Sept. 28, 1926.

1,601,690

M. M. MERRITT

ELECTROLYTIC DEPOSITION OF METALS

Filed August 20, 1925 3 Sheets-Sheet 1

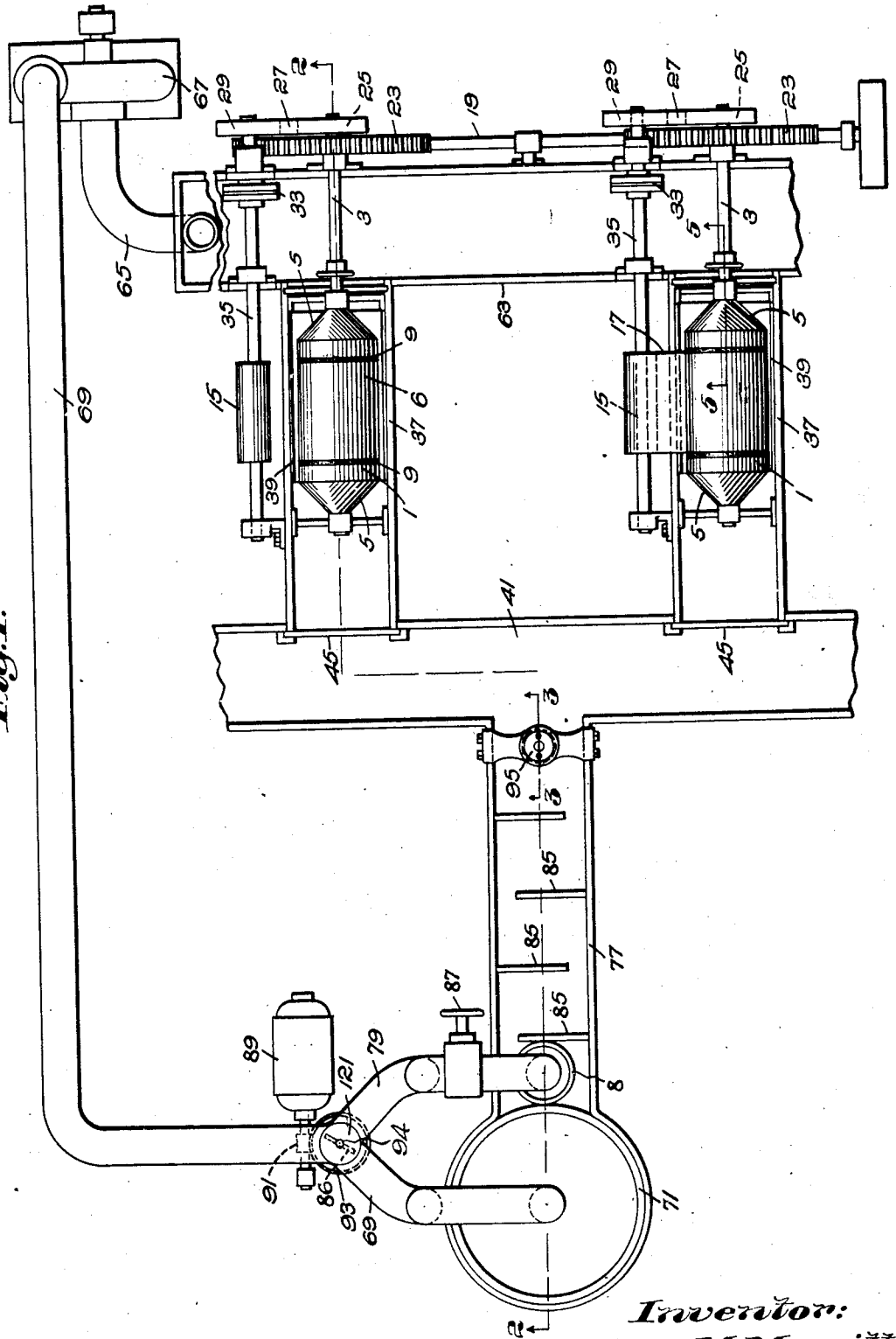


Fig. 1.

Inventor:
Matthew M. Merritt,
by Emery Booth Janney & Varney
Attys.

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M. M. MERRITT

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Fig. 3.

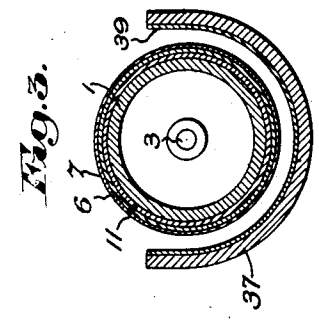


Fig. 2.

Inventor:
Matthew M. Merritt,
by Emery Booth Janney & Varney
Attys.

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M. M. MERRITT

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Fig. 6.

