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PROCESS FOR COATING METALS WITH ALUMINUM

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The protection of ferrous metals against corrosion and rusting has received a great amount of attention, and many different means of minimizing such corrosion have been devised, the particular means for so doing depending largely upon the particular environment in which the ferrous embodiment is to be used. For protection of ferrous metal shapes against atmospheric rusting, including the corrosive effects of highly acidic industrial atmospheres, galvanizing is employed widely, and corrosion-resisting paints, such as those having a red lead base, also are employed widely as protective coatings.

For many applications, the usual corrosion-protecting means have serious shortcomings. They may be imperfectly applied, and all have to be renewed at more or less frequent intervals. Efforts have been made to replace the zinc coatings of galvanized shapes with aluminum, because in various corrosion tests zinc has been found to have much lower corrosion resistance than aluminum which is due to a large measure to the type of oxide film formed.

For corrosion protection of ferrous metal shapes, aluminum offers definite advantages in hardness, ductility, and adherent oxide film on the exposed surface of the aluminum. There have been many attempts to use aluminum as a protective coating for ferrous metals, because of its permanence in air, because it possesses the property of retaining a bright and pleasing appearance which is permanent in brightness without being lacquered, and because it does not become tarnished or discolored through atmospheric effects as do other coating metals such as copper, zinc, tin or lead.

The use of aluminum as coating for ferrous metal shapes has been extremely restricted, however, because of the difficulty of producing an adherent coating of aluminum on ferrous metal bases, as compared with galvanized coatings; but as a coating metal, aluminum is the superior of the two metals, aluminum forming a continuous, adherent and inert oxide film, while zinc forms a hydrated, loosely adherent and readily separable oxide film, which fact renders a zinc coating rather temporary in its protective properties. For the same thickness of protective coating aluminum has the advantage that for each square foot of ferrous metal surface to be protected only about one-third of the weight of aluminum is required as compared with zinc. However, in the case of aluminum coatings applied to ferrous metal bases by procedures heretofore known, the aluminum coating flakes off from the ferrous

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metal base so that the base metal becomes exposed to corrosive influences, or it covers such base only imperfectly; and this is true regardless of the treatments to which the ferrous metal shapes have been subjected preparatory to receiving the aluminum coating. In fact, it has long been considered impractical to coat commercial ferrous shapes with aluminum owing to this difficulty.

As will be apparent from the foregoing considerations, the present invention has for an important object the provision of certain improvements in the art of coating ferrous metal shapes with aluminum in a commercially feasible manner in order to obtain the maximum desirable effects from metallic aluminum.

A further object of the invention is to provide an improved process for coating ferrous metal shapes with tightly adherent coatings of metallic aluminum which are continuous and free from pin holes, and which are uniformly tightly adherent to the base metal throughout all portions of the coating.

A still further object of the invention is to provide industrial coatings of aluminum on ferrous metal shapes which possess attractive and permanent brightness, tight adhesion and good corrosion resistance.

In accordance with the present invention, it has been discovered that when a base metal of cobalt, chromium, nickel, iron, or an alloy thereof, and most particularly a ferrous metal such as steel, is cleaned in accordance with conventional practices, and a fluxing composition of the present invention is applied thereto as an aqueous solution which is dried to leave a deposit of flux as a residue of desired thickness on the metal to be coated, it is possible to apply a tightly adherent, continuous coating of aluminum to the metal.

The fluxing composition employed in accordance with the present invention comprises a fluoride compound of zirconium or a fluoride compound of titanium, and advantageously a double salt of zirconium fluoride or titanium fluoride with an alkali metal such as potassium, e. g. potassium zirconium fluoride or potassium titanium fluoride.

In accordance with the present invention, the surface of the ferrous shape or article to be coated with aluminum first is cleaned in the usual manner, for example by mechanical cleaning procedures followed by degreasing in a grease solvent, e. g. carbon tetrachloride, pickling in dilute hydrochloride acid or sulphuric acid, wash-

ing with water, washing with an alkali solution to neutralize adhering acid, and water washing. The flux is then most advantageously applied by dipping the cleaned ferrous metal article into an aqueous solution containing a flouride compound of zirconium or titanium, such as zirconium fluoride itself or a complex zirconium fluoride salt with an alkali metal, e. g. potassium zirconium fluoride or sodium zirconium fluoride or lithium zirconium fluoride or the corresponding titanium compounds. After dipping in the aqueous solution of such flux, the water is allowed to evaporate to deposit an adherent coating of finely divided zirconium fluoride compound or titanium fluoride compound on the article to be coated, which then is dipped into a bath of molten aluminum. With the proper concentration of the solution of the zirconium fluoride compound, or titanium fluoride compound, which determines the thickness of the coating film of the salt on the surfaces of the article to be coated, the ferrous metal article, when immersed in a bath of molten aluminum, will receive a continuous, bright, attractive film of aluminum having a tight bond and high corrosion resistance.

