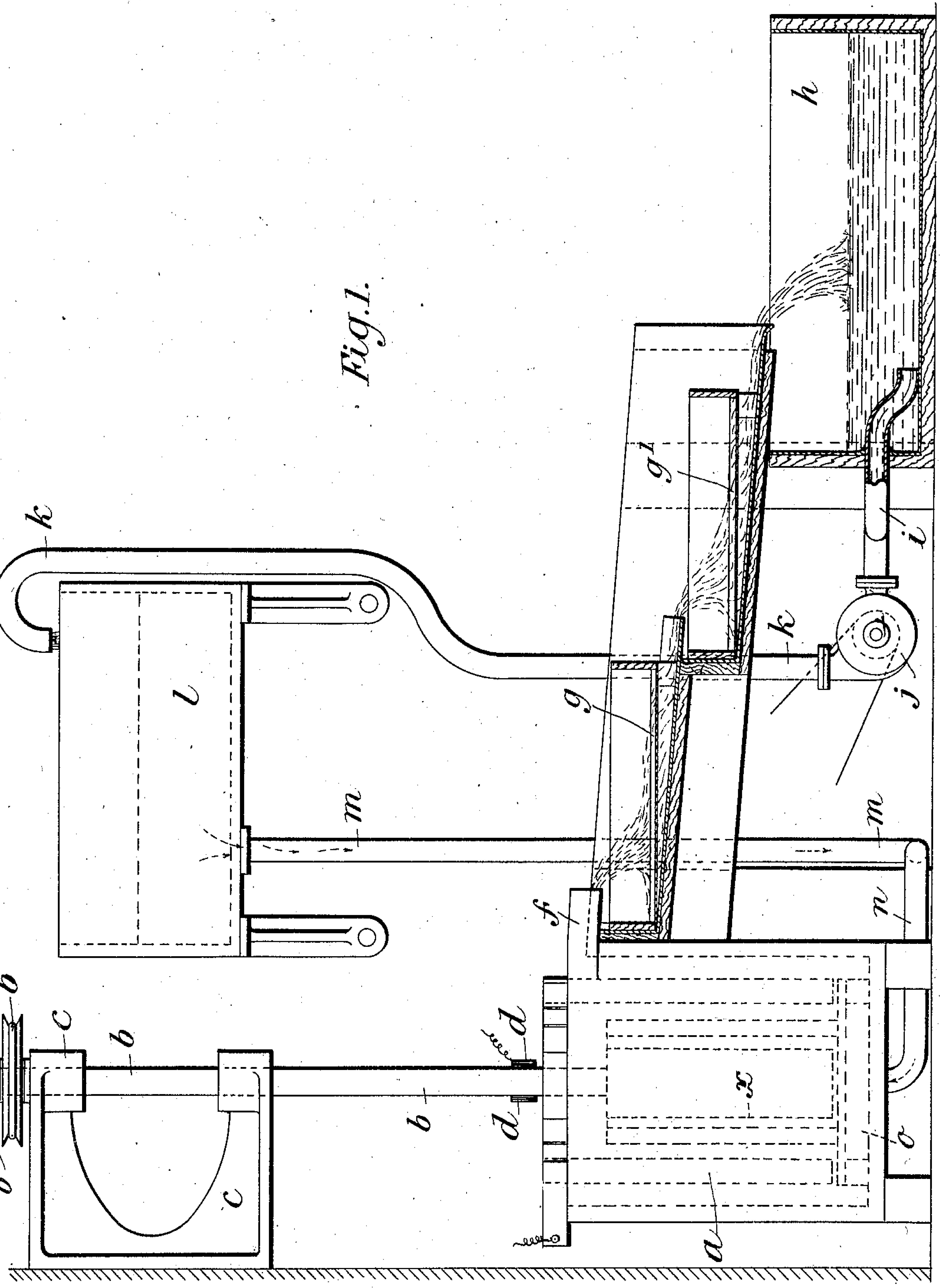
No. 791,341. PATENTED MAY 30, 1905.

H. C. HARRISON & J. DAY.

ELECTROLYTIC DEPOSITION OF METALS.

APPLICATION FILED JULY 19, 1901.

3 SHEETS—SHEET 1.



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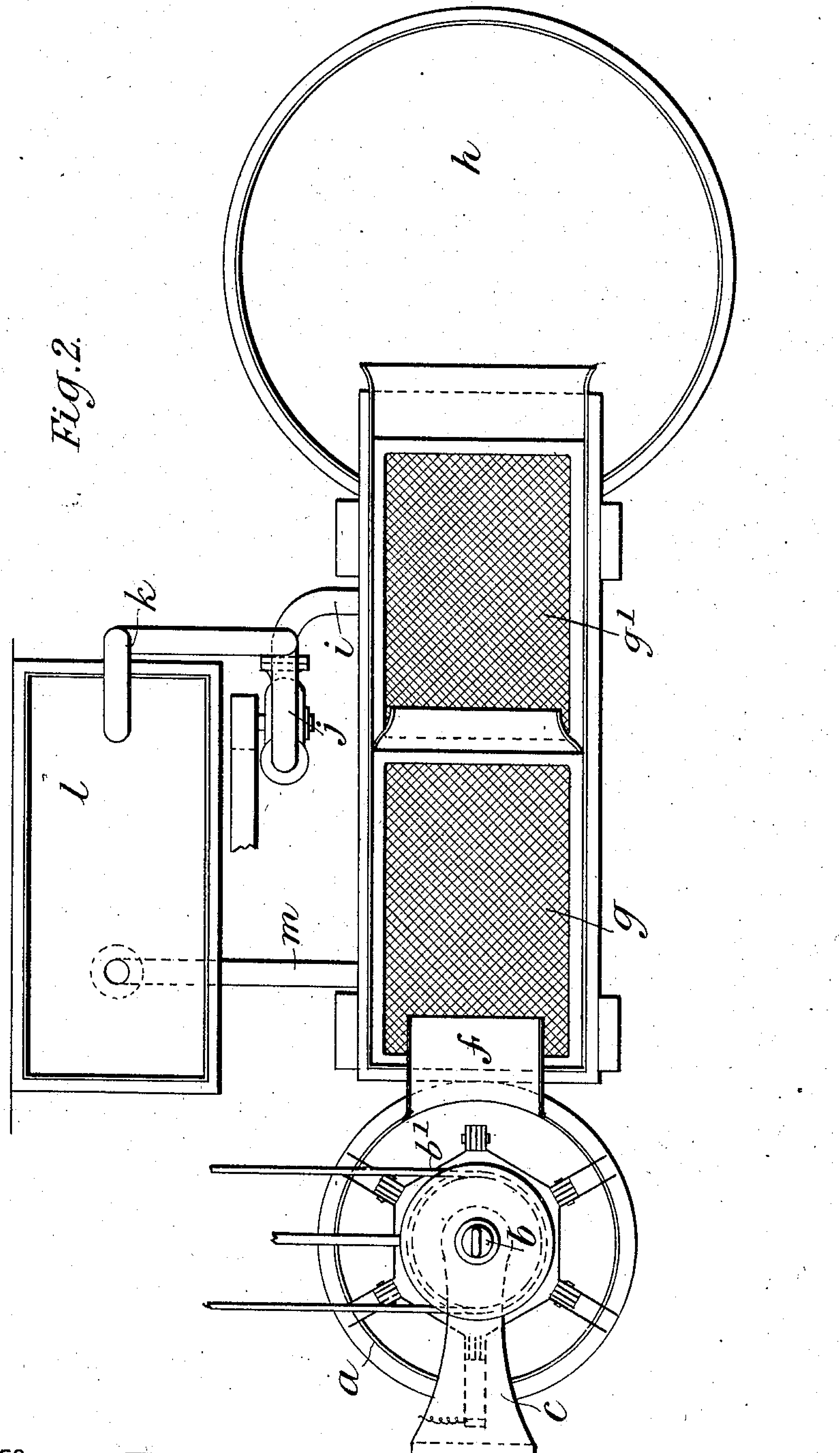

Fig. 2.

