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HOT DIP ALUMINUM COATING PROCESS

Allen W. Hodge, Columbus, Ohio, assignor, by mesne assignments, to Kaiser Aluminum & Chemical Corporation, Oakland, Calif., a corporation of Delaware

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The present invention relates to a method or process for coating basis metals with aluminum or its alloys. In particular, it relates to a new and novel method of improving the appearance of hot dip aluminum and aluminum alloy coatings and to increasing the economy, efficiency and use of hot dip coating methods of basis metals with aluminum and its alloys and to the resulting improved coated article per se.

In the art of hot dip coating of basis metals with aluminum or its alloys it is customary to employ molten fluxes such as mixtures of salts of halides and fluorides, or of gaseous fluxes such as hydrogen, chlorine or carbon monoxide, or of neutral atmospheres above the bath to facilitate the attainment of satisfactory coatings. The use of such fluxes or atmospheres with their associated equipment adds extra costs and difficulties to the hot dip aluminizing process. Moreover, certain aluminum alloys having beneficial properties cannot be used economically and satisfactorily in hot dipping due to the slow speed with which coatings are formed. It, also, has been found that certain basis metals cannot always be properly coated and that the molten baths drain improperly to result in uneven coatings. Further, the life of certain baths is limited due to metal buildup from the basis metal being coated.

Accordingly, one of the primary objectives of the present invention is to facilitate the use of aluminum or aluminum alloy hot dipping methods for coating fabricated articles without necessitating the employment of either liquid fluxes, such as molten mixtures of chlorides and fluorides, or gaseous fluxes, such as hydrogen, chlorine, or carbon monoxide, or of neutral atmospheres above the bath.

It is another important object of the present invention to so increase the rate of attack of molten aluminum or its alloys on ferrous or other basis metals that it becomes practical to use certain alloys for rapid continuous coating, where otherwise this could not readily be done.

It is still another object of this invention to provide an increase in the types of basis metals which can be successfully hot dipped.

A further object of the present invention is to enlarge the practical employment of aluminum or aluminum alloys for hot dip coating.

Other objects and advantages of the present invention are an increase in, or extension of, the useful life of a coating bath contaminated with the basis metal being treated, and better drainage of excess aluminum or aluminum alloys from coated articles or basis metals and therefore an improvement in their appearance, evenness and smoothness.

Still another object of the present invention is to provide a new and novel aluminum or aluminum alloy coated basis metal.

These and other objects and advantages of the present invention will become more apparent from the following detailed description and examples.

It has now been discovered that the addition of a minor

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amount of sodium or potassium or mixtures thereof to molten aluminum containing coating baths will avoid the difficulties alluded to above by increasing coating speeds, by eliminating protective coverings such as non-oxidizing or neutral atmospheres or salt fluxes, by increasing bath life and by permitting the coating of various basis metals in many forms and sizes. Improvements in evenness and smoothness of coatings are also obtained. These benefits have been achieved without a reduction in adherence, corrosion resistance or ductility of the coatings.

In general, a method of using the present invention is as follows:

Starting with a new bath of pure aluminum or of any desired aluminum alloy, the metal is made molten and brought to the preferred operating temperature. The bath is skimmed of dross, normally, although skimming is not necessary at this time. It will be noted that the surface of the bath is quite convex at the edges, since the oxide film always present on the bath surface resists wetting the refractory walls of the pot or crucible. Using an inverted crucible attached to a rod, or any similar device, a quantity of metallic sodium is plunged below the surface of the bath and stirred about. After a relatively short time some of the sodium will be absorbed into the bath and the excess either fumed away or converted to a dross on the bath surface. The bath is then skimmed carefully, and is ready for use. It will be noted that the edges of the aluminum bath are now practically level, or even concave, where the molten metal comes in contact with the pot or crucible walls. This is an indication of lowered surface tension and increased tendency to wet the crucible. Also, it will be noted that the bath surface is brighter than before the sodium treatment, and remains bright for a longer time after skimming. After skimming, the basis metal having a cleaned surface is immersed directly into the bath without a protective atmosphere or flux and withdrawn after a few seconds with an even and smooth aluminum containing coating thereon.

