W. E. GREENAWALT.

ELECTROLYTIC APPARATUS.

APPLICATION FILED MAY 24, 1909.

1,043,096. **Patented Nov. 5, 1912.**

2 SHEETS—SHEET 1.

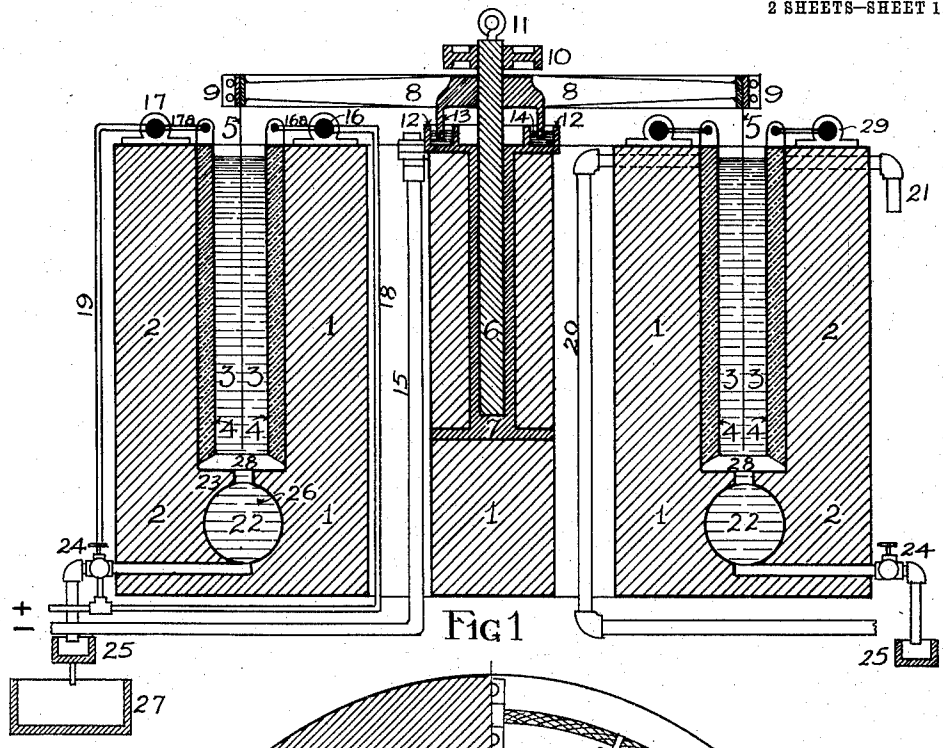

FIG 1

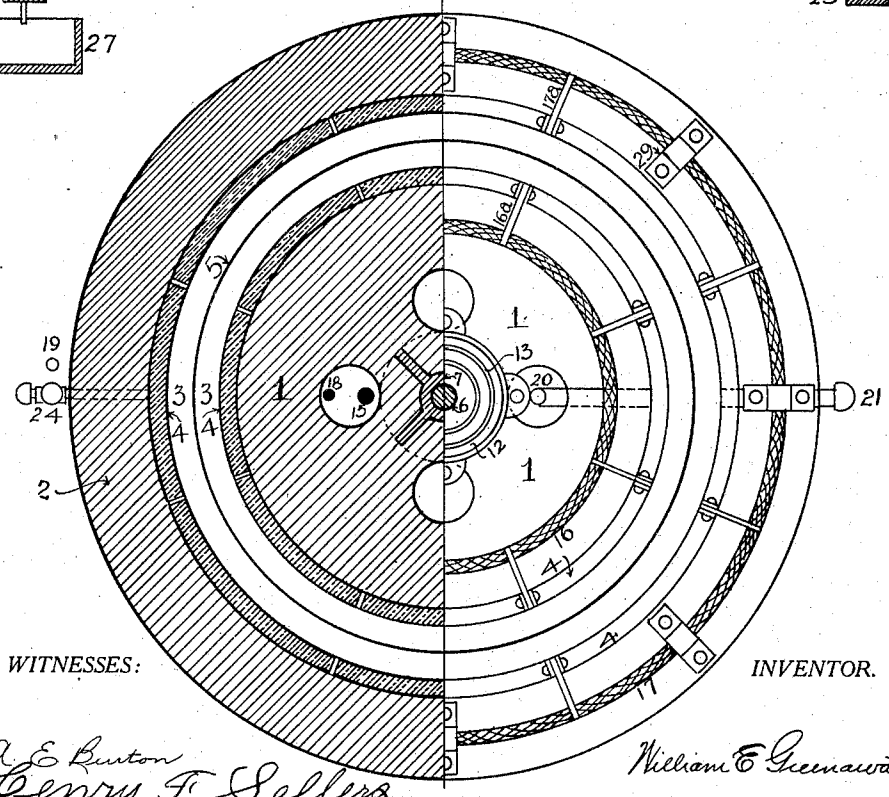

