No. 858,341. PATENTED JUNE 25, 1907.

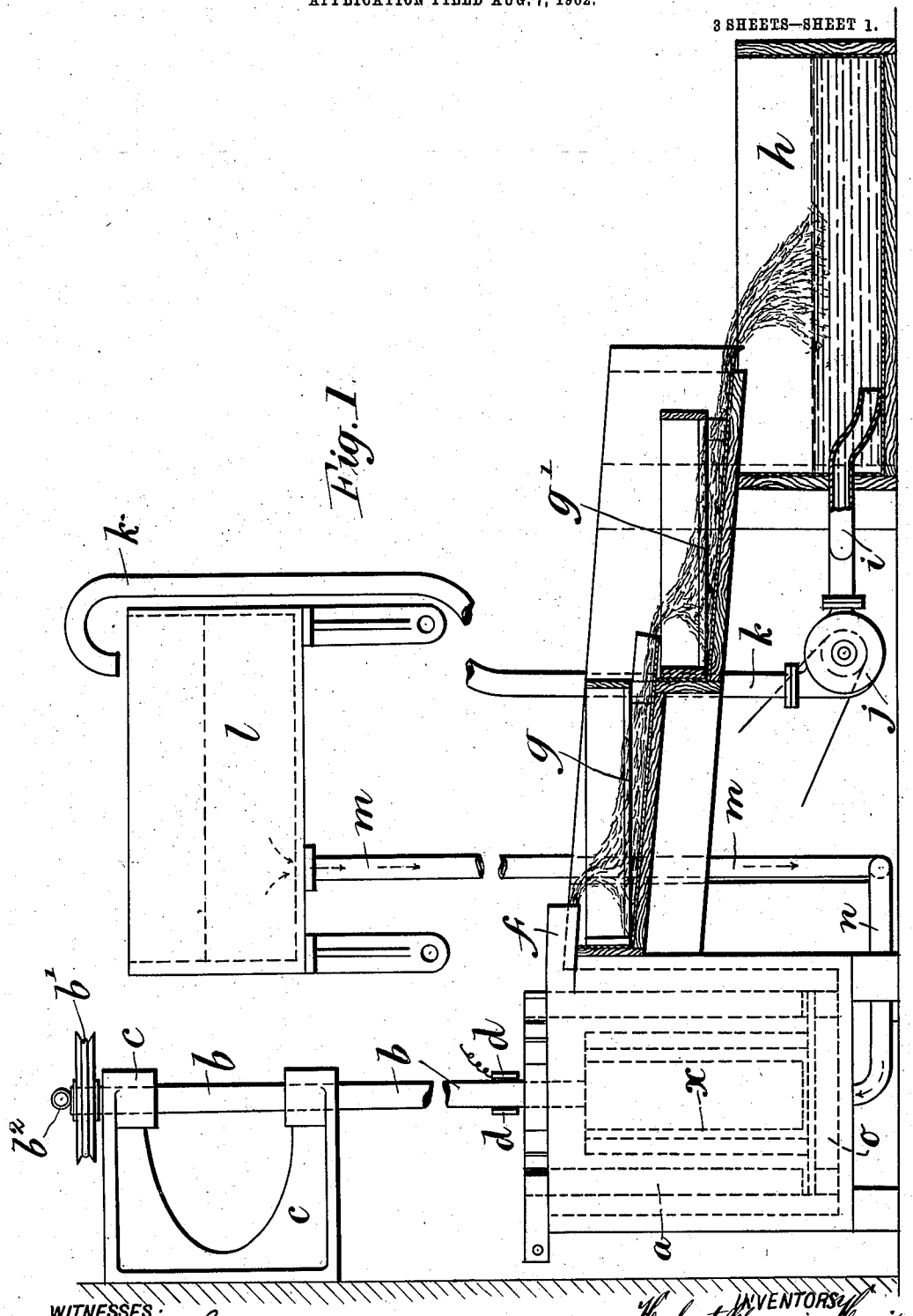
H. C. HARRISON & J. DAY.

APPARATUS FOR ELECTROLYTIC DEPOSITION OF METALS.

APPLICATION FILED AUG. 7, 1902.

3 SHEETS—SHEET 1.

Fig. 1.



WITNESSES:

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INVENTORS:

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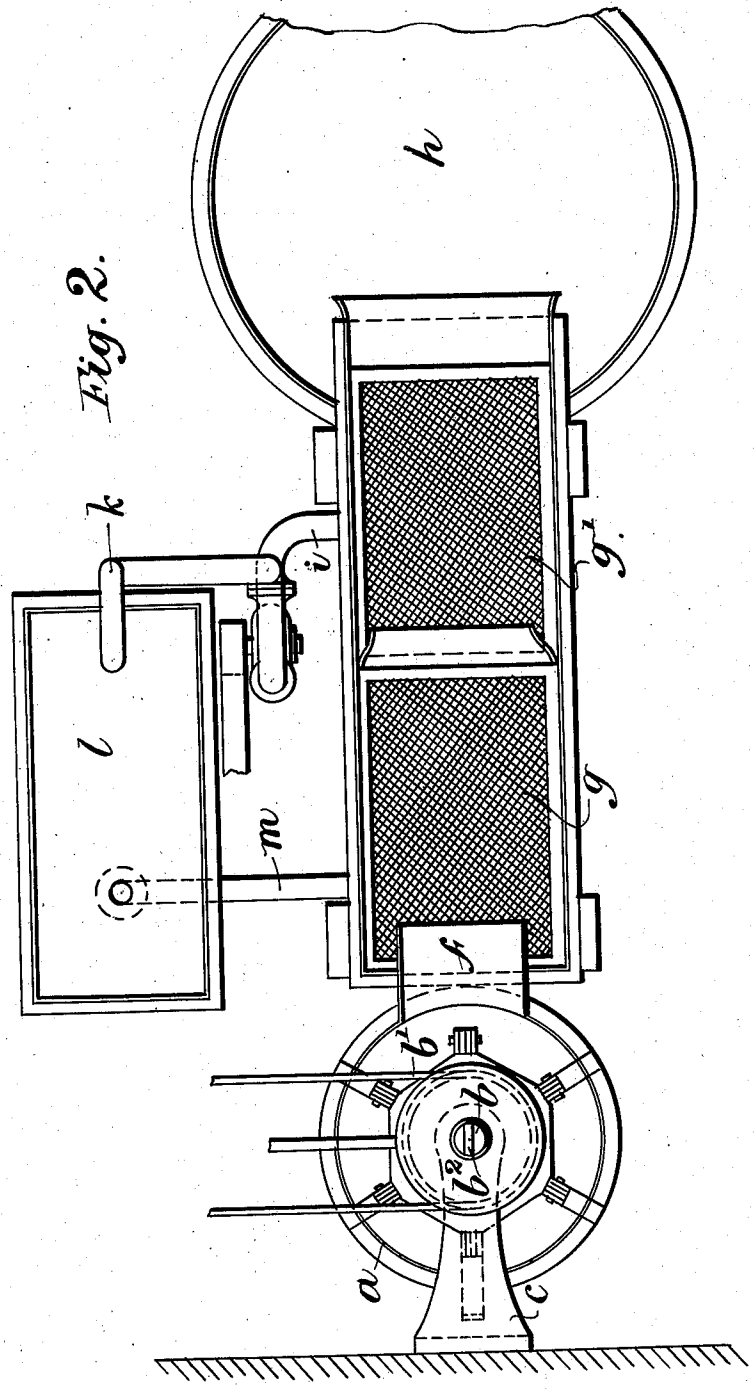
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APPLICATION FILED AUG. 7, 1902.

3 SHEETS—SHEET 2.

Fig. 2.



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No. 858,341. PATENTED JUNE 25, 1907

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APPARATUS FOR ELECTROLYTIC DEPOSITION OF METALS.

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3 SHEETS—SHEET 3.

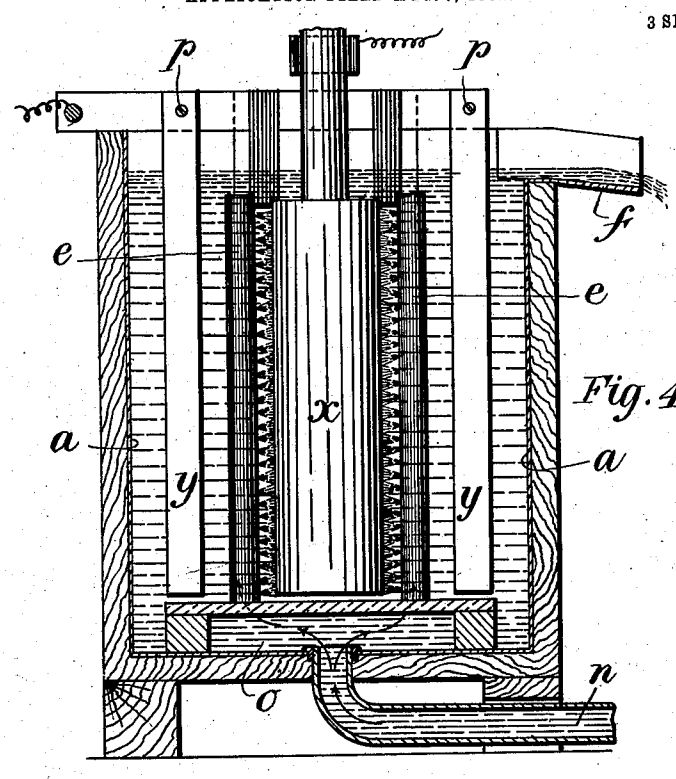
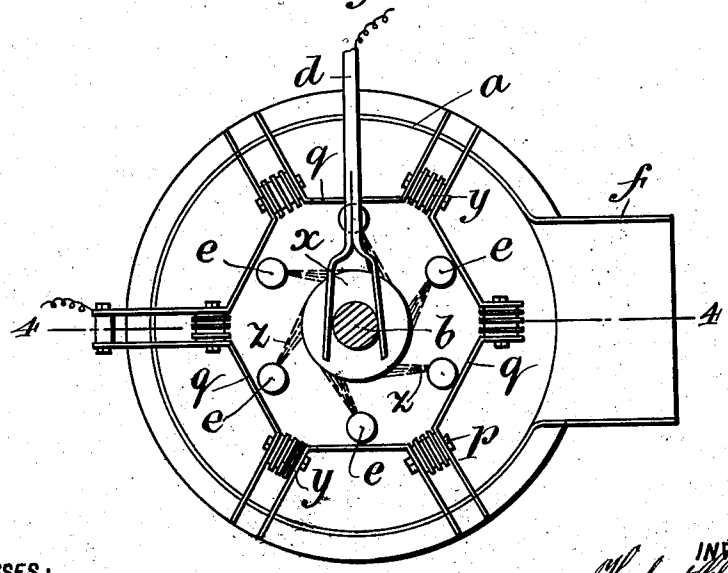


Fig. 4.

Fig. 3.



WITNESSES:

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UNITED STATES PATENT OFFICE.

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APPARATUS FOR ELECTROLYTIC DEPOSITION OF METALS.

No. 858,341. Specification of Letters Patent. Patented June 25, 1907

Application filed August 7, 1902. Serial No. 118,801.

To all whom it may concern:

Be it known that we, HERBERT CHAMPION HARRISON, gentleman, a subject of the King of Great Britain, residing at London, England, and JOSEPH DAY, civil engineer, a subject of the King of Great Britain, residing at Weston-super-Mare, England, have invented certain new and useful Improvements in the Electrolytic Deposition of Metals, of which the following is a specification.

Our invention relates to improvements in the electrolytic deposition of metals whereby though a high current density (involving correspondingly rapid deposition) is employed, nevertheless a tough and homogeneous deposit with smooth surface is obtained.

In the electrolytic deposition of metals from solutions of their salts particularly copper it is found that if the current density employed greatly exceeds that which is usually employed in the processes at present in use for the deposition of such metal from such solution the surface of the deposited metal deteriorates and at the same time the character of the deposited metal changes becoming at first less dense and often brittle, exhibiting a coarse fracture when broken, and that finally if the current density be sufficiently increased it the metal is deposited in a muddy incoherent form. Furthermore the deposited metal even if deposited at sufficiently low current density to be in a coherent form is usually in the shape of flat bars or plates which will first have to be re-cast before the metal can be used commercially for making tubes sheet or wire.

Many attempts have been made to produce a finished article of copper by one electrolytic process at a higher current density than that usually employed. Most of these have depended upon the mechanical consolidation (by mechanical pressure) of the metal during deposition while others aimed at obtaining dense tough and smooth deposits from the beginning without mechanical consolidation. However either the deposits have been found to be inferior and faulty in character or the processes have been attended by so much practical difficulty that hitherto the problem has not been satisfactorily and economically solved commercially.

Now according to our invention we are enabled to employ current densities greatly in excess of those usually employed and at the same time to obtain a tough smooth and homogeneous deposit in the form of a tube which is itself at once of commercial utility (without having to be re-cast unless desired) or the tube can be cut so as to give a sheet.

According to our invention we effect a continual, complete and rapid renewal, by displacement and replacement, of the layer of electrolyte immediately contiguous to a cathode circular in cross section and over the whole surface of the said cathode (*i. e.* throughout the whole length thereof and all round same) but more particularly over those parts exposed most directly to the action of the anode *i. e.* where the resistance between the electrodes is least and consequently the current density greatest. In other words we create a high differential velocity between the surface of the said cathode and the layer of electrolyte in contact with the same or immediately contiguous thereto and we continually renew this layer with clean and fresh unimpoverished electrolyte. For we have found that it is due to the impoverishing of this layer of electrolyte by a current of high density acting for any prolonged period and the non-renewal rapidly and continuously and completely of said impoverished layer that bad metal is deposited. To renew the whole contents of the depositing vat sufficiently rapidly to secure the continual renewal of this extremely thin layer is obviously impracticable and unnecessary, as is also to renew the whole volume of electrolyte between the anode and the cathode, since, except when deposits of extreme thinness are required, the anode must be at a workable distance (say one inch to four inches) from the cathode, this distance varying according to the current density employed, the rate of renewal and the thickness and smoothness of the deposits required.

In carrying out our invention we employ a cathode of circular cross-section for instance a cylindrical or conical cathode mounted vertically in the depositing vat and free to revolve about its own axis. The deposit is better if the surface of the cathode is highly polished. We renew the layer of electrolyte contiguous to the cathode by means of jets of electrolyte directed tan-

gentially to the surface of the cathode. Jets of electrolyte so employed most effectually displace and renew the liquid in the extremely small cavities or inequalities in or on the surface of an electrolytic deposit. The jets used by us may be obtained by surrounding the cathode with vertical spray-pipes of a material, such as vulcanite, which does not conduct electricity and which is not attacked by the solution employed. The spray-pipes are arranged parallel with the surface of the cathode to be deposited upon and are bored at intervals or so formed as to emit the electrolyte in a direction tangential to the surface of the cathode. The spray-pipes are kept constantly supplied with electrolyte under suitable pressure for instance either by a pump or by gravity from a vat placed at a suitable level and supplied by a pump. We have found that one jet will effectually renew this layer of electrolyte only over a given area and most effectually only close to where the jet impinges upon the circular cathode tangentially. If directed radially upon the circular cathode at the actual point of impact the electrolyte is very effectually renewed but the efficiency of renewal falls off more rapidly than in the case of a jet tangentially impinging. For various diameters of hole or nozzle for the projection of a tangentially impinging jet of electrolyte the width of band influenced has been determined experimentally by us and the influence of the jet was found to fall off from the center to the edge of the band influenced. We therefore bore or form the pipes so that the space between two adjacent jets is preferably half the width of the band influenced. By this means the effect of two adjacent jets is super-imposed where the influence of each tends to diminish.

Now each complete spray-pipe will influence a definite fraction of the circumference of the cathode of cylindrical or conical or other circular form in cross-section. A sufficient number of spray-pipes must therefore be employed all round the cathode and extending from end to end thereof to influence the whole surface of such cathode.

The anode is made of bars or groups of bars (either consisting of the metal to be deposited or—in cases where the deposit of metal on the cathode is to be obtained from the salts in solution in the bath without the metal of the anode dissolving in the bath—of a substance not liable to be attacked by the electrolyte) arranged around the cathode and so placed as to be directly opposite and parallel to the line of impact of the jets from each spray-pipe respectively. We thus secure that the bands upon the surface of the cathode exposed to the greatest current density are coincident with the bands where the jets from each spray-pipe impinge.

We find we obtain the best results by slowly rotating the cathode about its own axis so as to insure all parts of the cathode being evenly coated.

By this invention we secure an effective and continual renewal of the layer of electrolyte immediately contiguous to the cathode and at the same time a partially localized action of the current so that the greatest current densities are distributed over those parts of the cathode surface subjected to the greatest action of the jets, the current density falling off as the effect produced by the jets falls off from the point of their greatest efficiency. We also secure that the solution around the cathode is concentrated, while after it has been impoverished by the current it is forced to pass the anode without again coming into contact with the cathode until its strength has been renewed.

The closer the anode is to the cathode the lower becomes the resistance of the depositing vat and the less the electro-motive force necessary to work at any particular current density. But the closer the anode to the cathode the sooner the surface of the deposit will deteriorate in smoothness so that the thicker the deposit required the greater must be the distance between the anode and the cathode, always remembering that each anode bar or group of bars however near or remote from the cathode should be directly opposite the sphere of greatest influence of the corresponding spray-pipe.

Raising the temperature of the electrolyte will reduce the resistance of the depositing vat and so reduce the electro-motive force necessary.

It will be found advantageous in most cases to use the strongest solution possible; and, where acidified, a strongly acid one; avoiding in every case a solution so strong as to be in danger of crystallizing out. Thus for example in the deposition of copper we find it advantageous to use a solution containing about 180 or 190 grams of hydrated copper sulfate and 110 to 120 grams of sulfuric acid per liter.

Where necessary means should be adopted to collect the anode sludge, and we find it advantageous to keep the solution clear by filtration or otherwise. And in order that our invention may be the more easily understood and readily carried into practice we will proceed to describe same with reference to the drawings hereunto annexed.

Figure 1 is a view in side elevation of apparatus according to and for carrying out the present invention. Fig. 2 is plan thereof. Fig. 3 is local plan—on an enlarged scale—of the vessel with the cathode and anode therein. Fig. 4 is vertical sectional view on line 4—4 Fig. 3.

a is suitable vat or vessel adapted to hold the electrolyte.

b is the vertical spindle journaled in brack-

ets *c c* and provided with means to slowly rotate said spindle such as the pulley b^1 and means (such as the eye b^2) by which to bodily raise the cathode *x* on said vertical spindle *b* above the vat and to lower the spindle until said cathode *x* is immersed in the electrolyte; *d* is the brush.

e e are series of vertical pipes spaced-apart equidistant from one another and advantageously disposed concentrically around the cathode *x* and parallel to the longitudinal direction thereof; these vertical pipes *e* (which are closed at their upper ends) are provided at frequent intervals along same with holes or nozzles (see Fig. 4) in such position and in suchwise that the said nozzles will direct the jets *z* issuing therefrom in a direction tangential to the surface of the cylindrical cathode *x*—see Fig. 3. For example in practice we have found that we can successfully carry out our invention and deposit copper on a cathode of or about 3 inches diameter by employing vertical pipes located at or about 2½ inches from the center of such cathode, and spaced-apart at or about 2½ inches from one another concentrically all round such cathode, and the size of each of the series of holes in each such vertical pipe may be 3/32 of an inch and such holes may be provided at intervals of ½ an inch from one another throughout the vertical length of the pipe; but in other cases with differing conditions then the distance of the vertical pipes from one another and from the cathode and the size of the holes in said vertical pipes and the distance apart of said holes will vary according to the requirements in each case which can be readily ascertained (in the manner hereinbefore described) by any person skilled in the art and need not therefore be here further described.

The electrolyte is forced by any suitable means into the pipes *e* and issues therefrom in the form of jets *z* all round and tangential to the surface of the cathode *x;* in the arrangement shown in the drawings the electrolyte overflowing from the spout *f* of the vessel *a* flows through the filters *g* g^1 into the suction tank *h* and then is withdrawn through the suction pipe *i* by means of any suitable pump (such as the centrifugal pump *j*) which may either force the electrolyte direct into the vertical pipes *e* or said pump may force the electrolyte through the pipe *k* into a reservoir or tank *l* at any suitable height adapted to give the required pressure to the jets *z* from which tank *l* the electrolyte passes through the connecting pipe *m* and through the pipe *n* leading to the chamber *o* from which latter the electrolyte is forced into the vertical pipes *e*.

The anode of copper (or other suitable metal adapted to be electrolytically deposited) may be of any suitable form or shape but in the case of copper we have found a series of narrow vertical bars of crude copper to be very suitable and in the case illustrated we have shown the anode *y* formed of groups of such copper bars, each said group being secured together at their upper ends by bolts *p* passed through eyes formed in the upper end of each said group of copper bars and all the said groups coupled up by the connections *q*—thus the electric current flows through the connections *q* and through each of the groups of copper bars same being all in electrical connection and forming the anode.

Although our invention is primarily designed for the electrolytic deposition of copper and simultaneous refining thereof yet it may be carried into practice with any other metal or metals to which same may be applicable.

By the use of the expression "tangential" or "tangentially" herein we do not wish to be understood to confine ourselves to the strict mathematical definition of a tangential line—as in practice we find it advantageous to direct the jets toward a point on the cathode slightly nearer to the pipe discharging such jets than the point where the true tangential line from said pipe would touch said cathode but always so as not to direct the jets radially against said cathode, in other words we find it advantageous to direct the jets toward the cathode in a direction (toward the cathode) between the radial line and tangential line formed from said discharging pipe to the cathode.

Having now described our invention what we claim as new and desire to secure by Letters Patent of the United States is:—

1. In the electrolytical deposition of metals upon a cathode, the combination with a cathode, of a plurality of anodes arranged around the cathode in elements consisting of one or more anode bars, and means parallel to the axis of the cathode for producing jets of electrolyte adapted to impinge against the cathode so that the greatest action of the jets upon the cathode will take place at those points of the cathode nearest the elements of the anode where the resistance between the electrodes is least and, consequently, the current density greatest.

2. In the electrolytical deposition of metals, the combination with a vertically-mounted cathode, of a plurality of perforated pipes parallel to the axis of the cathode, disposed equidistant from one another, and disposed concentrically around and spaced apart equally all around said cathode, adapted to issue jets of electrolyte so as to impinge in a tangential direction against the surface of the cathode all around the latter and throughout the length thereof, and a plurality of anodes exterior to said vertical pipes.

3. In the electro deposition of metals upon a revolving cathode of circular cross-section—the combination with such cathode of the

anode arranged round the cathode in elements consisting of one or more anode bars, and pipes for directing the jets of electrolyte arranged in suchwise that the greatest action of the jets upon the cathode will take place at those points on the cathode nearest the elements of the anode where the resistance between the electrodes is least and consequently the current density greatest, and means to revolve the said cathode during electro deposition thereon.

4. In an apparatus for electrolytically depositing metals, the combination, with a cathode of circular cross-section, of a series of pipes spaced apart equidistant from one another and disposed concentrically about said cathode and provided with a series of holes or nozzles which direct the jets of electrolyte issuing from said pipes in a direction tangential to the surface of the cathode, and an anode located exteriorly of said series of pipes.

5. In an apparatus for electrolytically depositing metals, a vat, a revoluble cathode of circular cross-section vertically mounted in said vat, a plurality of spaced electrolyte-discharging pipes arranged concentrically about and parallel to said cathode, each of said pipes being perforated so as to cause the electrolyte to be projected in jets against the cathode in a direction approximately tangential thereto, and an outer series of spaced, depending, inter-connected anode-bars also arranged concentrically about and parallel to said cathode, said bars being disposed opposite the points of impingement of the jets upon the cathode.

In witness whereof we have hereunto set our hands in presence of two witnesses.

HERBERT CHAMPION HARRISON.
JOSEPH DAY.

Witnesses:
H. D. JAMESON,
F. L. RAND.