Only a very minor amount of sodium or potassium is required to be maintained in the baths to provide the novel results of the present invention. Amounts as low as 0.0005% by weight of the bath have proved effective. The solubility of sodium in liquid aluminum usually decreases from about 0.13% at 800° C. (1472° F.) to about 0.1% at 700° C. (1292° F.). Pure aluminum melts at a temperature of about 1220° F., a 12% silicon balance aluminum alloy melts at about 1070° F., and other aluminum alloys used in hot dip coating baths melt at from 1070° to 1220° F. Since aluminum and aluminum alloy coating baths normally operate at temperatures between about 1150° F. and about 1375° F., depending on the particular coating bath composition, any addition of sodium to the bath beyond about 0.13% is immediately rejected and wasted to form surface dross and/or fumes. The fuming is of relatively short duration and causes no appreciable loss in overall bath preparation time. Nevertheless, in the practice of this invention, it is sometimes desirable to add an excess of sodium, up to a total of about 0.2% of the bath weight, in order to more quickly saturate the aluminum bath with sodium. The excess of sodium is lost as a yellowish or gray dross on the bath surface, and as a white fume expelled into the surrounding air. Such procedures are better than to add the metal slowly in small amounts to avoid fuming which is time consuming. For the best results as to coating speed, drainage and so forth, it is preferred to maintain in the molten bath from 0.001 to 0.10% by weight of sodium and/or potassium based on the weight of the bath. Moreover, sodium and potassium can be used together in the form of mixtures or alloys thereof with obtainment of the same results.

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It is preferred to immerse the sodium or potassium directly in the body of the bath wrapped in aluminum foil in order that it will readily dissolve in and disperse throughout the molten metal. However, it may be introduced into the body of the melt as a liquid, or as a vapor to bubble through the melt, from a suitable boiler outside the bath. It also can be introduced as a master alloy, for example, as a pig containing about 12-14% Si, about 0.01% Na, and the balance aluminum where Si is to be an important constituent of the alloy coating.

Following a period of use, some deterioration, slight at first, will be noticed in the action of the bath. The surface of the bath may become convex and the coating characteristics poorer. At this time, the sodium treatment should be repeated. It has been found that satisfactory results are obtained by using a smaller amount of sodium in the second, and subsequent treatments. Usually, it is preferable to add from about 0.005% to 0.05% of the bath weight of sodium in these subsequent treatments. Large baths, kept molten continuously, seem to require retreatment at approximately weekly intervals. Smaller baths may need more frequent treatment. Probably the relations between bath surface and bath volume, and temperature, are the factors controlling duration of the sodium effect.

Basis metals treated according to the present invention are those which will form an interfacial layer when dipped in an aluminum or aluminum alloy melt and, thus, will be provided with a coating to protect it from corrosion, friction, and other attack. This invention is also applicable to basis metals which are provided with merely decorative aluminum or aluminum alloy coatings. While the present invention will be described with particular reference to ferrous metals and their alloys that is, cast iron, plain carbon steels and alloy steels such as those containing molybdenum, tungsten, vanadium and stainless steels of chromium and chromium and nickel, it is obvious that other metals can be very desirably coated with aluminum according to the present invention and therefore the present process will also cover basis metals such as chromium, cobalt, molybdenum, nickel, tantalum, titanium, tungsten, vanadium, zirconium and their alloys. Fabricated or unfabricated basis metals, for example, castings, sheet, strip and wire can also be used. The present invention is particularly applicable to basis metals which are fabricated of thin gauge metal, for example, fabricated stove parts of thin sheet steel. The additive in the present baths permits very good drainage from fabricated parts so that an even coat is provided on all exposed surfaces with no undesirable buildup of metal which must be later removed by expensive grinding or machining operations.

Prior to hot dipping, the basis metal is provided with a surface receptive to the hot coating metal. Such may be accomplished by a combination of any of several methods well known in the art which leave a chemically clean, etched surface, that is a surface free of oil, grease, dirt, oxides and slightly etched. It may be degreased or deoiled by treatment with a hydrocarbon solvent, for example, carbon tetrachloride or vapor degreased using trichloroethylene. After degreasing, the basis metal may also be washed with a strong soap or alkali solution such as a 20% NaOH solution which has been found very desirable. Finally, the basis metal may be pickled in an acid solution such as a 50-50 concentrated HCl-H₂O solution. In some cases, the surface need only be oxidized and then pickled; where cast iron is used, the surface may be decarburized although specific decarburization processes are not always required. Simple sand blasting is sufficient preparation in most cases.