FIG 2

WITNESSES:

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Henry F. Sellers

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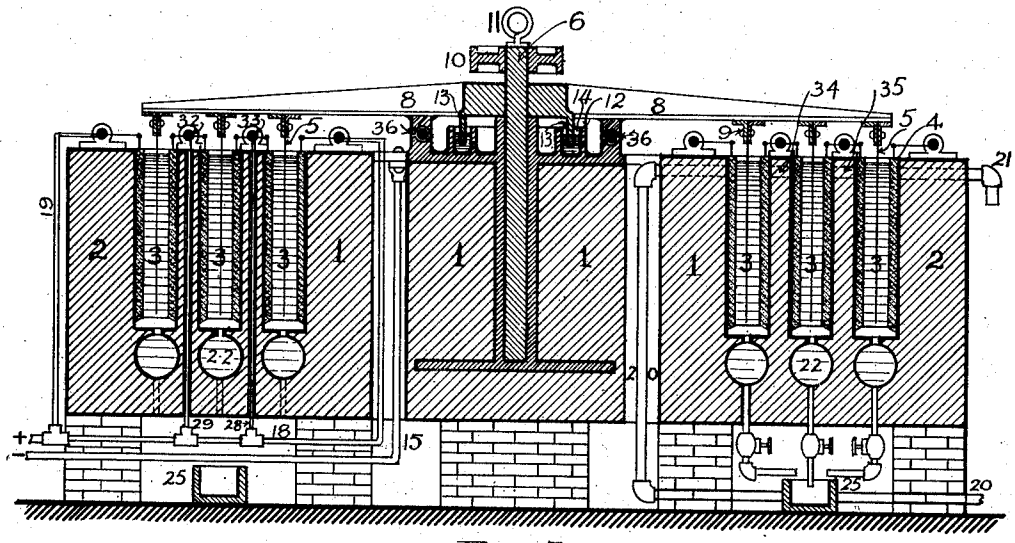

