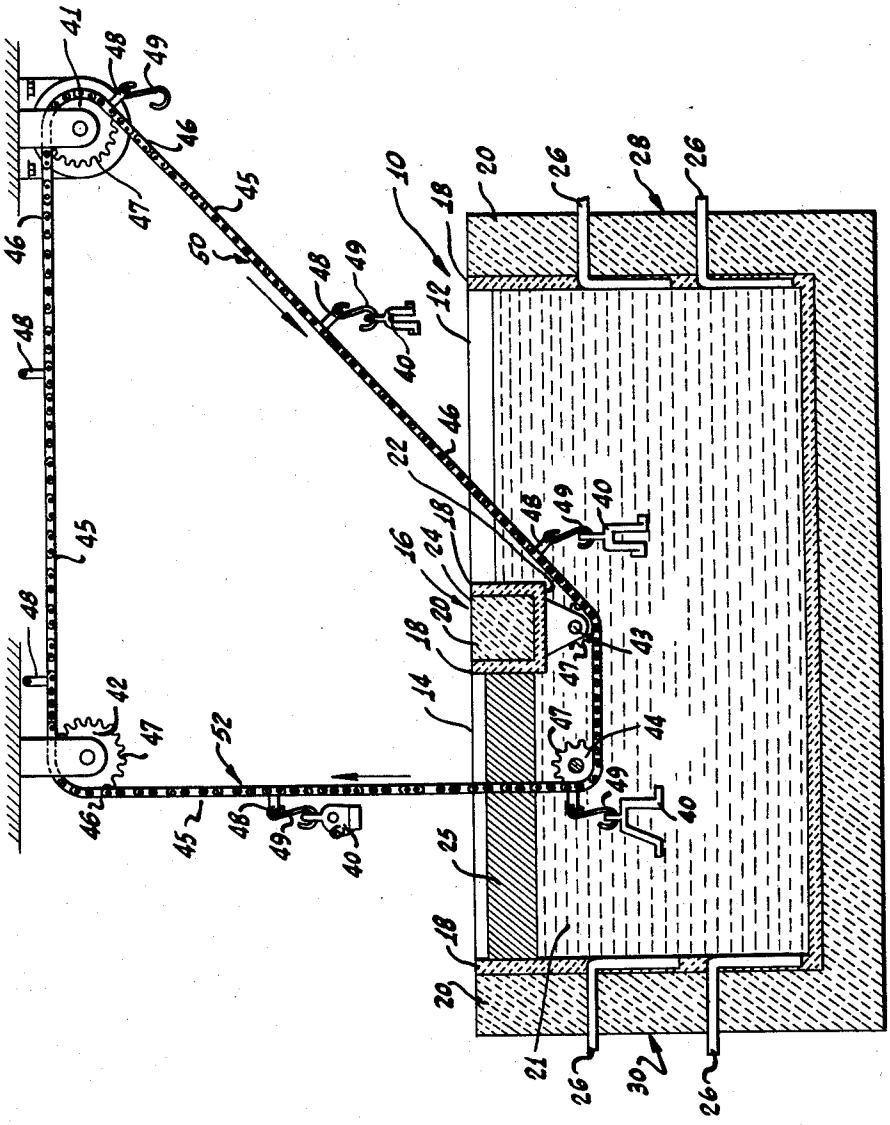
May 3, 1960 D. W. MITCHELL 2,935,419

METHOD OF ALUMINIZATION AND PRETREATING MEDIUM THEREFOR

Filed Aug. 27, 1956



INVENTOR.
DAVID W. MITCHELL
BY Fulwider Mattingly & Hunitzky
ATTORNEYS

United States Patent Office 2,935,419
Patented May 3, 1960

2,935,419

METHOD OF ALUMINIZATION AND PRETREATING MEDIUM THEREFOR

David W. Mitchell, Beverly Hills, Calif., assignor to American Mollerizing Corporation, Beverly Hills, Calif., a corporation of Nevada

Application August 27, 1956, Serial No. 606,514

11 Claims. (Cl. 117—51)

My invention relates generally to the coating of metals, and more particularly to a method and composition of matter for eliminating surface oxides from metals to be aluminized.

