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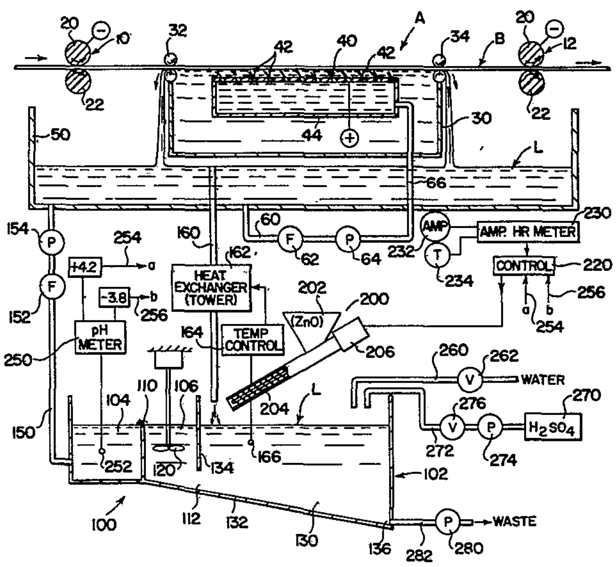
(54) **Method of supplying zinc to a sulfuric acid containing electrolyte.**

(57) A method of supplying zinc to a sulfuric acid containing electrolyte (L) used between an anode (40) and a moving metal cathode (B) for depositing zinc onto the cathode (B). The method includes directing the electrolyte (L) to a holding tank (30) where zinc oxide particles of about. 3 micron or less and a purity of at least 99% zinc oxide is added to the electrolyte (L) and allowed to dissolve in the electrolyte to provide the zinc compound used in electroplating between the electrodes (A, B). Thereafter, the electrolyte (L) is directed to the area between the anode (40) and cathode (B) for the zinc plating process.



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METHOD OF SUPPLYING ZINC TO A SULFURIC ACID CONTAINING ELECTROLYTE

Disclosure

The present invention relates to the art of plating zinc onto a moving metal object, such as a moving strip and more particularly to a method of supplying zinc to a sulfuric acid containing electrolyte used between an insoluble anode and a moving metal cathode. The invention is particularly applicable for use in coating zinc onto at least one surface of a moving steel strip and it will be described with particular reference thereto; however, it is appreciated that the invention has broader applications and may be used in other instances wherein a zinc containing electrolyte is required for a plating process between an insoluble anode and a moving metal cathode.

BACKGROUND OF INVENTION

In recent years, there has developed a substantial demand for a steel strip plated on one or both sides by zinc. This material is used extensively in the production of motor vehicle bodies for the purpose of reducing the corrosion tendency of certain portions of the vehicle body. Because of this demand, substantial effort is being directed toward improving the effeciency and operability of plating processes for applying zinc to a moving metal strip. Generally, the metal strip is conveyed through a plating tank and in close relationship with an anode formed from zinc. An electrolyte, including sulfuric acid, is in the tank and provides an electrical conductive path from the zinc anode to the cathodic moving metal strip. Zinc is electrically released from the anode and is carried in the electrolyte as zinc sulfate. The zinc sulfate disassociates to provide zinc ions that diffuse to the moving strip cathode on which they are electrodeposited. In this type of process, the zinc anode must be replaced periodically. This presents substantial difficulty and increases the down-time of the plating installation. In addition, zinc anodes tend to introduce zinc into the electrolyte at a faster rate than zinc is electrodeposited onto the cathode moving strip. Because of this discrepancy, the zinc sulfate concentration tends to increase in the electrolyte and to eventually exceed the optimum concentration for the best result of zinc electrodeposition. To prevent excessive increase in zinc sulfate concentration, some of the electrolyte must be discarded so as to maintain the optimum concentration and such action is wasteful of zinc. Furthermore, soluble zinc anodes may release small particles of zinc which do not dissolve rapidly in the electrolyte and can move to deposit on the moving strip to cause "particle roughness". Consequently, the use of a sulfuric acid type of electrolyte between a zinc anode and a moving metal strip cathode is wasteful of zinc, requires special means to avoid particle roughness and necessitates periodic addition of anodes to replace those consumed and removal of anode "stubs" that are too worn down to remain in proper position to the moving strip.

