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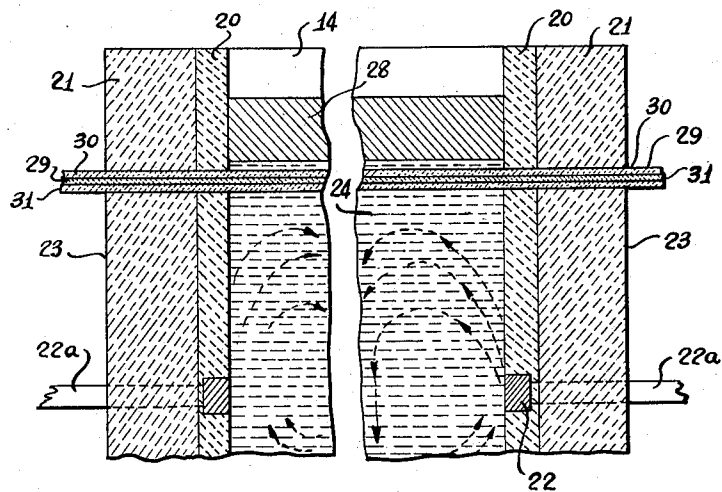
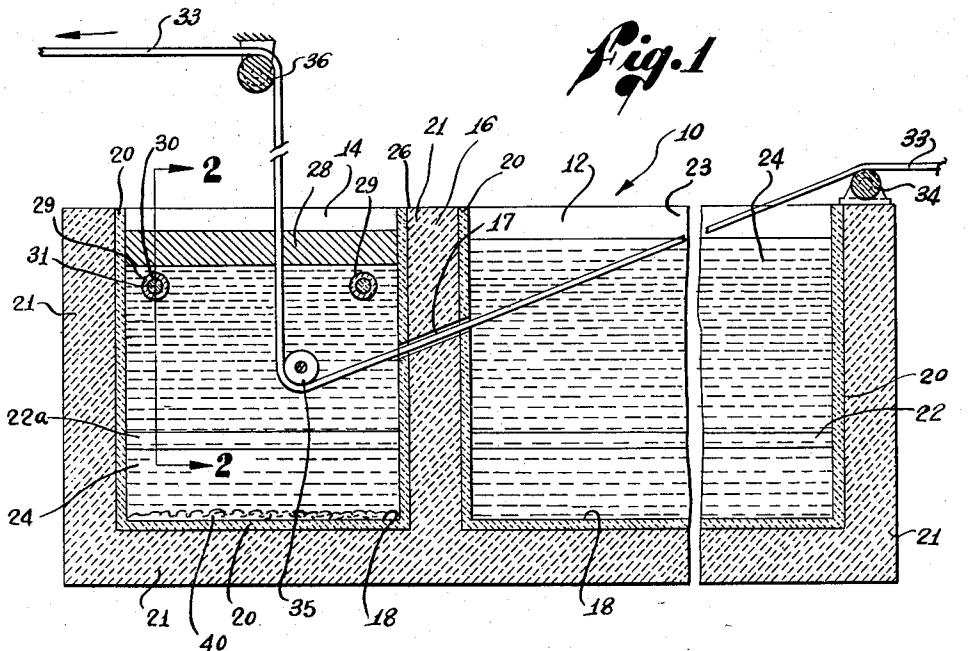


Fig. 2

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METHOD AND MEANS OF COATING OBJECTS WITH ALUMINUM

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This invention relates generally to a method and means for aluminizing metal objects, and more particularly to a method and means for obtaining impurity-free and oxide-free coatings of aluminum on metal.

The term "aluminization" as used in this specification and in the 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 itself.

Aluminization processes of the hot-dip type in which a molten aluminum coating layer overlies a heavier molten salt bath are highly advantageous. Such processes are exemplified by the process disclosed in the Moller Patent No. 2,315,725, entitled "Process for Metallization Especially Aluminization of Iron Articles," issued April 6, 1943. In this process, the base metal to be aluminized is first passed through a predominantly halide molten salt bath upon which rests a layer of molten aluminum or aluminum alloy, the base metal thereafter being withdrawn through the overlying aluminum layer. Both the molten coating metal and the molten salt bath are usually contained in a refractory crucible furnace.