FIG. 3

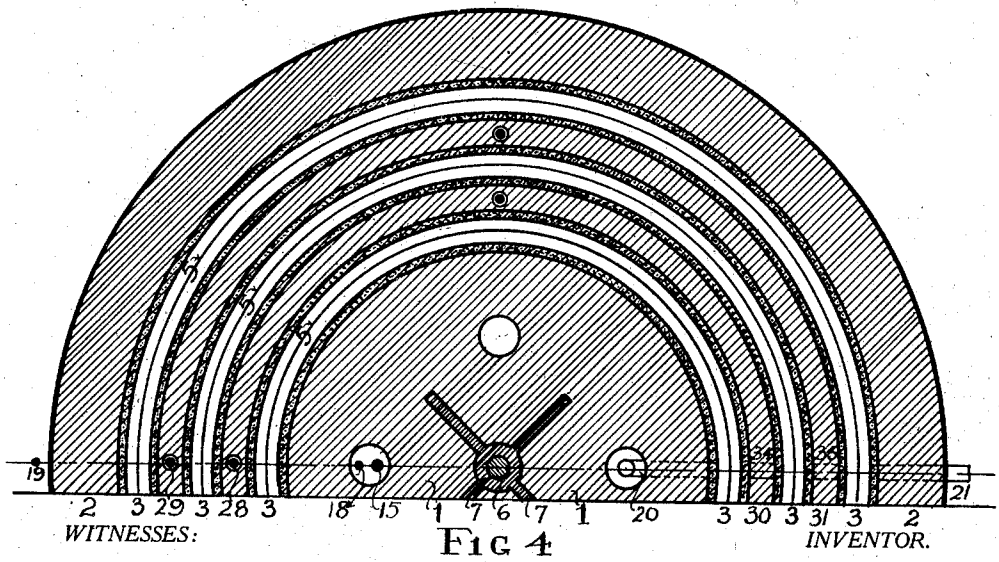

FIG 4

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ELECTROLYTIC APPARATUS.

1,043,096. Specification of Letters Patent. Patented Nov. 5, 1912.

Application filed May 24, 1909. Serial No. 498,081.

To all whom it may concern:

Be it known that I, WILLIAM E. GREENAWALT, a citizen of the United States, residing at Denver, in the county of Denver and State of Colorado, have invented certain new and useful Improvements in Electrolytic Apparatus, of which the following is a specification.

The apparatus may be used for the electrolytic decomposition of any of the metals which are capable of being deposited from a sulfate solution. It may also be used in the refining of copper and other metals. I shall, however, describe the apparatus more particularly with reference to the electrolysis of copper sulfate solutions in which lead is used as an insoluble anode, and having in mind copper sulfate solutions containing more or less impurities.

It is well known that no really satisfactory insoluble anode for the deposition of metals from sulfate solutions has yet been discovered. Lead has answered the purpose fairly well, and has been used in commercial operations, but the lead wears away rapidly under the oxidizing influence of the anode reactions. About one half pound of lead is peroxidized in the deposition of one pound of copper. The peroxid of lead adheres to the anode for some time, thus increasing the voltage of the process, and finally it drops to the bottom of the cell where it frequently gives trouble by causing short circuits of the electric current.

In the deposition of copper from impure sulfate solutions, the difficulties at the cathode are no less than those at the anode. A reguline deposit cannot be obtained under ordinary conditions from an impure electrolyte, except at the lowest current densities, and even under these conditions, trouble is likely to occur. It is desirable in all commercial installations, that the current density be fairly high, and that a reguline deposit be obtained from foul solutions, so that the cathode may be built up to any extent desired before it should be necessary to renew it. Moreover, the plant should be reasonably compact, and the output per unit of electrode area, reasonably large.

The accompanying drawings show, somewhat in detail, the improvement invented by me to overcome the difficulties enumerated, and embody the conditions thought to be desirable.

It is well known that cathodes rotating at a high speed greatly facilitates the deposition of reguline copper, and appears to be more effective than agitation of the electrolyte with a stationary cathode. The apparatus devised by me is so arranged that the cathode can be rotated at any speed desired, while at the same time the flow of fresh electrolyte and the electric current is uninterrupted. For the present purpose, lead anodes may be assumed to be in the apparatus and that the usual peroxidation takes place. Instead, however, of inclosing the anodes in bags or simply letting the peroxid drop to the bottom of the tank and there give trouble, arrangement is made to keep the anodes reasonably free from the peroxid, and to collect it in pockets in the bottom of the electrolyzer. When it has accumulated in sufficient amounts, it is washed out of the pockets, reduced to metallic lead, and again cast into anodes. The cost, therefore, of collecting the peroxid is practically *nil*, and notwithstanding that the wear of the anodes is considerable, the only cost of renewing them is in the reduction of the peroxid to metallic lead and recasting of the anodes, which per pound of copper deposited, is almost a negligible factor.