The term "aluminization" as used in this specification and claims refers to the coating of metals with molten aluminum or with molten aluminum alloys, while the term "aluminum" is used generically to include any substance which comprises, as a predominant constituent thereof, aluminum, examples being the aluminum alloys, and of course, pure aluminum.

In the past, metal surfaces have been made relatively free of oxides, preparatory to being aluminized, by being dipped into pickling solutions of bases or acids at temperatures below or at their boiling point, examples of appropriate acids being sulphuric acid and hydrochloric acid, and examples of an appropriate base being caustic soda.

The metal to be aluminized is then necessarily washed with water or an aqueous flux solution to remove the acid or base clinging to the metal in order to prevent the contamination thereby of the aluminum coating bath, as the object is immersed therein. However, after washing, and prior to the coating step, the water must be removed from the base metal in order to avoid explosions which might otherwise occur by reason of the intense reaction between the molten aluminum and water adhering to the base metal. The usual method of removing the water is by a drying operation, which, however, results in a re-oxidation of the metal surface.

The substantially complete elimination of oxides from the metal surfaces to be aluminized and is essential to the success of the process. For example, even very thin oxide films on the metal cause relatively poor adherence of aluminum coating thereto.

Aluminization processes in the past have recognized that the surface oxide problem exists, and various means of solving it have been suggested, none of which substantially completely eliminates the presence of surface oxides immediately prior to aluminization. For example, referring to the hot dip aluminization process disclosed in the Moller Patent No. 2,315,725, entitled "Process for Metallization, Especially Aluminization of Iron Articles," issued April 6, 1943, the metal to be aluminized is dipped into a predominantly halide molten salt bath upon which rests a layer of molten aluminum or of an aluminum alloy. The halide salt bath contains some fluoride salts which have a dissolving effect upon the oxides on the metal surface, and also upon the aluminum oxides formed in the aluminum layer. However, the metal oxides on the surface of the metal to be aluminized are not completely removed by the fluorides, and while such processes as the Moller process have greatly improved the standard hot-dipping method of aluminization in many ways, they have not provided an ultimate solution to the surface oxide problem.

Accordingly, it is a major object of the present invention to provide a method and a means of aluminization

of metals wherein substantially all the surface oxides of the metal are eliminated.

It is another object of the present invention to provide a method and means of eliminating the last traces of oxides from the surface of the metals to be aluminized immediately prior to the aluminizing step.

It is another object of the present invention to provide a method and means of pre-treating metals for aluminization in which a reducing agent, dissolved in a non-aqueous mixture of fused salts, attacks the surface oxides of the metal to be aluminized immediately prior to the aluminization step.

It is yet another object of the present invention to provide in a hot-dip method of aluminization a composition of matter which is capable of chemically reducing the last traces of oxides from the surfaces of metals to be aluminized immediately prior to the aluminization thereof.

It is still another object of the present invention to produce an aluminum-coated metal substantially completely devoid of oxides at the aluminum-base metal interface.

These and other objects and advantages of the present invention will become apparent from the following description and the accompanying single figure, in which an apparatus is shown in cross-section adapted to pretreat and aluminize metals according to the principles of my invention.

In general, the method and means of aluminization of metals of the present invention finds their greatest use in hot-dipping processes wherein the molten coating layer of aluminum or its alloys directly contacts the pretreating salt bath, as by floating thereon, in the manner disclosed by the above-identified Moller patent. By utilizing this type of process, the metal to be aluminized may be withdrawn from the improved pre-treating salt bath of the present process, after the virtually complete elimination of the oxides thereon, directly into the coating aluminum layer without any possibility of intervening oxidation immediately prior to the coating step.

The apparatus whereby the method and means of the present invention is advantageously utilized is designated in the figure by the numeral **10**. The apparatus **10** is a furnace, preferably rectangular, and comprises two sections or compartments, the right-hand or pre-treating section **12**, and the left-hand or coating section **14**, separated by a partition wall **16** terminating above the furnace **10**.