While the above-described Moller process has many advantages, various types of oxides are formed or deposited in the salt bath, which, if not removed in some manner, may contaminate the coating obtained. For example, the molten aluminum layer is necessarily exposed to air in order that the coated metal be withdrawn therefrom, aluminum oxides thus forming in the aluminum layer. Aluminum oxide, being heavier than the aluminum, sinks through the aluminum layer and may precipitate upon the base metal passing upwardly to be coated, such precipitation of oxides preventing contact of the base metal to be coated with aluminum. The net result is that the coating sometimes lacks uniformity. Metallic oxides are also sometimes present in the molten salt bath due to the fluxing action of the salts upon the base metal to be coated and may also similarly contaminate the base metal.

The salt bath of the above-described Moller process generally comprises chloride and fluoride salts, though the salts of other halides may also be used. These salts all have a solvent effect on the aluminum and iron oxides, thus preventing some precipitation within the salt bath. The fluoride salts have a substantially greater solvent effect than the other halide salts, especially for aluminum oxides. However, when the salt bath is substantially saturated with oxides and impurities, oxide and impurity precipitation from the salt bath solution commences, the precipitation occurring in the coldest zones of the salt bath due to the decreased solvent power of the halides for oxides and other impurities at lower temperatures. Since in the conventional furnace the heat gradient in the salt bath is such that the coldest zone is just below the aluminum layer, the excess oxides (that is, those present in an amount above the saturation amount) will precipi-

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tate just below the aluminum layer, thus interfering with the contact of aluminum upon the base metal just prior to its withdrawal into the coating metal.

While the addition of more oxide-dissolving fluoride salts increases the solvent power of the salt bath for oxides, and therefore might be believed to remove more oxides from the salt bath, these salts cannot be added in any substantial quantities since, when so added, they have an extremely corrosive effect on refractory furnace materials and are highly poisonous.

It can thus be seen that the halide salts, and the fluorides in particular, while partially eliminating the oxide and impurity problem as outlined above, do not provide an ultimate solution to the problem of oxide and impurity precipitation on the base metal just prior to its withdrawal into the coating metal.

Bearing in mind the foregoing facts, it is a major object of the present invention to provide an improved method and means for the aluminization of metallic materials whereby the uniformity of the aluminum coating is substantially improved.

It is another major object of the present invention to provide a hot-dip aluminum process of the type described wherein substantially all of the oxides and impurities in the salt bath are prevented from precipitating on the base metal as it is being drawn therethrough, thereby improving the uniformity of aluminization of the base metal.

Another object of the present invention is to provide a hot-dipped aluminization process of the type described wherein the efficiency in the reduction of the amount of oxide contamination of base metal, by a given amount of halide salts employed in the aluminization process, is substantially increased.

It is a further object of the present invention to provide a hot-dip aluminization process of the type described in which maximum elimination of the interfering oxides and impurities is obtained with a minimum amount of oxide-dissolving fluoride salts.

Still another object of the present invention is to provide a hot-dip aluminization process of the type described wherein oxides and impurities in the salt bath are precipitated at a point remote from the region of passage of the material to be aluminized.

A further object of the present invention is to provide a furnace apparatus for aluminization of metals according to the process of the type described which is so designed as to aid in the elimination of interfering oxides and impurities from the base metal.

It is still a further object of the present invention to provide a furnace apparatus for aluminization of metals according to the process of the type described in which the temperature distribution within the salt bath is such as to minimize the precipitation of oxides and other impurities on the base metal, as it is being withdrawn through the salt bath of the furnace.

These, and other objects of the present invention will be more readily understood by referring to the following description, and to the drawings, in which:

Figure 1 is a fragmentary cross-section, in side elevation, of a furnace apparatus embodying my invention; and

Figure 2 is a fragmentary cross-section along the line 2—2 of Figure 1.