Aluminum or aluminum alloy baths used to coat basis metals according to the method of the present invention can be pure aluminum melts considered as having 99+% or more aluminum, balance adventitious materials or

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aluminum alloy melts containing as little as above about 50% aluminum and the balance a metal which improves, modifies, etc., the aluminum and which can be at least one metal selected from the group consisting of beryllium, cerium, chromium, copper, cobalt, magnesium, molybdenum, silicon, titanium, vanadium, zinc and so forth.

The basis metal whether fabricated or unfabricated can be coated by automatic or manual processes. When automatically dipping articles, instead of using hand or manual dipping methods, the articles can be mounted on jigs or other suitable apparatus and by conveying means lowered into the melt, held there momentarily, raised to permit drainage, and then carried onto the next fabricating step. When continuous methods are used for coating strip or wire, the strip, for example, is introduced into the bath and carried around means such as a pulley immersed some distance in the bath. When hand or manually dipping articles, it is customary to skim the bath before dipping and removing the article in order to avoid staining and entrapment of occlusions. In continuous methods, skimming is performed usually at the beginning of operations. Moreover, since in continuous coating of, for example, wire or strip, it may be desirable to preheat the basis metal before introducing it into the bath, preheating furnaces using neutral or non-oxidizing atmospheres may be employed above or in conjunction with the bath incorporating this invention.

The time of immersion will vary from a few seconds when coating strip to possibly several minutes where massive fabricated parts are used. The time should be sufficient so that the article will arrive at the coating temperature and form the necessary bond or interfacial layer by diffusion. The times and temperatures for coating are obvious to those skilled in the art although customary times are reduced by the present invention. However, it will be appreciated that they should be conducted so as to avoid a large interface layer yet to be of a sufficient length to provide an even and smooth coating, unless only the interface or compound layer is desired.

The following examples will serve to illustrate the invention with more particularity to those skilled in the art:

Example I

A fresh 1455 gram heat of 99.75% pure aluminum was melted in a new graphite crucible and held at 1350° F. A few panels were unsatisfactorily coated and the behavior of the bath was typical for pure aluminum coating baths used in open air. The minimum immersion time for these panels was about 5 minutes. Sodium, 0.4 gram (about 0.03%), was then wrapped in aluminum foil and immersed in the bath. After a few minutes, the bath was skimmed. The final surface was brighter and smoother than on the originally pure aluminum bath. Panels coated in this bath without the use of a protective atmosphere or flux were smooth and bright without any pin holding and were obtained in a coating time of as little as 15 seconds.

Example II

During trial runs it was difficult to obtain a uniform flaw free coating on either cast iron or sheet metal using an alloy bath containing by weight 0.25% beryllium, 2.0% silicon, 0.2% chromium, and the balance aluminum. The bath was then treated with sodium. After treatment, the bath became more active, and without using a protective atmosphere or flux, the samples were immersed, resulting in good adherent coatings being obtained on steel panels, although unacceptable coatings were formed on cast iron. These samples had been sand blasted as the only preparatory cleaning. Additional sample cast iron panels were vapor degreased and then treated in a nitrate-nitrite salt bath (Houghton's Draw Temp No. 275) for ten minutes at 750° F. to decarburize them. They were next quenched in water and rinsed to

remove the salt. After drying, the cast iron samples were dipped into this unprotected treated coating bath for a few minutes after which they were removed with a very good coating. After 48 hours water immersion, coatings showed no discontinuities.

Example III

1455 grams of 99.75% aluminum were melted in a new graphite crucible and 0.4 gram of metallic sodium wrapped in aluminum foil was plunged below the surface. Steel panels were coated throughout the day in this unprotected bath with excellent results. The bath was held at 1350° F. over night and afterwards again coated a steel panel very well. During the following night the furnace failed. On the next morning, the bath was remelted and again found to coat test panels smoothly and very rapidly although no additional sodium had been added thereto.