THE INVENTION

In accordance with the present invention, the disadvantages of normal procedures for depositing zinc onto a moving cathode strip are completely overcome in a manner to eliminate wastage of zinc due to excess anode dissolution of soluble zinc anodes at a greater rate than electrodeposition and to eliminate efforts to maintain zinc anodes in optimum surface area relative to the moving strip surface area.

In accordance with the invention, there is provided a method of supplying zinc to a sulfuric acid containing electrolyte used between an anode and a moving metal cathode for depositing zinc onto the moving cathode. This method includes the steps of directing the electrolyte to a holding tank, adding to the electrolyte in the tank small particles of a compound of zinc, such as zinc carbonate, zinc hydroxide or zinc oxide. In accordance with the preferred embodiment the material is zinc oxide particles having a small particle size, such as about .3 micron or less and a purity of at least about 99% zinc oxide, allowing the zinc oxide to dissolve in the electrolyte and then directing the electrolyte back to the plating apparatus so that it can be used between the anode and cathode. In this manner, the zinc used in the plating process is provided by the zinc oxide which is a commercially available, relatively inexpensive material. It is not necessary to utilize a consumable zinc anode which must be replaced periodically, since the zinc itself is provided externally of the plating apparatus by zinc oxide particles being added to the electrolyte remote of the apparatus.

In accordance with another aspect of the present invention, the rate of adding the zinc oxide to the sulfuric acid electrolyte is controlled by the amount of zinc deposited onto the moving cathode strip. This use of zinc can be recorded or measured in a variety of ways, one of which is by use of a standard amp-hour meter. As is well known, the ampere hours used in a zinc plating process indicates the amount of zinc being deposited from the electrolyte onto the moving metal cathode. By using an ampere-hour meter, the amount of zinc being deposited is continuously measured and this measurement is used to control the rate at which zinc oxide powder is added to the sulfuric acid electrolyte in the holding tank.

In accordance with still a further aspect of the present invention, the rate of adding zinc oxide powder is controlled by the pH of the electrolyte solution. It is desirable to maintain the electrolyte with a pH in the general vicinity of 4.0. If the electrolyte becomes more basic and the pH increases, the rate of adding the zinc oxide is decreased. The opposite is true if the electrolyte becomes more acidic and the pH decreases below a certain value. This control function is used in combination with the device for measuring the rate of zinc used in the plating process.

In accordance with still a further aspect of the present invention, the electrolyte is cooled to maintain a general temperature value. Since the electrolyte is circulated to and from an external holding tank, it is possible to control the temperature of the electrolyte by a heat exchanger, such as a cooling tower, which can have a controlled rate of flow or cooling rate. This rate of cooling is controlled by the temperature of the electrolyte itself at a selected position, such as in the holding tank. In this manner, the electrolyte can be maintained at the desired optimum temperature which in the illustrated embodiment of the invention is approximately 150°F.

In accordance with still a further aspect of the present invention, the electrolyte solution is circulated through the holding tank at a relatively rapid rate so that the zinc oxide particles or powder being added to the electrolyte in the holding tank is added at a rate less than the dissolution rate of the zinc oxide in the electrolyte. In practice, the dissolution rate is approximately .62 gram per liter per minute of zinc oxide in the electrolyte.

In accordance with still a further aspect of the invention, the zinc oxide is substantially continuously added to the holding tank which contains the circulating electrolyte. Consequently, enhancement of the electrolyte with zinc oxide is a continuous process and the circulation of the electrolyte from the plating installation to the holding tank and back to the plating installation is a continuous, parallel, off-stream system.

By providing a system for maintaining the zinc concentration in the electrolyte exterior of the actual plating installation, a single system can be used to supply replenished or regenerated electrolyte of several separate and distinct plating tanks or installations. Consequently, a single system using the present invention can be employed for creating electrolyte for several plating installations wherein zinc is plated by current flow from an anode to a cathode. The anode used in the present invention is inert and may be lead or other material which practically does not dissolve in the electrolyte.