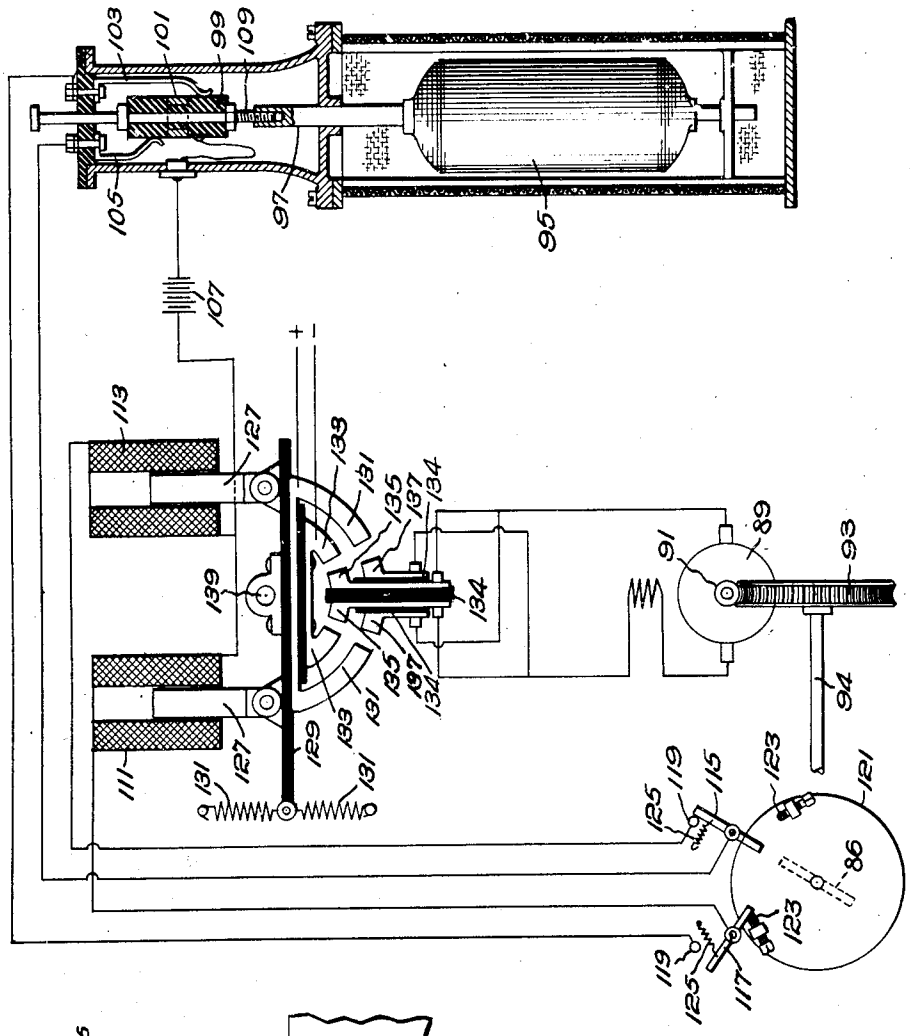


Fig. 4.

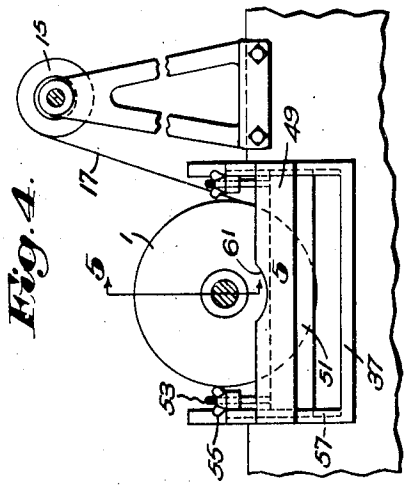
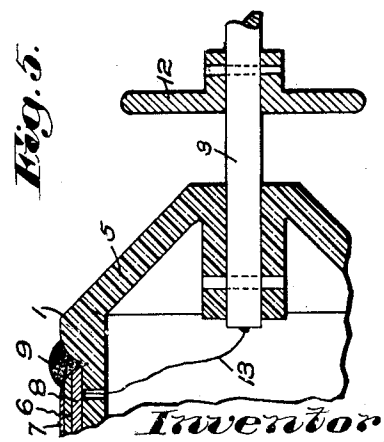


Fig. 5.



Inventor:
Matthew M. Merritt
by Emery Booth Janney & Varney
Attys.

Patented Sept. 28, 1926. 1,601,690

UNITED STATES PATENT OFFICE.

MATTHEW M. MERRITT, OF MIDDLETON, MASSACHUSETTS, ASSIGNOR TO INDUSTRIAL DEVELOPMENT CORPORATION, OF PORTLAND, MAINE, A CORPORATION OF MAINE.

ELECTROLYTIC DEPOSITION OF METALS.

Application filed August 20, 1925. Serial No. 51,377.

My invention pertains to improvements in electrolytic methods and apparatus, and particularly to methods and apparatus for making sheet metal by electro-deposition.

My invention will be best understood from the following description when read in the light of the accompanying drawings of one specific embodiment of my invention selected for illustrative purposes, while the scope of my invention will be more particularly pointed out in the appended claims.

In the drawings:—

Fig. 1 shows a plan of apparatus arranged according to my invention;

Fig. 2 is a section on the line 2—2 of Fig. 1;

Figs. 3 and 4 respectively are sections on the lines 3—3 and 4—4 of Fig. 2;

Fig. 5 is a fragmentary section on the line 5—5 of Fig. 1; and

Fig. 6 more or less diagrammatically illustrates the mechanism for controlling the proportion of electrolyte flowing through the soluble anode.

I have elected to illustrate my invention as applied to a battery of metal depositing units. Referring to the drawings I have shown a plurality of drums 1 each of which is mounted for rotation on a horizontal shaft 3, the drums being cylindrical and having the frusto-conical end portions 5. As illustrated the drums are formed of wood, porcelain or other suitable non-conducting material, and intermediate their length are provided with a conductive surface serving as a cathode upon which the sheet material to be formed is deposited. Preferably as illustrated by Figs. 3 and 5 the cathode consists of an endless sheet of copper 6 surrounding the drum and having its surface treated with mercury to form a coating of amalgam 7 for the purpose of preventing adherence of the deposited sheet to the cathode during the stripping operation hereinafter described. Preferably the copper sheet 6 is supported on a lead sheet 8, both sheets being received in an annular recess in the drum. For the purpose of aiding stripping of the deposited sheet from the cathode and for giving the deposited sheet a well formed edge the sides of the sheet 6 abut against a ring of rubber or other suitable non-conductive material carried by the drum.

For placing the cathode in electrical communication with the source of electromotive force indicated at 10 in Fig. 2 I have shown a brush 11 cooperating with a ring 12 on the shaft 3, the latter being connected to the sheet 8 (Fig. 5) by means of a conductor 13.

For stripping from the cathodes the sheets being continuously deposited thereon as the cathodes slowly rotate I provide rotating drums 15 to which the ends of the deposited sheets are secured, rotation of the drums 15 acting to strip the deposited sheets from the cathodes and to wind the sheets on the drums.

For rotating the drums 1 and 15 I have indicated a shaft 19 which carries worms 21 (Fig. 2) meshing with worm gears 23 on the ends of the shafts 3 carrying the drum 1, the shafts 3 carrying pulleys 25 belted by means of belts 27 to pulleys 29. The pulleys 29 drive shafts 31 which are connected by means of a friction drive device 33 of well known construction to shafts 35 which carry the drums 15. The speed of rotation of the pulleys 29 relatively to the speed of rotation of the pulleys 25 is such that the friction drive device 33 tends to rotate the drums 15 at a peripheral speed somewhat greater than the peripheral speed of the drums 1, in consequence of which the sheets 17 are maintained under tension, which facilitates the stripping operation and winds the sheets tightly on the drums 15.

As indicated by Figs. 1, 2 and 3 the drums 1 rotate in troughs 37 preferably lined with sheet lead 39 or other suitable conductive material, the sheet lead constituting an anode which is insoluble in the electrolyte and being uniformly distributed in relatively close proximity to the surface of the rotating cathode upon which the sheet of metal is deposited.

The electrolyte is fed to the various troughs 37 from a trough like conduit 41, the electrolyte flowing from the conduit 41

to the troughs 37 down aprons 43, and through the troughs lengthwise of the rotating cathodes in a swift-flowing continuous stream.

For regulating the amounts of electrolyte fed to the troughs 37 of each unit I provide suitable gates 45. The amount of electrolyte entering each trough 37 conveniently is sufficient to cause the electrolyte to contact with each rotating cathode to a depth of approximately one-third of its diameter, the level of the electrolyte being indicated by the dotted line 47 in Fig. 2.

To insure maintaining the level of the electrolyte substantially horizontal or parallel to the axis of the drum 1 so as to cause the sheet to be of uniform thickness I preferably provide each trough at the discharge side of the drum with a weir or dam best illustrated in Figs. 2 and 4. As shown the dam comprises a fixed plate 49 which extends across the trough and a second plate 51 similarly positioned but supported by screws 53 and nuts 55 and sliding at its ends in vertical grooves 57 so that it can be raised and lowered. The major portion of electrolyte discharges, as is indicated by the dotted lines 59 in Fig. 2, beneath the movable plate 51 of the dam, while a small portion of the electrolyte flows over the plate 49, the upper edge of the plate 49 for this purpose being preferably notched as is indicated at 61. The frusto-conical portions 5 of the drum heretofore referred to promote a uniform and uninterrupted flow of the electrolyte.

The electrolyte discharging from the troughs 37 falls into a trough 63, and leaving this trough by a pipe 65, is pumped by a pump 67 through a pipe 69 so as to elevate it and discharge it into a replenishing conduit herein shown as a tower 71. The tower contains suitable material 73 for replenishing the electrolyte, as for example ore, suitable salts, or scrap metal preferably the latter. The electrolyte after passing downwardly through the material 73 leaves the lower portion of the tower 71 through suitable orifices 75 and flows by gravity down a trough 77 in communication with the trough 41 it being observed that by the means just described the electrolyte is continuously circulated past the cathode and over the surface of the electrolyte replenishing material 73.

The negative terminal of the battery 10 or other source of direct current electro-motive-force is connected to the cathode as hereinbefore explained, while the positive terminal is connected to the insoluble conductive lining 39 of the trough 37 constituting an anode by a contact which runs the entire length of the lining. The metal-bearing material 73 in the tower 71 is maintained at substantially the same potential as that of lining 39 by reason of the fact that the circulating electrolyte being a conductor places the material 73 in electrical communication with conductive lining 39. Preferably a common source of electro-motive-force is employed for all of the units comprising a cathode 6 and insoluble conductive trough 39, the cathodes and troughs being connected in parallel to the respective terminals of said source. Provided a sufficient potential is impressed on the metal-bearing electrolyte replenishing material 73, the metal of said material will dissolve in the electrolyte as will hereinafter be more fully explained, while the depositing current flowing across the space between the lining 39 of the troughs and cathodes 6 will cause metal to be deposited from the electrolyte on the cathode.

My method and apparatus is not limited to the deposition of any particular metal or metals, being applicable to all metals below hydrogen in the electro-motive series. It will be understood however that the electrolyte, the metal-bearing material for replenishing the electrolyte, and the impressed voltage, must be suited to the particular metal or metals to be deposited. When my method and apparatus are used for depositing sheet copper on the cathodes the electrolyte employed is preferably a copper sulphate solution containing a low percentage of free sulphuric acid, and the material in the tower for replenishing the metal content of the electrolyte is preferably scrap sheet copper. For copper I have found that in order to obtain best results with an insoluble anode the impressed voltage should not be less than one and one-half volts although with a soluble anode it is possible to employ very much lower voltages. It will be understood that metallic copper is insoluble in dilute sulphuric acid at ordinary temperatures, although at higher temperatures it is soluble in concentrated acid with the formation of objectionable sulphur dioxide. I have found that by impressing a suitable voltage on the scrap copper in the tower 71 in contact with the electrolyte stream that I am able to effect dissolving of the copper at ordinary temperatures without formation of sulphur dioxide.

My explanation of the above phenomena discovered by me is that the impressed voltage on the copper has an effect analogous to that of raising the chemical valence of the copper by oxidization from zero to plus one or plus two at which value the copper will combine with the sulphate radical of the sulphuric acid of the electrolyte. For the present explanation the chemical valence of a metal in contact with an acid solution may be considered as the force, measured by the electrical charge of the ions of the metal which tends to cause the metal to enter into solution. This force I call for convenience

the "solution pressure" of the metal, which force, if the metal is to enter into solution when acted upon by an acid solution of the metal, I have found must be sufficient to overcome the counter force of the metal already in solution tending to prevent additional metal entering the solution. This counter force I call for convenience the "osmotic pressure" of the metal in solution, and I have found that by impressing on the metal in contact with the electrolyte a voltage sufficient to give the metal a "solution pressure" in excess of the "osmotic pressure" of the metal in solution, that I can replenish the metal content of the electrolyte to replace that deposited on the cathode. For a given amount of metal surface exposed to the action of the electrolyte apparently the rate of replenishment is directly proportional to the rate of electrolyte flow and preferably I vary the rate of replenishment while keeping the impressed voltage constant by varying the ratio of the amount of electrolyte to the amount of metal surface acted upon by the electrolyte, employing for this purpose means which will now be described.

For thus regulating the amount of metal dissolved by the electrolyte in the tower I have herein shown means for by-passing a portion of the electrolyte around the tower. For this purpose I have shown a pipe 79 in communication with the pipe 69 and discharging into a funnel 81 at substantially the same elevation as the discharge end of the pipe 69. The funnel 81 is in communication with a pipe 83 which discharges into the trough 77 adjacent the intake end of the trough, baffles 85 being placed in the trough 77 so as to thoroughly mix the stream of electrolyte discharging from the pipe 83 with that discharging through the openings 75.

I have found that best results can be obtained by preventing the metal content of the electrolyte from exceeding a maximum limit and from falling below a minimum limit. Preferably the amount of metal-bearing material in the tower and rate of electrolyte flow are such as to cause the electrolyte when all of it passes through the tower to dissolve metal faster than the metal is deposited on the cathodes. In operation sufficient electrolyte is caused to flow through the tower to effect solution of metal faster than deposition of metal until an upper limit of metal content of the electrolyte is approached or reached, then the flow through the tower is decreased to effect a solution of metal slower than deposition of metal until a lower limit of metal content is approached or reached, whereupon the flow through the tower is again increased again to increase the metal content of the electrolyte, this process of alternately increasing and diminishing the metal content of the electrolyte being continued throughout the run.

For regulating the amount of electrolyte diverted from the pipe 69 to the pipe 79 for by-passing electrolyte around the metal-bearing material in the tower 71, I have indicated a butterfly-valve 86 at the point of communication of these two pipes. As will be obvious movement of the valve 86 from its position shown in Fig. 1 in a counter-clockwise direction will divert more electrolyte to the pipe 79, which pipe for better regulating the flow therethrough is provided with a manually controlled valve 87 at its discharge end.

If desired the butterfly valve 85 may be operated manually, but as herein shown I have indicated it as operated by means of an electric motor 89, the shaft of which carries a worm 91 meshing with a worm gear 93 on the valve stem 94 of the valve so that when the motor is rotated the valve will be slowly turned.

If desired the motor 89 can be controlled automatically in response to changes in the specific gravity of the electrolyte, the specific gravity as will be understood being a direct function of the metal content of the electrolyte. For controlling the motor 89 in response to changes in specific gravity of the electrolyte I have shown at the discharge end of the trough 77 a float or hydrometer 95, with which float is associated mechanism for effecting rotation of the motor to turn the valve 86 for diverting more electrolyte through the pipe 79 when the specific gravity increases to a desired value, and to effect rotation of the motor 89 in an opposite direction to turn the valve 86 for diverting less electrolyte through the pipe 79 when the specific gravity decreases to a desired value.

Referring to Fig. 6 I have shown the float 95 provided with a stem 97 for raising and lowering a block of insulating material 99 carrying a contact ring 101 for placing the spring contacts 103 and 105 respectively in electrical communication with one terminal of the battery 107 when the float falls and rises, the block of insulating material 99 being preferably adjustably secured to the stem 97 by means of a rod 109 screw threaded into the end of the stem 97 so that by turning the rod 109 the distance between the float and the contact ring 101 can be varied. The terminal of the battery opposite that connected to the ring 101 is connected to one end of each of a pair of solenoids 111 and 113, the other ends of these solenoids being connected to switch arms 115 and 117 which cooperate with contacts 119 connected to the respective spring contacts 103 and 105. On the end of the valve stem 94 opposite the worm

gear 93 is a disk 121 of insulating material indicated in Figs. 1, 2 and 6. This disk as shown in Fig. 6 carries a pair of adjustable stops 123 which cooperate with the switch arms 115 and 117 so that when the valve 86 has turned through an angle determined by the adjustment of the stops one of the stops 123 will contact the associated switch arm and move it out of contact with its associated contact 119, while the other stop 123 permits a spring 125 associated with each switch arm to move the other switch arm into contact with its associated contact 119.

Assuming the parts in the position shown by Fig. 6 if the float 95 rises far enough to bring the spring contact 105 into contact with the ring 101 the solenoid 113 will be energized, and this by means of switch mechanism hereinafter described will cause the motor to rotate in such direction as to turn the disk 121 and butterfly-valve 86 as viewed in Fig. 6 counter-clockwise so as to divert more electrolyte around the tower 71. When the right hand stop 123 comes into contact with the arm 115 the latter will be moved from in contact with its contact 119 which will interrupt the circuit through the solenoid 113 and cause the motor to cease rotating. The movement of the disk 121 which took place while the motor was rotating will cause the left hand stop 123 to permit the switch arm 117 to move into contact with its associated contact 119 so that when the float falls due to a decrease in the specific gravity of the electrolyte and establishes communication between the contact ring 101 and the lower spring contact 103 the solenoid 111 will be energized to effect rotation of the motor and move the valve 86 and disk 121 back to the position shown by Fig. 6.

Each of the solenoids 111 and 113 has associated therewith an armature 127 attached to a plate of insulating material 129 normally held in horizontal position by a pair of springs 131. The plate 129 carries on its under side a pair of contacts 131 which as indicated are connected to one side of a source of electromotive force and a second pair of contacts 133 connected to the opposite side of the same source of electromotive force. Cooperating with the contacts 133 is a pair of contacts 135 and cooperating with the contacts 131 is a pair of contacts 137, these four contacts being insulated from each other by insulating strips 134. The opposite terminals of the motor are respectively connected to one contact of each the pairs of contacts 135 and 137 at opposite sides of the insulating strips 134 so that when the solenoid 113 swings the plate 129 about its pivot 139 to move the right hand contacts 131 and 133 into contact with the associated contacts 135 and 137 the motor will be rotated in one direction, and when the solenoid 111 swings the plate 129 in the opposite direction to bring the left hand contacts 131 and 133 into contact with the associated contacts 135 and 137 the motor will be rotated in the opposite direction.

As an example of the practice of my invention but without limitation thereto I have deposited on a single unit sheets of copper five and one-half thousands of an inch in thickness on a cylindrical cathode 24 inches in diameter and 5 feet long, the surface of the cathode being spaced from the surface of the trough lining approximately seven sixteenths of an inch and with an impressed voltage varying from 2.25 to 2.5 volts giving a current density of 250 amperes per square foot of cathode surface. The rate of rotation of the cathode was approximately one revolution in 76 minutes and the rate of electrolyte flow from 75 to 100 gallons per minute. About 875 pounds of sheet copper scrap three-eighths of an inch thick and cut in pieces two inches square was used for replenishing the metal content of the electrolyte the cross-sectional area of the mass of copper scrap transverse to the direction of the electrolyte flow being about two square feet, though in a plural installation as illustrated the amount of copper scrap would normally be considerably increased. In this example the copper content of the electrolyte was controlled to maintain it between lower and upper limits of approximately 26 and 32 ounces of copper sulphate crystals per gallon corresponding to maintaining the specific gravity of the electrolyte between approximately 1.18 and 1.24 in the presence of from 6 percent to 10 percent of sulphuric acid.