Preferably, either the article being coated or the aluminum is agitated during the coating operation, and best corrosion resistance is obtained with the aluminum bath maintained at a temperature of from about 1220° F. to about 1240° F., the conditions of temperature and time of immersion being variable, dependent upon the shape and size of the article to be coated, as will be pointed out hereinafter in greater detail.

The thickness of the aluminum coating can be controlled by regulating the rate of withdrawal of the shape from the molten aluminum. In general, the more rapidly the shape is withdrawn, the thicker is the coating.

The melting temperature of aluminum is high enough so that some annealing of cold-worked steel may occur as a result of it being immersed in the molten aluminum. Accordingly, to produce an aluminum-coated steel article of high tensile strength, the article after coating to a substantial thickness is plastically deformed sufficiently to reduce its cross-sectional area by at least the amount required to restore the hardness and tensile strength of the steel to the values prevailing prior to such annealing thereof as occurred in consequence of its immersion in the molten aluminum.

The solutions of zirconium fluoride or alkali zirconium fluoride, or corresponding titanium fluoride compound, may be applied to the cleaned surface of the ferrous article to be coated by dipping, spraying, painting, or in any other convenient way. Potassium zirconium fluoride solutions conveniently are applied by one dip of the article into a solution containing from approximately two to approximately eighteen grams of K_2ZrF_6 per 100 c. c. of water. Solutions of lower concentrations may be used if, by repeated applications, the required weight of zirconium salt is applied per unit area of the surface to be coated. Potassium zirconium fluoride has at 100° C. a high solubility of 23.5 grams K_2ZrF_6 per 100 c. c. of water, but at 20° C. the solubility is only 1.55 grams per 100 c. c. The increase in solubility is especially rapid from 90° to 100° C. It therefore is obvious that in order to use solutions of, for example 16 grams K_2ZrF_6 per 100 c. c. water, it is necessary to use hot solutions. The use of solutions heated to 95° C. to 100° C. has the advantage that the moisture in the salt film

quickly evaporates in the air. Normally, the surfaces of wire or sheet iron are dried in a stream of hot air. In cases where angle irons or other shapes of heavy cross section are coated, the drying operation becomes of less importance, because the moisture on the surface will evaporate in the air from heat accumulated in the shape during the dip in the hot flux solution. Though normally it is preferred to use one dip of the cleaned shape in a solution having a concentration of potassium zirconium fluoride of from approximately 8 to approximately 16 grams per 100 c. c. of water, good aluminum coatings have been obtained using one dip of the shape in a solution containing only 2 grams of K_2ZrF_6 per 100 c. c. of water.

The solubility of sodium zirconium fluoride, which also permits the obtaining of good aluminum coatings on ferrous metal shapes, at 100° C. is 1.67 grams per 100 c. c. of water. At 20° C. the solubility is 0.39 gram per 100 c. c. of water. Due to the low solubility it is found in practice that it is necessary to apply the desired weight of flux by two or several applications of a solution of the salt, with evaporation of the water between these applications. It therefore is apparent that though sodium zirconium fluoride can be used to produce good coatings of aluminum, the fact that it is difficult to apply the required weight of the salt on the shape by a single dip in the solution of the salt renders the sodium salt not so convenient and desirable as the potassium salt.

However, in no instance is the concentration of the zirconium fluoride compound critical, provided that a sufficient number of applications of the fluoride compound are employed. It is found in practice, that not less than 0.04 gram of zirconium fluoride salt per square foot of surface is required to produce the requisitely good coatings of aluminum on the shape being coated.

As has been indicated above, the factor which determines the quality of the aluminum coating is the quantity of zirconium fluoride compound or titanium fluoride compound present per unit area of the ferrous metal surface to be coated. When bright, cold-rolled steel sheets degreased and pickled, are dipped in vertical position in hot solutions of potassium zirconium fluoride at a temperature of from 95° to 100° C. and allowed to drain, the residual salt present on the sheets will depend on the concentration of the potassium zirconium fluoride solution. Thus, in one series of tests, it was found that with 40 grams per liter K_2ZrF_6 solution, there will be left 0.11 gram of K_2ZrF_6 per square foot of surface; with 80 grams per liter K_2ZrF_6 solution there will remain 0.25 gram K_2ZrF_6 per square foot, and with 160 grams per liter K_2ZrF_6 solution, there will remain 0.53 gram K_2ZrF_6 per square foot. On the basis of these tests, since one long ton of 12-gauge wire has 2080 square feet of surface, the total quantity of potassium zirconium fluoride present on the surface of one ton of such wire after one dip in 80 grams per liter solution is 1.14 pounds K_2ZrF_6.