Referring to the drawings, Figure 1 represents a section through a simple electrolyzer, and Fig. 2 the plan. Fig. 3 represents a section through a compound electrolyzer, and Fig. 4 the corresponding plan. The simple and compound electrolyzers are essentially the same, except that the compound electrolyzer has a greater capacity and is more efficient than the simple electrolyzer.

In the drawings, 1 represents a central circular pier supporting the revolving mechanism on which the cathode is suspended, and containing openings or conductors for the introduction of the solution to the electrolyte compartment, and conductors for the electric current to the inner row of anodes and to the revolving cathode.

2 is the outer wall of the electrolyzer, concentric with the central pier, and 3 a space formed by the circular central pier 1 and outer wall 2, which contains the electrodes and the electrolyte.

4 shows concentric rows of anodes, intended, in the electrolysis of copper sulfate solutions with insoluble anodes, to be of lead, and lining the central pier, on one side and the outer wall on the other.

5 is the cathode revolving in the space between the two rows of anodes.

6 is a shaft, carrying the spindle 8, from which the cathode 5, is suspended.

7 is a socket built into the central pier, in which the shaft revolves.

8 is the spindle attached to the shaft, carrying the cathode 5, and 9 is a clamping arrangement to fasten the cathode to the spindle in cylindrical shape. The material of the cathode when electrolyzing copper sulfate solutions will ordinarily be sheet copper, made in lengths to conform to the diameter of the middle of the circular space containing the electrolyte.

10 is a pulley by means of which the revolving mechanism is driven.

11 is a hook or eye for removing the revolving mechanism, by lifting it from the socket containing the shaft. The revolving mechanism is removed from the cell when it is desired to change the cathode.

12 is a circular metal channel containing mercury 14, and 13 is a flange from the spindle dipping into the channel and the mercury, thereby making electrical contact between the stationary channel or conductor, and the revolving cathode. With the mercury contact, electrical connection is always assured when the revolving mechanism is in place, and when it is desired to remove the revolving mechanism, the mercury offers no delay.

15 is the electric conductor passing through the central pier, and connecting with the cathode through the spindle and mercury contact.

16 and 17 are electric conductors connecting with the anodes by means of the short bars 16^a and 17^a.

18 is the electric conductor passing through the central pier and communicating with the interior row of anodes.

19 is the exterior conductor, connecting with the exterior row of anodes.

20 is a pipe or conduit passing through the central pier for the introduction of the sulfate solution into the electrolyte compartment, and 21 is the exit pipe for the electrolyzed solution.

In the operation of the electrolyzer, the electric current flows through the conductors 18 and 19 and the circular rods 16 and 17 and thence through the anodes 4, decomposes the metal sulfate solution into metal, which is deposited at the cathode, and the acid radical, which is liberated at the anode, passes through the cathode 5, into the spindle 8, and, by means of the mercury contact 12, 13, and 14, passes out of the apparatus and back to the dynamo by means of the conductor 15. The solution, entering the electrolyzer by means of pipe 20, passes downwardly, under the revolving cathode, and then upwardly on the other side, and flows out through the exit pipe 21. If desired, the solution may be made to enter the electrolyte compartment at 21 and overflow at 20, but the first direction is preferred, especially in the compound electrolyzers.

29 are clamps attached to the electrolyzer for the purpose of holding the electric conductors in place.

Lead anodes, used in depositing copper from sulfate solutions, have proved the most satisfactory. The greatest objection to lead, as an insoluble anode, is its rapid wear, due to peroxidation of the lead. Instead of attempting to overcome this difficulty of peroxidation, it is my object, in this apparatus, to recognize it as a condition, and make provision to minimize the expense incident thereto by automatically collecting the disintegrated lead, whatever its form, reducing it again to metallic lead, and again casting it in anodes. In doing this, a pocket 22 is provided below the electrolyte space, and below the anodes and cathodes, so that the disintegrated lead, as it forms on the anodes may drop off and by the agitation of the electrolyte due to the revolving cathode, find its way down to the pocket, where the electrolyte is comparatively quiescent. By this arrangement there is no danger of electric short circuits, and the disintegrated lead may accumulate until it is convenient to remove it, which will ordinarily be at times when the cathode is replaced. The agitation of the electrolyte due to the revolving cathode, tends to remove the disintegrated anode material as fast as it is formed, and in this way the electromotive force required for electrolysis is less than it would be under similar conditions in a quiet electrolyte. If soluble anodes are used, as in the electrolytic refining of copper, the anode slime is similarly taken care of and finds its way down into the pockets where the agitation of the electrolyte in the electrolyte compartment will no longer affect it.

