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PROCESS FOR COATING AND UNITING METAL SHAPES WITH ALUMINUM

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6 Claims. (Cl. 29—189)

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The present application is a division of my co-pending application Serial No. 121,894, filed October 17, 1949, now abandoned.

The present invention relates generally to the art of metal coating operations wherein a metal base is provided with a protective coating of a dissimilar metal for the purpose of inhibiting corrosion, enhancing appearance, and for other desirable results. More particularly, the present invention relates to the production of protective aluminum coatings of commercial quality and of tight adherence upon ferrous metal bases.

A still further object of the invention is to provide a process for the obtaining of tightly adherent, ductile coatings of aluminum on ferrous metal articles for corrosion inhibition of the ferrous metal base, which coatings are of commercial quality as regards their continuity and their adhesion to the ferrous metal base, but which also act as joining means by which adjacent shapes may be joined together in a firm and strong manner by the tightly adherent aluminum coating acting as a bond between adjacent overlapping edges or surfaces of the shapes which are to be joined together by the tightly adherent aluminum coating acting as the uniting medium.

A principal object of this invention, therefore, may be said to be the production on ferrous articles of tightly adherent aluminum coatings, while disposing adjacent articles in overlapping relation and applying a tightly adherent, continuous aluminum coating over the overlapping surfaces to bridge and to unite together such surfaces in a substantially integral manner.

A still further object of the invention is to produce on ferrous articles continuous and tightly adherent aluminum coatings and simultaneously producing on such articles strong seams by filling the space between overlapping edges on the ferrous articles with such tightly adherent and continuous coatings of aluminum.

Further objects of the invention will become apparent as the description proceeds, and the features of novelty will be pointed out in particularity in the appended claims.

In accordance with the present invention, the surface of the ferrous articles to be coated with aluminum first are cleaned in the usual manner, such as mechanical cleaning, followed by degreasing in a grease solvent, e. g. carbon tetrachloride, pickling in dilute hydrochloric acid or sulphuric acid, washing with water, washing with an alkali solution to neutralize adhering acid, and water washing. The cleaned ferrous metal article is then dipped into an aqueous solution

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containing a zirconium fluoride compound, or a titanium fluoride compound, such as zirconium fluoride itself, or a complex zirconium fluoride salt with an alkali metal, such as 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 solutions of zirconium fluoride or alkali zirconium fluoride, or corresponding titanium fluoride, may be applied to the clean surface of the ferrous article to be coated by dipping, spraying, painting, or any other convenient way. Potassium zirconium fluoride solutions conveniently are applied by one dip in solution containing from approximately two to approximately eighteen grams of K_2ZrF_6 per 100 cc. 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 cc. of water, but at 20° C. the solubility is only 1.55 grams per 100 cc. 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 cc. 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 cc. 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 cc. 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 makes it possible 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, the sodium salt is 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° C. to 100° C. and allowed to drain, the residual salt present on the sheets will depend on the concentration of the potassium fluoride solution. Thus, with 40 gms. per liter K_2ZrF_6 solution, there will be left 0.11 gram of K_2ZrF_6 per square foot of surface; with 80 gms. per liter K_2ZrF_6 solution there will remain 0.25 gram K_2ZrF_6 per square foot, and with 160 gms. per liter K_2ZrF_6 solution, there will remain 0.53 gram K_2ZrF_6 per square foot. As one long ton of 12-gage wire has 2080 square feet of surface, the total quantity of potassium zirconium fluoride present on the surface of one ton of wire after one dip in 80 gms. per liter solution is 1.14 lbs. 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-gage 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 travelling 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 gives a poor 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.

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.

In continuous coating of 15-gage wire with commercial aluminum at 1240° F., there are obtained coatings which are about 0.0017 inch thick. Using a temperature of 1230° to 1235° F. a heavier coating is obtained. On the other hand, a temperature of 1260°–1270° F. gives a definitely thinner coating.

Coatings applied at 1225°–1240° F. are generally heavier, but the alloy layer between the coating and base metal is quite thin and the coating will stand considerable bending before it cracks. 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 of from 8 to 12 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 time.

The present invention is directed to the application of the above-described aluminum-coating process to the joining of steel shapes while they are being coated. For example, a sheet of steel having a thickness of 0.025 inch is shaped in the form of a two-inch pipe with the two edges overlapping $\frac{1}{16}$ inch. The two edges are made straight and in contact along the whole length of the pipe. The pipe now is degreased, pickled in acid, washed in water, dipped in 95° C. solution containing 16 grams K_2ZrF_6 per 100 c. c. water, dried with 90° C. air and dipped in molten aluminum at 1250° F. for 15 seconds with agitation of the pipe. On removal from the aluminum bath, the pipe was found to be coated on the outside as well as on the inside with a smooth coating of aluminum. In addition, the aluminum had run into the space between the two overlapping edges forming a good, even, airtight seam on the pipe. Pipes can be joined end-to-end by this procedure, and the resulting air-tight seam is adequately strong for joining sections of downspouts and other light gage pipe.

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.

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. or below the melting point of aluminum, that 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

$$3K_2ZrF_6+4Al=6KF.4AlF_3+3Zr$$

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. As cryolite, as well as alkali zirconium fluorides are excellent fluxing compounds for aluminum, the thin film of flux covering the steel will effectively clean the aluminum surrounding the ferrous shapes, as well as the ferrous metal, and 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 will reduce the melting point to 565° C. for an eutectic. Anything which increases the AlF_3 content in the cryolite 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 potassium chloride, for instance the weight of KCl being 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 necessairily 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.

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 re-

acted. 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:

$$3K_2ZrF_6+4Al\rightarrow 6KF.4AlF_3+3Zr$$

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 melting 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 interface ferrous metal-aluminum 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 gms. per 100 cc. of solution, and at 100° C., the solubility is 12 gms. per 100 cc. 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, concentration of 50 to 100 gms./l., K_2TiF_6 are used, but good results have been obtained with concentrations as low as 20 gms./l., K_2TiF_6. One dip in a solution containing 50 gms./l., K_2TiF_6 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 salt film of titanium salt at a higher temperature. Drying in air at 80°–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 necessary, therefore, to dry in air having a temperature of 150° C. or higher. For example, when 0.020 inch thick sheet iron was dipped in a 50 gm./l., K_2TiF_6 solution at 95° C., it was necessary to dry the iron for 90 seconds when the temperature of the air current was 175° C. 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 capacity of the plant. Is also is possible to evaporate the water from the salt film by passing an electric current through the wire, strip, or similar stock provided that a current of air removes the evaporated moisture.

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 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 re-

moved by filtration. 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.

Furthermore, it has been found high advantageous to dip the cleaned ferrous articles in solutions containing a mixture of alkali zirconium fluoride and alkali titanium fluoride. For instance, it is found in practice that by using a solution containing 50 gms./l., K_2ZrF_6 and 50 gms./l., K_2TiF_6 aluminum coatings are obtained, which have a smoother surface than are obtained with solutions containing either 100 gms./l., K_2ZrF_6 or 100 gms./l., K_2TiF_6. The solutions containing alkali double fluoride salts of zirconium and titanium show two advantages. In the first place, 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 is only about 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, must 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 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, it is obvious that from a cost standpoint, the heating of a salt to its melting point is far more expensive than heating a solution of the salt to 90° C. to 100° C.

It may be mentioned that the actual chemistry involved in the present process of coating ferrous base metals with aluminum, is not very clearly understood. In carrying out the present invention, it has been observed that titanium and zirconium react rapidly with aluminum to form intermetallic compounds Al_3Ti.Al_3Zr, respectively. It may be that the bond layer between the aluminum coating and the ferrous base metal may be either a mixture of Al_3Ti and Ti, or Al_3Zr and Zr, but the exact composition of the bonding layer has not been established definitely.

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. Also, it will be understood that in the appended claims, the term "aluminum" is intended to include aluminum alloys as well as elemental aluminum.

The parent application of which this is a division is a continuation in part of my pending application Serial No. 53,370, filed October 7, 1948, 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.

What is claimed is:

1. The method of coating and joining together metal shapes of a base metal selected from the group consisting of cobalt, chromium, nickel, iron, and alloys thereof, which comprises thoroughly cleaning the surfaces of said shapes that are to be joined together, positioning such surfaces in substantially abutting relation, then applying to such cleaned and substantially abutting surfaces a flux selected from the group consisting of fluoride compounds of zirconium and fluoride compounds of titanium, then applying molten aluminum to and between such surfaces, and then cooling the aluminum so applied, whereby a continuous tightly adherent coating of aluminum is formed on and joins together said substantially abutting surfaces.

2. The method of coating and joining together metal shapes of a base metal selected from the group consisting of cobalt, chromium, nickel, iron, and alloys thereof, which comprises thoroughly cleaning the surfaces of said shapes that are to be joined together, positioning such surfaces in substantially abutting relation, then thoroughly wetting such cleaned surfaces with an aqueous solution of a fluoride compound of zirconium, then applying molten aluminum to and between such surfaces, and then cooling the aluminum so applied, whereby a continuous tightly adherent coating of aluminum is formed on and joins together said substantially abutting surfaces.

3. The method of coating and joining together metal shapes of a base metal selected from the

group consisting of cobalt, chromium, nickel, iron, and alloys thereof, which comprises thoroughly cleaning the surfaces of said shapes that are to be joined together, positioning such surfaces in substantially abutting relation, then thoroughly wetting such cleaned surface with an aqueous solution of potassium zirconium fluoride, then drying such surfaces, then applying molten aluminum to and between such surfaces, and then cooling the aluminum so applied, whereby a continuous tightly adherent coating of aluminum is formed on and joins together said substantially abutting surfaces.

4. The method of coating and joining together surfaces of ferrous metal shapes which comprises thoroughly cleaning such surfaces, positioning such surfaces in substantially abutting relation, applying to such surfaces a flux selected from the group consisting of fluoride compounds of zirconium and fluoride compounds of titanium, then causing molten aluminum to flow over and between such surfaces, and then cooling the aluminum adhering to such surfaces to below its melting point, whereby a continuous tightly adherent coating of aluminum is formed on and joins together said substantially abutting surfaces.

5. The method of coating and joining together surfaces of ferrous metal shapes which comprises thoroughly cleaning such surfaces, positioning such surfaces in substantially abutting relation, applying to such surfaces at least 0.04 gram per square foot of a flux selected from the group consisting of fluoride compounds of zirconium and fluoride compounds of titanium, then causing molten aluminum to flow over and between such surfaces, and then cooling the aluminum adhering to such surfaces to below its melting point, whereby a continuous tightly adherent coating of aluminum is formed on and joins together said substantially abutting surfaces.

6. The method of coating and joining together surfaces of ferrous metal shapes which comprises thoroughly cleaning such surfaces, positioning such surfaces in substantially abutting relation, applying to such surfaces an alkali metal double salt of zirconium fluoride, then causing molten aluminum to flow over and between such surfaces, and then cooling the aluminum adhering to such surfaces to below its melting point, whereby a continuous tightly adherent coating of aluminum is formed on and joins together said substantially abutting surfaces.

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