The furnace **10** is constructed of an inner liner **18** of suitable heat and chemical resistant material, such as a high density alumina refractory, and a backing layer **20** composed of a second refractory material, such as standard refractory brick, suitably reinforced as by an outer steel casing (not shown).

The partition wall **16** is also provided with a heat and chemical resistant liner **18** on each side face thereof, the liners being separated by the refractory backing layer **20**.

The pre-treating compartment **12** is preferably substantially longer than the coating compartment **14**, so that the base metal to be aluminized may be passed very rapidly through the pre-treating compartment **12** and still attain a temperature suitable for a high degree of cleaning and de-oxidation. Thus, for example, if the interior dimensions of the furnace **10** are 2 feet deep, 2 feet wide, and 30 feet long, the pre-treating compartment occupies from 20 to approximately 29.5 feet in length, 2 feet in width, and 2 feet in depth, whereas the coating compartment will comprise a volume of between 0.5 and 10 feet in length by 2 feet in depth, by 2 feet in width. Pre-treating compartment **12** is varied in length depending upon such factors as the composition of the salt bath used, the condition of the base metal, the purpose to which the product is to be put, and other factors.

The salt bath **21** of the present invention is introduced

into the interior of the furnace 10, the surface thereof lying above the lower edge 22 of the partition wall 18, but somewhat below the upper edge 24 thereof. A layer preferably 2–4 inches in thickness of aluminum coating metal 25 is provided within the coating section 14 of the furnace 10 and rests on the salt bath 21, the coating metal having a lower specific gravity than the salt bath.

Each compartment 12 and 14 is provided with a number of heating electrodes 26 embedded in the end walls 28 and 30 of the compartments 12 and 14, respectively, the electrodes being connected to a suitable electric source (not shown) whereby the salt bath 21 of the furnace 10 is maintained, in a molten state, at a specific desired temperature.

The molten salt bath 21 of the present invention comprises one or more chloride, bromide, iodide and fluoride salts, especially those of the alkali and alkaline earth groups, and the aluminum-containing fluorides, and one or more hydride salts, these salts together acting as the sole means of heat transmission to the aluminum layer 25 thereby maintaining it in a molten state in accordance with the principles set forth in the above-identified Moller patent.

The temperature of the salt bath required for aluminization ordinarily lies between about 1050° F., and 1650° F., the exact temperature depending upon such factors as the composition of the aluminum coating layer 25 and the thickness and ductility of the aluminum coating desired.

The preferred hydride salts that are employed in the pre-treating salt bath 21 are those of the alkali and alkaline earth group. In the temperature range between 1050° F. and 1650° F., however, these hydrides are generally relatively unstable, with the exceptions of calcium hydride, barium hydride and lithium hydride, and even these three at these temperatures must be considerably diluted to prevent substantial decomposition. It is therefore desirable to employ a small percentage, by weight, of the calcium, barium, and/or lithium hydrides dissolved in a predominantly halide salt bath. Preferably, the amount of calcium, barium, and/or lithium hydrides added to the salt bath is approximately 2% to 3%, by weight, of the total weight of the salt bath, although approximately as low as 0.01% has been employed in many instances with excellent results. Greater concentrations of hydrides have been, and may be, employed, but generally the greater concentration does not have any greater effect on the deoxidation of the piece to be coated.

The calcium, barium, and lithium hydride salts, which are extremely powerful reducing agents, at these temperatures, cooperate with the molten reducing halide salts, especially the fluorides, which are particularly effective in dissolving aluminum oxides, to substantially completely eliminate all traces of surface oxides from both the metal and the aluminum coating layer in the furnace 10.

The precise combination of halide salts used is determined primarily by the composition and density of the particular coating metal employed. It is preferable to support the aluminum coating metal on the salt bath 21 and therefore the composition of the halides in the salt bath is adjusted so as to have a density heavier than the aluminum coating metal, the relatively small percentage of hydrides employed contributing little to alter the overall density of the salt bath. In this connection, the barium halides as a group are heavier than the other alkali or alkaline earth metal halides, and an advantageous combination of halides therefore comprises a major percentage of barium halides with a lesser percentage of other lighter metal halides, other than a fluoride.