It will be understood that the percent sulphuric acid content of the electrolyte varies as an inverse function of the copper content, so that in the above example of the practice of my method when the copper content was at 32 ounces of copper sulphate crystals per gallon of electrolyte the acid concentration was at its lower limit of 6 percent and when the copper content was reduced to its lower limit of 26 ounces of copper sulphate crystals per gallon the sulphuric acid concentration was at its upper limit of 10 percent.

I have found that by passing the electrolyte in a rapidly flowing stream through the space between the insoluble anode and rotating cathode where the latter is in close proximity to the former I am able to use a low impressed voltage with high current density causing an exceedingly rapid deposition of metal on the cathode without the

presence of gas bubbles which would result in the formation of pin holes or other imperfections in the deposited sheet.

Although I have described for purposes of illustration one specific embodiment of an apparatus constructed and arranged according to my invention and one specific way of performing my method it is to be understood that I am not limited thereby to their particular details, but that within the scope of my invention wide deviations may be made therefrom without departing from the spirit of my invention.

Claims:—

1. Electrolytic apparatus comprising, in combination, a cathode providing a moving cathode surface, and conduit means of insoluble conductive material constituting an anode for guiding the electrolyte in a swift-flowing continuous stream in contact with said cathode surface.

2. Electrolytic apparatus comprising, in combination, a cathode providing a moving cathode surface, and conduit means of insoluble conductive material constituting an anode for guiding the electrolyte in a swift-flowing continuous stream substantially transverse to the direction of movement of said cathode surface and in contact therewith.

3. Electrolytic apparatus comprising, in combination, a cathode providing a moving cathode surface, and conduit means of insoluble conductive material constituting an anode for guiding the electrolyte past said cathode surface in contact therewith from one side thereof to the other in a swift-flowing continuous stream.

4. Electrolytic apparatus comprising, in combination, a cathode providing a moving cathode surface partially in contact with the electrolyte, and conduit means of insoluble conductive material constituting an anode for conducting the electrolyte in a swift-flowing continuous stream past the portion of said cathode surface in contact with the electrolyte.

5. Electrolytic apparatus comprising, in combination, a cathode providing a moving cathode surface partially in contact with the electrolyte, and conduit means of insoluble conductive material constituting an anode for conducting the electrolyte in a swift-flowing continuous stream substantially transverse to the movement of said cathode surface past the portion of said cathode surface in contact with the electrolyte.

6. Electrolytic apparatus comprising, in combination, a cathode providing a moving cathode surface partially in contact with the electrolyte, and conduit means of insoluble conductive material constituting an anode for conducting the electrolyte past the portion of said cathode surface in contact with the electrolyte from one side of said cathode surface to the other in a swift-flowing continuous stream.

7. Electrolytic apparatus for making sheet material comprising, in combination, means providing a slowly moving endless cathode surface, means for flowing the electrolyte in a swift, continuous stream in contact with said cathode surface comprising conduit means of insoluble conductive material constituting an anode, means for stripping from said cathode surface the sheet material deposited thereon, and means for replenishing the electrolyte with metal content.

8. Electrolytic apparatus for making sheet material comprising, in combination, means providing a slowly moving endless cathode surface, means for flowing the electrolyte transversely to the movement of said cathode surface in a swift continuous stream in contact with said cathode surface comprising conduit means of insoluble conductive material constituting an anode, means for stripping from said cathode surface the sheet material deposited thereon, and means for replenishing the electrolyte with metal content.

9. Electrolytic apparatus for making sheet material comprising, in combination, means providing a slowly moving endless cathode surface, means for flowing the electrolyte from one side of said cathode surface to the other in a swift, continuous stream in contact with said cathode surface comprising conduit means of insoluble conductive material constituting an anode, means for stripping from said cathode surface the sheet material deposited thereon, and means for replenishing the electrolyte with metal content.

10. Electrolytic apparatus for making sheet material comprising, in combination, means providing a slowly moving endless cathode surface, means for flowing the electrolyte in a swift, continuous stream in contact with a portion of said cathode surface from one side thereof to the other comprising conduit means of insoluble conductive material constituting an anode, means for stripping from said cathode surface the sheet material deposited thereon, and means for replenishing the electrolyte with metal content.

11. Electrolytic apparatus for making sheet material comprising, in combination, means providing a moving, endless cathode surface, means for flowing the electrolyte in a swift, continuous stream in contact with said cathode surface comprising conduit means of insoluble conductive material constituting an anode, means for stripping from said cathode surface the sheet material deposited thereon, and means for replenishing the electrolyte with metal content after

said electrolyte flows from in contact with said cathode surface.

12. Electrolytic apparatus for making sheet material comprising, in combination, means providing a moving, endless cathode surface, means for flowing the electrolyte substantially transverse to the movement of said cathode surface in a swift, continuous stream in contact with said cathode surface comprising conduit means of insoluble conductive material constituting an anode, means for stripping from said cathode surface the sheet material deposited thereon, and means for replenishing the electrolyte with metal content after said electrolyte flows from in contact with said cathode surface.

13. Electrolytic apparatus for making sheet material comprising, in combination, means providing a moving, endless cathode surface, means for flowing the electrolyte from one side of said cathode surface to the other in a swift, continuous stream in contact with said cathode surface comprising conduit means of insoluble conductive material constituting an anode, means for stripping from said cathode surface the sheet material deposited thereon, and means for replenishing the electrolyte with metal content after said electrolyte flows from in contact with said cathode surface.

14. Electrolytic apparatus for making sheet material comprising, in combination, means providing a slowly moving endless cathode surface, means for flowing the electrolyte from one side of said cathode surface to the other in a swift, continuous stream in contact with a portion of said cathode surface comprising conduit means of insoluble conductive material constituting an anode, means for stripping from said cathode surface the sheet material deposited thereon, and means for replenishing the electrolyte with metal content after said electrolyte flows from in contact with said cathode surface.

15. Electrolytic apparatus for making sheet material comprising, in combination, means providing a moving endless cathode surface, means comprising an insoluble conductive material constituting an anode the surface of which is in close proximity to said cathode surface for passing the electrolyte in a swift-flowing continuous stream transverse to the movement of said cathode surface, a body of soluble metal-bearing material, and means for flowing the electrolyte in contact with said metal-bearing material after the electrolyte leaves said cathode surface.

16. Electrolytic apparatus for making sheet material comprising, in combination, means providing a moving endless cathode surface, means comprising an insoluble conductive material constituting an anode the surface of which is in close proximity to said cathode surface for passing the electrolyte in a swift-flowing continuous stream from one side of said cathode surface to the other, a body of soluble metal bearing material, and means for flowing the electrolyte in contact with said metal bearing material after the electrolyte leaves said cathode surface.

17. Electrolytic apparatus comprising, in combination, means providing a moving cathode surface, a body of soluble metal bearing material, means for circulating the electrolyte in contact with said material and said cathode surface, said means causing said electrolyte to flow over said cathode surface in a swift, continuous stream and comprising a conduit of insoluble conductive material constituting an anode in relatively close proximity to said cathode surface.

18. Electrolytic apparatus comprising, in combination, means providing a moving cathode surface, a body of soluble metal bearing material, means for circulating the electrolyte in contact with said material and a portion of said cathode surface, said means causing said electrolyte to flow over said portion of said cathode surface in a swift, continuous stream and comprising a conduit of insoluble conductive material constituting an anode in relatively close proximity to said cathode surface.

19. Electrolytic apparatus comprising, in combination, means providing an endless moving cathode surface, a body of soluble metal bearing material, means for circulating the electrolyte in contact with said material and said cathode surface, said means causing said electrolyte to flow over said cathode surface from one side thereof to the other in a swift, continuous stream and comprising a conduit of conductive material constituting an anode in relatively close proximity to said cathode surface.

20. Electrolytic apparatus comprising, in combination, means providing an endless moving cathode surface, a body of soluble metal bearing material, means for circulating the electrolyte in contact with said material and a portion of said cathode surface, said means causing said electrolyte to flow over said portion of said cathode surface from one side thereof to the other in a swift, continuous stream and comprising a conduit of insoluble conductive material constituting an anode in relatively close proximity to said cathode surface.

21. Electrolytic apparatus for making sheet metal comprising, in combination, means forming an endless moving cathode surface, a trough in which said cathode surface moves, said trough being of insoluble conductive material constituting an anode the surface of which is distributed in rela-

tively close proximity to said cathode surface, means for passing the electrolyte through said trough between the anode and cathode surfaces in a swift-flowing continuous stream in contact with said both surfaces, a body of soluble metal-bearing material, means for replenishing the electrolyte with metal content comprising means for flowing the electrolyte through said body in contact therewith after the electrolyte leaves said trough, and means for stripping from said cathode surface the sheet of metal deposited thereon.

22. Electrolytic apparatus for making sheet metal comprising, in combination, means forming an endless moving cathode surface, a trough in which said cathode surface moves, said trough being of insoluble conductive material constituting an anode the surface of which is distributed in relatively close proximity to said cathode surface, means for passing the electrolyte through said trough from one end thereof to the other between the surfaces of said cathode and anode in a swift-flowing continuous stream in contact with both surfaces, a body of soluble metal-bearing material, means for replenishing the electrolyte with metal content comprising means for flowing the electrolyte through said body in contact therewith after the electrolyte leaves said trough, and means for stripping from said cathode surface the sheet of metal deposited thereon.

23. Electrolytic apparatus for making sheet metal comprising, in combination, means forming a moving endless cathode surface, a trough in which said cathode surface moves, said trough being of insoluble conductive material constituting an anode the surface of which is distributed in relatively close proximity to said cathode surface, means for passing the electrolyte through said trough in a swift-flowing continuous stream between said cathode and anode surfaces, said cathode surface in the direction in which it moves being partially immersed in said stream, a body of soluble metal-bearing material, means for replenishing the electrolyte with metal content comprising means for flowing the electrolyte through said body in contact therewith after the electrolyte leaves said trough, and means for stripping from said cathode surface the sheet of metal deposited thereon.

24. Apparatus for depositing sheet metal comprising, in combination, a cathode presenting a moving surface, conduit means for guiding an electrolyte in a swift-flowing continuous stream past a portion of said cathode surface, said conduit means presenting an electrically conductive trough constituting an anode in relatively close proximity to the cathode surface.

25. Electrolytic apparatus for making sheet metal comprising, in combination, means forming a moving endless cathode surface, a trough in which said cathode surface rotates, said trough having a surface of insoluble conductive material constituting an anode; means for circulating the electrolyte through said trough between and in contact with said cathode and anode surfaces, comprising means for causing the electrolyte to flow through said trough in a swift-flowing continuous stream; and means for stripping from said cathode surface the sheet of metal deposited thereon.

26. Electrolytic apparatus for making sheet metal comprising, in combination, means forming a moving endless cathode surface, a trough in which said cathode surface rotates, said trough having a surface of insoluble conductive material constituting an anode; means for circulating the electrolyte through said trough between and in contact with the cathode and anode surfaces, comprising means for causing the electrolyte to flow through said trough from one end thereof to the other in a swift-flowing continuous stream; and means for stripping from said cathode surface the sheet of metal deposited thereon.

27. Electrolytic apparatus for making sheet metal comprising, in combination, means forming a moving endless cathode surface, a trough in which said cathode surface moves, said trough having a surface of insoluble conductive material constituting an anode, means for circulating the electrolyte causing it to flow through said trough in a swift-flowing continuous stream in contact with the cathode and anode surfaces, means for replenishing the electrolyte with metal content after it leaves said trough and before it again returns thereto, and means for stripping from said cathode surface the sheet of metal deposited thereon.

28. Electrolytic apparatus for making sheet metal comprising, in combination, means forming a moving endless cathode surface, a trough in which said cathode surface moves, said trough having a surface of insoluble conductive material constituting an anode, means for circulating the electrolyte causing it to flow through said trough from one end thereof to the other in a swift-flowing continuous stream between and in contact with the cathode and anode surfaces, means for replenishing the electrolyte with metal content after it leaves said trough and before it again returns thereto, and means for stripping from said cathode surface the sheet of metal deposited thereon.

29. Electrolytic apparatus comprising, in combination, a cathode, metal-bearing material for replenishing the electrolyte, means for circulating the electrolyte to cause it to contact said cathode and material in series, and means for varying the ratio of the

amount of electrolyte to the amount of surface of said material on which said electrolyte acts.

30. Electrolytic apparatus comprising, in combination, a cathode, a circulatory electrolytic bath carrying an impressed voltage, soluble anodic metal-bearing material in contact with the stream of electrolyte, the impressed voltage being such that the solution pressure of the metal of the metal-bearing material exceeds the osmotic pressure of the metal in solution, and means for maintaining the impressed voltage substantially constant while varying the effect thereof by changing the ratio of the amount of electrolyte to the amount of surface of metal bearing material on which the electrolyte acts.

31. Electrolytic apparatus comprising, in combination, a cathode for deposition thereon of metal from the electrolyte, means for replenishing the electrolyte with metal content comprising circulating the electrolyte through metal-bearing material, and controlling means for effecting an increase and decrease in the rate of replenishment.

32. Electrolytic apparatus comprising, in combination, a cathode for deposition thereon of metal from the electrolyte, means for replenishing the electrolyte with metal content comprising circulating the electrolyte through metal-bearing material, and means for varying the ratio of the amount of electrolyte to the amount of metal-bearing material through which the electrolyte flows.

33. Electrolytic apparatus comprising, in combination, a cathode on which metal is deposited, an electrolyte, a body of material for replenishing the metal content of the electrolyte, said electrolyte circulated in contact with said cathode and body of material in series, the electrolyte and the body of material both in excess of the amount necessary to replace in the electrolyte the amount of metal deposited at the cathode, and means for varying the effective ratio between the electrolyte coming in contact with the body of material and the amount of material with which such electrolyte contacts thereby to prevent increase and decrease of the metallic content of the electrolyte beyond the desired limits.

34. A method of electrodeposition comprising effecting deposition on a cathode, while circulating electrolyte thereby and while regulating the metal content of the electrolyte by controlling its action on a body of electrolyte replenishing metal-bearing material.

35. An electrolytic method which comprises depositing metal from a rapidly circulated electrolyte, while replenishing the metallic content of the electrolyte alternately at a rate faster and slower than the rate at which metal is deposited therefrom.

36. The method of electrolytically depositing metal, which comprises rapidly circulating in series the electrolyte past a cathode and past a body of material for replenishing the metallic content of the electrolyte while alternately increasing and decreasing the metallic content of the electrolyte to maintain such content between predetermined limits.

37. The method of electrolytically depositing metal, which comprises continuously and rapidly circulating the electrotyle in series past the cathode and through metal-bearing material for depositing metal on the cathode and for replenishing the electrolyte with metal in excess of that deposited on the cathode, and when a desired limit of the metallic content of the electrolyte is reached decreasing such content.

38. That method of electro-deposition, which comprises regulating the rate of replenishment of the metal content of an electrolytic cell during the process of depositing in said cell.

39. The method of controlling the metallic content of an electrolyte which is continuously circulated past a cathode and an electrolyte replenishing metal, which comprises increasing and decreasing the ratio between the amount of electrolyte circulated past the replenishing metal and the aggregate surface of the latter.

40. Electrolytic apparatus comprising, in combination, means providing a cathode surface, means providing a surface of conductive material constituting an anode distributed in relatively close proximity to said cathode surface, soluble metal-bearing electrolyte replenishing material, means for rapidly circulating the electrolyte between the cathode and anode surfaces and through said metal-bearing material, and means for varying the ratio of the amount of electrolyte to the amount of surface of metal-bearing material on which the electrolyte acts.

41. Electrolytic apparatus comprising, in combination, a cathode, metal-bearing material for replenishing the electrolyte, means for circulating the electrolyte to cause it to contact said cathode and material in series, and means for varying the ratio of the amount of electrolyte to the amount of surface of said material on which said electrolyte acts comprising a regulatable by-pass for diverting electrolyte around said material.

42. Electrolytic apparatus comprising, in combination, a cathode, metal-bearing material for replenishing the electrolyte, means for circulating the electrolyte to cause it to contact said cathode and material in series, a by-pass for the electrolyte around said material, and means responsive to the specific gravity of the electrolyte for regulating

the amount of electrolyte passing through said by-pass.

43. Electrolytic apparatus comprising, in combination, a cathode, a body of soluble metal-bearing material for replenishing the electrolyte, means for continuously circulating the electrolyte past said cathode and through said material, said means comprising a pump for elevating all the electrolyte passing said cathode to a level above said cathode and body of material, and a regulatable by-pass around said body of material for varying the amount of electrolyte passing through said material.

44. Electrolytic apparatus comprising, in combination, a cathode, a body of soluble metal-bearing material for replenishing the electrolyte, means for continuously circulating the electrolyte past said cathode and through said material, said means comprising a pump for elevating all the electrolyte passing said cathode to a level above said cathode and body of material, and regulatable means for varying the ratio of the amount of electrolyte to the amount of said material on which said electrolyte acts.

45. Electrolytic apparatus comprising, in combination, means providing a moving cathode surface, a trough, means causing the electrolyte to flow through said trough in a swift-flowing continuous stream, means causing said cathode surface to move through said trough with its surface distributed uniformly to the walls of said trough and entering and leaving said stream by way of the surface of said stream, and means for relatively adjusting the surface of said stream and said cathode surface to effect substantially equal emersion of said cathode surface in said stream at all sections of said surface transverse to said stream.

46. Electrolytic apparatus comprising, in combination, means providing a moving endless cathode surface, a trough, means for causing the electrolyte to flow in a swift stream through said trough, means including a generally horizontal drum for moving said cathode surface into and out of said stream, and means for maintaining the level of the electrolyte in said trough substantially parallel to the axis of said drum.

47. Electrolytic apparatus comprising, in combination, means providing a moving endless cathode surface, a trough, means for causing the electrolyte to flow in a swift stream through said trough, means including a generally horizontal drum for moving said cathode surface into and out of said stream, and means for maintaining the level of the electrolyte in said trough substantially parallel to the axis of said drum comprising an undercut weir in said trough at the discharge side of said drum.

48. Electrolytic apparatus comprising, in combination, means providing a moving endless cathode surface, a trough, means for causing the electrolyte to flow in a swift stream through said trough, means including a drum for moving said cathode surface into and out of said stream, and means for maintaining the level of the electrolyte in said trough substantially parallel to the axis of said drum comprising flow controlling means in said trough at the discharge side of said drum.

49. Electrolytic apparatus comprising, in combination, means providing a moving endless cathode surface, a trough, means for causing the electrolyte to flow in a swift stream through said trough, means including a generally horizontal drum for moving said cathode surface into and out of said stream, and means for maintaining the level of the electrolyte in said trough substantially parallel to the axis of said drum comprising means in said trough at the discharge side of said drum for restricting the flow of electrolyte at the surface level thereof.

50. Electrolytic apparatus comprising, in combination, a trough, a drum rotating in said trough, said drum having a cylindrical portion provided with a cathode surface and having tapered ends, the axis of said drum being lengthwise of said trough, and means for causing the electrolyte to flow in a swift continuous stream through said trough.

51. Electrolytic apparatus comprising, in combination, a plurality of electrolytic units each comprising a cathode for deposition thereon of metal from the electrolyte, means for replacing in the electrolyte the metal deposited therefrom on the cathodes of said units comprising a common body of metal-bearing material through which electrolyte from all of said units is passed, and means for controlling the rate of such replacement of metal.

52. Electrolytic apparatus comprising, in combination, a plurality of means each provided with a moving cathode surface, troughs of insoluble conductive material constituting anodes in which said cathode surfaces move, means for passing the electrolyte in a swift-flowing stream through said troughs in contact with said cathodes, a body of soluble metal-bearing material, means for circulating the electrolyte through said plurality of troughs and body of material, and means for controlling the rate of solution of metal into the electrolyte from said body of metal-bearing material.

53. Electrolytic apparatus comprising, in combination, a plurality of means each provided with moving cathode surfaces, troughs of insoluble conductive material constituting anodes in which said cathode surfaces move, means for passing the electrolyte in a swift-flowing stream through said troughs in contact with said cathodes, a body of soluble metal-bearing material, means for

circulating the electrolyte through said plurality of troughs and body of material, and means for varying the ratio of the amount of electrolyte to the amount of said material on which said electrolyte acts.

54. Electrolytic apparatus comprising, in combination, a plurality of means each provided with moving cathode surfaces, troughs of insoluble conductive material constituting anodes in which said cathode surfaces move, a body of soluble metal-bearing material, means for circulating the electrolyte through said plurality of troughs in a swift-flowing stream in contact with said cathodes and through said body of material, and a by-pass for diverting a portion of the electrolyte around said body of material.

55. Electrolytic apparatus comprising, in combination, a plurality of electrolytic units each comprising a cathode and an anode of insoluble conductive material, a tower containing soluble metal-bearing material, means for circulating the electrolyte through said units and tower comprising a pump for elevating the electrolyte and causing it to flow through said tower and hence to said units by gravity.

56. Electrolytic apparatus comprising, in combination, a plurality of electrolytic units each comprising a cathode and an anode of insoluble conductive material, a tower containing soluble metal-bearing material, means for circulating the electrolyte through said units and tower comprising a pump for elevating the electrolyte and causing it to flow through said tower and hence to said units by gravity, and means for varying the ratio of the amount of electrolyte to the amount of said material on which said electrolyte acts.

57. Electrolytic apparatus comprising, in combination, a plurality of electrolytic units each comprising a cathode and an anode of insoluble conductive material, a tower containing soluble metal-bearing material, means for circulating the electrolyte through said units and tower comprising a pump for elevating the electrolyte and causing it to flow through said tower and hence to said units by gravity, and a by-pass for diverting a portion of the electrolyte around said soluble material.

58. Electrolytic apparatus comprising, in combination, a trough through which the electrolyte flows, an endless conductor moving in said trough, a body of soluble metal-bearing material for replenishing the electrolyte, a chamber into which the electrolyte discharges from said trough by gravity, and a pump and conduit means for elevating the electrolyte from said chamber for effecting flow of electrolyte through said trough and body of soluble metal-bearing material.

59. That method of making metallic sheets by electro-deposition which comprises rotating a cathode in close proximity to an anode of insoluble conductive material circulating the electrolyte to cause it to pass in a continuous swift-flowing stream between the anode and cathode, and replenishing the electrolyte with metal content after it passes from between the cathode and anode.

60. The method of making metallic sheets which comprises moving a cathode in close proximity to an anode of insoluble conductive material, circulating the electrolyte to cause it to pass between said cathode and anode in a swift-flowing continuous stream and then to pass through soluble metal-bearing material.

61. The method of making metallic sheets which comprises moving a cathode in close proximity to an anode of insoluble conductive material, circulating the electrolyte to cause it to pass between said cathode and anode in a swift-flowing continuous stream, while part of the cathode is in contact therewith, and while passing the electrolyte in contact with soluble metal bearing material.

62. The method of making metallic sheets by electro-deposition which comprises moving a cathode in close proximity to an anode of insoluble conductive material, circulating the electrolyte to cause it to pass in a continuous swift-flowing stream between the anode and cathode, while part of the cathode is in contact therewith, and replenishing the metal content of the electrolyte after it passes from between the cathode and anode.

63. The method of electro-depositing copper which comprises circulating the electrolyte to cause it to flow between the surface of a cathode and the surface of insoluble conductive material in a swift continuous stream and to flow in contact with copper-bearing material on which is impressed a voltage of not less than one and one-half volts.

64. Electrolytic apparatus for making metal sheets, comprising, in combination, means providing a moving endless cathode surface bounded at its edges by a surface of non-conductive material, and means for stripping from the cathode surface the sheet deposited thereon.

65. Electrolytic apparatus for making metal sheets, comprising, in combination, means providing a moving endless cathode surface bounded at its edges by a surface of rubber, and means for stripping from the cathode surface the sheet deposited thereon.

66. Electrolytic apparatus for making metal sheets, comprising, in combination, means providing a rotating cylindrical cathode surface abutting at its ends with a ring of rubber, and means for stripping from the cathode surface the sheet deposited thereon.

67. That method of increasing the metal

content of an electrolyte which comprises allowing the electrolyte to act on metal-bearing material while controlling the rate of solution of metal by varying the ratio of the amount of electrolyte to the amount of surface of said material on which the electrolyte acts.

68. The method of increasing the metal content of an electrolyte which comprises allowing the electrolyte to act on metal-bearing material while controlling the rate of solution of metal by varying the amount of the electrolyte acting on said material.

In testimony whereof, I have signed my name to this specification.

MATTHEW M. MERRITT.