In general, the method and means of aluminization of metals of the present invention find 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 pretreating salt bath of the process di-

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rectly into the aluminum coating layer without any possibility of intervening oxidation due to the surrounding oxygen-containing atmosphere.

In general, according to the present invention, the increased efficiency of removal of interfering oxides and impurities by a given amount of halide salts in the salt bath, especially by the fluoride salts, is accomplished by incorporating an auxiliary heating means just below the aluminum layer in the salt bath furnace in such a manner that the hottest region of the furnace prevails at a point just below the aluminum coating layer and causing the continuous circulation of the hotter portions of the salt bath downwardly to the colder zones.

The majority of the heat input to the salt bath furnace is caused by heating electrodes installed within the lower zones of the furnace. These internal electrodes cause circulation of the entire salt bath. Auxiliary salt bath circulatory mechanisms may also be used for circulatory purposes in some cases.

If the salt bath is at or near saturation with oxides or impurities, in being circulated from the upper high temperature zones to the lower colder zones of the furnace, it will deposit therefrom a substantial amount of the dissolved oxides and impurities in the lower temperatured zones of the furnace because of the substantially decreased solvent power of the salt bath at the lower temperatures. Upon the release of the oxides in the low-temperature zones of the furnace, they, being heavier than the salt bath, immediately sink to the bottom of the furnace. In this manner, the oxides and impurities are prevented from contacting the base metal to be coated which is passed only through the upper high-temperature zones of the furnace.

The halide salts, after releasing a substantial percentage of the oxides in the lower region of the furnace, are circulated upwardly to the high-temperature zones, just below the aluminum layer, due to the heat or auxiliary circulating means, to again become saturated with oxides. They then move downwardly again to repeat the cycle of deposition as above described.

Referring now to Figure 1, the salt bath furnace, embodying one preferred form of my invention, is there shown and designated generally by the numeral 10. The furnace 10 is preferably rectangular and comprises two sections or compartments, the right hand or pretreating section 12, and the left hand or coating section 14, separated by a baffle wall 16 having a passage or slot 17 formed in the central section thereof. The passage 17 is angled with respect to the floor 18 of the furnace 10, and its cross-section is slightly larger than the cross-section of the material to be coated.

The furnace 10 is constructed of refractory liner 20 of high heat and chemical resistance, such as a high density aluminum refractory, and a backing layer 21 composed of a second refractory material, such as standard refractory brick, suitably reinforced as by an outer steel casing (not shown). The baffle wall 16 is also provided with the heat and chemically resistant liner 20 on each face thereof, the liners being separated by the refractory backing layer 21.

Each compartment 12 and 14 is provided with a pair of individual internal heating electrodes 22, 22a, respectively, imbedded in the lower sections of each of the side walls 23 of each of the compartments, the electrodes being connected to a suitable electric source (not shown) whereby a salt bath 24 (to be described) is maintained in a molten state in the furnace 10 at a specific desired temperature. The number of heating electrodes may be increased depending upon the depth, geometry, and insulation of the particular salt bath furnace employed. Due to the presence of the electrodes 22, 22a, the salt bath 24 will undergo substantial circulation from the upper to the lower zones of the furnace 10, as shown by the arrows in Figure 2.

The salt bath 24 is introduced into the interior of

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the furnace 10, the surface thereof lying somewhat below the upper edge 26 of the baffle wall 16. A layer of aluminum coating metal 28, preferably one to four inches in thickness, is provided within the coating section 14 of the furnace 10 and floats on the salt bath 24, the coating metal having a lower specific gravity than the salt bath. The salt bath comprises one or more chlorides, bromides, iodides, and fluoride salts, especially those of the alkali and alkaline earth groups, and the aluminum-containing fluorides, these salts together acting as the sole means of heat transmission to the aluminum layer 28, thereby maintaining it in a molten state in accordance with the principles set forth in the above-identified Moller patent.

Specific salt bath compositions that have been employed with excellent results in the coating of metals with pure aluminum and its alloys at salt bath temperatures ranging between 1050° F. to 1650° F., comprise 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% sodium chloride by weight
0.1-10% aluminum fluoride by weight

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

If the oxide concentration in the salt bath is low, it is sometimes not necessary to employ any fluoride salts in the process of the present invention, it being then desirable to rely only upon the solvent effects of other halides.