Bearing in mind these factors, salt bath compositions 21 that have been employed with excellent results in the coating of metals with pure aluminum and many of its alloys at salt bath temperatures ranging between 1050° and 1650° F. comprise the following:

I. 65–75% barium chloride by weight
15–25% sodium chloride by weight
0.0–10% sodium fluoride by weight (the fluoride may not be needed if the piece to be coated is relatively clean)
0.01–3% calcium hydride by weight

II. 65–75% calcium and/or barium bromide by weight
15–25% sodium bromide by weight
0.0–10% aluminum fluoride by weight
0.01–3% calcium hydride by weight

III. 65–75% potassium iodide by weight
15–25% sodium iodide by weight
0.0–10% sodium fluoride by weight
0.01–3% calcium hydride by weight

IV. 65–75% strontium chloride by weight
15–25% sodium chloride by weight
0.0–10% cryolite by weight
0.01–3% calcium hydride by weight

Composition I is presently preferred because of the relative cheapness of the chloride salts.

The metal to be coated in the apparatus 10 may be wire, strip, sheet, or other continuous material, or may be a discontinuous piece of material 40, as shown in the figure. The piece 40 is first pickled in an acid or base solution, for example, sulphuric acid solution, to remove heavy scale adhering thereto. It is then washed in an aqueous flux solution to remove the adhering aluminum-contaminating pickling solution, and dried, during which some re-oxidation occurs. The piece 40 is then ready for the final pretreating step and the coating step.

The conveying mechanism made of, for example, a suitable refractory material, by which the piece 40 is passed through the sections 12, 14, of the furnace 10 comprises a pair of spaced sprockets 41, 42 rotatably mounted above the furnace 10, and a pair of spaced sprockets 43, 44 rotatably mounted to the furnace below the surface of the salt bath 21, the sprocket 44 lying in the coating section 14 of the furnace 10. The sprockets 41, 42, 43 and 44 all lie in the same vertical plane, and the axis of the sprocket 42 lies vertically above the axis of the wheel 44.

An endless chain 45 is placed about the sprockets 41, 42, 43 and 44, the links 46 of the chain interlocking with the teeth 47 of each of the sprockets. The chain is thus movable by the rotation of any one of the sprockets 41, 42, 43 or 44. The upper sprocket 41 is axially connected to a driving means (not shown) whereby the rotation thus imparted to this sprocket drives the chain 45 in the direction indicated by the arrow.

The chain 45 has affixed thereto a series of spaced outwardly protruding eyes 48 adapted to receive removable hooks 49. The pieces 40 are removably affixed to the hooks 49 at a point prior to the entry of the chain 45 into the salt bath 21 of the furnace 10 as, for example, at point 50.

The metal piece 40 passes into and through the pretreating section 12, being heated, cleaned, and thoroughly de-oxidized therein by the action of the hydrides and halides, and is then withdrawn from the pre-treating section 12, around sprocket 43 into the coating section 14, around sprocket 44, thence vertically upwardly through the aluminum layer 25 to be removed, for example, at point 52 for quenching or other process steps.

The rate of travel of the metal piece 40 is adjusted so that, as the metal leaves the salt bath 21, its temperature is at least equal to the melting point temperature of the aluminum coating metal 25. Thus, an adequate alloying action between the base metal and the coating metal is assured.

Continuous materials, such as strip, wire and sheet, are

aluminized in substantially the same manner as described with reference to the individual piece **40**, the conveying means being considerably modified depending upon the particular type of material to be aluminized.

Another group of salt bath compositions with which good results have been obtained is the following:

35–57% potassium chloride by weight
24–45% sodium chloride by weight
0.0–20% sodium aluminum fluoride by weight
0.0–12% aluminum fluoride by weight
0.01–3% barium hydride

These salt bath compositions all have a specific gravity less than that of the aluminum coating layer so that the salt will lie thereupon. The chemical action of the hydrides and halides in these compositions is very similar to that of the previously described compositions. The elimination of virtually all the surface oxides on the metal surface as well as the aluminum oxides, is thus assured.

A process in which the second group of salt bath compositions described above can be utilized is the following: the piece to be coated is first immersed into a molten salt bath, then lowered into the submerged aluminum coating layer, and withdrawn after being coated, through the overlying salt composition bath. In this process the salt adheres to the aluminum coated piece and must be removed after the coating step.

The first-described method and composition of matter is more advantageous, inasmuch as substantially less diffusion between the base metal and the coating metal is encountered and a consequently thinner and more ductile interfacial alloy is obtained.

The metal hydride reducing agent employed in any of the above salt bath compositions is either added directly to the molten salt bath **21** in which it dissolves, or it may be generated in the halide salt by the simultaneous addition of hydrogen gas and lithium, calcium, and/or barium metal.

The types of metal that have been aluminized with especially excellent results include the elements iron, nickel, cobalt, manganese, titanium and cooper metals and alloys (e.g., steel) thereof. These metals, with the exception of titanium, fall in the transition group of elements and have atomic numbers ranging from 25 for manganese to 29 for copper. Titanium has an atomic number of 22.

The composition of matter above described is also employed in the single compartment Moller furnace illustrated and described in the above-identified Moller patent. Further, in some instances, it is advantageous to utilize the composition of matter in a multi-compartment salt bath furnace, each compartment interconnecting with the other, one compartment of the furnace containing the floating aluminum coating metal.

It will be understood that substantial modifications may be made in the specific embodiments shown and described which lie within the scope of the invention. Therefore, I do not wish to be bound by the specific embodiments shown and described, but only by the appended claims.

I claim:

1. A bath for treating base metals which comprises a layer of molten metal selected from the group consisting of aluminum and aluminum alloys and a layer of molten salts containing approximately 97 to 99.99% molten halide salts, the remainder being hydride salts selected from the group consisting of calcium, barium and lithium hydrides, said molten layers being in contiguous underlying-overlying relationship.

2. A salt bath for pretreating metals to be aluminized, said salt bath being in direct contact with a molten aluminum-containing coating layer, which comprises by weight:

65–75% barium halide
15–25% sodium halide selected from the group consisting of chlorides, bromides and iodides
0.0–10% sodium fluoride

and at least one hydride which comprises 0.01–3% of the total weight of said salt bath, said hydride being selected from the group consisting of calcium, barium, and lithium hydride.

3. The salt bath of claim 2 characterized in that the barium halide is barium chloride, and the 15–25% sodium halide is sodium chloride.

4. A salt bath for pretreating metals to be aluminized, said salt bath being in direct contact with a molten aluminum-containing coating layer, wihch comprises:

37–57% potassium chloride
25–45% sodium chloride
0.0–20% sodium aluminum fluoride
0.0–8% aluminum fluoride

and at least one hydride which comprises 0.01–3% by weight of the salt bath, said hydride being selected from the group consisting of calcium, barium, and lithium hydride.

5. A method of coating a base metal with molten coating metal from the group consisting of an aluminum and an aluminum alloy, which comprises the steps of: pretreating the metal to be coated in a molten bath comprising a major percentage of molten halide salts, approximately 97 weight percent, and a minor percentage of hydrides selected from the group consisting of calcium, barium, and lithium hydride, to thereby substantially completely eliminate the oxides from the surface of said metal; and passing said oxide-free base metal directly into, and through, an aluminum molten bath without any intervening oxidation.

6. A method of coating a base metal with a molten coating metal selected from the group consisting of an aluminum and an aluminum containing alloy which comprises: dipping the metal to be coated into a molten pretreating bath comprising 97–99.99% of molten halide salts selected from the group consisting of chlorides, bromides, iodides and fluoride salts, and 0.01–3% of hydride selected from the group consisting of calcium, barium, and lithium hydride, to thereby substantially completely eliminate the oxides from the surface of said metal; and passing said oxide-free metal directly into, and through, an interconnecting aluminum-coating layer to thereby coat said base metal.

7. A method of coating a base metal selected from the group consisting of the transition elements having an atomic number of from 25 to 29, and titanium, with a molten coating metal selected from the group consisting of an aluminum and an aluminum alloy bath which comprises: immersing the base metal in a molten pretreating salth bath comprising, by weight,

65–75% barium halide
15–25% sodium halide, other than fluoride
0.0–10% sodium fluoride, and

0.01–3% of a hydride selected from the group consisting of calcium, barium, and lithium hydride to substantially completely eliminate the oxides from the surface of said metal; and passing said oxide-free base metal directly into, and through, said aluminum coating bath interconnecting and overlying said salt bath to thereby coat said base metal.

8. A method of coating a base member selected from the group of a transition element having the atomic numbers of 22, 25, 26, 27, 28 and 29, with a molten coating metal selected from the group consisting of aluminum and an aluminum coating alloy bath which includes the steps of: immersing the base metal in a salt bath comprising

37–57% barium chloride
25–45% sodium chloride
0.0–20% sodium aluminum fluoride
0.0–8% aluminum fluoride
0.01–3% barium hydride

to thereby substantially completely eliminate the oxides

from the surface of said base metal; and passing said oxide-free base metal directly into, and through, a lower interconnecting aluminum layer to thereby coat said base metal.

9. A method of continuously aluminizing continuous metallic material with a molten coating metal selected from the group consisting of aluminum and its alloys, which comprises: passing the material to be aluminized into a pre-treating molten salt bath maintained at a temperature higher than the melting point of said coating metal, and having a density higher than the density of said coating metal, said salt bath comprising a major percentage of halide salts, approximately 97 weight percent, selected from the group consisting of chloride, bromides, and fluorides, and a minor percentage of a hydride selected from the group consisting of calcium, barium, and lithium hydride, said pre-treating salt bath substantially completely eliminating oxides from the material to be aluminized; passing said material through said salt bath at a rate such that the temperature of the material immediately prior to its exit from said salt bath is above the melting point of the coating metal; and withdrawing said pretreated material, having its surface completely free of oxides, directly into and through an overlying coating metal layer to thereby aluminize the continuous material.

10. A method of coating continuous metallic materials with a molten coating metal selected from the group consisting of aluminum and its alloys, which comprises the steps of: passing the material to be coated into a pretreating molten salt bath maintained at a temperature higher than the melting point of said coating metal, and having a density higher than the density of said coating metal, said salt bath comprising 65–75% barium chloride, 15–25% sodium chloride, 0.0–10% sodium fluoride, and 0.01–3% of a hydride selected from the group consisting of calcium, barium, and lithium hydride, said pretreating salt bath substantially completely eliminating surface oxides from said material to be aluminized; passing said material through said salt bath at a rate such that the temperature of the material immediately prior to its exit therefrom is above the melting temperature of the coating metal; and withdrawing said pretreated oxide-free material directly into, and through an overlying metal of coating material to be thereby aluminized.

11. A method of coating a base metal with molten coating metal selected from the group consisting of an aluminum and aluminum alloys, which comprises the steps of: pretreating the metal to be coated in a molten bath comprising a major percentage of molten halide salts, approximately 97–99.99 weight percent, and a minor percentage of hydrides, approximately 0.01–3.0%, selected from the group consisting of calcium, barium and lithium hydride, at a temperature of between 1050° F. and 1650° F., to thereby substantialy completely eliminate the oxides from the surface of said metal; and passing said base metal directly into, and through, an aluminum molten bath without any intervening oxidation.

References Cited in the file of this patent

UNITED STATES PATENTS

2,315,725	Moller	Apr. 6, 1943
2,377,876	Gilbert	June 12, 1945
2,702,281	Gibb	Feb. 15, 1955

OTHER REFERENCES

Gibb: Journal of Chem. Education, vol. 25, October 1948, pp. 577–582.