United States Patent

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[73] Assignee **National Steel Corporation**

[54] **REDUCING ELECTROLYTIC SLUDGE FORMATION**
18 Claims, 2 Drawing Figs.

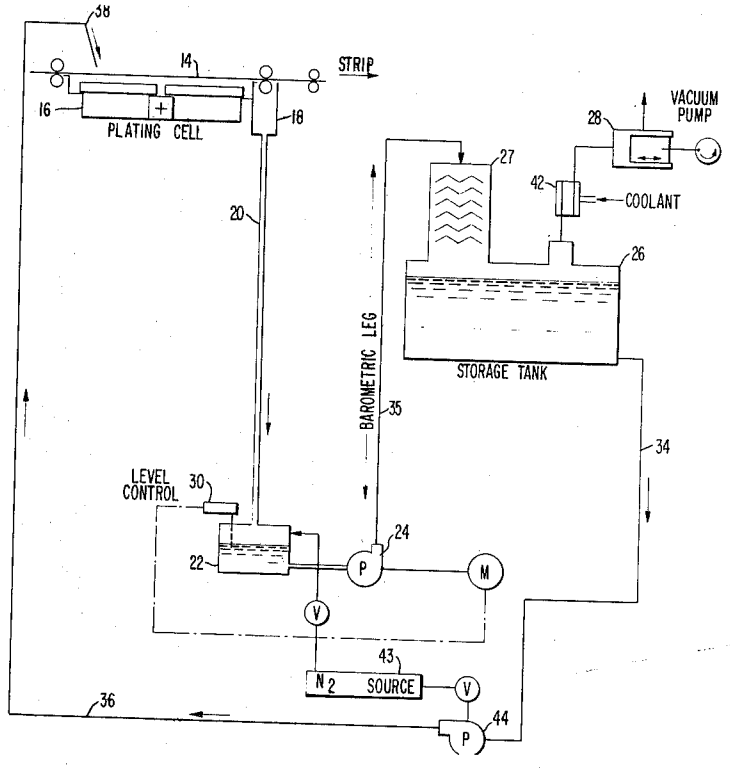
[52] **U.S. Cl.** **204/28,** 204/54, 204/206, 204/237
[51] **Int. Cl.** **C23b 5/58,** C23b 5/68
[50] **Field of Search** 204/27, 28, 206, 234, 236, 237, 239, 232, 54

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ABSTRACT: Method and apparatus for decreasing sludging in a stannous-tin electrolyte used in continuous-strip electroplating by continuous deaeration of the electrolyte which removes gases absorbed when the electrolyte is exposed to ambient atmosphere and by decreasing the opportunity for the electrolyte to absorb oxygen. A barometric leg, or other suitable pressure isolation means, is arranged to separate the path for continuous replenishment of electrolyte into an atmospheric pressure loop and a subatmospheric pressure loop. Desorption performance and efficiency is increased by operation at or below the vapor pressure of the electrolyte at the operating temperature for the system and by use of a vapor condenser on the vacuum side of the deaeration means used. Improved results are obtained by providing an inert gas shield during collection of electrolyte splash-over and carryout from the plating cells and also by injection of an inert gas into the electrolyte after deaeration and prior to exposure of the electrolyte to ambient atmosphere. The inert gas steps operate to reduce the opportunity for oxygen absorption.



