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METHOD OF ELECTRODEPOSITING ALUMINUM

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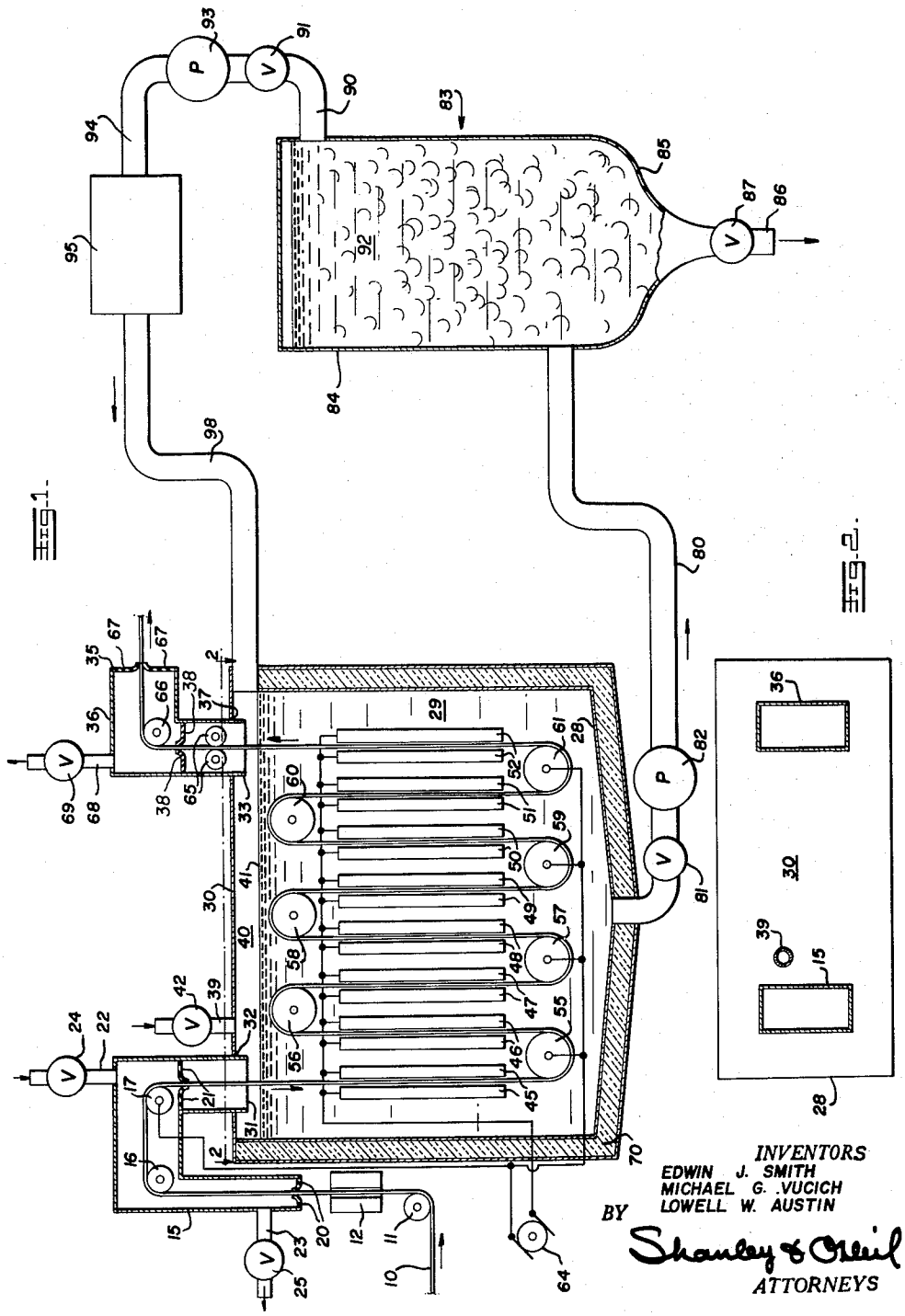


Fig. 1.

Fig. 2.

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METHOD OF ELECTRODEPOSITING ALUMINUM

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This application is a continuation-in-part of our copending applications Serial No. 826,997, filed July 14, 1959, for "Method and Apparatus for Removing Contaminants" and Serial No. 92,002, filed February 27, 1961 for "Electrolyte and Method of Electroplating," both now abandoned.

This invention broadly relates to a novel method and improved apparatus for treating an electorlyte to reduce the concentration of a dissolved iron salt contaminating the same. The present invention further relates to a novel method and improved apparatus for the electrodeposition of aluminum-containing material and, in one of its more specific aspects, to electroplating an aluminum-containing coating on a ferrous metal base wherein an electrolyte is treated to remove contaminating iron salts.

The present invention will be described and illustrated hereinafter with specific reference to a process and apparatus for the electrodeposition of an aluminum-containing coating on ferrous metal strip from a fused electrolyte containing a major proportion of aluminum chloride and the remainder one or more alkali metal chlorides. However, it will be apparent to those skilled in the art that the principles of the invention are applicable to other substrates, including metal bases or forms of metal bases, coating metals and electrolytes which present the problems solved by the present invention.

A fused electrolyte bath having an aluminum chloride content of approximately 75–85% by weight and the remainder sodium and/or potassium chloride is useful in producing aluminum electroplate. The electrolyte composition may be of the binary or ternary type. A satisfactory binary electrolyte is a composition containing by weight 80% aluminum chloride and 20% sodium chloride, and a satisfactory ternary electrolyte is a composition containing by weight 80% aluminum chloride, 10% sodium chloride and 10% potassium chloride. Although a fused electrolyte bath containing 80–85% aluminum chloride produces objectionable visible fuming in the presence of water, an electrolyte containing more than 85% aluminum chloride fumes excessively and the plating results usually are not improved by increasing the aluminum chloride content above this value. However, if the aluminum chloride content falls below about 75% by weight, poor plating may result when using unmodified direct current in the absence of special plating conditions and such electrolyte compositions are not usually preferred. In some instances, it may be possible to use electrolyte compositions containing less than 75% aluminum chloride and the remainder alkali metal chloride when using special plating condition and/or by using low current densities. When using a fuming fused aluminum chloride-alkali metal chloride electrolyte bath, such as a bath containing 80% by weight aluminum chloride, 10% by weight sodium chloride and 10% by weight potassium chloride, current conditions up to 100 amperes per square foot and often as high as 100–400 amperes per square foot may be used with straight direct current, and current conditions for special plating conditions may be equally satisfactory or even better.

Still other baths for electrodepositing aluminum are known to the art and may be used in practicing the present invention. For example, one or more of the chloride

salts of the electrolyte baths mentioned herein may be replaced with other suitable halide salts such as aluminum bromide, sodium bromide, and potassium bromide in amounts to maintain the same molar proportions. Also, the aluminum halide may be complexed with other complexing agents such as ammonia and organic amines or their salts in a manner somewhat similar in effect to the complexing of aluminum chloride with potassium and/or sodium halide. An aluminum chloride-ammonia bath contains complexed aluminum chloride which is thought to be in the form of $AlCl_3 \cdot NH_3$ or possibly higher members of the ammonia series with varying amounts of free aluminum chloride being dissolved therein in the case of a fuming bath. Further, aluminum chloride may be complexed by means of organic amines and their salts such as ethyl pyridinium bromide to produce the complex ethyl pyridinium bromide–$AlCl_3$. This material may contain dissolved free aluminum chloride. The various aluminum electroplating baths discussed above may be considered to be, broadly speaking, fused salt electroplating baths containing aluminum halide and a complexing agent, with the aluminum halide complex being in the molten state and preferably having dissolved therein free aluminum halide in proportions causing fuming at the operating temperature.

It is understood that when substituting other halides for the chlorides in the electroplating baths discussed herein, the substitutions may be made in molar proportions rather than in proportions by weight so as to provide the same molar proportion of aluminum halide, the complexing agent and the free dissolved aluminum halide. Unless specifically stated to the contrary, the parts and percentages of the specific electrolyte bath ingredients are in parts or percentages by weight. If desired, substitution of other materials may be made on a molar basis, as mentioned above. When electroplating an aluminum-containing coating on a substrate which is a conductor of electricity in accordance with the teachings of the present invention, the above electroplating baths may be used under the same general conditions as used by the prior art with the exceptions noted hereinafter.

The above-mentioned visible fuming is due to a reaction between the fused aluminum halide-containing electrolyte and atmospheric water vapor or water from some other source. The reaction products thus produced are highly corrosive and tend to corrode metallic apparatus, ferrous metal strip passing through the electrolyte, and other metallic materials contacted thereby. This results in the electrolyte bath being gradually contaminated with the corroded metals and especially with iron from the ferrous metal strip being electroplated. Thus, after continuously operating the electroplating line over an extended period of time, iron salts present on the strip surface as it enters the electrolyte or produced upon contact with the electroylte are disolved therein and may build up to a substantial level. While metals other than iron such as copper, zinc, nickel, etc. tend to contaminate the electrolyte bath and deleteriously affect the plated product, iron is usually the most difficult metallic contaminant to control in the electroplating of ferrous metal strip.

When electroplating ferrous metal strip using a fused salt electrolyte such as discussed above, it was discovered that with continued operation over an extended period of time and especially when the electrolyte bath is contaminated with water, the concentration of dissolved iron salts may increase to a level where the electroplated coating takes on a color varying from gray to black. Additionally, there is a pronounced tendency for a black undercoating to deposit initially that adversely affects the adherency of the aluminum coating. On the other hand, in instances where only iron-free salts are used in prepar-

ing the electroplating bath or the electroplating bath is purified to be entirely free of iron, it was further discovered that unsatisfactory crystalline, dendritic electrodeposits may be produced which were unexplainable prior to the present invention.

It has been further discovered that the abovementioned deficiencies of prior art aluminum electroplated substrates may be prevented by proper levels of iron compounds dissolved in the electrolyte. For example, electroplate produced from electrolyte baths containing more than about 0.02% iron exhibit poor adhesion of the aluminum coating and have an uneven, dark appearance which render the product unsatisafctory for many commercial applications. Additionally, when the dissolved iron content of the electrolyte falls below about 0.001% by weight, crystalline, dendritic electrodeposits may be produced which are not entirely satisfactory.

In accordance with one important aspect of the present invention, improved aluminum electroplate is produced from a novel aluminum electroplating bath containing a soluble iron compound in an amount providing about 0.001–0.02% by weight of dissolved iron. Also, improved apparatus and a novel method are provided whereby the dissolved iron content of an electrolyte may be reduced and/or maintained at the proper dissolved iron concentration by intimate contact with metallic aluminum other than anodes. In accordance with another aspect of the invention, improved apparatus and a novel method of plating are provided wherein dissolved iron in the electrolyte may be effectively controlled at a desired predetermined level by intimately contacting the electrolyte with metallic aluminum other than the anodes to thereby precipitate excess iron-containing material. It has been further discovered that the precipitated iron-containing material does not deleteriously affect the plating process so long as it does not redissolve in the electrolyte. Thus, in a method of electroplating a substrate with an aluminum-containing coating, particles of precipitated iron-containing material may be suspended in the electrolyte so long as it is not allowed to redissolve in the electrolyte to provide a dissolved iron content above about 0.02% by weight.

It is an object of the present invention to provide a novel electroylte bath for electroplating aluminum on a substrate.

It is a further object of the present invention to provide a novel method of electroplating an aluminum-containing coating on a substrate.

It is still a further object of the present invention to provide a novel method and improved apparatus for maintaining an electrolyte bath for electroplating an aluminum-containing coating at the proper iron concentration.

It is still a further object of the present invention to provide a novel method and improved apparatus for electroplating an aluminum-containing coating on ferrous metal wherein the electrolyte bath is contacted with metallic aluminum other than an anode to maintain the proper iron concentration.

It is still a further object to provide a novel method and improved apparatus for reducing the concentration of an iron salt dissolved in an electrolyte.

It is still a further object of the present invention to provide a novel method and improved apparatus for electroplating an aluminum-containing coating on a ferrous metal base using a fused salt electrolyte containing aluminum halide and alkali metal halide wherein the electrolyte is treated to remove contaminating iron salts and assure production of adherent coatings free of discoloration.

Still other objects and advantages of the present invention will be apparent to those skilled in the art upon reference to the following detailed description and the drawings, wherein:

FIGURE 1 is a diagrammatic side elevational view partially in cross section of one arrangement of apparatus satisfactory for use in practicing the present invention; and

FIGURE 2 is a cross-sectional view taken along the line 2—2 of FIGURE 1 but omitting a showing of the strip, the sealing flaps, the rolls, the electrodes and conduits including cooperating apparatus for withdrawing contaminated electrolyte and returning purified electrolyte to the bath.

Referring now to FIGURES 1 and 2 of the drawings, which illustrate a specific embodiment of the invention, ferrous metal strip **10** is shown passing under roll **11** after receiving a wet prior art pretreatment or other suitable pretreatment such as cathodic cleaning in an ortho-sil solution (Na_4SiO_4) employing a treating time of 1–2 seconds at a current density of 35 ampere seconds per square foot, followed by, in sequence, brushing and spraying with water, anodic pickling in a suitable electrolyte such as aqueous 35% sulfuric acid for 2–3 seconds at 80–100 amperes per square foot, scrubbing and washing with water and drying to remove all traces of water. The strip **10** then passes upwardly through heater **12** where it is heated sufficiently to completely evaporate any free water remaining on the strip surface. The heated ferrous metal strip **10** passes upward through strip conditioning unit **15** where it is thoroughly dried to remove any remaining traces of free water and then passes over rolls **16** and **17**. If desired, the ferrous metal strip **10** may be treated within strip conditioning unit **15** in a reducing atmosphere or otherwise treated for the purpose of further conditioning the strip surface and assuring absolute removal of free water, combined water and substances forming water under the conditions present in the electroplating unit. It also may be desirable to preheat the strip to a temperature about the temperature of the bath at the time plating is commenced. Two pairs of suitable sealing flaps **20** and **21** are provided near the entrance and exit ends, respectively, of strip conditioning unit **15** to prevent undue loss of any dry gaseous treating agent which may be employed in strip conditioning unit **15**, as well as in aiding in preventing entry of atmospheric water vapor. The dry gaseous treating agent may be supplied to strip conditioning unit **15** by means of conduit **22** and withdrawn by means of conduit **23**. The flow rate of dry gaseous treating agent to strip conditioning unit **15** via conduit **22** is controlled by means of valve **24**, while the withdrawal rate via conduit **23** is controlled by means of valve **25**. Any suitable dry gaseous treating agent may be employed in strip conditioning unit **15**, depending upon the nature of the treatment desired. However, it is essential that the treatment be such so as to insure that the surface of ferrous metal strip **10** is free of free water, combined water such as hydrated ferrous metal salts, or substances reacting under conditions present in the electroplating zone to form water upon exit from strip conditioning unit **15**. In addition, it is essential once the strip has been thoroughly dried and freed of all sources of water that the dry strip not be subjected to any source of water while passing from the drying step to the electrolyte. It is preferred to surround the strip at all times with a dry medium, such as a dry, non-reactive gas, during passage from the drying step to the electroplating bath. In instances where a special conditioning treatment is not necessary, the gaseous treating agent may be dry air, nitrogen, carbon dioxide, argon, etc. Usually, it is preferred that the gaseous treating agent be supplied to strip conditioning unit **15** at about atmospheric pressure.

The ferrous metal strip **10** passes downward from strip conditioning unit **15** into electroplating tank **28** containing, for example, the novel aluminum electroplating electrolyte described herein. The fused electrolyte **29** may contain a predominant proportion by weight of aluminum chloride such as for example 80% aluminum chloride, about 0.001–0.02% and preferably 0.003–0.01% dissolved iron, and the remainder equal parts of sodium chloride and

potassium chloride and when such an electrolyte is used it fumes in the presence of water or water vapor under the operating conditions. A hood **30** is positioned above electroplating tank **28**, as best seen in FIGURE 2. The exit end **31** of strip conditioning unit **15** extends downward a short distance through opening **32** in hood **30** and, similarly, the entrance end **33** of unit **36** extends downward a short distance through opening **37** in hood **30**, thereby providing an entrance and an exit, respectively, to electroplating tank **28** for ferrous metal strip **10**. The hood **30** is joined to both strip conditioning unit **15** and unit **36** in air-tight relationship, and since sealing flaps **21** and **38** are provided near ends **31** and **33**, respectively, this combination of elements substantially seal off electrolyte **29** from the surrounding atmosphere. A gas or gaseous mixture such as dry nitrogen, carbon dioxide, argon or air is fed by means of conduit **39** into space **40** within electroplating tank **28** and above level **41** of electrolyte **29** and the undersurface of hood **30**. A valve **42** is provided in conduit **39** for the purpose of controlling the feed rate of dry gas that is fed to space **40**.

Electroplating tank **28** is provided with spaced pairs of aluminum-containing anodes **45** and **46–52**. The ferrous metal strip **10** passes downward from roll **17** into fused electrolyte **29** and is subsequently passed between the spaced pairs of anodes by means of a path established by rolls **55** and **56–61**. The spaced pairs of anodes are electrically connected to the positive side of generator **64** (or other suitable source of current), while ferrous metal strip **10** is made electro-negative between contact rolls **17**, **55**, **57**, **59** and **61**. The ferrous metal strip **10** is electroplated with a coating containing aluminum of any suitable desired thickness.

When the electrolyte contains by weight 80% aluminum chloride, about 0.001–0.02% dissolved iron, and the remainder equal parts of sodium chloride and potassium chloride, the bath **29** may be at a temperature of about 250–400° F. and, preferably, about 300–350° F. Current density, preferably, should be from 20 to about 100 amperes per square foot. However, under optimum conditions of operation, current densities up to about 100 to 400 amperes per square foot are possible and may be used when desired. The electroplating conditions for use in accordance with the present invention need not differ in any respect from those of the prior art for electroplating aluminum other than in providing the proper level of dissolved iron in the electrolyte bath and/or providing for purification of the electrolyte in accordance with the invention. It is understood that plating conditions will necessarily vary somewhat from electrolyte to electrolyte. However, suitable conditions for a given prior art electrolyte for the electroplating of an aluminum-containing coating are well known to those skilled in the art.

After passing under roll **61**, the ferrous metal strip **10** passes upward through electrolyte **29** and after emerging therefrom passes between squeegee rolls **65**, which reduce the amount of dragout of electrolyte to some extent. The ferrous metal strip **10** continues to pass upwardly through unit **36** and is then passed horizontally over roll **66**. A pair of sealing flaps **67** are provided at the exit end **35** of unit **36** for the purpose of sealing off the exit and thereby allowing a slight suction to be applied to unit **36** through exhaust conduit **68** when this may be desired, as well as preventing entry of atmospheric water vapor which would have a detrimental effect on the aluminum chloride content of the electrolyte. The exhaust conduit **68** is provided with valve **69** for the purpose of controlling exhaust of unit **36** in instances where it is exhausted. The plated ferrous metal strip **10**, after passing over roll **66**, passes from the exit end of unit **36** and then may be washed with water and dried or given other subsequent treatments. If desired, the plated strip may be roll-brightened.

For the purpose of minimizing loss of heat, electroplating tank **28** may be surrounded by an insulating material **70**. Additionally, and in order to maintain the fused electrolyte **29** at the proper operating temperature, heating means (not shown) may be employed as is conventional in the art. For example, immersion heating may be employed in the conventional manner wherein the heating units are immersed directly in the electrolyte or, preferably, the insulating material **70** may be spaced from the electroplating tank **28** and the electroplating tank surrounded within the space thus formed by suitable heating means such as fin-type strip electrical heaters.

The gas or gaseous mixture fed through conduit **39** must be dry, but it may be at any suitable convenient temperature such as room temperature. The pressure employed within space **40** may be atmospheric pressure or slightly above although any suitable convenient pressure may be applied. It is only necessary to replace the atmosphere within space **40** with a dry gas. A slight suction may be maintained, if desired, on strip conditioning unit **15** and unit **36** by means of exhaust conduits **23** and **68**, respectively, to aid in the escape through flexible sealing flaps **21** and **38** of gas fed to space **40** together with any moisture or water content. It is not necessary that the gas be supplied under pressure or the atmosphere within space **40** be maintained under a substantially elevated pressure. However, a pressure above atmospheric pressure may be preferred in some instances for best results. The composition of the specific dry gas or dry gaseous mixture supplied to space **40** may vary widely. It is only necessary that the dry gas or gaseous mixture be substantially non-reactive under the conditions of operation of the electroplating line with the electrolyte **29**, the strip **10** or the apparatus contacted by the gas or gaseous mixture.

With continued operation of the above described apparatus, the concentration of iron salts dissolved in the electrolyte bath rises sufficiently to result in poor adherence or off-colored electroplated coatings. When the concentration of iron salts exceeds about 0.02% dissolved iron, then unsatisfactory electroplate from the standpoint of an adherent coating and color of the coating is produced and it is necessary to purify the electrolyte. This may be conveniently accomplished in accordance with the invention by withdrawing electrolyte including any sludge from the bottom of the electroplating tank **28** via conduit **80** provided with control valve **81** and pumping the withdrawn electrolyte by means of pump **82** into an intermediate portion of vessel **83**. The bottom of the electroplating tank **28** slopes downward slightly to thereby allow the sludge to collect in the vicinity of conduit **80** and be withdrawn for passage to vessel **83**. This assures removal of the maximum amount of contaminating substances in a given volume of withdrawn electrolyte.

The vessel **83** may be provided with a generally cylindrical upper portion **84** and a conical lower portion **85** which terminates in a conduit **86** provided with control valve **87** for withdrawing sludge from vessel **83**. The uppermost portion of vessel **83** is provided with conduit **90** including control valve **91** for withdrawal of purified electrolyte. Also, the vessel **83** is packed with metallic aluminum **92** such as aluminum turnings, aluminum wire or other metallic aluminum materials preferably of a type assuring a relatively large surface area for a given weight of aluminum. The aluminum turnings are in intimate contact with the withdrawn electrolyte and thereby result in the precipitation of iron-containing material which tends to pass downward in the vessel **83** with purified electrolyte rising to the upper portion of vessel **83**. A sludge containing precipitated iron-bearing material is withdrawn from vessel **83** via conduit **86** and is discarded.

The purified electrolyte withdrawn via conduit **90** is pumped by means of pump **93** via conduit **94** to filter **95**. The filter **95** also is packed with aluminum turnings or other suitable form of metallic aluminum providing a relatively large surface area for a given weight of aluminum. The metallic aluminum is preferably in a

form such as to aid in the filtration of small particles of precipitated iron-bearing material withdrawn along with electrolyte from vessel 83. While aluminum turnings are a preferred form of aluminum for this purpose, other forms of aluminum may be used and a suitable filter element such as glass wool may be substituted for or combined with the aluminum turnings. For preferred results, metallic aluminum should be present in the filter in order to prevent redissolving a portion of the precipitated iron-bearing material in the electrolyte. The filtered and purified electrolyte is withdrawn from filter 95 and recycled to the electrolyte bath via conduit 98 with conduit 98 preferably entering the electrolyte tank at about the electrolyte level 41 so as to prevent cascading.

The electrolyte withdrawn via conduit 80 and passed to vessel 83 may be contacted with at least 0.035 sq. ft. of aluminum surface for each gallon of electrolyte. This will assure removal of sufficient iron-containing salts to provide a dissolved iron content in the electrolyte below 0.02% and thereby allow good plate to be produced. However, better results may be obtained with higher ratios of aluminum surface area to a given volume of electrolyte, such as 0.25 sq. ft. of aluminum surface per gallon of electrolyte or higher. For example, 1, 5, 10, 15 or even 25 or more sq. ft. of aluminum surface may be in contact with each gallon of electrolyte to assure precipitation of a maximum amount of iron-containing material in a minimum period of time in instances where this is desirable. In instances where the ratio of aluminum surface to a given volume of electrolyte is relatively low, then the average residence time of the electrolyte within vessel 83 should be sufficiently long to assure a dissolved iron content of about 0.001–0.02% by weight in the purified electrolyte, while with higher ratios shorter residence periods are satisfactory to achieve this end. The electrolyte is withdrawn from the electroplating tank at a rate to assure that the dissolved iron content is maintained below 0.02% by weight, such as at about 0.001–0.02% by weight and preferably at about 0.003–0.01%. The iron-bearing material which is precipitated from the electrolyte in the form of metallic iron or other insoluble iron-bearing substances collects on the aluminum surface and eventually falls downward into the lower portion 85 of vessel 83.

Usually, it is preferred that contaminated electrolyte be withdrawn from the electroplating tank and then purified. However, it is possible to immerse metallic aluminum in electrolyte contained within the electroplating tank. For example, metallic aluminum in the form of sheet, wire, turnings, etc., may be placed along the sides or bottom of the electroplating tank. Suitable shielding means may be provided to assure that stray currents do not interfere with the plating operation, or glass lined plating tanks and other electrically insulated equipment may be used for this purpose. The metallic aluminum also may be placed in a non-conducting or electrically insulated container such as Teflon (polytetrafluoroethylene) so as to electrically insulate the aluminum turnings from the plating tank, contact rolls and other elements within the electroplating tank. In such event, the electrolyte in the electroplating tank may be circulated through the immersed Teflon container filled with metallic aluminum to thereby result in the precipitation of iron-bearing material.

Surprisingly, it has been discovered that precipitated iron-bearing material does not interfere with the production of adherent coatings of satisfactory color. However, the precipitated iron-bearing material exhibits a pronounced tendency to go back into solution in the absence of metallic aluminum and, preferably, metallic aluminum should be maintained in contact with the electrolyte at all times in an amount sufficient to maintain the dissolved iron content at an acceptable level, such as at about 0.001–0.02% by weight and preferably at about 0.003–0.01%. Therefore, maintaining the electrolyte in the presence of at least about 0.035 sq. ft. of aluminum surface for each gallon of the electrolyte will assure production of satisfactory aluminum plate from the electrolyte at all times. Even better results will be obtained at the higher ratios of aluminum surface to a given volume of electrolyte mentioned above.

While the electrodeposition of an aluminum coating has been specifically described herein, it is understood that aluminum-containing coatings in general may be electroplated in accordance with the teachings of the invention. Also, suitable electrolytes and/or plating conditions may be used other than the ones specifically described herein, such as disclosed in copending application Serial No. 34,923 now Patent No. 3,167,403, filed June 9, 1960, for "Method of Coating and Product" by Edwin J. Smith, Michael G. Vucich and Lowell W. Austin. The teachings of this copending application are incorporated herein by reference.

The foregoing detailed description and the following specific examples are for purposes of illustration only and are not intended as being limiting to the spirit or scope of the appended claims. All percentages appearing in the specification including the examples are percent by weight unless otherwise noted.

EXAMPLE I

Ferrous metal strip, after a wet pretreatment following the procedure described in connection with FIGURE 1, is passed at a speed of 10 feet per minute through plating apparatus similar to that illustrated in FIGURES 1 and 2 of the drawings. The temperature of the strip is about 325° F. and a feed of 72 cu. ft. per hour of dry gaseous nitrogen is passed into the space between the hood and the electrolyte level, as well as the strip conditioning unit, for the purpose of preventing water contamination of the electrolyte due to the entrance of atmospheric moisture. The ferrous metal strip is dry after the pretreatment and completely free of "free water," combined water such as hydrated metal salts and substances reacting under conditions present in the electroplating zone to form water and is maintained in this condition at the time of entering the electroplating zone.

The strip is introduced into a fused electrolyte containing by weight 80% aluminum chloride, about 0.001–0.02% dissolved iron and the remainder equal parts of sodium chloride and potassium chloride. The electrolyte is maintained at a temperature of 325° F. Aluminum anodes 10 feet in length are used employing a current density of 42.5 amperes per sq. ft. to thereby electroplate a coating 30 millionths of an inch thick of aluminum matte on the ferrous metal strip. After plating, the strip is fed from the electrolyte through the outlet zone and is washed in water and dried. The resulting white matte coating of aluminum is adherent and may be roll-brightened to produce a bright mirror-like surface, if desired.

During the above operation, electrolyte is withdrawn from the bottom of the electroplating tank via conduit 80 and is passed to the lower portion of vessel 83 containing aluminum turnings where the iron salt content is reduced by precipitation of metallic iron. The resulting purified electrolyte is withdrawn from the upper portion of vessel 83 and is passed to filter 95 via conduits 90 and 94 where suspended matter including iron-bearing material is filtered out in the presence of aluminum turnings. The resulting purified electrolyte is then passed back to the electrolyte tank via conduit 98. The vessel 83 contains about 0.25 sq. ft. of aluminum surface for each gallon of electrolyte. An iron concentration of 0.001–0.02% is maintained in the electrolyte in this manner.

When operating in the above manner with the dissolved iron concentration at 0.001–0.02% by weight, the aluminum coating is smooth, dense, adherent and of very satisfactory color. However, when valve 81 is closed and the electrolyte is no longer purified in vessel 83, the iron concentration rises above 0.02% and unsatisfactory, non-

adherent coatings of a dark to black color are produced. The rise in iron concentration is much more rapid when water is not excluded from the bath and it is more difficult to maintain the iron concentration within the above prescribed limits. Thus, this example illustrates the preferred operating practice wherein all sources of water are excluded from the bath in combination with treatment of the electrolyte to maintain the iron concentration within acceptable limits. When the electrolyte is purified to an extent that the iron concentration is reduced below 0.001% by weight then unsatisfactory crystalline, dendritic electrodeposits are obtained.

EXAMPLE II

A fused salt electrolyte bath containing by weight 80% aluminum chloride, varying percentages of dissolved iron as noted below, and the remainder equal percentages of potassium chloride and sodium chloride was prepared and placed in a 2000/ml. laboratory electrolytic cell. The bath was maintained at a temperature of 310–320° F. and samples were plated with varying concentrations of iron chloride dissolved in the electrolyte bath. The anodes used were 2S–F grade aluminum with a cathode to anode spacing of 1½ inches using a current density of about 25 amperes per square foot. The cathode plated area was about 3" x 5" on each face. The cathodes were formed from Type L steel strip and prepared for plating using the following procedure:

(A) 15 second cathodic cleaning in hot 2 oz./gal. orthosil solution at 100 amps/sq. ft.

(B) Cold spray rinse.

(C) Anodic pickle in cold 35 wt. percent H_2SO_4 at 80–100 amps/ft.^{2} for 2–3 seconds.

(D) Cold spray rinse.

(E) Hot water rinse.

(F) Roll dry with rubber rolls.

(G) 10 second immersion in fused plating salts before electrodepositing aluminum.

The data obtained appears in Table I below.

TABLE I

Sample No.	Percent Iron in Melt by Analysis	Cathode Efficiency	Remarks
1	0.0005	94.0	Crystalline, dendritic deposit.
2	0.007	94.5	White matte deposit and very dense coating; improvement over Sample I.
3	0.013	92.0	Smooth white matte deposit.
4	0.021	91.0	Some discoloration.
5	0.041	89.5	Metallic gray coating which is beginning to blacken; some staining of deposit.
6	0.103	84.5	Gray metallic-black stained panel.
7	0.22	65.0	Samples very dark to gray-black; deposits slightly powdery.

It is apparent from the foregoing that a small amount of dissolved iron salts in fused salt electrolytes greatly affect the coating. Discoloration of the coating occurs at iron concentrations above 0.02% and the coating also is adversely affected in that it is not as adherent. As the iron concentration increases, the discoloration deepens until the coating is black. Also, it was noted that a black deposit formed between the panel surface and the aluminum plate and the amount of this black initial coating increased with increasing iron concentration. At dissolved iron concentrations below about 0.001% by weight, crystalline, dendritic coatings are obtained.

EXAMPLE III

Two electrolyte baths were prepared containing by weight 80% aluminum chloride, 10% sodium chloride, and 10% potassium chloride. The baths were maintained at 325° F. in a conventional laboratory cell and varying amounts of iron added by anodic electrolysis. Immediately after electrolyzing the iron impurity into the baths, the anode and cathode were removed, a cover placed over the baths, and the baths allowed to sit for about three-quarters of an hour. Then, samples of the baths were taken and analyzed for iron followed by immersion of metallic aluminum in the baths. Additional samples of the baths were taken periodically and analyzed for iron. Also, the visual effects of the immersed aluminum were noted. The data thus obtained for the two baths are recorded below in Tables II and III.

TABLE II

[Removal of iron impurity from the melt by immersion of aluminum in the first bath]

Area of immersed aluminum, .37 sq. ft.
Weight of Bath, 5.6 lbs.
Liquid Volume (cylindrical), 5½" dia. x 4⅞" high.
Temperature of Bath, 325° F.

Time in Hours	Weight percent Iron in Bath by Analysis	Remarks
Start	.206	Bath is black with many suspended particles.
1	.175	Do.
3	.110	Do.
5	.059	Do.
21	.007	Bath is light tan with black material on immersed aluminum surfaces and at bottom of the cell.
28	.0004	Bath is water clear with black material on immersed aluminum surfaces and at bottom of cell.

TABLE III

[Over-all effect on second bath and immersed aluminum]

Percent iron added by anodic electrolysis to the second bath (calculated by weight loss), .32%.
Area of Immersed aluminum, 0.37 sq. ft.
Operating temperature, 325° F.
Weight of Bath, 5.6 lbs.
Liquid volume (cylindrical), 5½" dia. x 4⅞" high.

Time in Hours	Weight percent Iron by Analysis	Remarks
Start—No aluminum immersion.	.249	Bath is black in color with dispersed particles.
18	.288	a. Bath appears deep red to black, but clear of particles. b. Sublimed solids on transite cover are a deep straw color. Analyzed at .88% $FeCl_3$, 97.6% $AlCl_3$.
42	.307	Bath appears deep red to black.
42	Aluminum Immersed in the Fused Bath.	
59	.002	Bath almost water clear with black particles on the immersed aluminum surfaces and at the bottom of the cell.
59	Aluminum removed from the Fused Bath.	
140	.232	Bath is a clear red melt with black particles at the bottom of the plating cell.
184		The melt is deeper red but clear and the black particles are starting to rise from the bottom of the cell and disperse through the melt.

When the aluminum strips were immersed in the baths, a black material formed on the surface which eventually dropped to the bottom of the cell as a sludge. The black particles were tested and found to be magnetic and to evolve hydrogen when dropped into nitric acid. Thus, the particles were metallic iron. After the bath was purified to an iron concentration below 0.02% iron, good deposits could be obtained from the bath even in the presence of the black particles. At iron concentrations above 0.02%, unsatisfactory deposits were obtained.

What is claimed is:

1. A method of electrodepositing aluminum on an iron-containing metallic substrate comprising intimately contacting the substrate with a body of nonaqueous fused electrolyte for electrodepositing aluminum, the electrolyte containing dissolved iron-containing material formed at least in part in situ from the said substrate, electrodepositing aluminum on the substrate while it is intimately contacted with the body of electrolyte, and con-

tinuously maintaining the said iron-containing material dissolved in the electrolyte in a concentration resulting in not less than about 0.001% and not more than about 0.02% by weight of iron in solution in the electrolyte while the aluminum is being electrodeposited.

2. The method of claim 1 wherein the iron-containing material is maintained dissolved in the electrolyte in a concentration resulting in not less than 0.003% and not more than 0.01% by weight of iron in solution in the electrolyte while the aluminum is being electrodeposited.

3. A method of electroplating aluminum on a ferrous metal substrate comprising immersing the ferrous metal substrate in a body of nonaqueous fused electrolyte for electroplating aluminum, the electrolyte containing dissolved iron-containing material formed at least in part in situ from the ferrous metal substrate, electroplating aluminum on the substrate while it is immersed in the body of electrolyte, and continuously maintaining the said iron-containing material dissolved in the electrolyte in a concentration producing a smooth and adherent aluminum coating and resulting in not less than about 0.001% and not more than about 0.02% by weight of iron in solution in the electrolyte while the aluminum is being electroplated.

4. The method of claim 3 wherein the iron-containing material is maintained dissolved in the electrolyte in a concentraction resulting in not less than 0.003% and not more than 0.01% by weight of iron in solution in the electrolyte while the aluminum is being electroplated.

5. The method of claim 3 wherein the electrolyte comprises aluminum halide and alkali metal halide.

6. A method of electroplating aluminum on a ferrous metal substrate comprising immersing the ferrous metal substrate in a body of nonaqueous fused electrolyte for electroplating aluminum, the electrolyte consisting essentially of aluminum chloride, alkali metal chloride and a dissolved iron-containing compound formed at least in part in situ from the ferrous metal substrate, electroplating aluminum on the substrate while it is immersed in the body of the electrolyte, and continuously maintaining the said iron-containing compound dissolved in the electrolyte in a concentration producing a smooth and adherent aluminum coating and resulting in not less than about 0.001% and not more than about 0.02% by weight of iron in solution in the electrolyte while the aluminum is being electroplated.

7. The method of claim 6 wherein the iron-containing material is maintained dissolved in the electrolyte in a concentration resulting in not less than 0.003% and not more than 0.01% by weight of iron in solution in the electrolyte while the aluminum is being electroplated.

8. The method of claim 6 wherein the electrolyte consists essentially of at least 75% by weight of aluminum chloride and the remainder substantially alkali metal chloride and the dissolved iron-containing compound.

9. A method of electrodepositing aluminum on an iron-containing metallic substrate comprising immersing the substrate in a body of nonaqueous fused electrolyte for electrodepositing aluminum, the electrolyte containing dissolved iron-containing material formed at least in part in situ from the said substrate, electrodepositing aluminum on the said substrate while it is immersed in the body of the electrolyte, and while the aluminum is being electrodeposited, continuously maintaining the said iron-containing material dissolved in the electrolyte in a concentration resulting in not less than about 0.001% and not more than about 0.02% by weight of dissolved iron by intimately contacting the electrolyte with metallic aluminum other than as an anode to precipitate iron-containing material at dissolved iron concentrations exceeding about 0.02% by weight.

10. The method of electrodepositing aluminum of claim 9 wherein the said iron-containing material is dissolved in the electrolyte in a concentration resulting in not less than 0.003% and not more than 0.01% by weight of dissolved iron.

11. The method of claim 9 wherein each gallon of the electrolyte is in intimate contact with metallic aluminum having a surface area of at least 0.035 sq. ft.

12. The method of claim 9 wherein each gallon of the electrolyte is in intimate contact with metallic aluminum having a surface area of at least 0.25 sq. ft.

13. The method of claim 9 wherein electrolyte containing the dissolved iron-containing material is withdrawn from the said body of nonaqueous fused electrolyte, the withdrawn electrolyte is intimately contacted with metallic aluminum to precipitate iron-containing material therefrom, the precipitated iron-containing material is removed from the electrolyte, and the resulting electrolyte having a reduced concentration of dissolved iron content is recycled to the said body of electrolyte to thereby maintain the dissolved iron content within the said range.

14. A method of electrodepositing aluminum on an iron-containing metallic substrate comprising immersing the substrate in a body of nonaqueouse fused electrolyte for electrodepositing aluminum comprising aluminum halide and alkali metal halide, the electrolyte containing dissolved iron-containing material formed at least in part in situ from the said substrate, electrodepositing aluminum on the said substrate while it is immersed in the body of the electrolyte, and while the aluminum is being electrodeposited, continuously maintaining the said iron-containing material dissolved in the electrolyte in a concentration resulting in not less than about 0.001% and not more than about 0.02% by weight of dissolved iron by intimately contacting the electrolyte with metallic aluminum other than as an anode to precipitate iron-containing material at dissolved iron concentrations exceeding about 0.02% by weight.

15. The method of electrodepositing aluminum of claim 14 wherein the said iron-containing material is dissolved in the electrolyte in a concentration resulting in not less than 0.003% and not more than 0.01% by weight of dissolved iron.

16. A method of continuously electrodepositing aluminum on ferrous metal strip comprising continuously passing the ferrous metal strip through a body of fused salt electrolyte for electrodepositing aluminum consisting essentially of at least 75% by weight of aluminum chloride and the remainder substantially alkali metal chloride and a dissolved iron compound formed at least in part in situ from the ferrous metal strip, continuously electrodepositing aluminum on the ferrous metal strip as it is passed through the body of electrolyte, and while the aluminum is being electrodeposited, continuously maintaining the said iron compound dissolved in the electrolyte in a concentration resulting in not less than about 0.001% and not more than about 0.02% by weight of dissolved iron by intimately contacting the electrolyte with metallic aluminum other than as an anode to precipitate iron-containing material at dissolved iron concentrations exceeding about 0.02% by weight.

17. The method of continuously electrodepositing aluminum of claim 16 wherein the said iron compound is dissolved in the electrolyte in a concentration resulting in not less than 0.003% and not more than 0.01% by weight of dissolved iron.

18. The method of claim 16 wherein each gallon of the electrolyte is in intimate contact with metallic aluminum having a surface area of at least 0.035 sq. ft.

19. The method of claim 16 wherein each gallon of the electrolyte is in intimate contact with metallic aluminum having a surface area of at least 0.25 sq. ft.

20. The method of claim 16 wherein electrolyte containing the dissolved iron compound is withdrawn from the said body of electrolyte, the withdrawn electrolyte is intimately contacted with metallic aluminum to precipitate iron-containing material therefrom, the precipitated iron-containing material is removed from the electrolyte, and the resulting electrolyte having a reduced concentration of dissolved iron is recycled to the said body of

electrolyte to thereby maintain the dissolved iron content within the said range.

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