Example IV

A new 12% silicon, balance aluminum alloy bath was made up. After adding 0.4 gram of sodium to this bath an improvement in results was obtained comparable to those in the pure aluminum bath of Example III.

Example V

An alloy bath containing 0.2% chromium, 0.2% molybdenum, 0.06% titanium, balance aluminum when new was kept in a cast iron pot until it contained an excessive amount of iron. Part of the bath was transferred to a graphite crucible. Steel panels dipped into this bath without a protective cover obtained no coating whatever. About 0.5% of the bath weight of Misch metal was then dissolved in the bath, but still no coating whatever could be obtained on test panels. Then about 0.2% of the bath weight of sodium was added and after a few minutes the surface skimmed. Immediately, panels dipped into this bath were completely coated. Later, the metal in the crucible was solidified, the crucible broken off, and the metal button analysed for iron. The upper half of the button was found to contain 1.83% to 2.11% iron and the lower half 5.40% to 9.37% iron. Although the iron distribution in the liquid bath was undoubtedly more uniform, sodium had effectively extended the useful life of this bath.

Example VI

Cast malleable iron is notoriously difficult to coat by hot dip aluminizing methods. A bath, similar in composition to the original bath of Example V, would not coat cast malleable pipe fittings until a small amount of sodium was added. After the sodium addition, the pipe fittings could be coated easily. Similar results were obtained using an aluminum-5% silicon bath.

Example VII

An attempt was made to coat a stove part such as a corrugated SAE 1040 18 gauge steel flue passage with an alloy containing 0.2% beryllium, 3.0% silicon, 0.1% molybdenum, 0.1% chromium, balance aluminum. No coating could be obtained. Complete, even coverage was obtained after adding a minor amount of sodium to the melt, which drained better from the part.

Example VIII

When a 4600 pound 0.2% Cr, 0.2% Mo, 0.03% Ti and balance aluminum bath was first put in operation, good coatings were obtained on gray iron before sodium additions if the iron was immersed for 10 minutes or more, but the surface oxide was too heavy for successful use with light gauge steel. Addition of about .015% sodium overcame the difficulties caused by tenacious oxide films, allowing the thin steel to be wetted easily by the bath. Many gray iron castings were coated in this sodium treated bath, with no prior treatment other than sand blasting.

Example IX

Steel wire for farm fence wire was being coated with an alloy of 0.2% Be, 3% Si, 0.1% Mo, 0.1% Cr, balance Al. The coating was incomplete and rough. While the coating machine was running, sodium was added to the bath. Immediately, the coating became complete, smooth and entirely satisfactory. Ductility remained.

Moreover, a bath of the type of Example VIII, was treated with potassium which produced the same results as with sodium. A bath containing 0.2% Be, 3.0% Si, 0.1% Mo, 0.1% Cr and the balance aluminum was treated with lithium, without exhibiting any improvement in coating characteristics over an untreated bath.

Further, molten baths of the types shown above were treated with sodium and successfully coated various metals such as bronze sheet, molybdenum wire, Nichrome wire (Tophet A 80 Ni—20 Cr and Tophet C 60 Ni—15 Cr—25 Fe as manufactured by the W. B. Driver Co.), rolled titanium and stainless steels samples such as Nos. 302, 304 and 430.

It, therefore, is seen from the above examples that by the addition of an alkali metal such as sodium or potassium or alloys or mixtures thereof to hot dip aluminum or aluminum alloy coating baths it is possible to produce coatings on massive as well as thin fabricated or unfabricated basis metals at increased speeds without loss of ductility or corrosion resistance. The coatings obtained by the new and novel process disclosed herein are complete, even and smooth. Fluxes and protective atmospheres are eliminated when the baths are treated with sodium. The novel sodium treatment of the present invention does not change the character of the coatings formed by the coating baths to which it is added. Therefore, a bath that could produce ductile coatings without sodium will also produce ductile coatings with sodium. Likewise, the brightness, ductility and resistance to corrosion of the coating remain unchanged. Moreover, it has been found that some of the most desirable aluminum alloys for coating ferrous and other metals either will not produce continuous, complete coatings at all, or will produce such coatings only when quite new and free of the basis metals, that naturally accumulate in the bath through use. Such alloys can be made to produce continuous, complete coatings after treating baths thereof with sodium. Further, the life of baths is lengthened by treatment with sodium.

