously contacting said coating metal, said salt bath comprising at least one halide salt; withdrawing said pretreated base metal, after it has reached substantially the temperature of said salt bath, directly into a molten coating metal layer, overlying a portion of said salt bath, without intervening oxidation; and withdrawing said coated base metal immediately from said coating metal.

2. A process of continuously coating metals with a coating metal selected from the group consisting of aluminum and the aluminum alloys, which comprises the steps of: immersing said metal in a pretreating molten salt bath, said base metal being immersed in said salt bath without previously contacting said coating metal, said salt bath being composed of at least 90% of halide salts, other than fluoride salts, and up to 10%, by weight, of fluoride salts; passing said pretreated metal from said salt bath, after it has reached the temperature of said salt bath, directly into a salt bath of a coating section, said coating section having an aluminum layer from two to four inches in thickness, overlying said salt bath in said coating section; and passing said metal vertically through said coating section salt bath and normal to, and through, said molten aluminum layer to be coated thereby.

3. A process of continuously coating base metals selected from the group consisting of iron, nickel, cobalt, manganese, titanium, copper and alloys thereof with a coating metal selected from the group consisting of aluminum and aluminum alloys, which comprises the steps of: immersing the base metal material in a pretreating molten salt bath maintained at a temperature above the melting point of the coating metal, said base metal being immersed in said salt bath without previously contacting said coating metal, passing said material from said salt bath directly into an interconnected salt bath of a coating section which supports an overlying aluminum layer one to four inches in thickness thereon, each of said salt baths being maintained at a temperature above the melting point of said aluminum layer and being composed of halide salts; and passing said material, after it has attained substantially the temperature of said salt bath, vertically through said molten aluminum layer to be coated thereby.

4. The process of coating continuous metal materials as defined in claim 3, characterized in that the salt bath comprises halide salts selected from a group consisting of alkali and alkaline earth fluorides, chlorides, iodides, and bromides.

5. A process for coating a base metal with a coating metal selected from the group consisting of aluminum and aluminum alloys, which comprises the steps of: immersing the base metal to be coated in a salt bath having a temperature of between 1000° F. and 1650° F., said base metal being immersed in said salt bath without previously contacting said coating metal, said salt bath comprising at least one halide salt; withdrawing said base metal, after it has reached at least the melting point temperature of said coating metal, into said coating metal, without intervening oxidation, said coating metal overlying a portion of said salt bath and being maintained in its molten state, and withdrawing said coated base metal immediately from said molten coating metal.

6. A process for coating a base metal with a coating metal selected from the group consisting of aluminum and aluminum alloys, which comprises the steps of: immersing a metal to be coated in a salt bath having a temperature above the melting point of said coating metal, said base metal being immersed in said salt bath without previously contacting said coating metal, said salt bath comprising at least one halide salt; withdrawing said base metal, after it has reached substantially the temperature of said salt bath, into said coating metal, without intervening oxidation, said coating metal overlying a portion of said salt bath and being maintained in its molten state; and withdrawing said coated base metal immediately from said molten coating metal.

7. A process of continuously coating a continuous base metal material with a coating metal selected from the group consisting of aluminum and aluminum alloys,

which comprises the steps of: immersing the continuous base metal material in a molten salt bath maintained at a temperature above the melting point of the coating metal, said base metal being immersed in said salt bath without previously contacting said coating metal; passing said base metal material from said salt bath into an interconnected salt bath of a coating section which supports an overlying molten aluminum-containing layer one to four inches in thickness thereon, each of said salt baths being maintained at a temperature above the melting point of said aluminum layer and being composed of at least one halide salt; and passing said material, after it has attained at least the melting point temperature of said coating metal, through said aluminum layer to be coated thereby.

8. The process of coating continuous base metal materials as defined in claim 7, characterized in that the salt bath comprises a halide salt selected from a group consisting of alkali and alkaline earth fluorides, chlorides, iodides and bromides.

9. A process for coating base metals with a coating metal selected from the group consisting of aluminum and aluminum alloys, which comprises the steps of: immersing said base metal in a molten salt bath having a temperature at least equal to the melting point of said coating metal, said base metal being immersed in said salt bath without previously contacting said coating metal, said salt bath comprising at least one halide salt and being heavier than said coating metal; immersing said base metal, after it has reached at least approximately the melting point temperature of said coating metal, into

said molten coating metal, overlying a portion of said salt bath, without intervening oxidation, any salt, transferred to said coating metal, by means of said base metal, sinking below said coating metal; and withdrawing said coated base metal immediately from said coating metal.

10. An apparatus for coating continuous base metal materials which comprises: a rectangular refractory pot having a floor, a pair of end walls, and a pair of elongated side walls; a transverse partition wall affixed to said side walls and spaced from said end walls to form a pretreating and a coating section, said partition wall terminating above said floor to form a lower interconnecting passage between said sections; means for conveying said continuous material diagonally downwardly through said pot through said passage, and approximately vertically upwardly through said coating section, said conveying means comprising roller means affixed onto one of said walls of said pot; heating electrodes embedded in the lower portions of the end wall of each compartment; and means for transferring heat from said electrodes to said material passing through said compartments, said means comprising a molten salt.

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CERTIFICATE OF CORRECTION

Patent No. 2,918,388 December 22, 1959

Goran August Moller

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 69, for "preheating" read -- pretreating --; column 6, line 57, for "state," read -- state; --.

Signed and sealed this 28th day of June 1960.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents