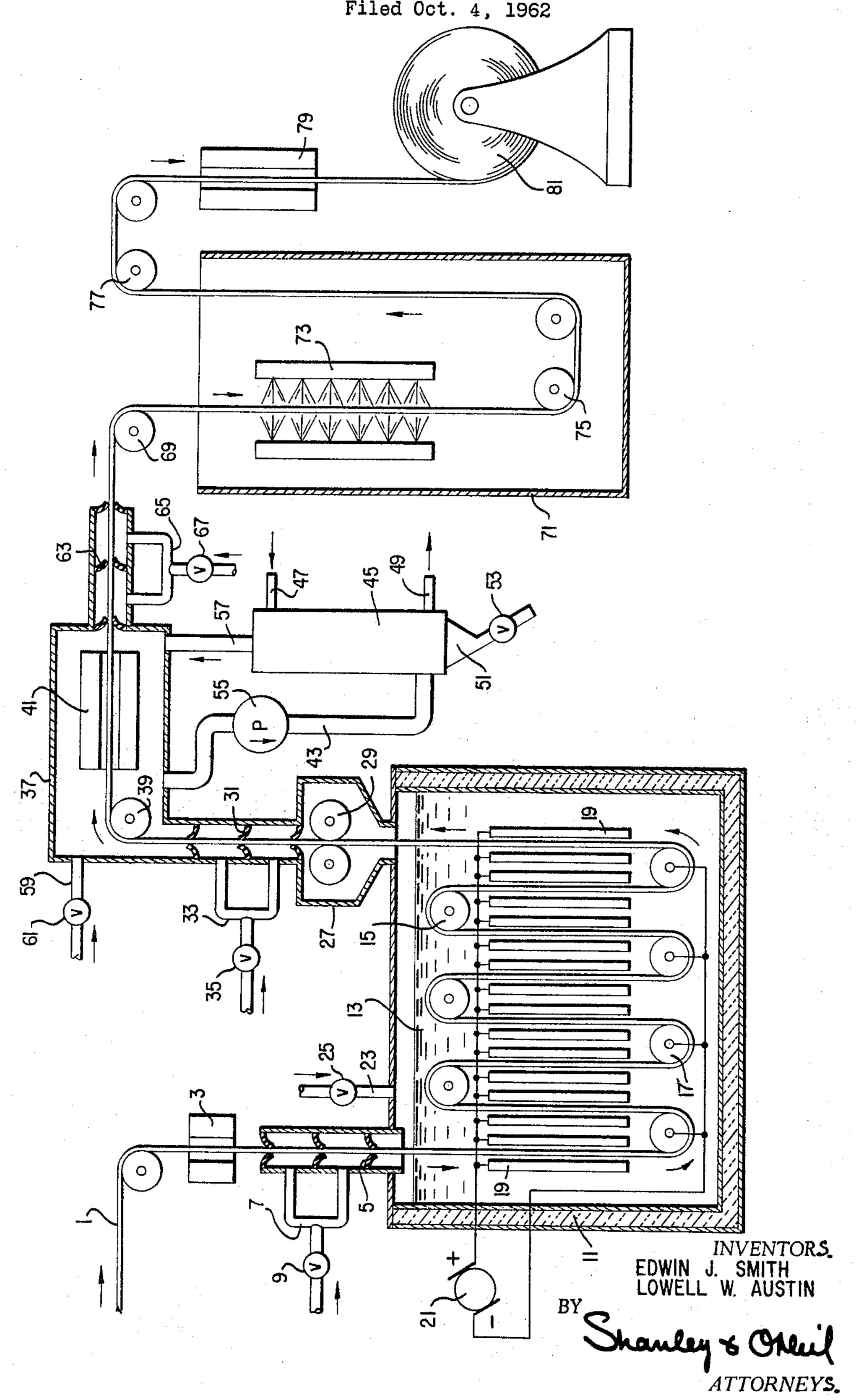
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METHOD OF RECOVERING ALUMINUM HALIDE FROM METAL STRIP ELECTRODEPOSITED WITH AN ALUMINUM-CONTAINING COATING FROM A FUSED SALT BATH Filed Oct. 4, 1962



3,267,008 METHOD OF RECOVERING ALUMINUM HALIDE METAL STRIP ELECTRODEPOSITED FROM WITH AN ALUMINUM-CONTAINING COATING FROM A FUSED SALT BATH

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The present invention relates to the electrodeposition of aluminum, more particularly the electrodeposition of an aluminum coating on a continuously moving metal strip from a fused salt electrolyte bath containing aluminum halide. By "aluminum" is meant pure aluminum 15 and aluminum alloyed with other metals.