A pair of auxiliary tube-like heating electrodes 29 are provided extending through the salt bath 24 of the coating compartment 14 just below the aluminum layer 28. The ends of the tube electrodes 29 are each embedded in opposite side walls 23 of the furnace 10. The tube electrodes 29 are preferably composed of an outer highly heat-resistant shell 30 such as fused alumina, the shell having contained therewithin a resistance heating element such as a silicon carbide rod 31 connected to a source of electric current (not shown). The region of the coating compartment 14 just below the aluminum layer 28 is maintained, by the auxiliary heating means 29, at a higher temperature than the lower zone of the furnace 10. However, the circulation pattern of the salt bath in the coating section 14, due to the internal heating electrodes 22a, as described, is not appreciably disturbed by the presence of the relatively minor heat input due to the auxiliary heating means 29. Thus, the colder portions of the salt bath 24, upon coming into the vicinity of the electrodes 22a will be heated and circulated upwardly into the hotter upper zone, and the hotter portions will be carried downwardly, following the main circulation path of the salt bath 24 as shown by the arrows in Figure 2, into the lower colder zone of the salt bath 24. The circulation of the salt bath 24 in this manner may be aided, if desired, by mechanical agitation means, such as a salt bath pump (not shown).

It is found that halides generally, and cryolite or other oxide-dissolving fluoride salts in particular, have

a substantially greater solvent power for oxides, especially aluminum oxides, at higher temperatures than at lower temperatures. Thus, halide salts, which are saturated or nearly saturated with oxides and/or other impurities at high temperatures, in circulating downwardly, release some of the oxides that they hold in solution in the lower colder zone of the furnace 10. These oxides, being heavier than the salt bath, will precipitate upon the bottom 18 of the furnace, the precipitate being designated by the numeral 40.

The halide salts, now cooled, move upwardly in the coating compartment 14 into the upper zone thereof where they again dissolve more oxides and other impurities at the higher temperature because of their greater solvent capacity at these higher temperatures. The halide salts, now heated, again move downwardly and deposit oxides therefrom in the manner above-described. The deposition step followed by the dissolving step is continuously repeated until substantially all excess oxides and impurities have been removed from the upper high-temperature zone of the salt bath 24.

The temperature gradient between the high and low-temperature zones may be as little as 10° F. or as much as 100° F. in practical use. The upper limit is dictated mainly by the fact that the hotter the salt bath 24 immediately below the aluminum layer 28, the hotter will be the aluminum and the greater the alloying of the aluminum with the base metal, resulting in a brittleness of product. Thus, a balance must be met between too high a temperature in the high-temperature zone and too low a temperature gradient. If the end use of the product is such that brittleness is not a factor, a 100° F. temperature difference or more can be employed.

It has been found that the salt bath 24, within the range of compositions heretofore described, and at temperatures in the range of 1000°-1650° F., possesses approximately a 25-50% change in solvent power for aluminum oxides for a temperature change of between 50 to 100° F.

The temperature of the salt bath 24 in the lower zone of the coating compartment 14 is maintained preferably between about 1050° to 1260° F., while the temperature in the upper high temperature zone is usually maintained from 10° to 100° F. higher by means of electrodes 29. The pretreating compartment 12 may or may not be maintained at the same temperature as the high- or low-temperature zones of the pretreating compartment 12 depending upon the nature of the metal being coated, the amount of pretreatment desired, and the end use to be made of the product. The improvement in aluminization of metals, caused by different-temperatured compartments is disclosed in co-pending U.S. patent application, Serial No. 611,333, entitled: "Method and Means for Continuously Hit-Dip Aluminizing of Materials."

