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METHOD OF ELECTROLYZING A SOLUTION OF NICKEL SALT.

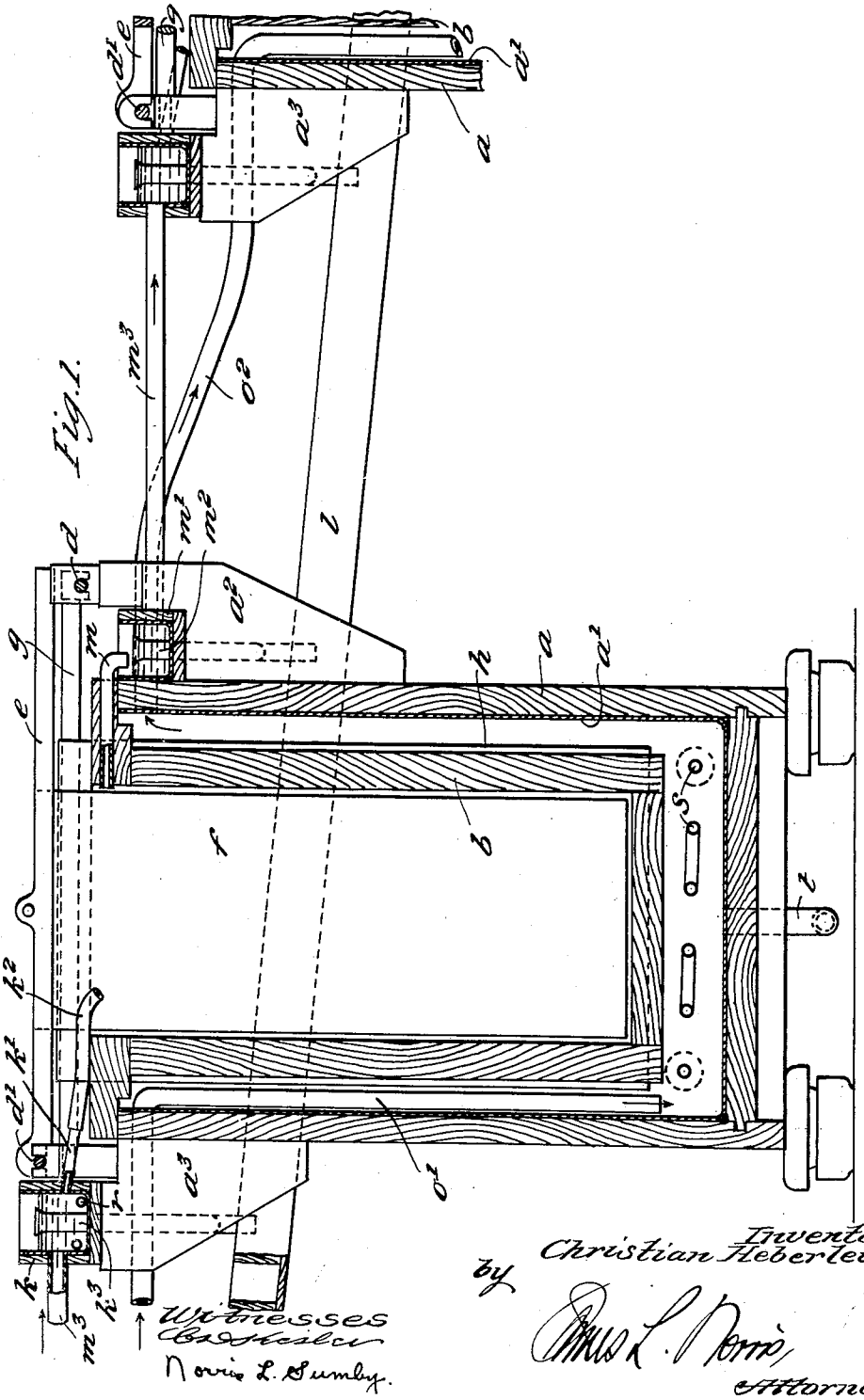
APPLICATION FILED DEC. 7, 1918.

1,389,829.

Patented Sept. 6, 1921.

2 SHEETS—SHEET 1.

Fig. 1.



Witnesses
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Fig. 3.