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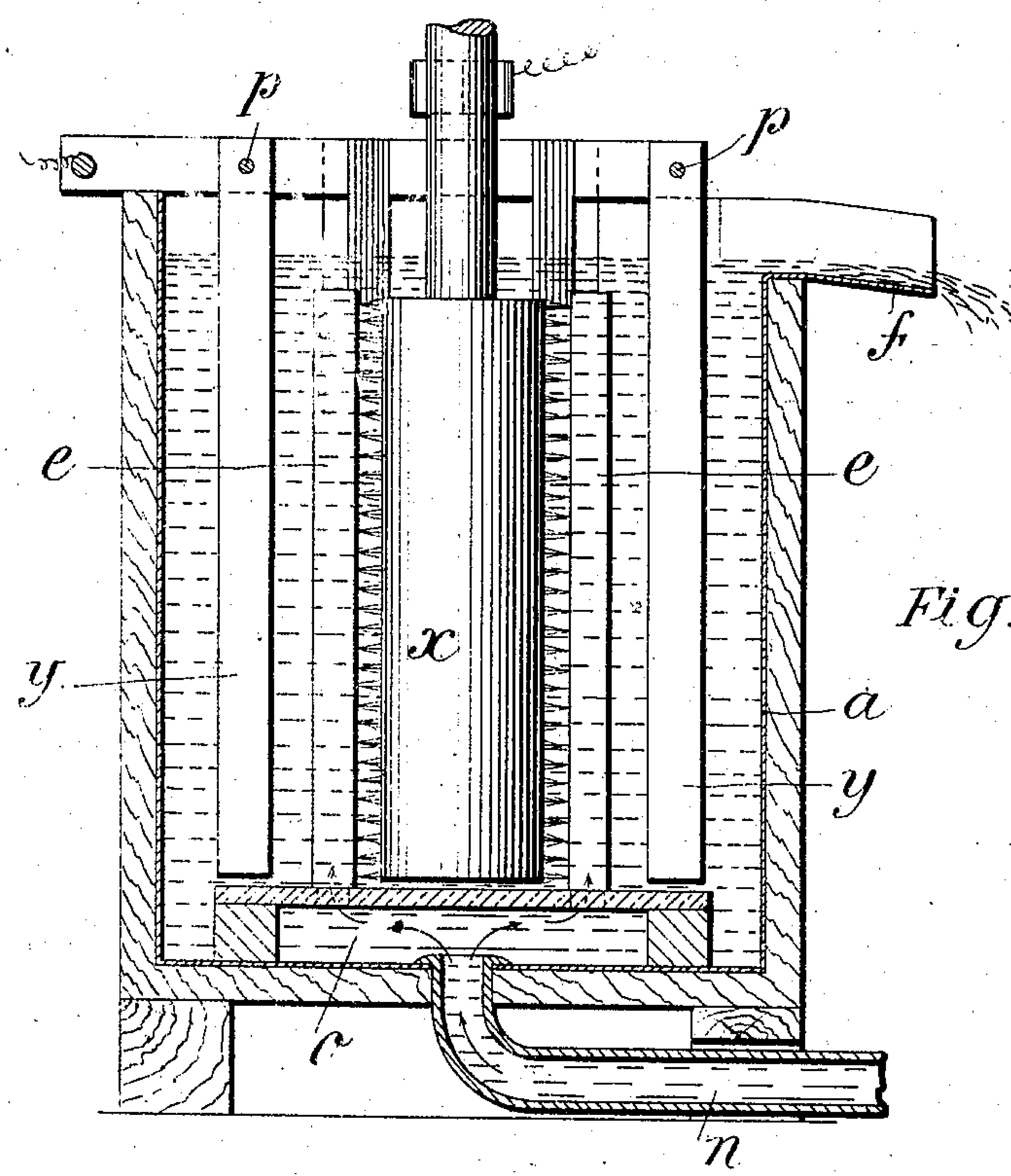
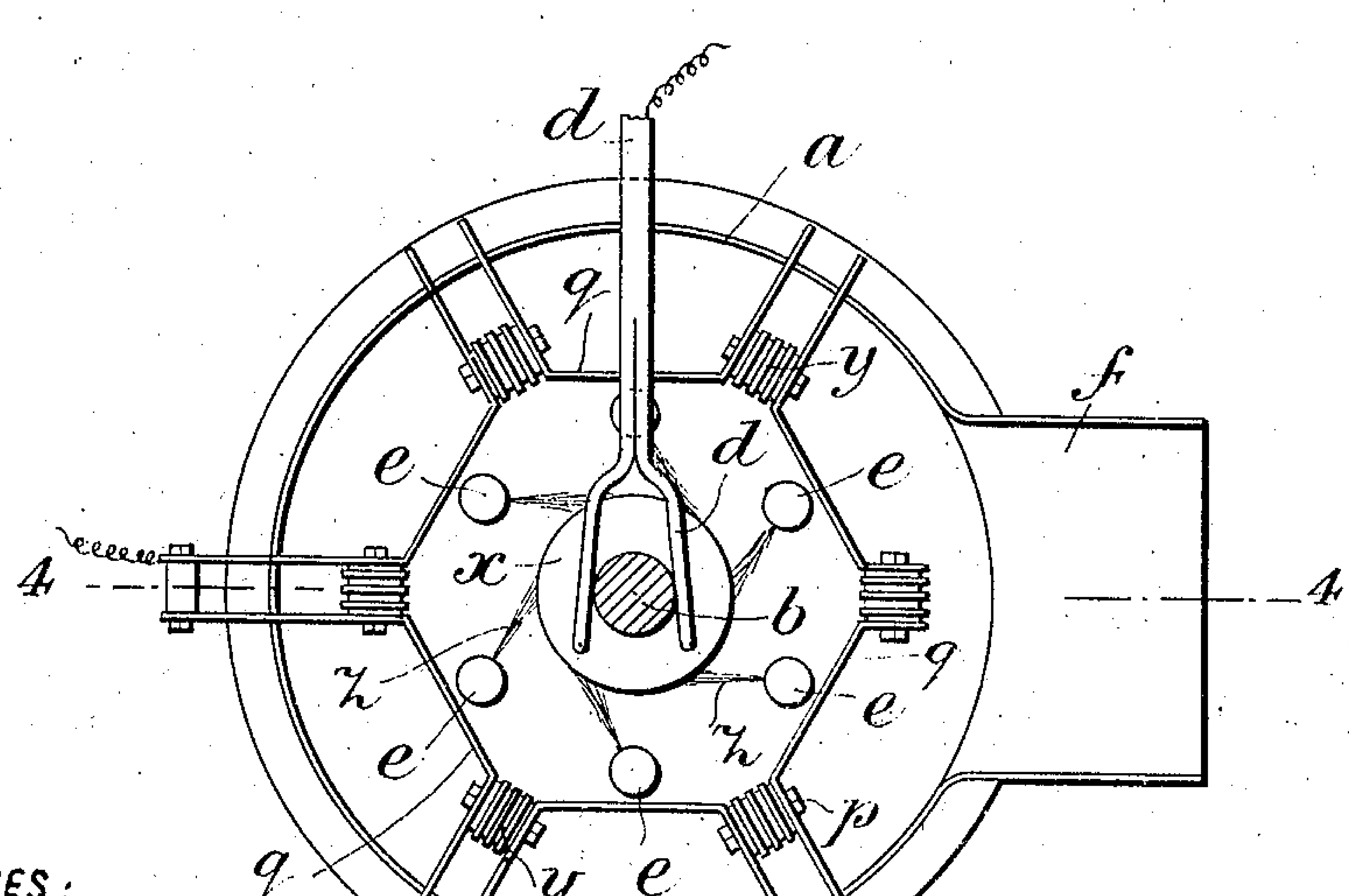