22 shows the pockets for the accumulation of disintegrated anode material, 23 projections for the support of the anodes, which also form a slot to more thoroughly separate the pocket from the influence of the agitated electrolyte. In order to still further maintain quiescence in the pockets, partitions 26 are placed at intervals which stop the flow of electrolyte in the direction of the rotating electrode. The pockets are provided at intervals with outlet pipes and valves 24, so that when the disintegrated anode material accumulates in sufficient quantities for its removal, these outlets are opened and the contents of the pockets washed into a launder 25, and from thence into a settling tank 27, where it is accumulated and washed. It is then charged into a furnace, with a reducing agent, and the resulting lead again cast into anodes.

28 are strips of some suitable material, such as wood or earthenware, spanning the slot to the pocket, and beveled at both ends so as to keep the anodes in position, flanking the pier and walls, while at the same time any anode may be removed without disturbing the others. The strips also act to further isolate the pocket from the electrolyte compartment.

In the way described, the only expense of the anodes is in the accumulation of the peroxid, reducing it to metallic lead, and recasting it into anodes, which should be a small item in the operation of a commercial plant. The lead is not consumed or lost, so that after the first cost of the lead, it remains permanently in the plant, allowing, of course, for a small unavoidable loss in manipulation.

Fig. 3 shows a section through a compound electrolyzer, and Fig. 4 the corresponding plan, in which there are several rows of anodes and corresponding rows of cathodes, embodied in one machine. It is in no way essentially different from that shown in Figs. 1 and 2, but simply modified in some of the details to make its working practical for larger units.

In Figs. 3 and 4, two interior circular walls 30 and 31 are shown, dividing the electrolyte space into three compartments. Penetrating these walls at intervals are ducts or openings through which, by means of the conductors 28 and 29, the electric current is supplied to the circular rods 32 and 33, which in turn supply the electricity to the respective anodes. The current to the respective cathodes is supplied through the mercury contact 12, 13, and 14, as in Figs. 1 and 2. The solution, entering the electrolyzer through the pipe 20, enters the inner compartment of the electrolyte space, flows downwardly, under the cathode, then upwardly on the other side, through the opening 34 in wall 30, into the intermediate electrolyte compartment, flows downwardly again under the intermediate cathode and upwardly again on the other side, through the opening 35 in the wall 31, into the outer electrolyte compartment, downwardly again under the cathode and up again on the outer side, and flows out through pipe 21. It will be noticed that by this method of circulating the electrolyte about the electrodes the lineal speed of rotation is somewhat proportional to the amount of copper in the electrolyte, and also, in a measure, proportional to the current density. The current density can always be controlled by the number of anodes placed in the concentric rows. The electrolyte is the richest in metal content on entering the electrolyzer, at the interior row of anodes, where the rotation in feet per minute, is the slowest, while the outgoing electrolyte, where the speed of rotation is the fastest, is the leanest in metal content. As the electrolyte is impoverished in circulating through the electrolyzer, the lineal speed of rotation is increased, so that the metal ions coming in contact with the electrodes, may be quite constant. The deposition of metal on the cathode is therefore quite uniform, notwithstanding the progressive impoverishment of the electrolyte as it passes through the electrolyzer.

In order to relieve the shaft of the great weight in the larger apparatus, the revolving mechanism is supported on ball bearings as shown at 36, Fig. 3. The shaft in such cases is simply used to steady the rotation. The ball bearing, like the shaft, is supported by the socket embedded in the central pier. If it is desired to renew the cathodes, the entire revolving mechanism is lifted up by a traveling crane, and taken away, while a duplicate revolving mechanism, with the cathode sheets already attached, is immediately put into place, all of which can be done in a few minutes. The mercury contact automatically makes electric connection when the revolving mechanism is in place. The socket in the central pier may be used either for the shaft or for the ball bearing, or for both, for carrying the revolving mechanism which carries the cathode.

I am aware that in many electrolyzers for the decomposition of metal sulfates, as in the refining of copper, a suitable space is provided in the tank below the electrodes for the accumulation of anode slimes without short circuiting the electric current. Such an arrangement is not comprehended in the meaning of the term "pocket," which is intended to be confined to a space somewhat aside from the main body of the tank, and more or less undisturbed by the agitation caused by the revolving electrodes.

In the construction of the apparatus, the central pier will usually be built of concrete with the socket embedded in it. The holes for the various conductors of electricity and electrolyte can readily be provided for by embedding porcelain tubes in the cement. The conductors may be embedded in the cement without tubing of any kind, but this would be disastrous in the event at any time, that it would be found necessary to replace the conductors. The outer wall will ordinarily be of cement also, but may be constructed of wood. An ordinary round wooden tank with a circular concrete pier built up in the middle will answer the purpose fairly well for a simple apparatus. As cement is attacked by acids, it is advisable to thoroughly paint the electrolyte compartments with a hydrocarbon paint, or better, line it with suitable glazed brick laid in asphalt or tar. The intermediate walls may be made of cement, painted, or of special shaped brick so as to give true and concen-

tric circles. The electric conductors passing up through the intermediate walls are protected from the electrolyte by porcelain or rubber tubes.

A simple modification of the apparatus would be to have the cathodes stationary and revolve the anodes, as the agitation of the electrolyte due to the revolving anodes would be sufficient to give a reguline deposit on a stationary cathode. Nevertheless, while such a modification is possible, the results are not to be compared with those of the revolving cathode, between stationary anodes.

It is not necessary to build the central pier in one solid mass. Convenience and economy will determine the details of construction.

I claim:—

1. In electrolytic apparatus the combination of a central circular pier; an outer wall concentric with the central pier; a space between the outer wall and central pier forming a circular channel concentric with the outer wall and central pier and adapted to contain the electrolyte; anodes immersed in the electrolyte and adjacent to the vertical walls of the channel thereby forming two concentric rows of anodes; means of supplying electricity to the interior and exterior rows of anodes; cathode revolving between said rows of anodes; suitable electrical connections between the stationary conductor and the revolving cathode, and means of circulating the electrolyte down and up about the cathode while the cathode is revolving about a vertical axis between the anodes.

2. In electrolytic apparatus the combination of a central circular pier; an outer wall concentric with the central circular pier; a space between the outer wall and central pier forming a circular-channel and adapted to contain the electrolyte; anodes immersed in the electrolyte and adjacent to the vertical walls of the channel thereby forming two concentric rows of anodes; perforations through the central pier for the passage of electrolyte and electric current; cathode revolving between said rows of anodes; suitable electrical connections between the stationary conductor and the revolving cathode, and means of circulating the electrolyte down and up about the cathode while the cathode is revolving between the anodes.

3. In electrolytic apparatus the combination of a central circular pier; an outer wall concentric with the central pier; a space between the central pier and outer wall; intermediate walls dividing the space into compartments thereby forming concentric circular channels adapted to contain the electrolyte; anodes immersed in the electrolyte and adjacent to the vertical walls of the channels thereby forming two concentric rows of anodes for each compartment; cathodes revolving between the respective rows of anodes; means of supplying electricity to the respective rows of anodes; means of supplying electricity to the respective revolving cathodes, and means of introducing the electrolyte into the inner compartment of the electrolyzer, circulating it about the respective cathodes and withdrawing it from the outer compartment.

4. In an electrolytic apparatus the combination of a central circular pier; an outer wall concentric with the central pier; a space between the central pier and outer wall; intermediate walls dividing the space into compartments thereby forming concentric circular channels adapted to contain the electrolyte; anodes immersed in the electrolyte and adjacent to the vertical walls of the channels thereby forming two concentric rows of anodes for each compartment; cathodes revolving between the respective rows of anodes; means of supplying electricity to the respective rows of anodes; means of supplying electricity to the respective revolving cathodes; means of introducing the electrolyte into the inner compartment of the electrolyzer, circulating it about the respective electrodes, and withdrawing it from the outer compartment; and electrodes arranged in concentric circles so that the lineal speed of the respective rotating cathodes will be greater as the electrolyte becomes impoverished in the metal being deposited.

5. In electrolytic apparatus the combination of a central circular pier; an outer wall concentric with the central pier; a space between the outer wall and central pier forming a circular channel adapted to contain the electrolyte; anodes immersed in the electrolyte and adjacent to the vertical walls of the channel thereby forming two concentric rows of anodes; cathode revolving between said rows of anodes; means of supplying electricity to the interior row of anodes through perforations in the central pier; suitable electrical connections between the stationary conductor and the revolving cathode; means of circulating the electrolyte about the electrodes by introducing it on one side of the cathode and withdrawing it from the other; and pockets located below the electrolyte space for the accumulation of disintegrated anode material.

6. In electrolytic apparatus the combination of a central circular pier; an outer wall concentric with the central pier; a space between the outer wall and central pier; intermediate walls dividing the space into compartments thereby forming concentric circular channels adapted to contain the electrolyte; anodes immersed in the electrolyte and adjacent to the vertical walls of the channels thereby forming two concentric rows of anodes for each compartment; cathodes revolving between the respective

rows of anodes; means of supplying electricity to the respective anodes; means of supplying electricity to the respective cathodes; means of introducing the electrolyte into the inner compartment of the electrolyzer, circulating it about the cathodes and withdrawing it from the outer compartment; and pockets located below the electrolyte space for the accumulation of disintegrated anode material.

7. In electrolytic apparatus the combination of a cathode revolving about a vertical axis; concentric rows of anodes on either side of the cathode, and means of introducing the electrolyte on one side of the cathode circulating it down and up and then withdrawing it from the other side of the cathode.

8. In electrolytic apparatus the combination of a cathode revolving about a vertical axis; concentric anodes on either side of the cathode, and means of circulating the electrolyte down and up vertically about the cathode while the cathode is revolving about a vertical axis between the anodes.

9. In electrolytic apparatus the combination of a plurality of circular electrolyte compartments communicating with one another; anodes adjacent to the side walls of the compartments thereby forming concentric rows of anodes in pairs; and cathodes revolving between the respective pairs of rows of anodes so that the lineal speed of the respective cathodes becomes greater as the electrolyte is impoverished in the metal being deposited.

10. In electrolytic apparatus the combination of a plurality of circular electrolyte compartments communicating with one another; electrodes of one sign adjacent to the side walls of the respective compartments thereby forming two concentric rows of electrodes for each compartment; and means of revolving electrodes of the opposite sign between the rows of stationary electrodes so that the lineal speed of the respective revolving electrodes will be greater as the electrolyte in the respective compartments becomes impoverished in the metal being deposited.

11. In electrolytic apparatus the combination of an electrode of one sign revolving about a vertical axis; stationary electrodes of the opposite sign arranged in concentric circles about the revolving electrode, and means of circulating the electrolyte down and up vertically about the revolving electrode while the revolving electrode is revolving between the stationary electrodes.

12. In electrolytic apparatus the combination of a series of concentric rows of anodes arranged in pairs; cathodes revolving between each pair of rows of anodes; and means of introducing the electrolyte into the compartment at the interior row of anodes, circulating it about the intermediate electrodes, and withdrawing it at the outer row of anodes.

WILLIAM E. GREENAWALT.

Witnesses:

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