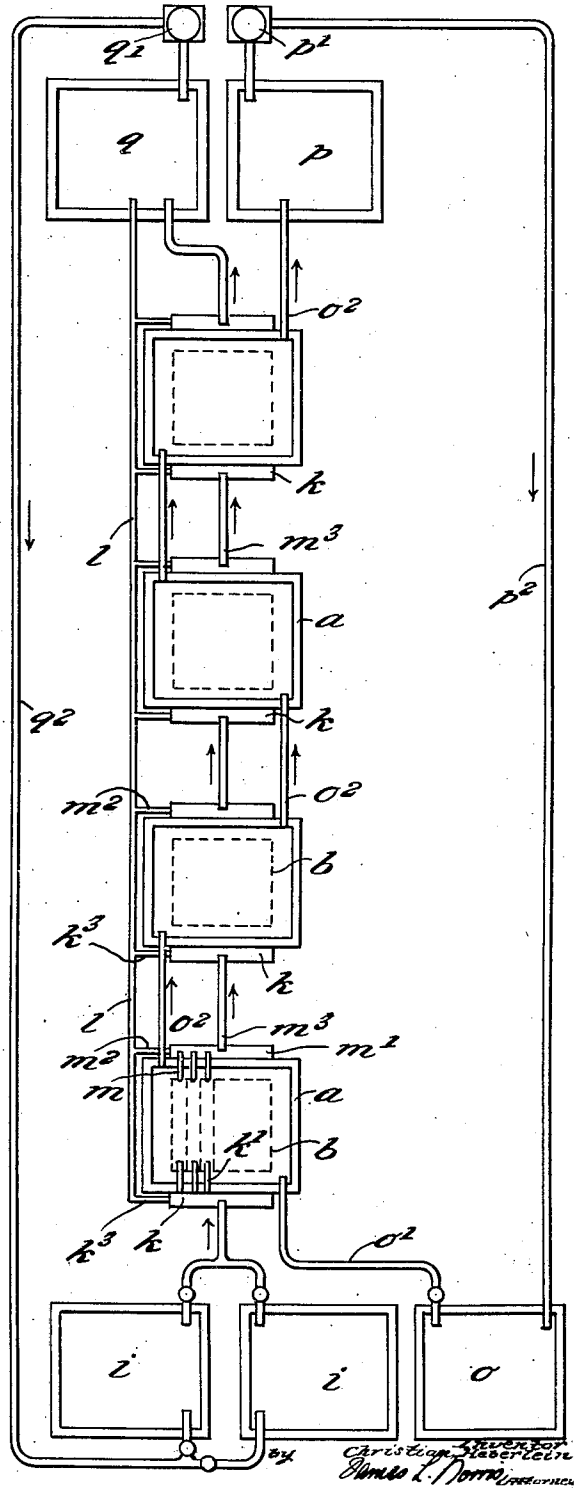
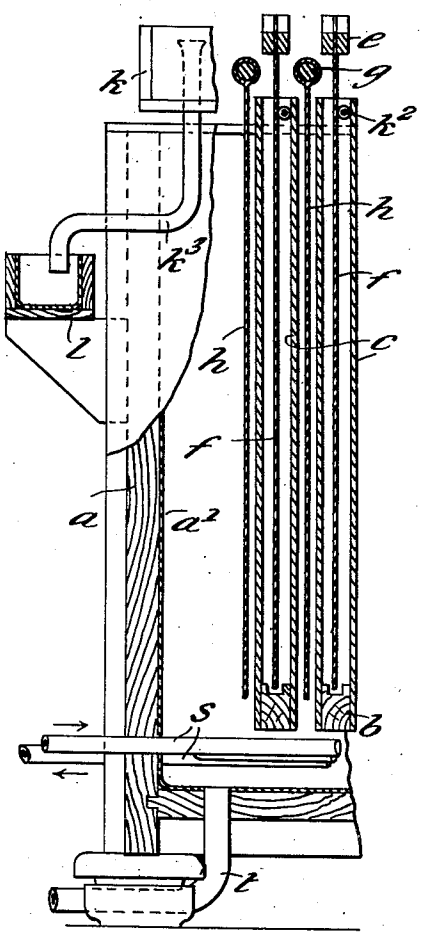


Fig. 2.



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UNITED STATES PATENT OFFICE.

CHRISTIAN HEBERLEIN, OF LONDON, ENGLAND.

METHOD OF ELECTROLYZING A SOLUTION OF NICKEL SALT.

1,389,829. Specification of Letters Patent. Patented Sept. 6, 1921.

Application filed December 7, 1918. Serial No. 265,746.

To all whom it may concern:

Be it known that I, CHRISTIAN HEBERLEIN, a citizen of the Swiss Republic, residing in London, England, have invented a certain new and useful Improved Method of Electrolyzing a Solution of Nickel Salt, of which the following is a specification.

This invention relates to an improved method for electrolyzing a solution of a nickel salt.

In all processes for the electrolytic deposition of metallic nickel from a solution of a nickel salt in which insoluble anodes are used, it has not hitherto been possible commercially to continue the deposition of the nickel after a comparatively small fraction of that present in solution has been deposited, owing to the accumulation of free acid in the electrolyte, because it stands to reason that if the electrolyte becomes too acid the free acid will redissolve the electrolytically deposited nickel. On the other hand a certain amount of free acid must always be present to prevent the formation of nickel oxid which would interfere with the formation of a smooth deposit.

In order to improve these conditions it has been the practice to separate the electrodes by a diaphragm, to restrict the increase of acidity to the anolyte.

However a certain transfusion of the anolyte into the catholyte takes place and unduly increases the acidity of the latter.

In order to prevent this it is the practice to circulate the electrolyte and to replace it by fresh liquor and although a number of proposals have been made in this direction, as far as I am aware, the exact conditions for working on a commercial scale in an economical manner with insoluble anodes have never been formulated.

Now I have examined the conditions as regards the acidity in the electrolyte in relation to the current efficiency in order to find out the most economical conditions for working in a continuous manner on a large scale.

The following table shows the results of my experiments with insoluble anodes, nickel sulfate and a current density of 10 amperes per square foot:—

Cathode efficiency.		Anode efficiency.	
% free acid in electrolyte.	% cath. eff.	% free acid in electrolyte.	% anode eff.
Neutral— .10% Av. .05%	100 %	Neutral—.05	97%
.10— .3 % Av. .20%	98 %	.05—.1	87%
.30— .45% Av. .37%	88.6%	.1 —.2	76%
1.5 %	45 %	.2 —.3	66%
1.7 %	28 %	.3 —.4	63%
2.0 %	21 %		

It can be seen from the above table that whereas at 0.1% of free acid in the electrolyte the cathode efficiency is 100%, with 2% free acid in the electrolyte the cathode efficiency is already reduced to 21%, and that the optimum conditions as regards cathode efficiency are between 0.1% and 0.4% free acid.

It will be noticed that, as the acidity of the electrolyte increases the anode efficiency decreases more rapidly than the cathode efficiency.

It is true that by working with very high current density, the electrolysis may be carried on in presence of a higher acidity, Professor Guess Report of the Royal Ontario Nickel Commission, page 479, having stated that the economic limit is attained with a current of 250 amperes per square foot when the free acid is 4.4% but the current efficiency under these conditions is only 50%.

Having once ascertained the optimum conditions as regards the acidity of the electrolyte in relation to the optimum current efficiency, the next step was to devise a method for maintaining these conditions when working on a large scale.

In order to keep down the acidity of the catholyte it is the practice to use a number of cells with diaphragms and to circulate the catholytes and anolytes.

Now if a number of cells are used in which the catholytes are passed from one cell to the next in series, the catholyte will soon become exhausted *i. e.* considerably re-

duced in nickel and if the anolyte be passed from one cell to the next in series, its acidity will rapidly increase and by transfusion through the diaphragm into the catholyte, increase the acidity above the required optimum.

It is of course feasible to regulate the circulations so that the acidity in the catholyte is maintained at the optimum; but such a method would require an elaborate system for controlling the circulation in each cell and owing to the relatively small amount of deposition of nickel on the cathodes it would not be economically possible to work this process on a large scale, apart from the disadvantages of requiring a considerable number of mechanical and electrical connections between the various cells.

Similar disadvantages would be encountered in circulating the catholytes and anolytes in parallel.

In accordance with the present invention a series of electrolytic vats are used, each vat containing a plurality of cathode compartments containing a similar number of stationary cathodes separated by electrolytic diaphragms from insoluble anodes arranged between said cathode compartments, the whole being arranged in a single anode compartment, which is formed by the vat.