The primary object of the present invention is the provision of a method for creating electrolyte to be used in a zinc plating installation, wherein the zinc compound for the electrolyte is maintained by zinc oxide particles or powder at a location remote to the actual plating installation.

Another object of the present invention is the provision of a method for replenishing the zinc in an electrolyte solution, wherein the zinc is formed into a zinc sulfate without the use of soluble anodes.

Still another object of the present invention is the provision of a method of regenerating a zinc plating electrolyte, which method replenishes the electrolytically decomposed zinc compound of the electrolyte at a position remote to the cathode and anode of the plating installation.

Yet another object of the present invention is the provision of a method of regenerating plating electrolyte for use in a zinc plating process, which method uses a relatively inexpensive source of zinc that is readily dissolvable in a sulfuric acid electrolyte.

These and other objects and advantages will become apparent from the following description.

BRIEF DESCRIPTION OF DRAWINGS

The single Figure in the present application illustrates schematically the preferred embodiment of the invention and its use with a schematically illustrated system for plating zinc onto a moving strip of the type used in producing body components for motor vehicles, appliances and similar consumer products.

PREFERRED EMBODIMENT

Referring now to the drawing wherein the showings are for the purpose of illustrating a preferred embodiment of the invention only and not for the purpose of limiting same, a plating device A is used for plating at least one side of a moving strip B. In this device, strip B is conveyed between two longitudinally spaced roll sets 10, 12, which sets each include an upper conductive roll 20 and a lower support roll 22. By an appropriate known arrangement, the conductive rolls are electrically negative and render the strip B cathodic for the plating process. By providing the upper rolls as the conductive rolls, any zinc deposits which accumulate on these rolls can be easily cleaned from the rolls. Of course, the conductive rolls 20 are cylindrical in shape and lie flat against the upper surface of strip B to provide the strip with a negative charge without arcing or undue marring of the strip surface. In accordance with the illustrated embodiment, a plating tray 30 is provided with longitudinally spaced dam roll sets 32, 34 which allow the overflow of electrolyte L from tray 30 at either end of the tray. The strip is maintained under tension by the conveying system used in this type of plating apparatus to reduce the tendency of the strip to droop between roll sets 32, 34. An insoluble anode 40 extends across the width of the strip and includes rearwardly directed orifices 42 and a plenum chamber 44. An appropriate electrical connection is provided to allow the anode 40 to be electrically positive. Below tray 30 there is provided an electrolyte reservoir 50 which contains a supply of electrolyte L of the sulfuric acid type. Sulfuric acid electrolyte is commonly used in zinc plating of steel strip. In the illustrated embodiment, plating device A includes a pipe 60 for directing electrolyte through filter 62 to the inlet of pump 64. The pump 64 pumps electrolyte through outlet conduit 66 to the interior of plenum chamber 44. From the plenum chamber, electrolyte L is forced from apertures or orifices 42 against the lower surface of strip B. The electrolyte L includes zinc sulfate which is used to deposit zinc onto the under surface of strip B as the strip passes over anode 40, which anode is non-consumable and may be formed from lead or steel plated with an insoluble metal or any other nonconsumable anode material. As so far described, at least the under surface of strip B is plated with zinc as it moves across tray 30 between roll sets 32, 34. Of course, a plurality of trays 30 could be supplied from a single reservoir 50 or additional reservoirs could be used for one or more trays 30. In practice, several of the plating trays 30 are provided so that the speed of the strip B can be increased and still obtain the desired thickness of zinc deposited by the plating process onto one or both surfaces of the metal strip. The tray arrangement shown in the Figure is primarily applicable for plating zinc onto a single side of the moving strip and is shown for illustrative purposes.