The invention will be described and illustrated with reference to the electroplating of an aluminum-manganese alloy on ferrous metal strip using a fused electrolyte containing a major proportion of aluminum chloride and 20 the remainder of one or more alkali metal chlorides such as sodium or potassium chloride. It will be understood, however, that the principles of the invention are applicable to other metal bases and to other fused salt electrolytes containing aluminum halide.

A fuming fused electrolyte bath composition having an aluminum chloride content of approximately 75-85% by weight with the remainder being sodium and/or potassium chloride is useful in producing good aluminum electroplate. The electrolyte composition may be of the binary or ternary type, with a satisfactory binary electrolyte composition being exemplified by a composition containing by weight 80% aluminum chloride and 20% sodium chloride and a satisfactory ternary electrolyte being exemplified by 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 results when using unmodified direct current and in the absence of special plating conditions. Thus, such electrolyte compositions are not usually preferred. However, it is possible to use electrolyte compositions containing less than 75% aluminum chloride and the remainder 50 alkali metal chloride when using special plating conditions and/or by using low current densities. For example, nonfuming baths maintained in the molten state at a temperature of about 190-200° C. and containing less than 70% aluminum chloride, e.g. substantially no 55 free aluminum chloride, may be used to electroplate satisfactory adherent nonpowdery aluminum deposits when using straight direct current at current densities less than one ampere per square foot, or at current densities less than one ampere per square foot when using polarity 60 reverse current, or at current densities up to 2 amperes per square foot when using pulse direct current and up to 15 amperes per square foot when using a hot cathode maintained at a temperature much higher than the bath temperature. At higher bath temperatures within the 65 operative range, current densities may be raised to some extent without incurring the deposition of powdery deposits or deposits having other imperfections. With slightly fuming aluminum chloride-alkali metal chloride baths, i.e. electrolyte baths containing about 70% alu- 70 minum chloride and the remainder alkali metal chloride and having a free aluminum chloride content of about

0.5-1.5%, the current density may be up to 5 amperes per square foot when straight direct current is used, up to 10 amperes per square foot when polarity reverse current is used, above 15 amperes per square foot when using a hot cathode maintained at temperatures much higher than the bath, and considerably above 18.6 amperes per square foot when using pulse direct current. When using a fuming aluminum chloride-alkali metal chloride bath, such as a bath containing 80% aluminum chloride, 10% sodium chloride, and 10% potassium chloride, current densities 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, with the current densities for special plating conditions being equally satisfactory or even better. Thus, it is apparent that a wide variety of aluminum chloride-alkali metal chloride electrolyte baths are suitable for the electrodeposition of aluminum on a metal base such as ferrous metal and that any suitable one of these baths may be used in practicing the present invention. In general, the electrolyte baths for use in practicing the present invention are prior art fused salt

aluminum electroplating baths.

Still other aluminum electroplating baths 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 baths mentioned herein may be replaced with other suitable halide salts such as aluminum bromide, sodium bromide and potassium bromide in the molar proportions existing in the above-mentioned baths. Also, the aluminum chloride may be complexed with other complexing agents such as ammonia, organic amines, or their salts in a manner somewhat similar in effect to the complexing of aluminum chloride in the foregoing baths with potassium and/or sodium chloride. An aluminum chloride-ammonia bath contains complexed aluminum chloride which is thought to be in the form of AlCl₃.NH₃ or possibly higher members of the ammonia series with varying amounts of free aluminum chloride being dissolved therein in the case of the fuming bath, or a nonfuming bath may be used as discussed above for the more common aluminum chloride-alkali metal chloride baths. Further, aluminum chloride may be complexed by means of organic amines and their salts such as the ethyl pyridinium bromide to produce the complex ethyl pyridinium bromide-AlCl₃. This material may likewise have free aluminum chloride dissolved therein or it may be a nonfuming bath as discussed above.

The various aluminum electroplating baths discussed above may be considered to be, broadly speaking, fused salt electrolyte baths containing aluminum halide and a complexing agent therefor with the aluminum halide complex being in the molten state and having dissolved therein free aluminum halide in instances where it is present. Such fused salt electrolyte bath compositions known to the art to be suitable for the electroplating of aluminum are operative in practicing the present invention.

It is to be understood that when substituting other halides for chlorides in the electroplating baths discussed herein, the substitutions will 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 therefor and any free aluminum halide dissolved therein. The parts and percentages of the specific electrolyte bath ingredients mentioned herein are in parts or percentages by weight. If desired, substitution of other materials may be made on a molar basis.

Recently, bright aluminum deposits have been electroplated in the form of aluminum-manganese alloys and the above electroplating baths have been used under the same conditions as when electrodepositing aluminum matte. In fact, no substantial change in operating conditions is necessary, generally speaking, other than pro-

viding the proper additive concentration in the electrolyte bath. The present invention will be illustrated in connection with the electrodeposition of an aluminum-manganese alloy, it being understood, however, that the electrodeposition of this alloy is chosen simply because it is a highly suitable coating for purposes of illustrating the operation of the present invention, and not because the present invention is in any way restricted to the electrodeposition of an alloy of aluminum rather than aluminum matte.

A serious problem that attends the electrodeposition 10 of aluminum from a fused salt electrolyte bath is that moving metal strip emerging from the bath draws out of the bath on its surface a considerable quantity of fused salt which is at least initially in liquid phase. This "drag out" represents a considerable loss of electrolyte and is 15 costly in terms of lost electrolyte. Of course, it is possible to remove these electrolytes from the strip by washing with water, for they are water soluble. However, the aluminum halides and particularly aluminum chloride rapidly hydrolyze to the corresponding halide acid, so that 20 no way is known to recover the salt by washing with commonly used aqueous rinse media. It has been proposed that organic instead of aqueous solvents be used for removing the electrolyte from the strip, but this proposal has the drawback that such organic solvents are of course 25 more expensive than water and also that a separation system would be needed for separating the recovered salt from the organic solvent. Removal of the salt by boiling off the salts until the plated strip is free from drag-out salts is also unattractive, because the last of the alkali 30 halide salts does not boil away until above 2500° F.

The present invention comprises the discovery that a substantial proportion of the drag-out salts can be recovered by heating the strip, after it emerges from the electrolyte bath, to a temperature higher than the temperature 35 of vaporization of the aluminum halide but lower than the vaporization temperature of alkali metal halide. Most of the aluminum halide is thus vaporized; and the atmosphere adjacent the heating zone, containing vaporized aluminum halide is passed through a cooling zone to con- 40 dense vaporized aluminum halide. Preferably, the atmosphere in the heating zone is maintained substantially free of oxygen to avoid oxidation of the strip at such elevated temperatures. It is also preferred that that atmosphere, when stripped of a substantial proportion of its vaporized aluminum halide, be returned to the heating zone and be recycled through the heating and cooling zones in a substantially closed cycle.

It is particularly preferred that the aluminum halide be aluminum chloride. Aluminum bromide melts at about 207.5° F. and vaporizes at about 506° F., while aluminum iodide melts at about 376° F. and vaporizes at about 680° F. Upon condensation, the bromide and halide are initially liquid and solidify only upon considerable further cooling. By contrast, however, aluminum chloride sublimes at about 352° F. Aluminum chloride-alkali metal halide baths for the electrodeposition of aluminum are conventionally maintained at about 325° F., so that a strip emerging from such baths having a coating containing a substantial proportion of free aluminum chloride as a component of the electrolyte need not be heated greatly above its emergent temperature in order to sublime the aluminum chloride. Upon cooling of the gas from the heating zone, the aluminum chloride condenses in solid form very little below 352° F. and may be conveniently handled and stored in such solid form without the necessity of handling it first as a condensed liquid and then as a solid.

The electrolyte is largely a mixture of aluminum chloride and a complex salt of alkali metal-aluminum chloride, 70 such as sodium aluminum chloride or potassium aluminum chloride, the complex salts apparently containing the alkali metal halide and aluminum halide in equimolar proportion. When driving off aluminum chloride from such a mixed salt electrolyte, the aluminum chloride sub- 75

limes quite rapidly and thereafter the alkali metal aluminum chloride tends to decompose to aluminum chloride and the alkali metal chloride at a substantially slower rate than the sublimation rate of the aluminum chloride. Nevertheless, it must be borne in mind that not only is the free aluminum chloride recovered but also a portion of the alkali metal aluminum chloride is decomposed and its decomposition product of aluminum chloride is also recovered. Of course, the salt remaining behind on the substrate after removal of the aluminum chloride will be a mixture of alkali metal chloride and the complex salt; but as the sodium and potassium chlorides are extremely cheap in any event, and the aluminum chloride is the relatively expensive component of the mixture, the recovery of a substantial proportion of the aluminum chloride comprises the maximum utilization of the practically recoverable value of the drag-out salt. The salts remaining on the substrate after such vaporization by heating are of course easily removed by rinsing the same as were the drag-out salts prior to the advent of the present invention.

Accordingly, it is an object of the present invention to provide methods for electrodepositing on a continuously traveling metal strip an aluminum-containing coating from a fused salt electrolyte bath containing aluminum halide, characterized in that losses of electrolyte from drag out are kept to an economic minimum.

Other objects and advantages of the present invention will become apparent from a consideration of the following description, taken in connection with the accompanying drawing, in which the single figure is a diagrammatic side elevational view partially in cross section of one embodiment of a continuous aluminum electroplating line in accordance with the present invention.

Referring now to that drawing in greater detail, a specific embodiment of the invention is illustrated in which a ferrous metal strip 1 enters the cycle of the present invention after receiving a wet prior art treatment or other suitable pretreatment such as cathodic cleaning in an Ortho-Sil solution (Na₄SiO₄) 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, and scrubbing and washing with water and drying to remove all traces of water. Strip 1 then passes through a heater 3, which may be an induction or resistance heater, where it is heated sufficiently to evaporate completely any free water remaining on the strip surfaces. The heated strip 1, at a temperature of about 325°-350° F., then passes through a series of seals 5 within a hood, the seals assuring that no atmospheric air with its undesirable oxygen and water vapor is drawn into the coating operation by the strip. The space between seals 5 is provided with an inert gas such as nitrogen or argon under pressure through conduits 7 controlled by a valve 9. In speaking of an "inert gas" in connection with conduits 7 and other conduits similarly arranged downstream of conduits 7, it is to be understood that the gases need only be substantially free from oxygen and water vapor. Nitrogen is preferred because it is cheap and relatively inert. Argon and carbon dioxide, however, are also quite suitable. Such inert gases are supplied between seals 5 at atmospheric pressure or little above to assure the exclusion of air from the seal system.

Strip 1 then passes downwardly into electroplating tank 11 in which is maintained a fused aluminum electroplating electrolyte 13 which may for example be 80% aluminum chloride, 10% sodium chloride, and 10% potassium chloride on a weight basis. Such an electrolyte fumes in the presence of water or water vapor under the operating conditions, and for this reason tank 11 is closed. Tank 11 is also heated, in the manner and for the purpose disclosed in copending application Serial No. 72,382, filed November 29, 1960, now abandoned.

In tank 11, strip 1 follows a circuitous path through the molten electrolyte bath, passing alternately about upper rolls 15 and lower rolls 17. Tank 11 contains a plurality of pairs of aluminum-manganese alloy anodes 19, and a vertical run of strip 1 passes between. Alternatively, in order to deposit an aluminum-manganese alloy on strip 1, the anodes 19 may be of high purity aluminum and an auxiliary source of manganese may be provided as when manganese is added to the bath in the form of a manganese halide such as manganese chloride or other 10 suitable manganese mineral acid salts soluble in electrolyte 13. A still further alternative is the addition of manganese to the bath by dissolution of auxiliary anodes containing manganese in an auxiliary electrical circuit. These methods are described in greater detail in copend- 15 ing application Serial No. 819,298, filed June 10, 1959, now abandoned in favor of application Serial No. 34,923, filed June 9, 1960, now United States Patent No. 3,167,403 to which reference is had for a more complete disclosure of this subject matter in order to avoid the inclusion of 20 unnecessary detail in the present specification. Suffice it to say that the spaced pairs of anodes are electrically connected to the positive side of a generator 21 or other suitable source of electrical current, while strip 1 is made electronegative by connecting lower rolls 17 to the nega- 25 tive side of generator 21. Strip 1 is thus electroplated with a coating of aluminum-manganese alloy containing at least about 10% manganese and the remainder aluminum. The coating may be of any suitable desired thickness and will be bright in the as-plated condition regard- 30 less of the thickness of the coating, as the thickness of the electroplate appears to have little or no effect on its brightness.

The usual operating conditions may obtain in electroplating tank 11. Thus, for the bath described above, the bath temperature is preferably about 300-350° F., e.g. 325° F. The current density should preferably be from about 20 to about 100 amperes per square foot, although under optimum conditions of operation current densities up to about 100-400 amperes per square foot are possible 40 and may be used when desired. Needless to say, plating conditions will necessarily vary somewhat from electrolyte

to electrolyte.

As has heretofore been proposed, tank 11 is insulated and may if desired be heated to avoid the accumulation 45 of solidified deposits of electrolyte on the tank walls and cover. Similarly, a nonreactive atmosphere is maintained above the bath by means of a conduit 23 controlled by a valve 25 to permit the introduction of nitrogen, carbon dioxide, argon or other oxygen-free and 50 water-free gas above the bath as required.

Upon leaving the bath of electrolyte 13, strip 1 passes upwardly into a hood 27 and between a pair of squeegee rolls 29 that reduce to some extent the amount of drag out of electrolyte. From squeegee rolls 29, strip 1 con- 55 tinues through a series of seals 31 that prevent loss of the plating tank atmosphere. Conduits 33 controlled by a valve 35 supply a relatively inert gas such as nitrogen to the spaces between the seals in the manner previously explained.

From seals 31, strip 1 passes into a heater portion 37 of hood 27. Strip 1 passes about a roll 39 and thence through a heater 41 which may be of the induction or the resistance type. In the course of passing through heater 41, aluminum halide such as aluminum chloride 65 is vaporized from the strip and a portion of the complex aluminum halide-alkali metal halide salt is decomposed and the aluminum halide also vaporized. When the aluminum halide is aluminum chloride, which sublimes at 70 about 352° F. by itself, substantially complete sublimation of free aluminum chloride and partial breakdown of the complex salt with sublimation of its aluminum chloride can be achieved if strip 1 is heated in heater 41 to a temperature of at least about 375° F. and not more 75

than about 450° F., preferably not more than about 425° F. and most preferably not more than about 400° F. The other aluminum halides require corresponding higher temperatures. The strip should be held at this temperature for at least about 2 seconds, preferably about 3 seconds. It can be held at this temperature for longer periods of time, but the additional recovery of aluminum halide ordinarily does not justify the added expense. The length of heater 41 largely determines the time the strip will be maintained at such elevated temperature. For a strip traveling at a certain number of feet per second, heater 41 should have an effective length along strip 1 at least equal to that number of feet per second times the number of seconds the strip should be at the desired elevated temperature in the case of induction heating in which the strip almost instantaneously attains the desired temperature upon entering into heater 41. For radiant heating, in which the strip attains the desired temperature more slowly, the effective length of heater 41 is of

course correspondingly longer.

The control and handling of the atmosphere adjacent heater 41 is of primary importance in the present invention. Heater portion 37 of hood 27 is closed to the ambient atmosphere and the resulting controlled atmosphere within heater portion 37 is comprised partly of aluminum halide vaporized in heater 41. This aluminum halide is recovered by confining the atmosphere adjacent heater 41 and cooling it. Preferably, the cooled atmosphere from which a portion of the aluminum halide has been recovered is then recycled into heater portion 37 and is thus handled in what is substantially a closed cycle. To this end, atmosphere in heater portion 37 laden with vaporized aluminum halide is withdrawn through a conduit 43 and passes through a cooling unit 45 provided with a cooling inlet 47 and a cooling outlet 49 for a cooling fluid such as water. At least a portion of the aluminum halide carried in the withdrawn vapor is thus condensed and collected and removed for reuse in the cycle. To this end, cooling unit 45 has a discharge outlet 51 controlled by a valve 53. The drawing illustrates schematically equipment suitable for use when the aluminum halide is aluminum chloride, in which case the sublimed aluminum chloride in vapor phase condenses in cooling unit 45 in solid phase and falls to the bottom of cooling unit 45 for withdrawal through outlet 51 and additionally may be scraped from the condensing cooling surfaces by conventional mechanical means (not shown).

Circulation of the gas in heater portion 37 of hood 27 in a closed cycle is effected by a gas pump in the form of a fan 55 disposed in conduit 43. Accordingly, gas leaving cooling unit 45, freed of some of its aluminum halide but saturated with halide at the cold outlet temperature, passes through conduit 57 back to heater portion 37 where it is reheated and again approaches saturation with vaporized aluminum halide at the heater temperature, and so on through a plurality of cycles. It is important to note that when the gas is recycled, its aluminum halide content never falls below saturation at the lower temperature. Hence, substantially all the halide that is picked up in the heater is condensed in the cooling unit. Such gas as is lost from the cycle may be replenished through conduit 59 controlled by valve 61; and as before, this gas is free from water and preferably free from oxygen and may for example be nitrogen, carbon dioxide, argon or the like. The inert nature of the gas assures not only that there will be no water present to hydrolyze the aluminum halide to hydrohalic acid but also that the finish of the strip will not oxidize at the elevated temperatures reached in heater 41. It is not necessary to heat the gas in the closed cycle about heater 41, as there is very little introduction of cold gas through conduit 59 and because it is not necessary to change the

temperature of the gas much above or below the condensation temperature of the aluminum halide.

From heater 41, strip 1 passes through a further set of seals 63 between which an inert gas is introduced through conduits 65 controlled by a valve 67. Leaving seals 63, 5 strip 1 passes about a roll 69 and downwardly into a rinse tank 71, in which hot water sprays 73 play on opposite sides of strip 1 and wash off the remaining complex salt and any remaining aluminum halide. There is thus produced a weak solution of salt including aluminum halide, 10 that rapidly hydrolyzes to the corresponding hydrohalic acid. Further recovery of aluminum halide from the wash water accumulating in rinse tank 71 is therefore not attempted.

75 and 77 and through a heater 79 in which the water is evaporated and the strip dried, after which the strip is coiled on a coiler 81. On coiler 81, the strip has a bright plating of aluminum-manganese alloy and is dry and free from electrolyte salts or their decomposition or 20 hydrolysis products.

To enable those skilled in this art to practice the invention, the following illustrative example is given:

Example

Ferrous metal strip is passed through heater 3 and attains a temperature of 325° F. therein. It passes at a speed of 100 feet per minute into a bath of electrolyte in tank 11, which is sealed from contact with the atmos- 30 phere by means of passing a total of 72 cubic feet per hour of dry gaseous nitrogen through conduits 7 and 23. In this condition, the strip enters the electrolyte dry and free not only from "free" water, but also from combined water such as hydrated metal salts and substances 35 reacting under conditions present in the electroplating zone to form water. The electrolyte bath contains 80 parts aluminum chloride, 10 parts sodium chloride, 10 parts potassium chloride, and is at a temperature of 325° F. Aluminum manganese alloy anodes, 80% by 40 weight of aluminum and 20% by weight of manganese and 10 feet in length, are used with a current density of 42.5 amperes per square foot. A coating 30 millionths of an inch thick is deposited on the strip, the coating being bright and lustrous in the as-plated condition and having 45 a composition 80% aluminum and 20% manganese. The strip leaving the bath is coated with dragout salts having the same proportions as the salts in the electrolyte, and passes upwardly and through heater 41 where it is induction heated to a temperature of 400° F. by induction 50 heating through a path 5 feet long. Substantially all the free aluminum chloride sublimes, and a portion of the sodium aluminum chloride and potassium aluminum chloride complexes breaks down with sublimation of at least a portion of the aluminum chloride thus released. Vapors 55 at about 400° F. pass through conduit 43 to cooling unit 45 where they are cooled to about 325° F., at which temperature most of the aluminum chloride in the vapors deposits in solid phase in cooling unit 45 and is removed through outlet 51. The vapor thus depleted in aluminum 60 chloride is returned to the vicinity of heater 41. Salts remaining on the strip are rinsed off and the strip is dried and coiled and the rinse solution is sewered.

From a consideration of the foregoing disclosure, it 65 will be obvious that the initially recited object of the present invention has been achieved.

Although the invention has been described and illustrated in connection with a preferred embodiment, it will be understood that modifications and variations may be 70 resorted to without departing from the spirit of the invention, as those skilled in this art will readily understand. Such modifications and variations are considered to be within the purview and scope of the present invention as defined by the appended claims.

What is claimed is:

- 1. A method of electrodepositing on a continuously traveling metal strip an aluminum-containing coating from a fused salt electrolyte bath containing aluminum halide comprising passing the strip through the bath in electrical circuit with the electrolyte, withdrawing the strip from the bath with a coating of electrolyte on the strip, the withdrawn strip being insufficiently hot to vaporize all of the aluminum halide content of the coating of electrolyte, passing the strip through a heating zone remote from the electrolyte bath to heat the strip to a temperature above the vaporization temperature of the aluminum halide on the strip to vaporize aluminum halide from the strip, removing the heating zone vapors contain-The rinsed strip, wet but clean, then passes about rolls 15 ing vaporized aluminum halide, cooling the removed vapors to below the condensation temperature of the aluminum halide in a cooling zone to recondense the aluminum halide from the cooled vapors, and removing the recondensed aluminum halide from the cooling zone.
 - 2. A method as claimed in claim 1 wherein the cooled vapors from which aluminum halide has been removed in the cooling zone are returned to the heating zone.
 - 3. A method as claimed in claim 1 in which the aluminum halide is aluminum chloride.
 - 4. A method as claimed in claim 1 in which the gas in the heating and cooling zones is substantially free from oxygen.
 - 5. A method as claimed in claim 1 in which the gas in the heating and cooling zones is substantially free from water.
 - 6. A method of electrodepositing on a continuously traveling metal strip an aluminum-containing coating from a fused mixed salt electrolyte bath containing aluminum halide and an alkali metal halide that vaporizes at a higher temperature than the aluminum halide comprising passing the strip through the bath in electrical circuit with the electrolyte, withdrawing the strip from the bath with a coating of mixed salt electrolyte on the strip, the withdrawn strip being insufficiently hot to vaporize all of the aluminum halide content of the coating of mixed salt electrolyte, passing the strip through a heating zone remote from the electrolyte bath to heat the strip to a temperature above the vaporization temperature of the aluminum halide but below the vaporization temperature of the alkali metal halide on the strip to vaporize aluminum halide but not alkali metal halide from the strip, removing from the heating zone vapors containing vaporized aluminum halide, cooling the removed vapors to below the solidification temperature of the aluminum halide in a cooling zone to recondense aluminum halide from the cooled vapors, and removing the recondensed aluminum halide from the cooling zone.
 - 7. A method as claimed in claim 6 wherein the cooled vapors from which aluminum halide has been removed in the cooling zone are returned to the heating zone.
 - 8. A method as claimed in claim 6 in which the aluminum halide is aluminum chloride.
 - 9. A method as claimed in claim 6 in which the gas in the heating and cooling zones is substantially free from oxygen.
 - 10. A method as claimed in claim 6 in which the gas in the heating and cooling zones is substantially free from water.
 - 11. The method of claim 1 wherein the aluminum halide is aluminum chloride, and the withdrawn strip is heated in the heating zone to a temperature of about 375–450° F. and maintained at this temperature for at least 2 seconds.
 - 12. The method of claim 1 wherein the aluminum halide is aluminum chloride, the electrolyte bath has a temperature of about 300-350° F., and the withdrawn strip is heated in the heating zone to a temperature of about 375–450° F. and maintained at this temperature for 75 at least 2 seconds.

13. The method of claim 12 wherein the withdrawn strip is heated to a temperature of about 400-425° F. and maintained at this temperature for about 3 seconds.

14. The method of claim 6 wherein the aluminum halide is aluminum chloride, and the withdrawn strip is 5 heated in the heating zone to a temperature of about 375-450° F. and maintained at this temperature for at least 2 seconds.

15. The method of claim 6 wherein the aluminum halide is aluminum chloride, the mixed salt electrolyte 10 bath has a temperature of about 300-350° F., and the withdrawn strip is heated in the heating zone to a temperature of about 375-450° F. and maintained at this temperature for at least 2 seconds.

strip is heated to a temperature of about 400-425° F. and maintained at this temperature for about 3 seconds.

References Cited by the Examiner

UNITED STATES PATENTS

1,488,553	4/1924	Peacock	204—39
2,762,764	9/1956	Owen	20439
3,007,854	11/1961	Smith et al	20428

FOREIGN PATENTS

11/1959 Canada. 587,658

JOHN H. MACK, Primary Examiner.

16. The method of claim 15 wherein the withdrawn 15 R. L. GOOCH, T. TUFARIELLO, Assistant Examiners.

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