The process for coating metallic materials by means of the present invention consists of first immersing the metal object, which may be for example, wire, strip, or sheet 33 in the pretreating section 12, thence passing it through the passage or slot 17 of the partition wall 16 and upwardly through the coating section 14. The preferred conveying mechanism for this purpose consists of a guide roller 34 rotatably mounted on the end wall of the pretreating compartment 12, submerged guide roller 35, and a third roller 36, spaced tangentially above the submerged guide roller 35, rotatably mounted preferably substantially above the furnace 10 to allow cooling of the coated material to occur before it is bent about the upper roller 36.

The relative arrangement of the pretreating and submerged rollers 34 and 35, respectively, 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 upper rollers 36 is such that the metal 33 passes upwardly through the coating section 14 in a path that is

substantially perpendicular to the plane of the coating layer 28, the metal thus following the shortest possible path through the coating material, in order to minimize the metal-aluminum contact.

As previously described, a substantial percentage of all of the oxides formed are precipitated from the salt bath in the lower colder regions of the furnace 10. Since the wire, strip, or sheet 33 passes only through the upper regions, the precipitation of oxides thereon is substantially decreased even though the salt bath may be nearly saturated with oxides.

It can thus be seen that the circulation of halide salts from the upper, hotter zones of the furnace 10 to the colder, lower zones causes deposition and precipitation of oxides therefrom due to the decreased oxide solubility of the halide salts at lower temperatures, thus greatly increasing the amount of oxides that precipitate at a point remote from the aluminum layer. Further, the subsequent circulation of the halide salts upwardly to the hotter regions enables them to dissolve more oxides, thereby substantially decreasing the amount of oxides that might otherwise precipitate at a point just below the aluminum layer 28. Thus the maintenance of a heat gradient wherein the hotter portions of the furnace 10 are immediately below the aluminum layer, coupled with adequate circulatory means, greatly increases the effectiveness of the halide salts, especially the fluorides, in removing oxides and impurities which would otherwise contaminate the base metal 33. A substantially more uniform aluminum coating is thus produced.

Attention is drawn to the fact that 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 12, through an interconnecting passage, and upwardly through the coating section 14, the arrangement of the rollers and passage being modified to allow for the passage of these individual pieces. The apparatus and process for coating individual objects is otherwise substantially similar to that heretofore described.

Attention is also drawn to the fact that while the heat gradient in the coating compartment of the salt bath must be such that the upper regions thereof are substantially higher in temperature than the lower regions, it may still be desirable to have more heating electrodes in the lower regions of the furnace, depending on the depth, insulation and geometry of the furnace—provided the above-described heat gradient is maintained.

The above-described aluminization process has been advantageously employed with many types of base metals including especially iron, nickel, cobalt, manganese, titanium and copper.

While one preferred embodiment of my method and apparatus for aluminizing metals 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 molten coating metal selected from the group consisting of aluminum and aluminum alloys, wherein said molten coating metal overlies at least a portion of a heavier molten salt bath, which comprises the steps of: passing said base metal through a first zone only of said molten salt bath, the first zone being maintained at a higher temperature than a zone of said salt bath section; causing circulation of salt from the first hotter zone downwardly to the lower colder zone and thence upwardly to create a flow pattern in the salt bath; withdrawing said base metal through said molten coating metal which overlies at least a portion of the surface of said salt bath to be thereby coated, those oxides and impurities present in

an amount above the saturation point of the lower zone being precipitated within said lower zone of the salt bath remote from the path of said base metal.

2. The process as defined in claim 1 wherein said salt bath comprises a fluxing agent selected from the group consisting of fluoride, chloride, bromide, and iodide salts.

3. A method of coating metal material with a coating metal selected from the group consisting of aluminum and aluminum alloys wherein the molten coating metal overlies a heavier molten halide salt bath, the improvement which comprises: passing said material to be coated through the molten salt section of a first salt bath; passing said material into a second salt bath upon at least a portion of which floats said aluminum coating metal, said second salt bath having a high-temperature zone and a low-temperature zone, said high-temperature zone being maintained immediately adjacent and below said aluminum coating metal, said material passing through said high-temperature zone only; and causing circulation of said salt bath from said high-temperature zone to said low-temperature zone whereby oxides and impurities in solution in said high-temperature zone but that are present in an amount in excess of the saturation amount of the low-temperature zone of the salt bath precipitate in the low-temperature zone of the salt bath.