In continuous operations where wire or sheets are directed into the solution by pulleys or rolls, after leaving the dipping tank, the wire or sheet as a rule runs down through an inclined tunnel to the kettle or furnace holding the molten aluminum. Hot air passing through the tunnel removes the moisture from the surface. With air at a temperature of 85° C., the water will evaporate from a 12-gauge wire in from 15 to

25 seconds. The dipping tank, the tunnel, and the aluminum furnace should be so located that the wire does not get into contact with any pulleys or rolls in traveling from the last point of contact with the flux solution to the aluminum pot. Such contact would partially remove the coating of salt and therefore impair the aluminum coating. The wire or sheet or other shape should travel substantially in a vertical direction until the aluminum coatings have solidified in order to facilitate the draining of the excess of the molten metal back to the pot containing the aluminum. After the coating has solidified, it is quickly cooled by a quench in cold water for example, in order to retard the formation of a brittle aluminum iron alloy.

It has been pointed out above that particularly good coatings are obtained when the ferrous articles or shapes are coated with a film of zirconium fluoride and agitated in the molten aluminum. This agitation promotes the contact between the aluminum, the flux, and the ferrous shapes. Identical results are obtained when the molten aluminum in the immediate vicinity of the ferrous article is agitated. This agitation of the aluminum is easily obtained, as when the aluminum is melted in electric induction furnaces.

In this connection, it may be noted that it is a well-known fact that the temperature of the molten aluminum determines to a great extent the quality of the coating. High temperatures accelerate the formation of an alloy layer consisting of Al_3Fe between the iron and the outside coating of aluminum. This alloy compound is brittle, and as a rule, it is not desired.

If under conditions such that in continuous coating of 15-gauge wire with commercial aluminum at 1240° F. there is obtained a coating which is about 0.001 inch thick, then under the same conditions but at a temperature of 1230° F. a heavier coating will be obtained. On the other hand, a temperature of 1260° to 1270° F. gives a definitely thinner coating.

Coatings applied at 1225° to 1240° F. are generally heavier, but the alloy layer between the coating and base metal is quite thin and the coatings will stand considerable bending before they crack. The coatings applied at 1270° F. and higher are thinner but the alloy layer is quite thick and the coating may crack in 180° bending test. In practice, an immersion time from 2 to 15 seconds is used, usually, on base material 0.010 to 0.025 inch thick. A definite temperature and time of immersion cannot be specified, however, as the character of the articles treated, the composition of aluminum alloy used, the desired degree of ductility of the coating, determine these factors. The best corrosion resistance is obtained with low temperatures of the order of 1220° F. to 1240° F. Heavy angle shapes which do not require as ductile coatings as do sheets, for example, may be dipped at higher temperatures and for longer times.

For any given temperature of application of the aluminum, the thickness of the coating can be controlled within limits by regulating the rate at which the shape is withdrawn from the molten metal. A rapid rate of withdrawal is conducive to the formation of relatively thick coatings (up to about 0.002 inch and perhaps even somewhat thicker); whereas a slow rate of withdrawal of the shape from the molten aluminum leads to the formation of relatively thin aluminum coatings (below 0.001 inch). In a continuous coating process the rate of withdrawal of the shape from the molten aluminum is of course determined by its speed of travel therethrough; and the time of immersion may be independently regulated by suitable adjustment in the length of the path of travel of the shape below the surface of the molten aluminum.

The temperature at which the molten aluminum is brought in contact with the article to be coated is well above the temperature at which work-hardened steel and other common ferrous alloys undergo annealing. Even the short immersion time of two seconds in molten aluminum at temperatures from 1225° to 1240° F. is sufficient to effect considerable annealing of cold-rolled, cold-drawn, or otherwise work-hardened steel shapes, especially wires and thin gauge sheets or strips. For example, in coating a cold-drawn low carbon steel wire 0.077 inch in diameter by immersing it in molten aluminum at 1235° F. for only two seconds, the breaking strength of the wire was reduced from 470 pounds to 350 pounds (a decrease of over 25% in its tensile strength) and its elongation was increased from 1% to 18%. With longer times of immersion in the molten aluminum the breaking strength of the wire was decreased even more and the elongation was increased correspondingly. In producing aluminum-coated cold-finished steel shapes of high tensile strength, therefore, it is best to apply the aluminum coating before the shape has been brought to finished size, and then to cold work it to finished size after the aluminum coating has been applied. For example, in the production of aluminum-coated steel wire of high tensile strength, the best practice is to cold draw the wire to a ready-to-finish size, say, 5 to 6 Steel Wire Gauge size numbers larger than the desired finished size. Then the wire is coated with aluminum by the procedure herein described. It is desirable to make sure that the aluminum coating is of substantial thickness, by suitably regulating the rate at which the wire is withdrawn from the bath of molten aluminum. After the aluminum-coated wire has been cooled to room temperature, it is cold-drawn to the desired finished size. The aluminum adheres tenaciously to the underlying steel, so no particular problem is encountered in drawing the aluminum-coated wire. The extent to which the coated wire is reduced in size should be enough at least to restore the hardness and tensile strength of the wire to the values prevailing prior to such annealing as occurred when the wire was immersed in the molten aluminum. Generally cold drawing through 5 or 6 Steel Wire Gauge numbers suffices for this purpose. Of course, the wire may be more severely cold worked, after coating, if desired. In addition to increasing its hardness and tensile strength, the cold drawing of the coated wire has the further advantage of greatly improving the surface quality and appearance of the aluminum coating, and also of increasing the uniformity of the outside diameter of the coated wire along its length.

If the wire is to be cold-worked after being aluminum-coated, it is often desirable to anneal it prior to the coating operation, and to develop substantially the full desired extent of work-hardening by cold working after the coating operation is completed. By annealing the wire prior to coating, it is made soft and tractable for handling during the coating operation and progress of this operation is accordingly facilitated.

The above-described procedure for cold-work-

ing aluminum-coated wire is, of course, in principle applicable also to the treatment of aluminum-coated sheets and other shapes, except that instead of drawing, the cold working of such shapes is usually effected by a cold-rolling operation.

Depending upon the quantity of potassium fluoride used in the manufacture of the potassium zirconium fluoride, three different salts can be formed, viz., $KZrF_5.H_2O$; K_2ZrF_6; K_3ZrF_7. Only the first of these salts crystallizes with water of crystallization. In practice, this salt is less desirable to use as it rather quickly decomposes in water solutions to K_2ZrF_6 plus ZrF_4. The second of the above salts is the commercial product and most easily obtained. The third salt is formed when an excess of potassium fluoride is used in its production. In the employment of the present process, the second and third salts therefore are the ones that actually will be present and both have been found to give about the same results. A considerable excess of KF above K_3ZrF_7 is not desirable.

Potassium zirconium fluoride melts at approximately 600° C., i. e,, substantially below the melting point of aluminum, which is 659° C. Sodium zirconium fluoride and lithium zirconium fluoride also melt below the melting point of aluminum. These salts react with molten aluminum to give potassium, sodium, or lithium cryolite. With the salt K_2ZrF_6 the reaction is

$$3K_2ZrF_6+2Al\rightarrow 2K_3AlF_6+3Zr$$

The resulting potassium aluminum fluoride (potassium cryolite) formed contains 40 mol per cent of AlF_3 and has a melting point of 790° C., or higher than the normal operating temperature of the aluminum, which is about 700° C. Although the ultimate reaction product would be solid and as some time is required for a complete reaction, the potassium cryolite forms a mixture with unreacted K_2ZrF_6 that has a lower melting point than aluminum. Since cryolite, as well as alkali zirconium fluorides, are excellent fluxing compounds for aluminum, the thin film of flux covering the steel will effectively clean both the aluminum surrounding the ferrous shapes and the ferrous metal itself, and will assist in the wetting and coating of the ferrous article with aluminum.

A slight increase in the AlF_3 content in the potassium cryolite from 40 to 45 mol per cent produces a eutectic composition having a melting point of 565° C. Anything which increases the AlF_3 content in the cryolite up to this value, for instance a higher percentage of ZrF_4 in the potassium zirconium fluoride, will be beneficial as it reduces the ultimate melting point of the flux. A small addition of potassium chloride to the potassium zirconium fluoride solution also affects favorably the fluidity and the melting point of the potassium cryolite flux. When the weight of the potassium chloride in the solution is from three to fifty per cent of the weight of the potassium zirconium fluoride, improved results are obtained in practice; but with higher proportions of potassium chloride, for instance when the weight of KCl is 75% of the K_2ZrF_6 in the solution, duller and less shiny coatings are obtained. Other ways of modifying the melting point of the cryolite formed in the reaction will be obvious to one skilled in the art.

It has been observed that at least certain types of alkali zirconium fluoride hydrolyze in water solutions to some extent, forming a white precipitate. This white precipitate has no fluxing properties of itself, but it is not harmful if present in not too large quantities. As it accumulates it should ultimately be separated from the solution which is returned to the process. The hydrolysis of the alkali zirconium fluoride increases with temperature, and by using a solution heated to a lower temperature it is possible to avoid the hydrolysis to a great extent. The distinctly lower solubility of the alkali zirconium fluoride salt at lower temperatures may necessitate in such cases more than one application of the salt in case the ferrous articles which are to be coated have such surface, or chemical composition, that a relatively heavy application of zirconium fluoride compound per unit area is required.

The potassium zirconium fluoride which is preferred for use in the present process possesses good fluxing properties, high solubility in hot water, absence of water of crystallization in the crystals forming on evaporation of the solution on the ferrous metal shape being coated, low melting point, good adherence of the salt film formed on the metal surfaces on evaporation of the solution, non-hygroscopicity, and the characteristic that the solution hydrolyzes to a very small extent. Also, of importance is the ease with which the water in the film of solution on the metal evaporates in contact with warm air.

It has been mentioned that it is preferred to evaporate the water from the flux solution prior to immersion of the treated shape in the molten aluminum coating bath, but this is not a necessarily essential step, for good coatings have been obtained by dipping shapes to be coated in a solution containing eight grams of K_2ZrF_6 per 100 c. c. of water and immediately dipping the wet shape in molten aluminum. When the dipped shapes are to be dried, it is found that when zirconium fluoride alone is used as well as with sodium zirconium fluoride, viscous films are formed on the ferrous metal surfaces from which films the water is removed at a slower rate than it is from a film of potassium zirconium fluoride solution.

Drying of the flux solution may be accomplished in various ways, as by passing the shape, after dipping in the flux solution, through a current of heated air, or by passing an electric current through the wire, strip, or similar stock provided that a current of air removes the evaporated moisture.

When using zirconium fluoride alone, or alkali metal zirconium fluoride, as the flux, it has been determined that the flux is decomposed by the molten aluminum to produce zirconium metal during the reaction, which alloys with the aluminum coating in proportions which depend on the concentration of the flux solution, and the thickness of the aluminum coating. The percentage of zirconium in the aluminum coating ranges from a fraction of a per cent to several per cent. This does not exert any harmful effect on the properties of the coating, but in fact is beneficial because it increases markedly the corrosion resistance of the coating and produces a fine grain structure, with attendant marked reduction in intergranular corrosion in the coating, all of which improved effects are attributable to the presence of zirconium in the aluminum coating.

As has been indicated above, the present invention includes the use of titanium fluoride

compounds, such as alkali titanium fluorides, these being relatively stable at temperatures around 700° C. (1292° F.). The titanium double fluoride salts with potassium fluoride, sodium fluoride, and lithium fluoride have a relatively high solubility in hot water, melt below the melting point of aluminum, and react with molten aluminum to give cryolites, which during the few seconds of immersion of ferrous metal articles in molten aluminum form a flux with a low melting point in the presence of the salt which is not yet reacted.

The chemical reactions involved in coating steel with aluminum using zirconium or titanium fluoride compounds appear to be in accordance with the reaction given above. After degreasing, pickling, and washing in hot water, the ferrous surface is chemically clean. The dip into the potassium zirconium fluoride solution followed by drying in hot air produces a surface with a thin film of salt thereon. The ferrous metal of the shape being coated, however, always carries some occluded moisture and air (oxygen) on its surfaces, and when the ferrous metal shape enters the molten aluminum, these occluded gases cause a slight oxidation. The thin film of iron oxide reacts with the aluminum to give a thin film of aluminum oxide on the ferrous metal. At the same time, the potassium zirconium fluoride salt on the ferrous metal reacts to give cryolite:

$$3K_2ZrF_6+2Al\rightarrow 2K_3AlF_6+3Zr$$

This reaction is not instantaneous but requires at least ten seconds. The K_3AlF_6 which is formed during the reaction dissolves in not yet reacted K_2ZrF_6, and the salt gradually changes over to K_3AlF_6. The titanium fluoride compounds behave in similar manner.

It is well known that molten aluminum cryolite dissolves alumina. When a few crystals of potassium zirconium fluoride are dropped on the surface of molten aluminum the salt behaves very differently from other salts: it melts to a very fluid melt, which rapidly moves around on the surface of the aluminum, the behavior being somewhat similar to oil dropped on the surface of water. This rapid movement evidently is a surface tension phenomenon, and doubtless is enhanced by the fact that the surface tension of the salt continuously changes as the composition of the salt changes from entirely K_2ZrF_6 to entirely K_3AlF_6. When the fused salt rapidly spreads out on the surface of the aluminum, it pushes the oxide film on the metal ahead of the salt, and forms an area of clean metal on the surface.

Potassium titanium fluoride also readily melts in contact with aluminum and the molten salt behaves exactly like potassium zirconium fluoride. This rapid movement of the fused salt at the ferrous metal-aluminum interface appears to explain the good results obtained by the use of potassium zirconium fluoride and potassium titanium fluoride. When the steel actually has been coated with aluminum, the cryolite generated in situ is still in a fluid condition, due to some unreacted potassium zirconium fluoride and is dispersed in the surrounding aluminum. Gradually the cryolite rises to the surface of the aluminum. Therefore, when steel wire is being continuously coated with aluminum, the cryolite liberated in the aluminum surrounding the wire results in a continuous cleaning action on the aluminum.

While the optimum temperature of coating is from 1230° F to 1240° F., good coatings are obtainable over a wider range, for example, from approximately 1220° F. to 1260° F. When aluminum alloy coatings are applied to steel, a lower temperature usually will be used. Preferably, a temperature for coating is employed that is slightly above the melting point of aluminum or the aluminum alloy being used as the coating, and as some aluminum alloys have a lower melting point than aluminum itself, a lower temperature in the molten metal can be used in such cases. In connection with aluminum alloys, it is a well-known fact that certain binary and ternary alloys of aluminum give better corrosion resistance than ordinary aluminum. Thus, it is a well-known fact that aluminum containing 1.5% to 2.0% manganese has much better corrosion resistance than commercial aluminum, and in carrying out the present invention it has been found that definitely improved corrosion resistance is obtained by using an aluminum alloy containing 1.5% manganese, and 0.25% titanium.

In using titanium fluoride compounds as the flux, the preferred compound is potassium titanium fluoride, although the double fluorides of titanium with sodium and lithium are operative. Potassium titanium fluoride crystallizes with water of crystallization. The solubility of the salt at 20° C. is 1.2 grams per 100 c. c. of solution, and at 100° C., the solubility is 12 grams per 100 c. c. of solution, this being calculated as anhydrous salt. When this salt is used in coating steel with aluminum, the procedure is essentially the same as described above herein for potassium zirconium fluoride. The degreased, pickled and thoroughly washed ferrous surface is dipped in a hot aqueous solution of potassium titanium fluoride. Preferably, a concentration in the range from 50 to 100 grams per liter K_2TiF_6 is used, but good results have been obtained with concentrations as low as 20 grams per liter K_2TiF_6. One dip in a solution containing 50 grams per liter gives, after drying, a film of salt of about 0.2 gram K_2TiF_6 per square foot of surface.

It may be noted, however, that it is more difficult to remove the water from alkali titanium fluoride salts than from the corresponding alkali zirconium fluoride salts. For this reason, it is generally necessary to dry the film of titanium salt at a higher temperature. Drying in air at 80° to 100° C., which gives good results with potassium zirconium fluoride gives incomplete removal of the water or too slow drying with titanium fluoride solutions. It is best to dry in air at a temperature of 150° C. or higher. For example, when 0.020 inch thick sheet iron was dipped in a solution containing 50 grams per liter K_2TiF_6 at 95° C., it was necessary to dry the iron for 90 seconds in air at a temperature of 175° C. in order to effect substantially complete removal of the water. It is obvious that in continuous coating of wire or sheet, it is important to be able to remove the water in the salt film in a relatively short time in order to get the maximum output capacity of the plant.

When a ferrous article coated with a film of dry potassium titanium fluoride is immersed in the molten aluminum, it is found in practice that it is more important to agitate the ferrous article or the molten aluminum than when potassium zirconium fluoride is used, lack of agitation resulting in a rougher coating. This apparently is due to the fact that potassium titanium fluoride, although molten, is more viscous than the potassium zirconium fluoride, which, when it

melts, rapidly spreads out over the surface of the aluminum and the ferrous article.

When alkali zirconium fluoride salts are used in coating steel with aluminum, some of these salts, especially compounds having a zirconium content exceeding the amount corresponding to the formula A_2ZrF_6 (A=alkali metal) will form, due to hydrolysis, a white precipitate. This results in a loss of zirconium salt. Furthermore, this precipitate must be removed by filtration or otherwise. The precipitate can be prevented from forming by adding small quantities of alkali fluoride to the solution. In carrying out the present invention, it has been found that the formation of this precipitate can be prevented by adding some alkali titanium fluoride salt to the zirconium salt solution. Likewise, such precipitate if already formed can be dissolved by adding alkali titanium fluoride. Accordingly, it has been found highly advantageous to dip the cleaned ferrous articles in solutions containing a mixture of alkali zirconium fluoride and alkali titanium fluoride. By using a solution containing 50 grams per liter K_2ZrF_6 and 50 grams per liter K_2TiF_6, aluminum coatings are obtained, which have a smoother surface than are obtained with solutions containing either 100 grams per liter K_2ZrF_6 or 100 grams per liter K_2TiF_6. The solutions containing alkali double fluoride salts of zirconium and titanium thus show two advantages: First, the solution does not precipitate any zirconium compounds, and second, the appearance of the aluminum coating is improved.

As the aluminum coating on aluminized steel rarely exceeds 0.001 to 0.002 inch in thickness, it is evident that the corrosion resistance of the aluminum coating itself is of high importance. Therefore, elements which reduce the corrosion resistance of the aluminum coating, such as zinc or tin, should be absent from the aluminum bath being used for the coating.

It may be mentioned that, in accordance with the present invention, the valuable properties of zirconium and titanium fluoride compounds in coating steel were discovered by bending a clean specimen of sheet steel into a U-shape. A few crystals of potassium zirconium fluoride were placed in the bottom of the U-bend and the steel and salt were immersed for fifteen seconds in molten aluminum. It was found that this procedure gave a continuous coating of aluminum on the steel. If the cleaned steel is first dipped in molten potassium zirconium fluoride and then in molten aluminum, the result is the same, although the coatings formed in this manner have a somewhat coarse surface, and this procedure is relatively expensive, because the dips in the fused salt applies much more salt on the steel than is required. The use of the fused salt also introduces a problem, owing to the difficulty of finding a suitable material for a holding crucible that will keep the molten salt free from contamination. Under certain conditions, it may be found desirable to apply the potassium zirconium fluoride by dipping the steel in a fused salt bath of alkali chlorides containing a small percentage of alkali zirconium fluoride or alkali titanium fluoride. However, in the preferred manner of carrying out the process of the present invention, the zirconium and titanium fluoride compounds are applied to the steel as an aqueous solution, which enables the application of requisite small amounts of flux without any waste and without any container problem. Also, from a cost standpoint, the heating of a salt to its melting point is generally more expensive than heating a solution of the salt to 90° C. to 100° C.

While the foregoing description is limited to the coating of aluminum on steel, it likewise is to be understood that the process of the invention is applicable to chromium, nickel, cobalt or alloys thereof, such as stainless steel or other alloys in addition to iron and steel. Also, it will be understood that in the appended claims, the term "aluminum" is intended to include aluminum alloys as well as elemental aluminum.

This application is a continuation in part of my copending application Serial No. 121,894, now abandoned, filed October 17, 1949, which in turn was a continuation in part of my application Serial No. 53,370, filed October 7, 1948, now abandoned, entitled "Process for Coating Metals with Aluminum and Products Thereof."

While the invention in its preferred form is carried out in practice in accordance with the above-outlined procedures, it will be apparent that variations in procedural details will suggest themselves to one skilled in the art without departing from the inventive concept, as may be suggested by varying characteristics and compositions of the ferrous metal shapes being coated in accordance with the present invention; and it is found in practice that in addition to iron and steel shapes, the process may be employed to coat nickel, cobalt, and chromium, with aluminum if desired, the process producing adherent aluminum coatings on these metals as well as alloys thereof, in a manner similar to that described herein for coating ferrous metal shapes. Also, the term "aluminum" as used in the claims includes aluminum alloys in which aluminum is the major constituent. Accordingly, it is understood that it is intended and desired to embrace within the scope of this invention such modifications and changes as may be necessary to adapt it to varying conditions and uses, as defined by the appended claims.

I claim:

1. The method of forming a continuous tightly adherent coating of aluminum on a base metal selected from the group consisting of cobalt, chromium, nickel, iron, and alloys thereof, which comprises thoroughly cleaning the surface of said base metal, then applying to such cleaned surface an effective amount of a flux selected from the group consisting of fluoride compounds of zirconium and fluoride compounds of titanium, and then contacting such surface of the base metal with molten aluminum.

2. The method of forming a continuous tightly adherent coating of aluminum on a base metal selected from the group consisting of cobalt, chromium, nickel, iron and alloys thereof, which comprises thoroughly cleaning the surface of said base metal, then thoroughly wetting such cleaned surface with an aqueous solution containing a substantial amount of a flux selected from the group consisting of fluoride compounds of zirconium and fluoride compounds of titanium, and then contacting such surface of the base metal with molten aluminum.

3. The method of forming a continuous tightly adherent coating of aluminum on a base metal selected from the group consisting of cobalt, chromium, nickel, iron and alloys thereof, which comprises thoroughly cleaning the surface of said base metal, then thoroughly wetting such cleaned surface with an aqueous solution containing a substantial amount of a flux selected from the group consisting of fluoride compounds of zirco-

nium and fluoride compounds of titanium, then drying such surface of the base metal, and then immersing such dried surface in molten aluminum.

4. The method of forming a continuous tightly adherent coating of aluminum on a base metal selected from the group consisting of cobalt, chromuim, nickel, iron, and alloys thereof, which comprises thoroughly cleaning the surface of said base metal, then applying to such cleaned surface an effective amount of a fluoride compound of zirconium, and then contacting such surface of the base metal with molten aluminum.

5. The method of forming a continuous tightly adherent coating of aluminum on a base metal selected from the group consisting of cobalt, chromium, nickel, iron, and alloys thereof, which comprises thoroughly cleaning the surface of said base metal, then thoroughly wetting such cleaned surface with an aqueous solution containing a substantial amount of a fluoride compound of zirconium and then contacting such surface of the base metal with molten aluminum.