In accordance with the present invention, there is provided an off-stream, parallel electrolyte make-up supply system 100, which system provides the zinc compound within the electrolyte L for use in the electrical plating process insoluble anode 40 and cathodic strip B. In accordance with the illustrated embodiment of the invention, this off-stream parallel electrolyte make-up supply system includes a tank 102 with an outlet compartment 104 and a mixing compartment 106. The two compartments are connected by an overflow weir 110. A lower inlet opening 112 is used for directing electrolyte L into the mixing compartment 106, which includes an appropriate mixing device, schematically illustrated as standard motor driven mixing impeller 120. The main mixing compartment or holding tank 130 of the total tank 102 is formed adjacent tank 106 and includes a lower inclined wall 132 which also forms the lower wall of mixing chamber 106. Holding tank 130 is separated from mixing tank 106 by wall 134 which is spaced from the lower inclined wall 132 to create the inlet opening 112 which has been previously described. At the lower end of inclined wall 132 there is provided a sump area 136 which accumulates precipitates and other separable impurities, primarily ferric compounds which are precipitated from electrolyte L. To circulate electrolyte L through the holding tank 130 there is provided a conduit 150 including a filter 152 and a pump 154 which is communicated with the lower portion of outlet compartment 104. Pump 154 forces the electrolyte from compartment 104 into reservoir 50 for use in the plating process, as previously described. A stand pipe 160 directs electrolyte L from reservoir 50 to the holding tank 130. In the illustrated embodiment of the invention it is desirable to maintain the temperature of the electrolyte in holding tank

130 at a selected temperature compatible with dissolution of zinc oxide in the electrolyte. This temperature, in practice, is approximately 150°F. Since the current flow necessary for the plating process increases the temperature of the electrolyte, in practice, to a temperature above the desired 150°F, there is provided in return line or pipe 160 an appropriate heat exchanger 162 which can be a cooling tower having a flow rate or cooling capacity controlled by an appropriate temperature control arrangement 164. A thermocouple 166 within tank 130 indicated the temperature of electrolyte L in tank 130. As the temperature varies from a selected value, control 164 changes the cooling rate of heat exchanger 162 accordingly. This is standard temperature control practice in plating installation. In this manner, the electrolyte from stand pipe 160 is cooled before it is directed into holding tank 130 to maintain a selected temperature in tank 130. In accordance with the invention, a fine zinc oxide powder is fed into the electrolyte L in holding tank 100 where it dissolves and forms into zinc sulfate for use in the plating process. In accordance with the schematic illustration of the invention, as shown in the Figure, a hopper 202 is filled with a zinc oxide powder having a particle diameter of about .3 micron or less and a surface area of at least about 4.0 square meters per gram. This type of zinc oxide is available from American Smelting and Refining Company and is sold under the trade name AZO-55. This material is considered paint fine and approximately all the material passes through a standard 325 mesh screen. Of course, other small particle sizes for the zinc oxide could be used with a corresponding decrease in the dissolution rate. However, the size of the preferred embodiment provides a rapid dissolution rate. The zinc oxide powder is deposited manually or mechanically into hopper 202. The powder is continuously fed from the

hopper by an appropriate conveyor, indicated as a screw feed conveyor 204, driven by a variable speed motor 206. The motor will be driven continuously and the rate of the motor speed will determine the amount of zinc oxide deposited into holding tank 130. To control the rotational speed of motor 206 there is provided an appropriate variable speed motor control 220. It is anticipated that the speed of the motor 206 could be adjusted manually by testing the electrolyte periodically and then changing the speed of the motor to assure the proper pH and zinc concentration. However, in accordance with more limited aspects of the present invention the variable speed motor control 220 is controlled automatically so that the zinc oxide powder is fed by conveyor 204 into holding tank 130 at a desired rate which is indicative of the operating characteristics of the plating device A. In accordance with this aspect of the invention, an amp-hour meter 230 is provided. As is well known, the ampere-hour reading of meter 230 indicates the amount of zinc being deposited onto the strip. If system 100 is used for several different plating operations, the amp-hour (i.e. amperes-hour) measurement for the total system being supplied is recorded by meter 230. As the amp-hour meter indication varies, the continuous speed of motor 206 is changed by motor control unit 220. An ampere-meter 232 and a timer 234 are schematically illustrated as input of meter 230 to indicate that meter 230 records the actual amount of metal being deposited on the strip in the plating installation being supplied by the electrolyte from system 100. It has also been found that electrolyte L should have a pH within a selected range. In practice this range is between approximately 3.8 and 4.2. In accordance with the more limited aspect of the invention, the motor control 220 can also be adjusted by a reading of the pH value of electrolyte L, as it is being directed from system 100 to the reservoir 50. To illustrate this concept, a standard pH meter 250 is shown. This meter has a high level output line 254 and a low level output line 256, indicated as lines a, b. These lines are directed to motor control 220, as shown in the Figure. If the pH within tank 104, as sensed by meter 250 through probe 252, is greater than the set upper limit, in this instance 4.2, a signal is created in line 254. This decreases the speed of motor 206 so that the acidic nature of the electrolyte is increased. If the pH is less than a value, in the illustrated embodiment, 3.8, a signal is created in line 256. This increases the speed of motor 206 by motor control 220. It can be seen that the pH of the electrolyte is used to determine the speed at which the zinc powders are fed into holding tank 130 for regenerating the electrolyte to be used in the plating apparatus or device A. Holding tank 130 is provided with a make-up water line 260 having a valve 262 and a make-up sulfuric acid system including a supply tank 270, pump 274 and valve 276 which control the input of acid through line 272. At the start of the run, tank 130 is filled with water and sulfuric acid which is mixed with zinc oxide powders to create the initial electrolyte. Thereafter, the electrolyte is regenerated by the continued introduction of finely divided zinc oxide powders, as previously explained. In this manner, zinc oxide is used to create the zinc sulfate of the electrolyte.

As sludge accumulates in sump area 136, it is removed by pump 280 through line 282.

The zinc oxide powders used in the preferred embodiment will dissolve in electrolyte having a pH of approximately 4 and a temperature of approximately 150°F. at a rate of approximately .62 gram per liter per minute. The continuous circulation of electrolyte L between reservoir 50 and holding tank 130 creates sufficient flow to allow dissolution of most of the zinc oxide powder in tank 130 before it is conveyed into the mixing tank 106. In the mixing tank, the final dissolution takes place and the zinc laden electrolyte overflows weir 110 and is deposited into the outlet compartment 104 for pumping into the reservoir 50 of plating device or apparatus A.

EXAMPLE

In one example of the use of the present invention, a steel strip B having a width of 24 inches is passed across anode 40 at a speed of 100 feet/minute. A coating of .001 inch is to be deposited onto the lower surface of the strip. This may require several trays 30. As is known, it requires approximately 13.7 ampere-hours to deposit .001 inch of zinc on a square foot of steel strip. The number of plating units and the current between the strip and anode are sellected to obtain this deposition on the strip moving at 100 feet/minute. These aspects of this example do not form a part of the present invention, except to indicate that such an installation requires about 442 pounds of zinc per hour from the supply system 100 which utilizes the present invention. This quantity is obtained by multiplying the amount of zinc deposited per square feet, i.e. .59 ounces for .001, by the plating speed of 12,000 square feet per hour. This provides a zinc demand of 7080 ounces/hour or 442.5 pounds per hour. Consequently, system 100 is dimensioned and operated to provide at least 442.5 pounds of zinc for plating per hour. Sufficient zinc oxide powder is fed from hopper 202 by motor 206 to give this amount of usable zinc. The feed rate is controlled by ampere-hour meter 230 which determines the amount of zinc being deposited. In this example, this determined amount is 442.5 pounds/hour.

The zinc oxide powder of this example has the following properties:

(1) Particle size of less than about .3 micron.

(2) About 99.2 - 99.8 percent ZnO.

(3) Specific gravity of about 5.6

(4) Apparent density of 30-32 pounds/cubic foot

(5) Surface area of about 4.0 square meters/gram.

(6) Is paint fine, i.e. 99.9 passes a standard 325 mesh screen.

Zinc oxide powder having the above characteristics is available from American Smelting and Refining Company of Columbus, Ohio and is sold under the trade name AZO-55.

With these properties, the zinc oxide particles or powder dissolves at the rate of .62 gram/liter/minute in an electrolyte L of about 4.0 pH and at a nominal temperature of 150°F which is maintained by passing the electrolyte through heat exchanger 162 having a flow or cooling rate controlled by thermocouple 166 in tank 130. Since zinc oxide is approximately 80% zinc and the zinc oxide dissolves at a rate of about .62 gram/liter/minute, about 1800 gallons of electrolyte must be circulated per minute through system 100 to obtain the required amount of usable zinc. Consequently, in this example pump 154 is rated to pump 1800 gallons per minute and heat exchanger 162 has a corresponding capacity.

If the pH of the electrolyte in tank 104 measured by meter 250 increases above a value, in practice 4.2, line 254 decreases the speed of motor 206 by speed control 220. In a like manner, if the acid balance increases and the pH decreases to below a value, in practice 3.8, line 256 increases the speed of motor 206. This pH adjustment is minor and the motor speed is primarily controlled by the amount of zinc actually deposited as measured by meter 230.

During operation, some zinc plating electrolyte is carried out of the unit on the surface of the moving strip. Such dragged-out electrolyte is a loss that is replaced by addition of water from line 260 and of sulfuric acid from source 270 via line 272. The addition of sulfuric acid will decrease the pH in tank 102 which will be detected by the pH probe 252 so the pH meter 250 will instruct controller 220 to add zinc oxide via feeder unit 202-206. This drag out will require slightly more than .62 gram of zinc oxide to replace the zinc removed by drag out and deposited on the strip.

Having thus described the invention, it is claimed:

1. A method of supplying zinc to a sulfuric acid containing electrolyte used between an anode and a moving metal cathode for depositing zinc onto said cathode, said method comprising the steps of:

(a) directing said electrolyte to a holding tank;

(b) adding to said electrolyte in said tank zinc oxide particles;

(c) allowing said zinc oxide particles to dissolve in said electrolyte; and,

(d) then directing said electrolyte between said anode and cathode.

2. A method as defined in claim 1 including the additional step of:

(e) controlling the rate of said adding step by the amount of zinc deposited onto said moving metal cathode.

3. A method as defined in claim 1 including the additional step of:

(e) controlling the rate of said adding step by the pH of said electrolyte.

4. A method as defined in claim 1 including the additional step of:

(e) cooling said electrolyte.

5. A method as defined in claim 1 including the additional step of:

(e) circulating said electrolyte through said holding tank at a flow rate providing about .62 gram of zinc oxide for each liter per minute of electrolyte flow.

6. A method as defined in claim 1 wherein said zinc adding step substantially continuously adds zinc oxide to said electrolyte.

7. A method as defined in claim 2 wherein said zinc adding step substantially continuously adds zinc oxide to said electrolyte.

8. A method as defined in claim 3 wherein said zinc adding step substantially continuously adds zinc oxide to said electrolyte.

9. A method as defined in claim 4 wherein said zinc adding step substantially continuously adds zinc oxide to said electrolyte.

10. A method as defined in claim 5 wherein said zinc adding step substantially continuously adds zinc oxide to said electrolyte.

11. A method of supplying zinc to a sulfuric acid containing electrolyte used between an anode and a moving metal cathode for depositing zinc onto said cathode, said method comprising the steps of:

(a) directing said electrolyte to a holding tank;

(b) adding to said electrolyte in said tank zinc oxide particles having a particle size of about .3 micron or less and a purity of at least about 99% zinc oxide;

(c) allowing said zinc oxide particles to dissolve in said electrolyte; and,

(d) then directing said electrolyte between said anode and cathode.

12. A method of supplying zinc to a sulfuric acid

containing electrolyte used between an anode and a moving metal cathode for depositing zinc onto said cathode, said method comprising the steps of:

(a) directing said electrolyte to a holding tank;

(b) adding to said electrolyte in said tank zinc compound particles selected from the class consisting of zinc oxide, zinc hydroxide, zinc carbonate and mixtures thereof;

(c) allowing said zinc compound particles to dissolve in said electrolyte; and,

(d) then directing said electrolyte between said anode and cathode.

AMENDED CLAIMS

CLAIMS:

1. A method of regenerating electrolyte in a zinc plating process in which a metal cathode continuously moves through a plating bath containing electrolyte past an anode in said bath, such that zinc is deposited onto said cathode, said method comprising the steps of:

(a) continuously directing from said plating bath electrolyte of depleted Zn ion concentration into a zinc replenishing electrolyte pool in a holding tank;

(b) continuously adding zinc compound particles to said electrolyte pool in said tank;

(c) allowing said zinc compound particles to dissolve in said electrolyte pool and form, separate therefrom, a continuous supply of regenerated electrolyte in said tank; and,

(d) then continuously directing said regenerated electrolyte from said supply thereof into said plating bath directly between said anode and cathode such that said regenerated electrolyte does not mix with the existing electrolyte in said bath prior to being directed between said anode and cathode.

2. A method of regenerating electrolyte in a zinc plating process in which a metal cathode continuously moves through a plating bath containing electrolyte past an anode in said bath, such that zinc is deposited onto said cathode, said method comprising the steps of:

(a) continuously circulating said electrolyte between said plating bath and a pool of said electrolyte in a holding tank remote from said plating vessel via an intermediate reservoir of electrolyte;

(b) continuously adding zinc compound particles to the pool of said electrolyte in said tank;

(c) allowing said zinc compound particles to dissolve in said circulating electrolyte in said tank to continuously form therein a supply of regenerated electrolyte separate from the said electrolyte pool therein;

(d) continuously directing said regenerated electrolyte from the said supply thereof into the bottom of said intermediate reservoir; and,

(e) then continuously withdrawing the regenerated electrolyte in said reservoir from the bottom thereof and directing it into said plating bath directly between said anode and cathode, such that it does not mix with the existing electrolyte in said bath prior to being directed between said anode and cathode.

3. A method as claimed in claim 1 or 2, including the step of controlling the rate of said adding step by the amount of zinc deposited onto said moving metal cathode.

4. A method as claimed in any one of the preceding claims, including the step of controlling the rate of said adding step by the pH of said electrolyte.

5. A method as claimed in any one of the preceding claims, including the step of cooling said electrolyte.

6. A method as claimed in any one of the preceding claims, wherein said zinc compound particles comprise zinc oxide particles.

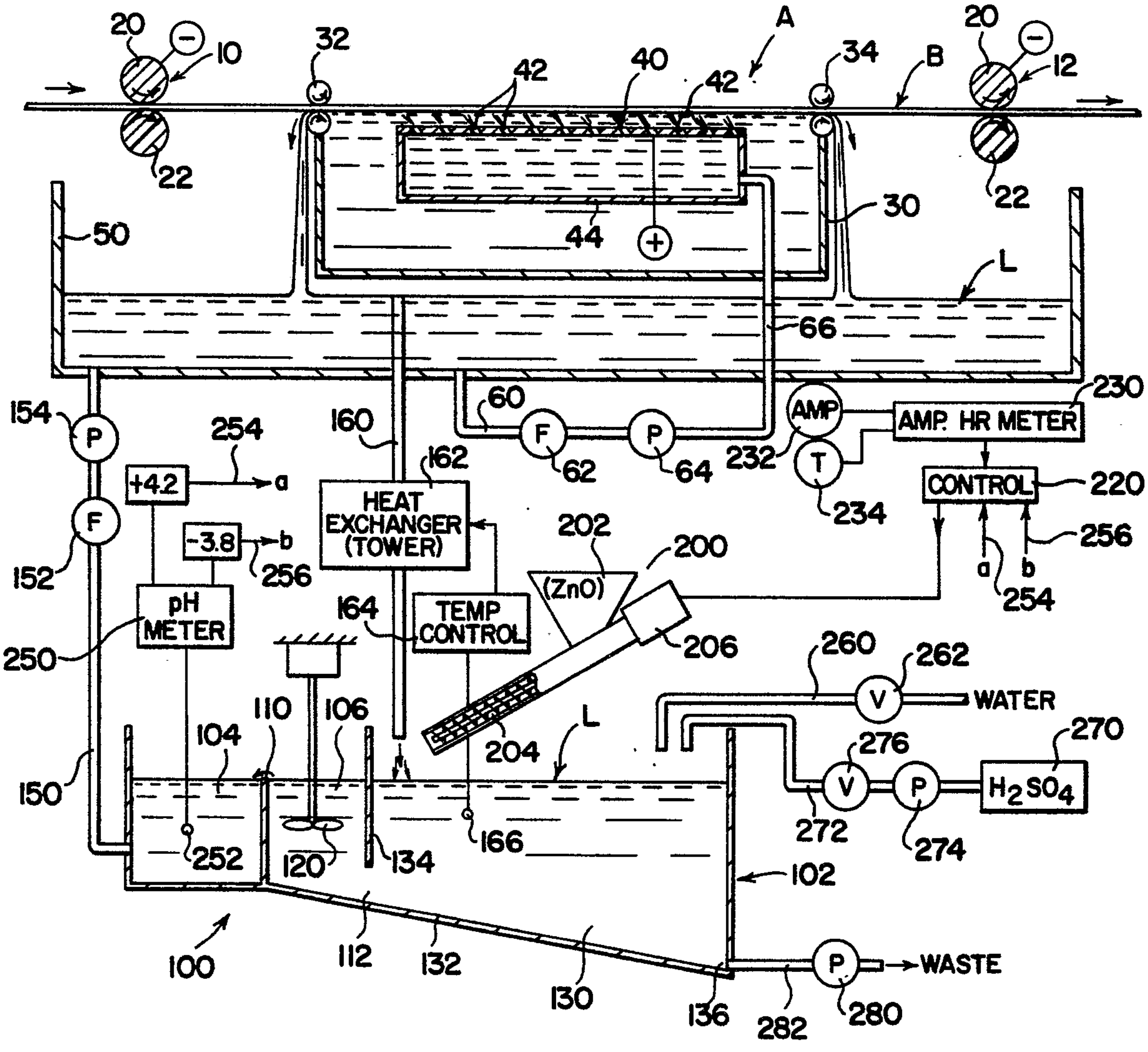
7. A method as claimed in claim 6, including the step of circulating said electrolyte through said holding tank at a flow rate providing about .62 gram of zinc oxide for each litre per minute of electrolyte flow.

AMENDED CLAIMS

8. A method as claimed in claim 6 or 7, wherein said zinc oxide particles have a particle size of about .3 micron or less and a purity of at least about 99% zinc oxide.

9. A method as claimed in any one of the preceding claims, wherein said zinc compound particles comprise particles of zinc oxide and/or zinc hydroxide and/or zinc carbonate.

10. A method as claimed in any one of the preceding claims, wherein the said regenerated electrolyte directed into said plating bath directly between the said anode and cathode is directed therebetween throughout substantially the entire opposing surface area zone of the anode and cathode.



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Application number EP 79 30 1224

EUROPEAN SEARCH REPORT

Category	DOCUMENTS CONSIDERED TO BE RELEVANT — Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.[3])
X	CHEMICAL ABSTRACTS, vol. 84, no. 8, Febr. 23, 1976, page 521 ref. 51500e Columbus, Ohio, US & JP - A - 75 85531 (NIPPON KOKAN K.K.) 10-07-1975 * Abstract *	1,2,6, 7,8,9, 12	C 25 D 21/14 C 25 D 3/22
X	CHEMICAL ABSTRACTS, vol. 84, no. 8, Febr. 23, 1976, page 521 ref. 51495g Columbus, Ohio, US & JP - A - 75 67238 (NIPPON KOKAN K.K.) 05-06-1975 * Abstract *	1,2,6, 7,8,9, 12	TECHNICAL FIELDS SEARCHED (Int.Cl.[3]) C 25 D 21/14 C 25 D 21/12 C 25 D 3/22 C 25 D 3/24
	DETTNER-ELZE, HANDBUCH DER GALVANOTECHNIK München, DE * Band II, page 306, Band I, page 433, Band I, page 478 *	1,3,4	
A	GB - A - 1 104 180 (GEIGY)		CATEGORY OF CITED DOCUMENTS
A	FR - A - 2 244 840 (DU PONT) * Page 6, lines 26-27 *	11	X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons &: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	25-02-1980	V. LEEUWEN

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