4. In a method of aluminization of metals wherein a molten aluminum coating layer overlies a heavier molten salt bath, the improvement which comprises: maintaining the upper zone of said salt bath adjacent the aluminum layer at a substantially higher temperature than the lower zone thereof; circulating salt from the hotter upper zone of the salt bath downwardly to the lower colder zone; precipitating oxides and impurities that are in solution in the upper hotter zone of said salt bath but present in an amount in excess of the saturation point of the lower colder zone of said salt bath, in the lower zone of said salt bath remote from said aluminum layer upon downward circulation of the salt in said hotter zone of the salt bath; circulating the salt from the colder zone of the salt bath upwardly to complete the cycle and dissolve more oxides and impurities for precipitation in the lower colder zone of the salt bath; and passing said metal to be coated, into said salt bath, above the precipitation level of the oxides and impurities only, and through said aluminum coating layer to be thereby coated without any appreciable precipitation of oxides and impurities thereon.

5. In a method of substantially reducing oxide contamination of a base metal to be coated, by chemical means in aluminization processes having an aluminum coating layer overlying a molten salt bath, the improvement which comprises: maintaining the salt in said salt bath at a substantially higher temperature in a zone immediately adjacent and just below said overlying aluminum layer than in the lower zone of said salt bath; causing circulation of the salt in said salt bath from said hotter upper zone to said lower low-temperature zone, thereby causing precipitation of a substantial amount of oxides and impurities, that are present in said salt bath, in said low temperature zone, the salt in the lower zone of said salt bath being moved upwardly to dissolve more oxides and impurities in said upper high temperature zone thus preventing their precipitation therein, the salt in the hot upper zone of the salt bath then moving downwardly to repeat the precipitation and solution cycle; and passing

said base metal to be coated into said salt bath, above the precipitation level of the oxides and impurities only, and through said aluminum coating layer to be thereby coated.

6. A process as defined in claim 5 characterized in that said salt bath comprises halide salts.

7. A process, as defined in claim 5 characterized in that said high temperature zone of said salt bath is from 10 to 100 degrees Fahrenheit above said low temperature zone.

8. A process as defined in claim 5 characterized in that said high temperature zone is maintained at a temperature from 1000 to 1650 degrees Fahrenheit and said low temperature zone is maintained at a lower temperature.

9. A process for coating base metals with a coating metal selected from the group consisting of aluminum and aluminum alloys, wherein said coating metal is molten and overlies at least a portion of a molten salt bath, which comprises the steps of: passing said base metal into a first zone only of a molten salt bath having both a first and second zone, said first zone being maintained at a higher temperature than said second zone; causing circulation of salt from said first zone to said second colder zone and thence recirculating salt to create a continuous flow pattern in said salt bath whereby oxides and impurities dissolved in said first zone are precipitated in said second zone; and passing said base metal through said first section and through said coating metal, which is molten and overlies at least a portion of the surface of said first zone of said salt bath, said coating metal being thus positioned at a point remote from the precipitation area of said oxides and impurities.

10. A process for coating base metals with a coating metal selected from the group consisting of aluminum and aluminum alloys, wherein said coating metal is molten and overlies at least a portion of a molten salt bath, which comprises the steps of: passing said base metal into a first zone only of said salt bath having a first and second zone, said first zone being maintained at an appreciably higher temperature than said second zone, said first zone being maintained at a temperature sufficiently high to dissolve oxides and impurities and said second zone being maintained at a temperature sufficiently low to cause precipitation of said oxides and impurities; and causing circulation of salt from said first zone to said second zone to create a continuous flow pattern in said salt bath whereby oxides and impurities dissolved in said first zone are precipitated in said second zone; and then passing said base metal from said salt bath through said overlying molten coating metal.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,953,473

September 20, 1960

David W. Mitchell

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 6, line 69, after "a" insert -- second --; same line 69, after "bath" strike out "section".

Signed and sealed this 11th day of April 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents