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APPARATUS FOR ELECTROLYTIC DEPOSITION.

APPLICATION FILED OCT. 31, 1913.

1,239,443. **Patented Sept. 11, 1917.**

Fig. 1.

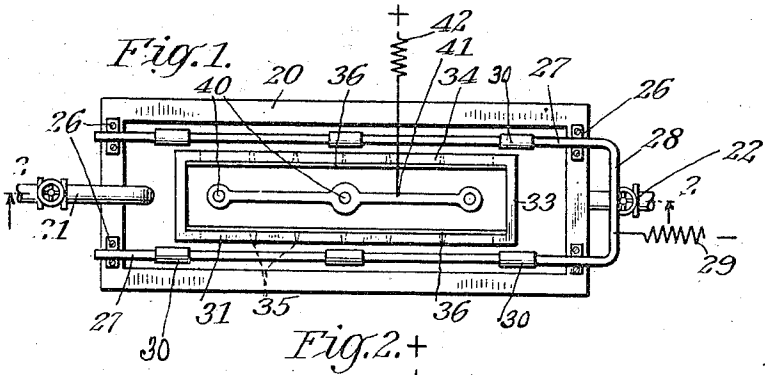


Fig. 2.

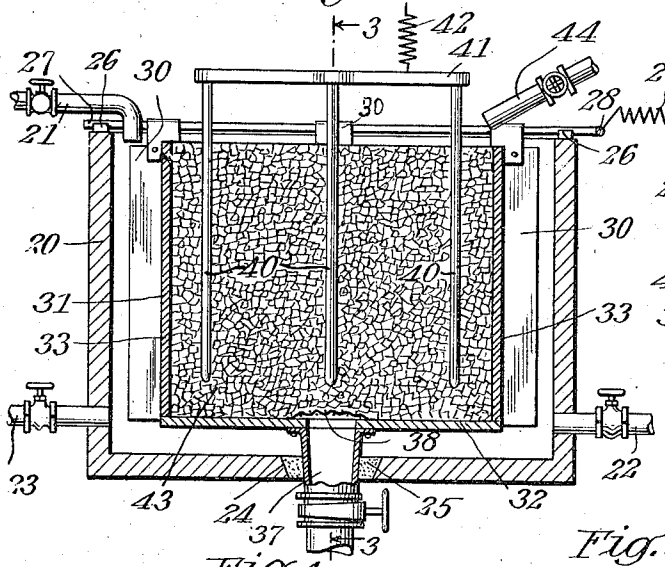


Fig. 3.

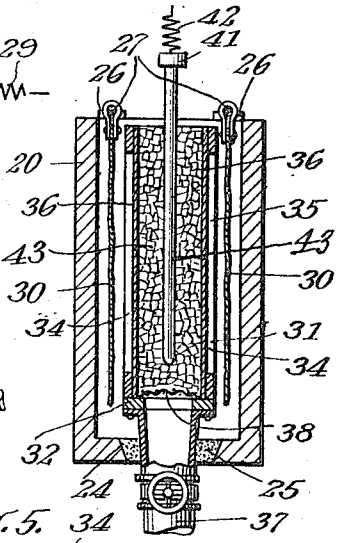


Fig. 4.

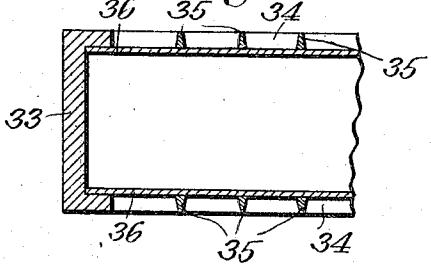
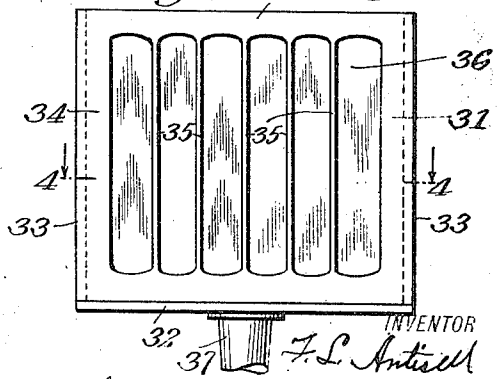


Fig. 5.



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APPARATUS FOR ELECTROLYTIC DEPOSITION.

1,239,443. Specification of Letters Patent. Patented Sept. 11, 1917.

Application filed October 31, 1913. Serial No. 798,410.

To all whom it may concern:

Be it known that I, FRANK L. ANTISELL, a citizen of the United States, and a resident of Perth Amboy, county of Middlesex, State of New Jersey, have invented certain new and useful Improvements in Apparatus for Electrolytic Deposition, of which the following is a specification.

This invention relates to anodes for plating out metals from solutions, for instance, copper that has been dissolved in excess of that plated out at the cathode of an electrolytic copper refinery vat, or that which has been leached out of its ore.

The objects of the invention will appear from the following description.

It is well known that when metal, copper for example, is plated from a sulfate solution with an insoluble anode, say of chemical or antimonial lead, a current of from 2 to 2½ volts is necessary and at the same time the ampere efficiency of the cell is low. That is to say, the amount deposited will be less than the theoretical amount in proportion to the metals in the solution that form as two or more sulfates. For instance, where iron is present as ferrous sulfate when it comes under the influence of the anode, it is oxidized to ferric sulfate, and being free to circulate between the electrodes, in course of time it comes under the influence of the cathode and is reduced back to ferrous sulfate, thus consuming some of the energy of the current in useless work besides tending to produce an inferior deposit. This loss of energy is increased with an increase of circulation and of temperature, both of which are desirable features of plating.

The voltage of a tank using an insoluble anode, lead for example, after being in service a short time is about 1.20 volts at the anode. In addition to this there is to be considered the ohmic resistance of the lead oxid that forms rapidly on the anode. In practice about ½ volt is required to overcome this ohmic resistance when operating at current density of about 16 amperes per square foot. In addition to these resistances there are other resistances, such as across the electrolyte, bus-bar contacts and metal circuit resistances, but these need not be considered here as they are approximately the same as or possibly a little greater than in my present invention.

I have discovered that the voltage of 1.20 is not a necessary characteristic of an anode when used in cupric sulfate solutions, and by constructing an anode according to my invention I am able to deposit copper or other metal from a solution at various voltages depending upon the current density of the cell. The counter electromotive force of my anode is about .35 of a volt, at which plating begins. At 5 amperes per square foot the voltage increases to about .85 of a volt, and at 10 amperes to 1.30 of a volt, while the ampere efficiency is maintained at practically 100 per cent. With this knowledge I am able to construct an apparatus that will deposit copper or other metal at a certain rate with a potential for example, of 1 volt. The economy of my construction is apparent when it is considered that the usual voltage of an insoluble anode is about 2.25 volts or 225 per cent. greater than when using the anode forming the subject-matter of my invention. Furthermore, there is an additional saving in the use of my invention due to the ampere efficiency maintained. Where a relatively small portion of copper is plated from a solution when using an insoluble anode, it has been considered good practice to obtain an ampere efficiency of between 80 and 85 per cent., which represents a charge to be added for liberating copper from solution as above stated, which makes the cost by the present practice about 275 per cent. more than is the case when my invention is used.

There are other advantages to be considered. For example, in the commercial electrolytic refining of copper as heretofore practised, about one-sixth of 1 per cent. of the amount of copper deposited on the cathode is present in the slimes as metallic colloidal copper due to a certain proportion of the copper dissolving in a cuprous state which in turn splits up into finely divided copper and sulfuric acid. This copper in the slimes is very expensive to remove. By the use of my invention and especially when my anode is fitted with a porous diaphragm, the solution which passes through the anode oxidizes any iron that may be in the solution, which may be from one-half to 1 per cent. This solution is then turned back into the cathode compartment and the ferric sulfate thus formed combines readily with the copper during the phase just described forming copper sulfate and ferrous sulfate. Of course, it is evident that only a small

amount of ferric sulfate is present and the solution may be maintained so that the ferric sulfate, which acts as a powerful oxidizer of copper in hot solutions, will not increase the corrosion of the electrodes.

In the prior practice as just referred to, at 2.25 volts per cell and 80 per cent. efficiency, about .92 of a pound of copper is produced per kw. hour, while by the use of my invention at 1 volt and 100 per cent. efficiency, 2.58 pounds of copper are produced per kw. hour.

There are two general systems in use in the art of recovering copper or other metals from solution. One is depositing copper out of the solution to a point where about 80 per cent. ampere efficiency may be maintained and the treated solution is conducted to a tank where the remaining copper is precipitated by iron or other reagents, some of the original impurities being precipitated with the cement copper. This operation has the disadvantage of necessitating the usual reagent, iron, to be cast into the form of plates that will hang more or less vertically in the tank; otherwise, a very large proportion of the impurities in the original solution will be precipitated with the cement copper. There is also an acid and by-product metal loss to be considered. This system can also be operated for recovering the by-products in the solution, but is complicated. Both operations are expensive and unsatisfactory and return a large amount of the impurities to the solution. The conditions must be favorable for a system which will recover by-products advantageously.

The other system is one where the copper is crystallized out of the solution as copper sulfate.

The advantages of my invention are, first, that it greatly decreases the voltage over that required by the insoluble anode now in use which is generally a sheet of chemical or antimonial lead. Second, when my anode is fitted with a porous diaphragm the current efficiency is increased as the diaphragm separates to a greater or less degree the analyte and cathalyte, limiting thereby the reaction at the anode where ferric sulfate is formed, which is again reduced to ferrous sulfate at the cathode, thus consuming a great amount of electrical energy in useless work. By this device copper can be plated from solutions containing large amounts of impurities, say for instance, iron, that would otherwise so contaminate a solution as to make it commercially prohibitive to use as an electrolyte owing to the low ampere efficiency due to the oxidization of the iron at the anode and its reduction at the cathode. In fact, I can successfully treat solutions containing as high as 50 grams of iron per liter when using the diaphragm type of my invention. Third, if I use a depolarizer such as H_2SO_3 a further increase in usefulness is possible and at the same time sulfuric acid is obtained as a by-product, or the apparatus may be used for oxidizing other solutions, for instance ferrous sulfate to ferric sulfate or the like, and I also increase the capacity of the system and further reduce the voltage. Fourth, the apparatus may be cheaply constructed and easily operated and all the parts are accessible. Other advantages will appear from the hereinafter description.

My invention is fully set forth in the following description taken in connection with the accompanying drawing which illustrates one embodiment of my invention, in which:

Figure 1 is a top plan view of a tank with one embodiment of my anode in place therein.

Fig. 2 is a cross section on line 2 of Fig. 1.

Fig. 3 is a cross section on line 3 of Fig. 2.

Fig. 4 is a cross sectional view on an enlarged scale on line 4 of Fig. 5.

Fig. 5 is a side view of the container forming part of my anode.

On the drawing the part marked 20 represents a tank of suitable construction and material for containing a solution. 21 is a pipe through which the solution is supplied to the tank, and 22 and 23 are outlet pipes. The bottom of the tank is provided with an opening 24, fitted with a bushing 25. Secured to the top of the tank are supports 26, made of suitable material, on which rest conducting rods 27, which are connected together at one end by the cross conducting rod 28, which may be integral therewith, and to which is connected a conducting wire 29. Suspended from each of the rods 27 is a cathode sheet 30. Supported inside the tank 20 and between the cathode sheets 30 is a receptacle or container 31, formed with a closed bottom 32, closed ends 33 and open sides 34, the latter being provided with a series of spaced ribs or bars 35. 36 represents sheets of rotary cut wood veneer or other suitable material which rest against the inner surface of the sides 34 and form porous walls or diaphragms for the container. To the bottom of the container is connected an outlet pipe 37, which extends through the opening 24 in the bottom of the tank 20 and around which fits the bushing 25, to make a water tight joint. The inner end of this pipe is covered by a screen or netting 38. 40 are rods of graphite or other suitable conducting material which extend into the container. The outer ends of these rods are connected to a conducting rod 41, to which is connected the conducting wire 42. Within the container and surrounding the rods 40 are particles of carbon (preferably gas house) or other suitable conducting material 43. The screen 38 covering the end of the outlet pipe 37 prevents the escape of

these carbon particles, and the rods or ribs 35 in the sides of the container assist in supporting the veneer diaphragms and prevent them from bulging out when the container is filled with the carbon particles. The receptacle or container with the conducting rods and the particles of carbon illustrates my preferred form of anode. 44 is a pipe which extends over the container and through which solution is supplied to the container.

In operation the valves in the outlet pipes 22 and 23 are closed and the valve in the pipe 21 is open so that the tank 20 can be filled with a solution containing copper or other metal to be recovered. When the tank is filled with this solution the valve in the outlet pipe 22 is open and the solution circulates in the tank, around the container 31 and out through the pipe 22. The valve in the outlet pipe 37 is also closed, and another or a similar solution is supplied to the container through the pipe 44, and when the container is filled with this solution the valve in the pipe 37 is open and the solution circulates through the loose particles of carbon contained in the receptacle, and passes out through the pipe 37. An electric current from a suitable source is supplied through the conducting wire 42, through the connecting rod 41, through the rods 40, which energizes the particles of carbon 43 within the container 31, passes through the solution or anolyte within the container, through the walls or diaphragms 36, then through the solution or catholyte in the tank 20, through the cathode sheets 30 to the conducting wires 27 and 28 and through the conducting wire 29 back to the source of supply. During this operation the current will continually deposit the metal out of the cathalyte, which is being continuously supplied to the tank 20, onto the cathode sheets 30. By energizing the particles of carbon or other suitable conducting material in the manner described I am able to reduce the voltage due to several reasons. One is that the numerous rough and jagged points, cells and pores of the carbon present an area with such a low surface tension that the oxygen particles are liberated mechanically, thereby reducing the resistance between the terminals of the anode and cathode. Another reason is that the surface of the anode is greatly increased, thereby facilitating the liberation of the oxygen gas. By the use of the veneer diaphragm which separates more or less the anolyte and catholyte, any ferrous iron in the solution will act as a depolarizer, and I am enabled to perform many important chemical changes that are useful in the art of metallurgy.

In some instances it is not necessary to separate the solutions in the container and in the tank. In that case the veneer diaphragm 36 may be substituted by a metal or other suitable perforated plate or sheet which permits the solution in the container to pass directly into the tank and will also permit the passage of the electric current but retains or holds the particles of carbon or other suitable conducting material within the container. In fact, in a simple form of my device the particles of carbon or other suitable material may be held in a screen or netting with the rods 40 projecting therein, and in fact, the said rods themselves may be made of cellular sticks of carbon or other suitable material to form the anode.

When a perforated member for holding the particles of carbon or other conducting material in position is used, the valves in the pipes 21 and 37 are closed so as to cut off the supply of solution to the tank and prevent the escape of the solution from the container 31. To permit the escape the valves in pipes 22 and 23 are open. The solution being supplied through the pipe 44 instead of passing out through the pipe 37, passes through the perforated members of the container or anode and out through the pipes 22 and 23. During this operation a much higher anodic efficiency is obtained. It is well known that the ordinary anodic efficiency is very low when depolarizing with SO_2 gas, a not unusual figure being five or six per cent. When using the veneer diaphragm this efficiency is raised to about 65 per cent., and when using the perforated diaphragm it is increased to about 80 per cent. with a consequent decrease in voltage.

By the use of my improved anode, especially when using the veneer diaphragm, I am able to obtain a good deposition of copper from a solution when the copper in the solution is as low as $\frac{1}{2}$ per cent., and at the same time increase the acid contents of the solution by the use of H_2SO_3 as a depolarizer and circulating the same through the anode. The treated solution can then be sent to the iron tank where the remaining copper (except the last traces thereof and the impurities held to a very large extent in the solution) will be precipitated, the resulting iron sulfate being discarded.

It is sometimes desirable to conduct the electrolyte from the anode compartment in which case the iron in the solution is oxidized. Another operation which may be desirable is to conduct the electrolyte, from the cathode compartment in which case the iron in the solution is reduced. In each operation it is evident what valves in the pipes are to be operated.

Having now described my invention, what I claim as new and desire to secure by Letters Patent is:

1. An anode consisting of a container open at its top for the passage of particles of conducting material, and also for the solution,

a bottom for supporting the particles of conducting material, but permitting the passage of the solution, closed ends and open sides, rotary cut veneer diaphragms forming the walls of the container, conducting rods extending into the container and fragments of conducting material within the container and surrounding the conducting rods and means for causing a circulation of the solution through the anode.

2. An anode consisting of a container having an opening in its top for the passage of particles of conducting material, and also for the solution, a bottom for supporting the particles of conducting material, but permitting the passage of the solution, closed ends and open sides, porous diaphragms covering said open sides, conducting members extending into the container to form a wet contact, and particles of conducting material inclosed within said container and surrounding said conducting members, means for causing a circulation of the solution through the anode.

3. An anode consisting of a container formed with a bottom constructed to support the conducting material, but to permit the passage of the solution, closed ends and open sides, diaphragms of veneer covering said sides, conducting members extending into the container to form a wet contact, and fragments of conducting material within the container and surrounding said conducting members, means for causing a circulation of the solution through the anode.

4. An anode consisting of a container open at one end for the passage of the fragments of conducting material and the solution formed with a bottom constructed to support the fragments of conducting material and permit the circulation of solution therethrough, closed ends and open sides, supporting rods connected to said sides, sheets of veneer within the container and supported by the sides and said rods, a conducting member extending into the container to form a wet contact, and fragments of conducting material within the container and surrounding said conducting member, means for causing a circulation of the solution through the anode.

5. An apparatus of the class described, a tank, means for supplying a solution to said tank, means for permitting the solution to pass out of said tank, conducting members connected to said tank, cathode sheets suspended from said conducting members and into the tank, an open ended receptacle between the cathode sheets, conducting members extending into the receptacle to form a wet contact, fragments of conducting material in said receptacle and surrounding the conducting members, and means for supplying a solution to the receptacle, means for causing a circulation of the solution through the anode.

6. An apparatus of the class described, a tank, means for supplying a solution to the tank, means for permitting the solution to pass out of the tank, cathode sheets suspended in the tank, a container within the tank between the cathodes, said container being formed with porous walls, an inlet and an outlet for said container, means for supplying a solution to the container, an electrical conducting member or members extending into the container to form a wet contact, and fragments of conducting material within the container and surrounding the conducting member or members, means for causing the circulation of the solution through the anode.

7. An apparatus of the class described, a tank, means for supplying a solution to said tank, means for permitting the solution to flow out of said tank, the bottom of the tank being provided with an opening, conducting rods supported by said tank, cathode sheets suspended in the tank from said conducting rods, a receptacle within the tank, means for supplying a solution to the receptacle, an outlet pipe connected to the receptacle and extending through the opening in the bottom of the tank to permit the circulation of the solution through the receptacle, sheets of veneer forming porous walls or diaphragms of the receptacle, a conducting member or members extending into the receptacle, and particles of conducting material in the receptacle and surrounding said conducting member or members.

In witness whereof I have hereunto set my hand at the city, county, and State of New York, this 29th day of October, 1913.

FRANK L. ANTISELL.

In presence of—

JOHN J. RANAGAN,
ISABEL R. RICHARDS.

Copies of this patent may be obtained for five cents each, by addressing the "Commissioner of Patents, Washington, D. C."