Fig.4.

Fig.3.



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UNITED STATES PATENT OFFICE.

HERBERT CHAMPION HARRISON, OF LONDON, AND JOSEPH DAY, OF WESTON-SUPER-MARE, ENGLAND, ASSIGNORS TO SAID HERBERT CHAMPION HARRISON.

ELECTROLYTIC DEPOSITION OF METALS.

SPECIFICATION forming part of Letters Patent No. 791,341, dated May 30, 1905.

Application filed July 19, 1901. Serial No. 68,897.

To all whom it may concern:

Be it known that we, HERBERT CHAMPION HARRISON, gentleman, residing at London, and JOSEPH DAY, civil engineer, residing at Weston-super-Mare, England, subjects of the King of Great Britain, 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 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 recast before the metal can be used commercially for making tubes, sheet, or wire.

Many attempts have been made to produce a finished article by an electrolytic process at a higher current density than that usually employed. Most of these have depended upon the mechanical consolidation 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 recast 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, 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 of said impoverished layer that bad metal is deposited.

In carrying out our invention we employ a highly-polished 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 tangentially 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. Furthermore, it is well known or a well-accepted theory that under the most favorable conditions for electrolysis the osmotic pressure of the ions in the electrolyte of the substance to be dissolved should be as low as possible, and therefore the concentration of the solution as low as possible in the neighborhood of the anode, while, conversely, that the osmotic pressure of the ions of the substance to be deposited should be as concentrated as possible in the neighborhood of the cathode. Our process partially, at least, fulfils these conditions, inasmuch as the electrolyte is constantly supplied in a concentrated form at the cathode and when impoverished by the action of the current is forced to escape past the anode without again coming in contact with the cathode until after having been restored to its normal strength.

The jets used by us may be obtained by surrounding the cathode with 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 to the surface of the cathode to be deposited upon and are bored at intervals or so formed to emit the electrolyte in a direction tangential to the surface of the cathode. The spray-pipes are kept constantly supplied with electrolyte, the same 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 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 superimposed 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 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 vertical 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 then slowly rotating the cathode about its own axis, so as to insure all parts of the cathode being evenly coated.

By the 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 electromotive 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 electromotive 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 one hundred and eighty grams of hydrated copper sulfate and one hundred and twenty 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.

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 a plan thereof.

Fig. 3 is a local plan of the vessel with cathode and anode therein on an enlarged scale. Fig. 4 is a vertical sectional view on line 4 4, Fig. 3.

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

b is vertical spindle journaled in brackets *c c* and provided with means to slowly rotate said spindle, such as the pulley *b'*, 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 disposed equidistant from one another and concentrically around the cathode *x*. 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 such wise 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 three inches diameter by employing vertical pipes located at or about two and one-half inches from the center of such cathode and spaced apart at or about two and one-half 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 three thirty-seconds of an inch, and such holes may be provided at intervals of one-half 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'* 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. The herein-described method for effecting, with high current density, the rapid electrodeposit of tough and homogeneous metal with a smooth surface, which consists in causing the electrolyte to impinge all around upon a vertically-mounted cylindrical cathode, by directing continually against every part of and all around the surface of said cathode and throughout the length thereof during deposition, a series of jets of electrolyte arranged certain distances apart around said cathode, whereby the rapid and continuous change of the electrolyte immediately contiguous to and all around the surface of the cathode and throughout the length thereof is effected.

2. The herein-described method for effecting, with high current density, the rapid electrodeposit of tough and homogeneous metal with a smooth surface, which consists in directing tangentially all around a vertically-mounted cathode and throughout the length

thereof, a series of jets arranged certain distances apart around said cathode so as to approach the surface of said cathode tangentially thereto, and cause a swirl of the impinged electrolyte all around the cathode, whereby the rapid and continuous change of the electrolyte immediately contiguous throughout the length of and all around such surface of the cathode is effected.

3. The herein-described method for effecting, with high current density, the rapid electrodeposit of tough and homogeneous metal with a smooth surface, which consists in simultaneously revolving the cathode and directing tangentially all around a vertically-mounted cathode, so as to approach the surface of said cathode tangentially and cause a swirl of the electrolyte at all points around the cathode and throughout the length thereof, a series of jets arranged certain distances apart, whereby the rapid and continuous change of the electrolyte immediately contiguous throughout the length of and all around such surface of the cathode is effected.

4. The herein-described method of electrodepositing metals, which consists in causing the electrolyte to impinge upon the entire surface of a vertically-mounted cathode, by directing horizontally throughout the length thereof a series of superposed jets of electrolyte arranged about said cathode.

5. The herein-described method of electrodepositing metals, which consists in causing the electrolyte to impinge upon the entire surface of a vertically-mounted cathode, by directing horizontally throughout the length thereof, a plurality of jets of electrolyte arranged in vertical rows about said cathode.

6. The herein-described method of electrodepositing metals, which consists in causing the electrolyte to impinge upon the entire surface of a vertically-mounted cylindrical cathode, by directing throughout the length thereof and approximately tangential thereto, a series of jets of electrolyte, the points of impingement of the electrolyte upon the cathode being at the shortest possible distance from the anodes.

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

HERBERT CHAMPION HARRISON.
JOSEPH DAY.

Witnesses:
FRANCIS W. FRIGOUT,
A. NUTTING.