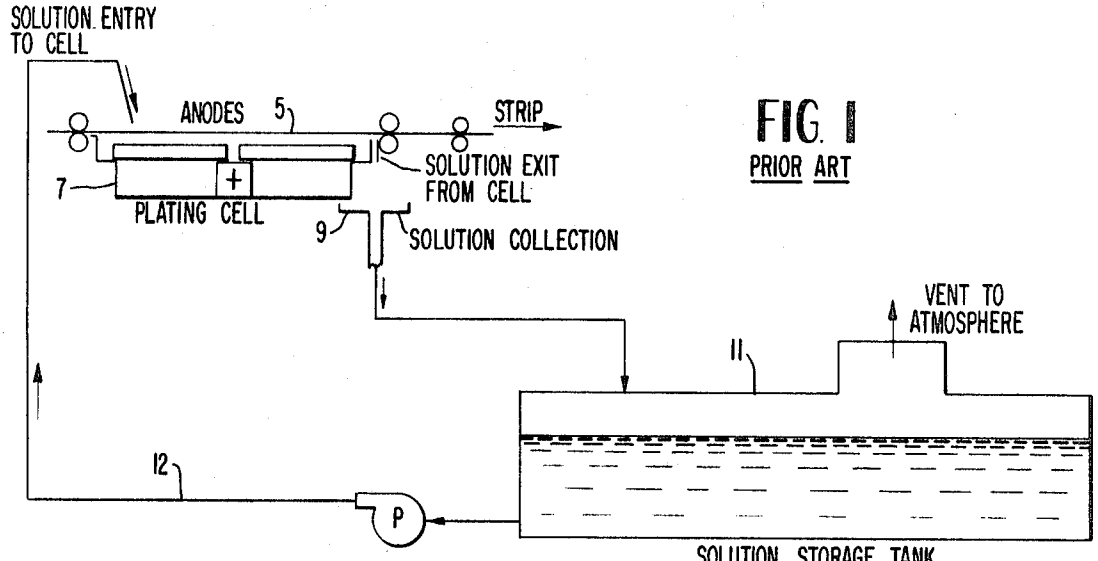


FIG. 1
PRIOR ART

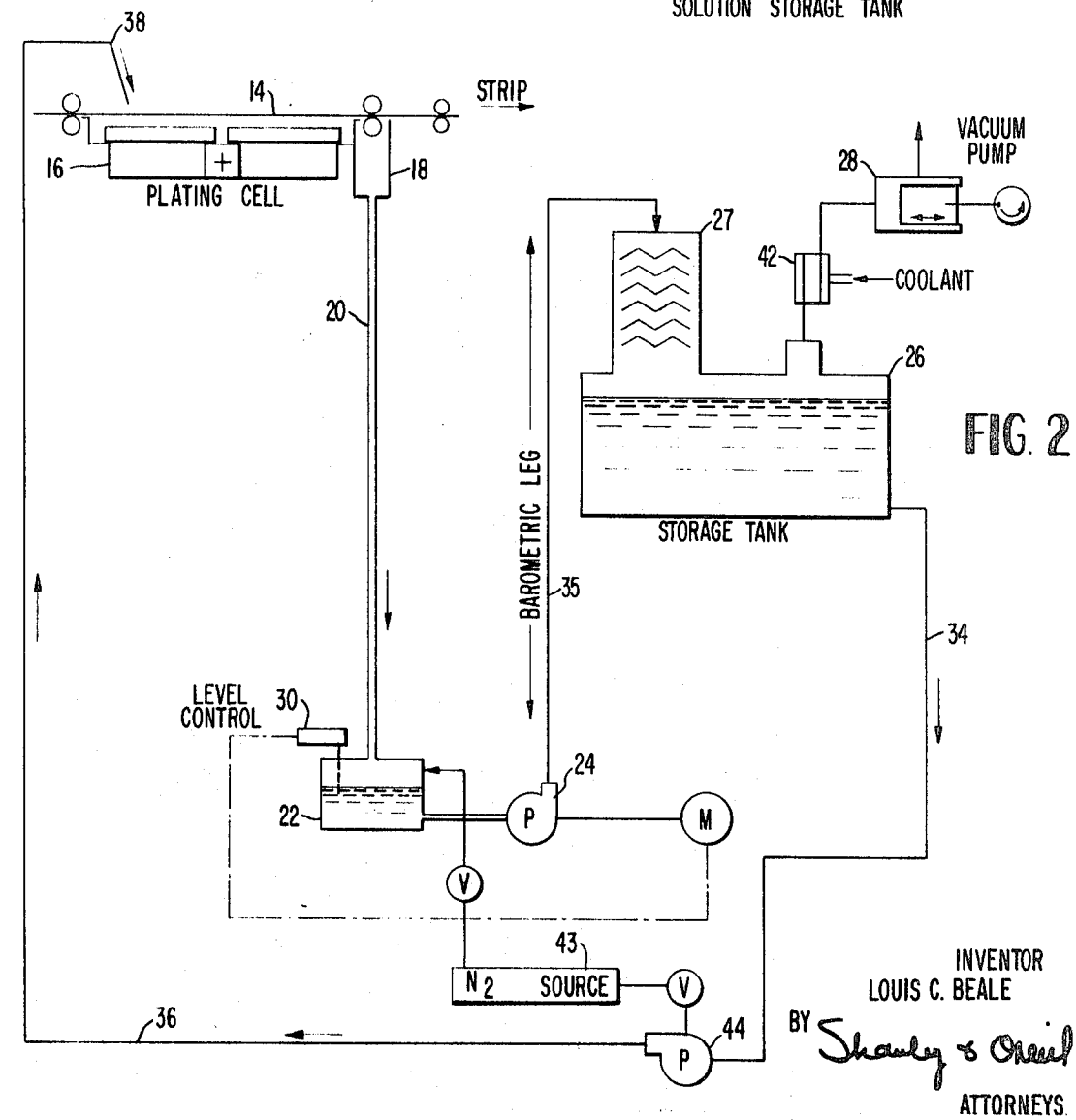


FIG. 2

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REDUCING ELECTROLYTIC SLUDGE FORMATION

This invention is concerned with reducing sludge formation in the electrolyte used in a continuous electrolytic operation.

Sludging in a stannous-tin electrolytic bath is deemed to be due to an oxidation reaction in which the stannous ion is converted to stannic ion:

$$2Sn^{+2}+0_2+4H^+ \rightarrow 2Sn^{+4}+2H_20$$

Sludging and an accompanying decrease in cathode efficiency are considered directly related to the amount of oxygen dissolved in the electrolyte. The economic detriment of sludging is clear cut since an otherwise completely continuous operation must be stopped periodically to remove accumulated sludge. In addition, replacing tin in the electrolytic bath chemically, for example as stannous chloride, is considerably more expensive than metallic tin as reclaimed from accumulated sludge.

This invention provides a novel combination of apparatus and process steps which eliminate major causes and opportunities for sludging.

The accompanying drawing will be used in describing the invention. In these drawings:

FIG. 1 is a schematic presentation of the prior art cycling of an electrolyte used in continuous-strip electroplating, and

FIG. 2 is a schematic presentation of apparatus for continuous-strip electroplating in accordance with the present invention.

