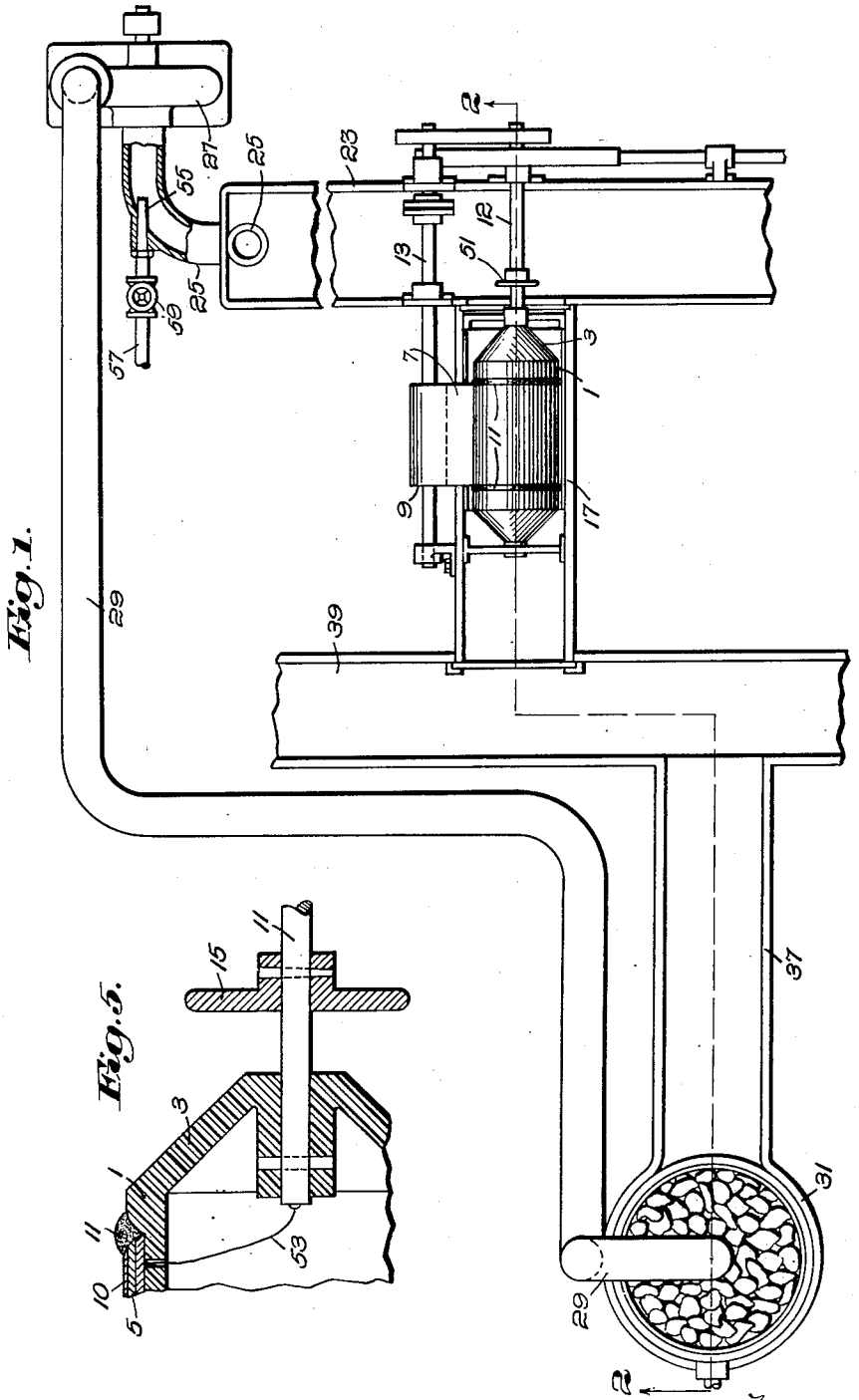
Sept. 28, 1926. 1,601,694

M. M. MERRITT

ELECTROLYTIC DEPOSITION OF METALS

Filed August 20, 1925 2 Sheets-Sheet 1



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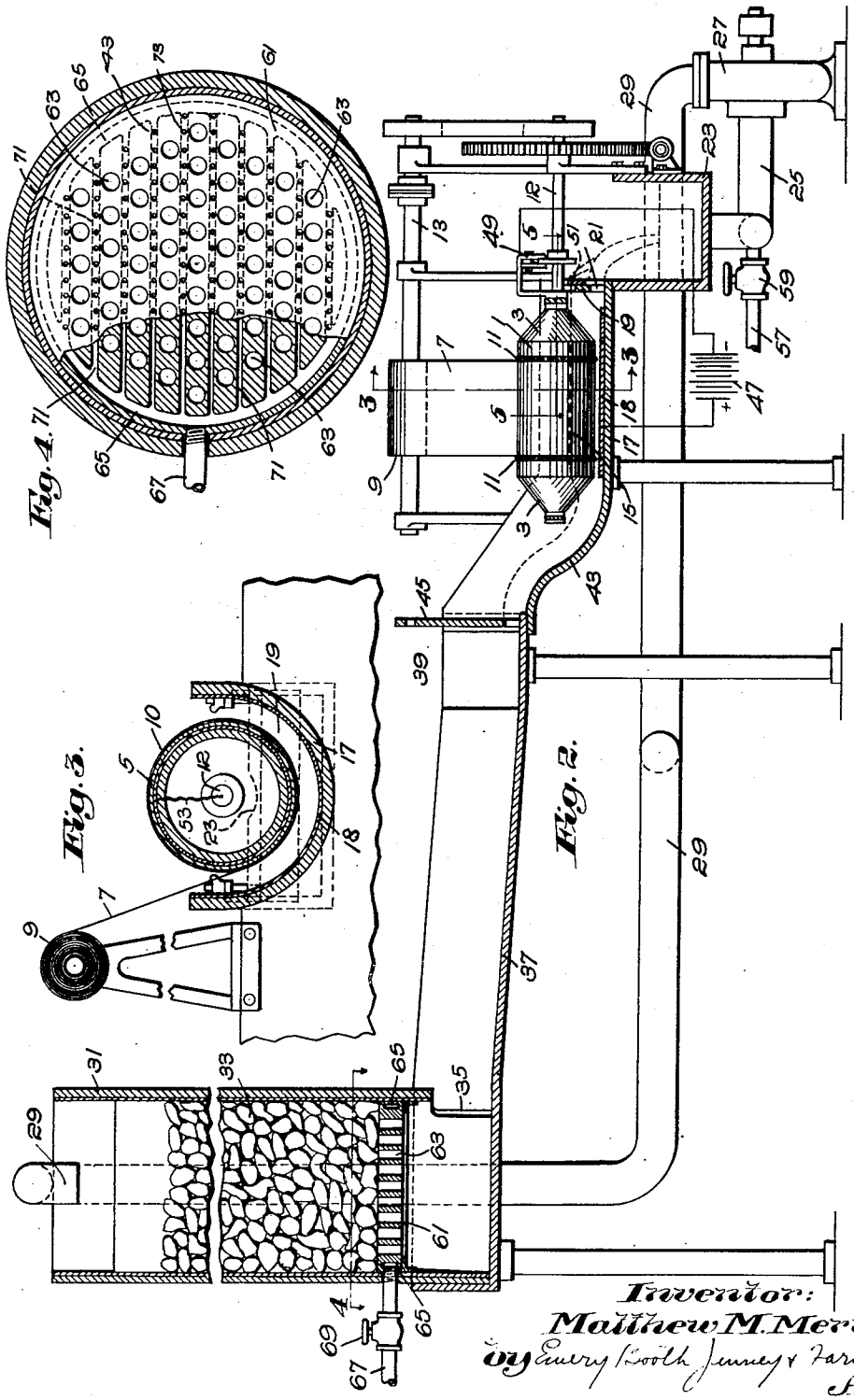

Fig. 4.

Fig. 3.

Fig. 2.

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UNITED STATES PATENT OFFICE

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ELECTROLYTIC DEPOSITION OF METALS.

Application filed August 20, 1925. Serial No. 51,381.

My invention pertains to improvements in electrolytic methods and apparatus and particularly but not exclusively to methods of 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:

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

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

Figs. 3, 4 and 5 are respectively sections on the lines 3—3, 4—4 and 5—5 of Fig. 2.