6. The method of forming a continuous tightly adherent coating of aluminum on a base metal selected from the group consisting of cobalt, chromium, nickel, iron, and alloys thereof, which comprises thoroughly cleaning the surface of said base metal, then thoroughly wetting such cleaned surface with an aqueous solution containing a substantial amount of a fluoride compound of zirconium, then drying such surface of the base metal, and then immersing such dried surface in molten aluminum.

7. The method of forming a continuous tightly adherent coating of aluminum on a base metal selected from the group consisting of cobalt, chromium, nickel, iron, and alloys thereof, which comprises thoroughly cleaning the surface of said base metal, then applying an effective amount of potassium zirconium fluoride to such cleaned surface, and then contacting the coated surface of the base metal with molten aluminum.

8. The method of forming a continuous tightly adherent coating of aluminum on a base metal selected from the group consisting of cobalt, chromium, nickel, iron, and alloys thereof, which comprises thoroughly cleaning the surface of said base metal, then thoroughly wetting such cleaned surface with an aqeuous solution containing a substantial amount of potassium zirconium fluoride, and then contacting such surface of the base metal with molten aluminum.

9. The method of forming a continuous tightly adherent coating of aluminum on a base metal selected from the group consisting of cobalt, chromium, nickel, iron, and alloys thereof, which comprises thoroughly cleaning the surface of said base metal, then thoroughly wetting such cleaned surface with an aqueous solution containing a substantial amount of potassium zirconium fluoride, then drying such surface of the base metal, and then immersing such dried surface in molten aluminum.

10. The method of coating a ferrous metal shape with aluminum, which comprises applying to the surface of such shape an effective amount of a flux selected from the group consisting of fluoride compounds of zirconium and fluoride compounds of titanium, then immersing the shape with flux thereon in molten aluminum, then withdrawing the shape from the molten aluminum with a continuous film of aluminum adhering thereto, and then cooling the resulting aluminum-

coated shape to below the melting point of aluminum.

11. The method according to claim 10, characterized in that the amount of flux applied to the surface of said shape is greater than 0.04 gram per square foot.

12. The method of coating a ferrous metal shape with aluminum which comprises applying to the surface of such shape an effective amount of an alkali metal double salt of zirconium fluoride, then immersing the shape with said salt thereon in molten aluminum, then withdrawing the shape from the molten aluminum with a continuous film of aluminum adhering thereto, and then cooling the resulting aluminum-coated shape to below the melting point of aluminum.

13. The method according to claim 12, characterized in that the amount of said zirconium salt applied to the surface of said shape is greater than 0.04 gram per square foot.

14. The method of producing an aluminum-coated steel article of high tensile strength which comprises applying an effective amount of a flux selected from the group consisting of fluoride compounds of zirconium and fluoride compounds of titanium to the surface of a steel shape, immersing the shape with said flux thereon in a bath of molten aluminum, withdrawing the shape from the molten aluminum and regulating the rate of such withdrawal so as to form on the shape a continuous adherent aluminum coating of substantial thickness, cooling the aluminum-coated shape to a temperature substantially below the melting point of aluminum, and thereafter plastically deforming the cooled aluminum-coated shape sufficiently to reduce its cross-sectional area by a substantial extent, whereby the hardness and tensile strength of the steel are substantially increased and the surface quality of the aluminum coating is substantially improved.

15. The method of producing an aluminum-coated steel article of high tensile strength which comprises applying an effective amount of an alkali metal double salt of zirconium fluoride to the surface of a steel shape, immersing the shape with said salt thereon in molten aluminum at a temperature of about 1220° to 1260° F., withdrawing the shape from the molten aluminum and regulating the rate of such withdrawal so as to form on the shape a continuous adherent aluminum coating of substantial thickness, cooling the aluminum-coated shape to below the melting point of aluminum, and thereafter plastically deforming the aluminum-coated shape substantially at room temperature sufficiently to reduce its cross-sectional area by at least the amount required to restore the hardness and tensile strength of the steel to the values prevailing prior to such annealing thereof as occurred in consequence of immersion of the shape in the molten aluminum.

16. The method of producing aluminum-coated steel wire of high tensile strength which comprises cold drawing a steel wire from an initial cross-sectional area to a smaller intermediate cross-sectional area, whereby the steel is hardened and its tensile strength is increased to a desired high value, then applying to the surface of said wire an effective amount of a flux selected from the group consisting of fluoride compounds of zirconium and fluoride compounds of titanium, then immersing the wire with flux thereon in molten aluminum, then withdrawing the wire from the molten aluminum and regulating the rate of such withdrawal so as to form

on the wire a continuous adherent aluminum coating of substantial thickness, then cooling the aluminum-coated steel shape substantially to room temperature, and thereafter cold drawing the aluminum-coated wire to a final cross-sectional area enough smaller than said intermediate cross-sectional area so as to restore the hardness and tensile strength of the steel to the values prevailing prior to such annealing thereof as occurred in consequence of immersion of the wire in the molten aluminum.

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