The exact mechanism by which aluminum hot dip coating baths are benefited by sodium treatments is not well understood. It is surmised that some metallic sodium is dissolved in the molten aluminum or aluminum alloy. At the air-metal interface the free sodium molecules may combine with oxygen from the air and with aluminum, or possibly with aluminum oxide already present. The presence of a minute, invisible amount of sodium compound formed in the oxide film, and constantly renewed as the film is broken, may cause this film to become more impervious to oxygen from the air, thus retarding film formation and avoiding the necessity of using a protective atmosphere or flux and it may also lower its surface tension. These effects could explain the decreased rate of film formation on the bath surface, while the lowered surface tension might permit more rapid wetting of an immersed basis metal. Since the basis metal thus was wetted more quickly by the molten metal, a chemical reaction between the basis metal and the aluminum could begin more rapidly, and the rate of coating would be increased. Again, lowered surface tension could permit more rapid and complete run-off or drainage of the still molten alloy after the basis metal is removed from the bath providing even and smooth coatings.

Furthermore, it has been found that under certain conditions, mixtures of sodium and potassium chlorides may be used to replace the metals as a means of furnishing the alkali metals to the molten bath. Because of the

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lower melting point, it is preferred to use mixtures of from about 60% NaCl—40% KCl by weight to 60% KCl—40% NaCl by weight. Sodium fluoride or sodium aluminum fluoride may be added to the salt mixture but no especial benefit has been observed from these additions. A small amount (about ½% to 2% of the weight of the bath) of these mixed salts may be added to a molten aluminum bath, and the bath temperature raised to about 1400° F. for periods varying from four hours to 24 hours. After again lowering the temperature to the working level and skimming the bath, results entirely similar to those obtained with metallic sodium have been observed indicating that the salt mixture furnishes alkali metal in effective amounts to the molten bath through at least partial reduction of the chlorides. The use of salt mixtures appears to recommend itself particularly with relatively small (up to 120 pounds) baths as opposed to large size commercial installations. Moreover, the salt may be deleterious to crucibles depending on the material thereof and its vapor may be injurious to steel equipment. For these reasons, and to avoid superheating of the bath and attendant loss of bath preparation time, the use of metallic sodium and/or potassium is preferred to the use of salt mixtures.

In summary, the present invention teaches that a remarkable improvement has been achieved in hot dip aluminum or aluminum alloy coating processes by the mere addition of a minor amount of sodium or potassium or alloys or mixtures thereof to molten baths of the same. Employing the method disclosed herein, an increase in coating speed and bath life can be realized; protective atmospheres and fluxes can be eliminated; a large number of basis metals can be coated whether of thin gauge or massive and whether fabricated or unfabricated; desirable coating baths can be utilized; and even and smooth coatings retaining their adherence, corrosion resistance and ductility can readily be produced. Moreover, the additives used are cheap raw materials and no complicated apparatus or special techniques are required to obtain the new results described herein. The present process is easier and simpler to use and, hence, not only better but cheaper than other well known methods.

Having thus described the invention, what is claimed as new and novel and is desired to be secured by Letters Patent is:

1. In the art of hot dip coating of basis metals with a metal selected from the group consisting of aluminum and its alloys, the improvement which comprises introducing alkali metal into a bath of a molten metal selected from the group consisting of aluminum and its alloys and wherein no protective atmosphere is employed over said bath, and passing said basis metal through the melt to provide said basis metal with a coating of said molten metal, the alkali metal being at least one metal selected from the group consisting of sodium, potassium and mixtures thereof and being introduced in a minor amount sufficient to enable said basis metal to be coated at a faster rate and the resulting coating to be complete, even and smooth as compared to a similar bath which has not been treated with said alkali metal, and to increase drainage and to extend bath life.

2. The method for increasing the quality and speed of hot dip coating of ferrous basis metals with a molten coating metal selected from the group consisting of aluminum and its alloys which comprises dissolving an alkali metal in a bath of a molten metal of the group consisting of aluminum and its alloys and wherein no protective atmosphere is employed over said bath, said alkali metal being at least one metal selected from the group consisting of sodium, potassium and mixtures thereof and being maintained in said bath in a minor amount sufficient to increase the rate of interaction between the basis metal and the molten metal of the bath, to increase drainage and to extend bath life up to the solubility of the alkali

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metal in the bath at the coating temperature, and rapidly passing said basis metal having a surface receptive to coating through the molten bath free of a protective covering to provide said basis metal with a coating of said molten metal, said alkali metal enabling said basis metal to be coated at a faster rate and the resulting coating to be complete, even and smooth as compared to a similar bath which has not been treated with said alkali metal.

3. The method for increasing the quality and speed of hot dip coating of ferrous basis metals with a molten coating metal selected from the group consisting of aluminum and its alloys according to claim 2 wherein the alkali metal is sodium which is maintained in said bath having a temperature of from 1150 to 1375° F. in a concentration of from 0.001% to 0.10% by weight of the bath.

4. The method for increasing the quality and speed of hot dip coating of ferrous basis metals with a molten coating metal selected from the group consisting of aluminum and its alloys according to claim 2 wherein the alkali metal is potassium and is maintained in said bath having a temperature of from 1150 to 1375° F. in a concentration of from 0.001% to 0.10% by weight of the bath.

5. The method for increasing the quality and speed of hot dip coating of ferrous basis metals with a molten coating metal selected from the group consisting of aluminum and its alloys according to claim 2 wherein the alkali metal is a mixture of sodium and potassium and is maintained in said bath having a temperature of from 1150 to 1375° F. in a concentration of from 0.001% to 0.10% by weight of the bath.

6. The method for increasing the quality and speed of hot dip coating of ferrous basis metals with a molten coating metal selected from the group consisting of aluminum and its alloys according to claim 2 wherein the alkali metal is introduced into the body of the molten bath as a liquid and at a rate sufficient to maintain a concentration of said alkali in said bath of from 0.0005 to 0.13% by weight of the bath.

7. The method for increasing the quality and speed of hot dip coating of ferrous basis metals with a molten coating metal selected from the group consisting of aluminum and its alloys according to claim 2 wherein the alkali metal is introduced into the body of the molten bath as a vapor and at a rate sufficient to maintain a concentration of said alkali in said bath of from 0.0005 to 0.13% by weight of the bath.

8. In the art of hot dip coating of basis metals with a metal selected from the group consisting of aluminum and its alloys, the improvement which comprises adding an alkali metal chloride mix to a bath of a molten metal selected from the group consisting of aluminum and its alloys and wherein no protective atmosphere is employed over said bath, the alkali metal chloride mix comprising from about 40 to 60% by weight of sodium chloride and the balance potassium chloride and being added in a minor amount to furnish sufficient alkali metal to the bath to increase the rate of interaction between the basis metal and the molten metal of the bath, to increase drainage and to extend bath life, and passing said basis metal through the melt to provide said basis metal with a coating of said molten metal, said alkali metal enabling said basis metal to be coated at a faster rate and the resulting coating to be complete, even and smooth as compared to a similar bath which has not been treated with said alkali metal.

9. In the hot dip coating of ferrous base metals with aluminum and aluminum base alloys, the improvement which comprises providing a bath of coating metal wherein no protective atmosphere is employed thereover and maintaining in the coating bath a minor amount of alkali metal selected from the group consisting of sodium, potassium and mixtures thereof sufficient to effectively increase the rate of coating and the quality thereof compared to that produced by the same bath not containing the alkali metal.

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10. A method according to claim 9 in which the alkali metal is maintained in the coating bath in amount from about 0.001% by weight of the bath to the limit of solubility thereof at the operating temperature of the bath.

11. A method according to claim 9 in which the alkali metal is maintained in the coating bath in amount from about 0.001% to 0.1% by weight of the bath.

12. A method according to claim 9 in which the alkali metal is added to the molten coating bath in metallic form as a solid.

13. In the hot dip coating of ferrous base metals with aluminum and alluminum base alloys, the improvement which comprises providing a bath of coating metal wherein no protective atmosphere is employed thereover and maintaining sodium in the coating bath in amount from

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about 0.001% to 0.1% by weight of the bath of effectively increase the rate of coating and the quality thereof compared to that produced by the same bath not containing the sodium metal.

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