In the prior art as shown in FIG. 1, a continuous strip 5 passes through a plating cell 7 in contact with the solution along the surface of the electrolyte in the plating cell. Electrolyte "splash-over" and "carryout" from a cell is collected in tray 9. Electrolyte from the plurality of cells in the conventional electrotinplating art is stored in solution storage tank 11 which is exposed to the atmosphere. The desired level of electrolyting plating cells is maintained by pumping solution from storage tank 11 via return line 12 to plating cell 7, and similar cells in the line.

Referring to FIG. 2, continuous strip 14 passes through plating cell 16. Electrolytic solution splashing over and carried from plating cell 16 by strip 14 is gathered at trough 18 and delivered through downcomer 20 for collection at sump 22. Pump 24 is controlled to transfer the electrolytic solution from sump 22.

In the prior art, a solution storage tank, such as tank 11 of FIG. 1, provided one of the main opportunities for the above sludging reaction to take place. An important teaching of the present invention is elimination of this opportunity for sludging by the novel step of immediate removal of oxygen from the electrolytic solution.

Referring to FIG. 2, removal of oxygen is carried out by deaeration of the solution in chamber 26. Vacuum pump 28 maintains deaeration chamber 26 substantially below atmospheric pressure. Prior to storage, this solution is deaerated rapidly utilizing a structure for increasing surface contact or exposure of the electrolytic solution to the vacuum. A suitable type of desorption means is shown schematically in FIG. 2 as spray tower 27. Thus oxygen is removed from the solution as soon as practicable after pickup, eliminating the storage tank sludging reaction of the prior art.

Solution collection means, including trough 18, downcomer 20 and sump 22 form part of the atmospheric pressure loop used in the handling of the electrolyte. This atmospheric pressure loop is pressure isolated from the subatmospheric pressure loop by isolation means located between the two loops. In FIG. 2, the isolation means takes the form of a barometric leg 35 located between sump 22 and the deaerating chamber 26. To form this barometric leg, sump 22 is located approximately 34 feet, or a greater distance, below the level of deaerating chamber 26. A level control means including sensor 30 can be used to control motor 32 driving pump 24 for transfer of electrolytic solution from the sump 22.

After deaeration, electrolytic solution from deaeration chamber 26 is returned to plating cell 16 by closed-circuit means including conduit 34 and 36 and cell entry means 38. These cooperate to return solution to the plating cell while preventing contact of the deaerated solution with ambient atmosphere prior to delivery into the plating cell.

Considering the deaeration, dissolved gases are removed by maintaining vacuum conditions in deaerating chamber 26. This subatmospheric pressure can extend below the vapor pressure of water at the plating solution temperature, in which case, solution boil occurs at the existing operating temperature without the necessity of raising the solution to its normal boiling temperature at atmospheric pressure. At the normal operating temperature of 150° F., the corresponding water vapor pressure would be 200 mm. By operating a deaerating chamber at 200 mm. of pressure, or slightly lower, the dissolved oxygen is removed rapidly due in part to the assistance of the solution boil.

Operation at such low pressures without loss of solution condensables is made possible by the disclosed structure including a condenser 42 between deaerating chamber 26 and vacuum pump 28. This recovers the condensable vapors from the electrolytic solution which can be returned directly to the solution. Condenser 42 also reduces the pumping capacity required for vacuum pump 28 in a given system. Sensible heat extracted in condensing solution vapors can also be returned to the electrolyte. However, under normal conditions encountered in a commercial electrotinplating line, circulation of solution is of such a volume that heat losses encountered in vaporizing a portion of the solution during deaeration ordinarily need not be returned to the system.

The benefits of the present invention can be supplemented by introducing an inert gas, such as nitrogen from source 43 at pump 44, in the return means for electrolytic solution. By adding an inert gas under pressure to the solution, oxygen pickup is reduced, that is this inert gas helps to delay oxygen pickup in the plating cell. Commercially pure nitrogen is preferred; other suitable inert gases include argon and carbon dioxide.

In accordance with the teachings of the invention, an inert gas can be used effectively to eliminate a major opportunity for oxygen absorption. Solution from plating cell 16 splashes into trough 18 and through downcomer 20. This provides increased surface exposure for absorbing oxygen. Oxygen absorption can also occur along the surface of the solution in sump 22. The present invention teaches enclosure of sump 22 with venting to the atmosphere through downcomer 20 and trough 18.

An inert gas is flushed through the above enclosed solution collection means. For example, nitrogen from source 43 is added under pressure to the space above the solution in sump 22. Nitrogen above the solution in sump 22 and exhausting upwardly through downcomer 20 and trough 18 will purge these structures of oxygen and prevent pickup of oxygen by the solution.

Various combinations of the above steps and structures can be relied on to obtain varying degrees of success in carrying out the invention. Also modifications and/or substitution of parts or steps will be evident to those skilled in the art based on the above teachings. Therefore the scope of the invention is not to be limited to the specific embodiments disclosed, but is to be determined from the appended claims.

What is claimed is:

1. For use in a continuous-strip electrotinplating operation, structure for reducing sludging by reduction of gas dissolution in the electrolyte comprising

plating-cell means for holding an electrolytic solution which is exposed to ambient atmosphere in the plating-cell means, the electrolytic solution being subject to sludge formation responsive to dissolved oxygen,

strip handling means for introduction of continuous strip to the plating-cell means and delivery from the plating-cell means,

means for replenishing electrolytic solution in the plating-cell means including solution collection means for receiving electrolytic solution from the plating-cell means,

deaerating means at subatmospheric pressure for receiving electrolytic solution collected from the plating-cell means and for removing gas dissolved in such electrolytic solution, and

conduit means connecting the deaerating means to the plating-cell means for delivery of deaerated electrolytic solution to the plating-cell means and for preventing contact of the electrolytic solution with ambient atmosphere prior to entry into the plating-cell means.

2. The apparatus of claim 1 wherein the deaerating means comprises a deaerating chamber at subatmospheric pressure for receiving electrolytic solution from the plating-cell means and further including pressure isolating means located between the solution collection means and the deaerating chamber.

3. The apparatus of claim 2 including vacuum pump means communicating with the chamber.

4. The apparatus of claim 2 including means for increasing surface exposure of the electrolytic solution upon entry into the deaerating chamber.

5. The structure of claim 1 in which the solution collection means includes sump means for receiving and accumulating electrolytic solution from the plating-cell means and further including

transfer means for delivering electrolytic solution from the sump means to the deaerating means, such transfer means including a barometric leg located between the sump means and the deaerating means permitting the deaerating means to be operated under vacuum conditions and to be pressure isolated from the plating-cell means and sump means.

6. The apparatus of claim 5 including level control means for the sump means for controlling delivery of electrolytic solution from the sump means.

7. The apparatus of claim 3 in which a condenser means is connected between the vacuum pump means and the deaerating chamber for condensing vapors from the electrolytic solution.

8. The apparatus of claim 7 including means for returning condensate to the deaerated electrolytic solution being returned to the plating-cell means.

9. The apparatus of claim 1 further including means for adding an inert gas to the solution collection means to at least partially shield electrolytic solution being collected from contact with oxygen.

10. The apparatus of claim 2 in which the solution collection means includes trough means for receiving splash-over and carryout of electrolytic from the plating-cell means, sump means for accumulating such electrolytic, and downcomer means interconnecting the trough means and sump means, with the sump means being enclosed and vented to the atmosphere through the downcomer means and the trough means, and

means for adding an inert gas under pressure to the sump means.

11. The apparatus means of claim 1 including means for introducing an inert gas into the deaerated electrolytic solution, such means being located to introduce inert gas into the conduit means for returning electrolytic solution to the plating-cell means between the deaerating means and the plating-cell means.

12. In a continuous-strip electrotinplating operation, utilizing an electrolyte subject to sludge formation responsive to oxygen dissolution, a process for reducing electrolytic sludging by reduction of gas dissolution in the electrolyte comprising the steps of

maintaining a deaerating means at subatmospheric pressure for receiving electrolytic solution after exposure to ambient atmosphere in plating-cell means,

deaerating electrolytic solution by circulating the electrolytic solution from the plating-cell means through the deaerating means, and

returning the deaerated electrolytic solution to the plating-cell while substantially preventing contact of the electrolytic solution with ambient atmosphere during and subsequent to deaeration prior to delivery into the plating-cell means.

13. The process of claim 12 in which deaeration of electrolytic solution is carried out by maintaining a deaerating chamber under vacuum conditions with the pressure range extending to below the vapor pressure of water at the temperature of the electrolytic solution, and

pressure isolating the deaerating chamber from the plating-cell means.

14. The process of claim 12 in which deaeration of the electrolytic solution is carried out by maintaining a deaerating chamber under vacuum conditions with the pressure range extending below the vapor pressure of water at the temperature of the electrolytic solution and further including the step of

condensing vapors from the electrolytic solution on the vacuum side of the deaerating chamber.

15. The process of claim 14 further including the step of returning condensate to the deaerated electrolytic solution.

16. The process of claim 12 further including the step of shielding the electrolytic solution after leaving the plating-cell means and before delivery to the deaerating chamber with an inert gas to substantially prevent contact of such solution with ambient atmosphere.

17. The process of claim 12 further including the step of injecting an inert gas under pressure into the electrolytic solution after exit from the deaerating chamber and before return to the plating-cell means.

18. The process of claim 13 including the step of increasing the surface area of the electrolytic solution exposed to the vacuum conditions upon entry into the deaerating chamber.

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