Referring to the drawings I have shown a cylindrical drum 1 provided with frusto-conical or tapered ends 3, the drum being formed of wood, porcelain, or other suitable non-conducting material and carrying intermediate its length an endless sheet 5 of copper or other suitable conductive material constituting a cathode on which the sheet metal to be formed is deposited from the electrolyte. The length of the cathode corresponds to the width of the deposited sheet indicated at 7. As the sheet is deposited on the cathode it is stripped therefrom by a rotating drum 9, the surface of the cathode being treated with mercury to form thereon a thin coating 10 of amalgam which facilitates the stripping operation. For further facilitating the stripping operation and for giving the sheet a properly formed edge the cathode abuts at each end with a ring 11 of rubber or other suitable non-conducting material carried by the drum. For rotating the drums 1 and 9 in order to strip the deposited sheet from the former and wind it upon the latter the same are respectively carried on shafts 11 and 13 which are conjointly rotated by suitable mechanism not necessary to be described herein.

The drum is in contact conveniently to a depth of approximately one-third its diameter with a swift-flowing continuous stream of electrolyte the level of which is indicated at 15 in Fig. 2. The electrolyte flows by the drum in a trough 17 having a lining 18 (Fig. 3) of lead or other suitable conductive metal insoluble in the electrolyte. The lining 18 constitutes an anode and has its surface uniformly distributed in relatively close proximity to the surface of the cathode 5. The level of the electrolyte in the trough is maintained substantially horizontal, that is parallel to the axis of the drum, by means of an adjustable dam 19 having a lower opening 21 through which the major portion of the electrolyte discharges from the trough, the remaining small portion of the electrolyte flowing over the dam through a notch 22 formed in its upper edge. The electrolyte leaving the trough 17 discharges into a trough 23, leaving the latter through a pipe 25 connected to a pump 27 which forces the electrolyte through a pipe 29 discharging into the upper end of an electrolyte replenishing chamber, herein illustrated as a tower 31 containing a body 33 of soluble metal-bearing material for replenishing the electrolyte. This soluble material may be in any suitable form as, for example, ore, suitable metallic salts, or metal scrap, preferably the latter.

The electrolyte discharges from the lower end of the tower through an orifice 35 into a downwardly inclined chute 37 which conducts the electrolyte into a distributing trough 39, the latter communicating with any desired number of troughs 17, only one of which, however, is illustrated in the drawings. For giving the electrolyte considerable velocity as it passes through the troughs 17 between the conductors constituting the cathode and the anode the chute connecting the trough 41 with the trough 17 at its bottom is constructed in form of an apron 43. The amount of electrolyte entering each trough 17, if a plurality of troughs 17 are provided, is controlled by a suitable gate 45.

In practice the negative terminal of a battery 47 or other source of direct current electro-motive force is connected to the cathodes by means herein conventionally illustrated as a brush 49 in contact with a slip ring 51 carried by the shaft 11 in electrical communication therewith, the shaft being placed in electrical communication with the cathode by means of a conductor 53 (Fig. 5). The positive pole of the battery 47 is connected to the insoluble lining 18 of the

trough by means of a terminal (not shown herein) running the length of that portion of the lining opposite the cathode 5.

It will be observed that with the battery connected to the cathode and anode as above described that the metal-bearing material 33 in the tower will be maintained at the same electrical potential as the lining 18 of the trough by reason of the fact that the electrolyte constitutes a conductor placing the two in electrical communication. I have found that by thus impressing sufficient potential on the metal-bearing material the metal of the same will enter into solution in the electrolyte, which enables me to replace in the electrolyte in whole or in part the metal deposited from the electrolyte upon the cathode. This method of replenishing the electrolyte by impressing a suitable potential on metal-bearing material in contact with which the electrolyte flows is applicable to all metals below hydrogen in the electromotive series. When depositing copper on the cathode I preferably use as electrolyte a copper sulphate solution containing a small percentage of free sulphuric acid, and for replenshing the metal content of the electrolyte I preferably use sheet metal scrap in the tower 31. I have found when using an insoluble anode that satisfactory results can be obtained when a positive electrical potential of not less than one and one-half volts is impressed on the copper scrap, although a much lower voltage can be employed when a soluble anode is used.

Apparently the rate of replenishment of the electrolyte effected by the impressed voltage is largely directly dependent upon the amount of electrolyte and the amount of surface of soluble metal-bearing material on which the electrolyte acts in a given time. Preferably the soluble metal-bearing material in the tower 31 is insufficient in amount compared to the amount of electrolyte flowing through the tower to effect, by action of the impressed potential alone, a rate of replenishment as great as the rate of deposition of metal on the cathode. For increasing the rate of replenishment above that effected by the impressed voltage I preferably cause the electrolyte to act on the soluble metal-bearing material in the presence of an oxidizing agent, and for this purpose I have herein illustrated means for introducing air into the electrolyte. In practice I preferably introduce enough air to effect in conjunction with the replenishment caused by the impressed voltage an aggregate rate of replenishment sufficient gradually to increase the metal-content of the electrolyte to a convenient maximum limit, and when this limit is reached interrupt the supply of air to the electrolyte until the metal-content of the electrolyte decreases to a desired minimum limit, whereupon air is again introduced into the electrolyte again to raise the metal-content to the desired maximum limit, this operation being repeated throughout the run. As an example of the practice of my method but without limitation thereto I have found that satisfactory results can be obtained when the upper limit of metal-content of the electrolyte corresponds to 32 ounces of copper sulphate crystals per gallon of electrolyte and the lower limit of metal-content corresponds to 26 ounces of copper sulphate crystals per gallon, the sulphuric acid concentration at these limits being respectively 6 and 10 per cent, and these limits of metal and acid content corresponding respectively to electrolyte specific gravities of 1.24 and 1.18.

For introducing air into the electrolyte I have illustrated the pipe 25 as provided with an interiorly located nozzle 55 supplied with compressed air by a pipe 57 controlled by a valve 59, it being obvious that the amount of air introduced into the electrolyte by the nozzle 55 may be controlled by the degree of opening of the valve 59. It will be observed that the pipe 25 constitutes the suction pipe of the pump 27, the latter preferably being of the centrifugal type so as to intimately mix the air with the electrolyte as the latter passes through the pump.

I also have illustrated means for introducing air into the electrolyte at the tower 31. To this end I have shown the metal-bearing material in the tower 31 supported on a grate 61 having openings 63 through which the electrolyte passes after desceding through the metal-bearing material. The grate consists of a disk having an internal circumferential conduits 65 in communication with a pipe 67 supplying the conduit with compressed air and controlled by a valve 69 for regulating the amount of air entering the conduit. Extending across the grate I provide internal conduits 71 in communication at opposite ends with the circumferential conduit 65, the conduits 71 being placed in communication with the upper surface of the grate by rows of perforations 73, which construction permits the compressed air to escape from the grate through the perforations and pass upwardly through the electrolyte and body of metal-bearing material, the excess of air discharging from the top of the tower.

My explanation of the action of the air introduced into the electrolyte in effecting solution of the metal of the metal-bearing material is that the air oxidizes the metal to form an oxide readily soluble in the acid of the electrolyte.

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. That method of increasing the metal content of an electrolyte which comprises allowing the electrolyte to act on metal-bearing material in the presence of an oxidizing agent for accelerating the solution of said material.

2. That method of increasing the metal content of an electrolyte which comprises allowing the electrolyte to act on metal-bearing material on which is impressed a positive electrical potential in the presence of an oxidizing agent for accelerating the solution of said material.

3. That method of increasing the metal content of an electrolyte which comprises allowing the electrolyte to act on metal-bearing material in the presence of air introduced into the electrolyte for accelerating the solution of said material.

4. That method of increasing the metal content of an electrolyte which comprises introducing air into the electrolyte for accelerating solution and allowing said air and electrolyte to act on metal-bearing material on which is impressed a positive electrical potential.

5. That method of electro-deposition which comprises rapidly flowing the electrolyte past a cathode for deposition thereon of metal from the electrolyte, and replenishing the metal content of the electrolyte by flowing the electrolyte in contact with soluble metal-bearing material in the presence of an oxidizing agent for accelerating the solution of said material.

6. That method of electro-deposition which comprises flowing the electrolyte past a cathode for deposition thereon of metal from the electrolyte, and replenishing the metal content of the electrolyte by flowing the electrolyte in contact with soluble metal-bearing material in the presence of an oxidizing agent for accelerating the solution of said material and while impressing on said soluble material a positive electrical potential.

7. That method of electro-deposition which comprises flowing the electrolyte past a cathode for deposition thereon of metal from the electrolyte, and replenishing the metal content of the electrolyte by introducing air into the electrolyte for accelerating solution and flowing it in contact with soluble metal-bearing material.

8. That method of electro-deposition which comprises flowing the electrolyte past a cathode for deposition thereon of metal from the electrolyte, and replenishing the metal content of the electrolyte by introducing air into the electrolyte for accelerating solution and flowing it in contact with soluble metal-bearing material on which is impressed a positive electrical potential.

9. That method of electro-deposition which comprises circulating the electrolyte to effect flow thereof rapidly between the opposed surfaces of metallic conductors and then in contact with soluble metal-bearing material in the presence of an oxidizing agent for accelerating the solution of said material, while maintaining said conductors at different electrical potentials.

10. That method of electro-deposition which comprises circulating the electrolyte to effect flow thereof rapidly between the opposed surfaces of metallic conductors and then in contact with soluble metal-bearing material, introducing air into the electrolyte for accelerating the solution of said soluble material, and maintaining said conductors at different electrical potentials.

11. That method of electro-deposition which comprises circulating the electrolyte to effect flow thereof rapidly between the opposed surfaces of metallic conductors one of which is insoluble in the electrolyte and then in contact with soluble metal-bearing material in the presence of an oxidizing agent for accelerating the solution of said soluble material, while the insoluble conductor is connected to the positive pole of a source of direct-current electro-motive-force and the opposed conductor is connected to the negative pole of the same source.

12. That method of electro-deposition which comprises circulating the electrolyte to effect flow thereof rapidly between the opposed surfaces of metallic conductors one of which is insoluble in the electrolyte and then in contact with soluble metal-bearing material, introducing air into the electrolyte for accelerating the solution of said soluble material, while the insoluble conductor is connected to the positive pole of a source of direct-current electro-motive-force and the other conductor is connected to the negative pole of the same source.

13. That method of electro-deposition of copper which comprises circulating a sulphuric acid electrolyte to effect flow thereof rapidly between the opposed surfaces of metallic conductors one of which is insoluble in the electrolyte and then in contact with copper-bearing material in the presence of a copper oxidizing agent for accelerating solution of said material, while the insoluble conductor is connected to the positive pole of a source of direct-current electro-motive-force and the other conductor is connected to the negative pole of the same source.

14. That method of electro-deposition of copper which comprises circulating a sulphuric acid electrolyte to effect flow thereof rapidly between the opposed surfaces of

metallic conductors one of which is insoluble in the electrolyte and then in contact with copper-bearing material, introducing air into the electrolyte for accelerating solution of said copper-bearing material, while said insoluble conductor is connected to the positive pole of a direct-current source of electromotive-force and the other conductor is connected to the negative pole of the same source.

15. That method of controlling the metal-content of an electrolyte from which metal is deposited on a cathode which comprises allowing the electrolyte to act on soluble metal-bearing material in the presence of varying amounts of an oxidizing agent, the latter acting to accelerate solution of said soluble material.

16. That method of controlling the metal-content of an electrolyte from which metal is deposited on a cathode which comprises allowing the electrolyte to act on soluble metal-bearing material in the presence of varying amounts of air introduced into the electrolyte, said air acting to accelerate solution of said soluble material.

17. That method of controlling the metal-content of an electrolyte from which metal is deposited on a cathode which comprises allowing the electrolyte to act on soluble metal-bearing material on which is impressed a positive electrical potential in the presence of varying amounts of air introduced into the electrolyte for accelerating solution of said soluble material.

18. That method of electro-deposition which comprises passing the electrolyte between the opposed surfaces of conductors one of which constitutes an anode and the other a cathode for deposition on the latter of metal from the electrolyte, replenishing the metal-content of the electrolyte by allowing it to act on soluble metal-bearing material in the presence of air introduced into the electrolyte for accelerating solution of said soluble material, and controlling the effective rate of replenishment by varying the amount of air introduced.

19. That method of electro-deposition which comprises depositing metal from the electrolyte and replenishing the metal-content of the electrolyte by circulating the electrolyte to effect flow thereof rapidly between the opposed surfaces of metallic conductors one of which constitutes an anode and the other a cathode and then in contact with soluble metal-bearing material in the presence of air introduced into the electrolyte for accelerating solution of said soluble material, and controlling the effective rate of replenishment by varying the amount of air introduced.

20. That method of electro-deposition of copper which comprises depositing copper on a cathode from a sulphuric acid electrolyte by circulating the electrolyte to effect flow thereof between the opposed surfaces of conductors one of which constitutes said cathode and the other of which is insoluble in said electrolyte and constitutes an anode, replenishing the metal-content of the electrolyte by allowing it while circulating to act in the presence of air introduced thereinto on soluble metal-bearing material, and controlling the effective rate of replenishment by varying the amount of air introduced.

21. That method of replenishing the metal-content of a circulating electrolyte from which metal is deposited on a cathode, which comprises allowing the electrolyte to act on soluble metal-bearing material on which an electrical potential is impressed to effect thereby replenishment of the electrolyte at a rate slower than the rate of deposition on the cathode, while introducing air into the electrolyte to effect thereby additional replenishment to increase the aggregate rate thereof to a value at least equal to the rate of deposition.

22. That method of replenishing the metal-content of a circulating electrolyte from which metal is deposited on a cathode, which comprises allowing the electrolyte to act on soluble metal-bearing material on which an electrical potential is impressed to effect thereby replenishment at a rate slower than the rate of deposition on the cathode, and intermittently increasing the aggregate rate of replenishment to a value greater than the rate of deposition by introducing air into the electrolyte.

23. That method of electro-deposition which comprises depositing metal from a circulating electrolyte on a cathode, maintaining the metal-content of the electrolyte between upper and lower limits by allowing the electrolyte to act on soluble metal-bearing material on which an electrical potential is impressed to effect thereby a rate of replenishment of the metal-content of the electrolyte slower than the rate of deposition on the cathode, and when the lower limit of metal-content is reached introducing air into the electrolyte in amount sufficient to effect thereby additional replenishment for raising the metal-content to the upper limit.

24. Electrolytic apparatus comprising in combination, a cathode, soluble metal-bearing material on which is impressed an electrical potential, means for circulating the electrolyte in contact with said cathode and soluble material for depositing metal from the electrolyte on said cathode and replenishing the metal-content of the electrolyte from said material, the amount of electrolyte acting on said material relatively to the amount of said material being insufficient to effect replenishment of the metal-content as fast as it is decreased by deposition on

said cathode, and means for intermittently increasing the rate of replenishment of the metal-content of the electrolyte to a value greater than the rate of deposition of metal on said cathode comprising means for introducing air into said electrolyte.

25. Electrolytic apparatus comprising in combination, conductors constituting a cathode and an anode, a body of soluble metal-bearing material for replenishing the electrolyte, means for circulating the electrolyte to effect flow thereof between said cathode and anode and in contact with said soluble material, and means for introducing air into said electrolyte in amount sufficient to effect substantial acceleration of the rate of solution of said material in the electrolyte.

26. Electrolytic apparatus comprising in combination, conductors constituting a cathode and an anode, a body of soluble metal-bearing material for replenishing the electrolyte, means comprising a pump for circulating the electrolyte to effect flow thereof between said cathode and anode and in contact with said soluble material, and means for introducing air into the electrolyte to effect mixture of the two by said pump.

27. Electrolytic apparatus comprising in combination, conductors constituting a cathode and an anode, a body of fragments of metal-bearing material for replenishing the electrolyte, means for circulating the electrolyte between said cathode and anode and through said body, and means for introducing air into said body in amount sufficient to effect substantial acceleration of the rate of solution of said material in the electrolyte.

28. Electrolytic apparatus comprising in combination, conductors constituting a cathode and an anode, a body of fragments of metal-bearing material for replenishing the electrolyte, means for circulating the electrolyte between said cathode and anode and downwardly through said body, and means for introducing air into the lower portion of said body for passage upward therethrough in amount sufficient to effect substantial acceleration of the rate of solution of said material in the electrolyte.

29. Electrolytic apparatus comprising in combination, conductors constituting a cathode and an anode, a body of fragments of metal-bearing material for replenishing the electrolyte, means for circulating the electrolyte between said cathode and anode and through said body, said means comprising an open conduit containing said body, and means for introducing air into said body at the lower portion thereof for passage upwardly through said body in amount sufficient to effect substantial acceleration of the rate of solution of said material in the electrolyte.

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

MATTHEW M. MERRITT.