The cathode liquor is passed through the cathode compartments of each vat in parallel in order to maintain uniform concentration and acidity of the catholyte therein. From each vat the catholyte is passed in series to the next vat, its acidity decreasing as it progresses.

This decreasing acidity is maintained within the limits of the optimum acidity by utilizing the increase in the acidity of the anolyte which transfuses slightly through the diaphragm into the catholyte, the anolyte being, for this purpose, passed through the vats in series.

In order to explain the method, supposing the cathode liquor issuing from the plurality of the cathode compartments of the first vat,—which owing to the parallel flow of the catholyte irrespective of the number of cathode compartments used, is of the same concentration and acidity,—has been reduced in acidity from 0.4% to 0.2% (which depends on the rate of flow of the cathode liquor), then passed in parallel into the plurality of cathode compartments of the second vat, the electrolytic action will reduce the acidity of the cathode liquor in this second vat from 0.2% to a lower figure.

On the other hand the anode liquor, which is passed through the anode compartment of each vat in series increases in acidity, for instance from neutral to 3% acidity in the first vat. On entering the second vat the anolyte transfuses slightly through the diaphragm and thus makes up the loss of acidity of the catholyte of this vat and maintains it at approximately the 0.2% of the entering cathode liquor.

In the third vat the acidity of the catholyte coming from the second vat will be reduced below 0.2% acidity, but owing to the transfusion of the anolyte of the third vat, which in the meanwhile has increased in acidity to say about 9%, into the cathode compartments of this vat, the acidity in said compartment is again made up to be within the limits of the optimum acidity.

To prevent any further increase of acidity in the cathode compartments of the following vat by transfusion of the strongly acid anode liquor into the cathode compartment, a certain amount of the anode liquor is withdrawn and replaced by new neutral anode liquor, whenever the acidity of the anolyte has reached a degree which would be incompatible with the maintenance of the optimum acidity of the catholyte.

The strongly acid anode liquor withdrawn is used in a well known manner for the extraction of further quantities of nickel from ore or matte, while the cathode liquor, which has again reached the required optimum acidity, but is reduced in nickel contents, is withdrawn from the cathode compartments of the last vat and pumped back to the cathode compartments of the first vat admixed with fresh neutral liquor obtained from the above-mentioned extraction of nickel from ore or matte, by the strongly acid anode liquor withdrawn from the anolyte.

It is necessary to use a plurality of cathode compartments because if only one cathode compartment, containing a plurality of cathodes were used, the nickel deposit would, in the case of stationary cathodes, be unsatisfactory, because the hydrogen formed on the cathode would remain occluded thereon.

By this process the deposition of nickel can be continued if desired until, for instance, in a liquor containing originally 10 per cent. of nickel, the free sulfuric acid amounts to 15 per cent. Inasmuch as a liquor containing 10 per cent, of sulfuric acid suffices for extracting nickel from a further portion of the material under treatment, it is easy to obtain by the invention suitable liquor for a cyclic process without concentration and at the same time to economize in power and electrolytic plant.

The accompanying drawings illustrate an apparatus suitable for carrying out the process.

Figure 1 is a vertical transverse section through a vat and a cathode compartment contained therein.

Fig. 2 is a part longitudinal vertical section through the said vat and two of the cathode compartments.

Fig. 3 is a plan of the electrolytic plant of which the said vat forms a unit.

The wooden vat a has a lead lining a' and supports on its sides a number of wooden frames b constituting the ends and bottom of the cathode compartments, the sides of which are sheets of asbestos millboard c stretched on the frame and fastened thereto.

Supported in electrical insulation on two or more brackets a^2, a^3 on each side of the vat a, are electrically conducting bars d, d', parallel to the sides. The bar d is connected with the positive pole of the source of electric current, the bar d' with the negative pole. Supported at one end by, and electrically connected with, bar d' are electrically conducting pairs of bars e, one pair extending longitudinally over each cathode compartment. These bars are supported at the other end on electrically insulating material carried by the brackets a^2, and between each pair of bars is clamped an iron cathode f depending in the middle of the cathode compartment beneath the pair. Electrically connecting bars g extend across the vat, one above each of the spaces between the cathode compartments. These bars are supported by, and electrically connected at one end with, the bar d and are supported at the other end by electrically insulating material carried by the brackets a^3. From each bar g in electrical connection therewith depends a lead anode h in the space between two cathode compartments.

Thus the vat forms a single anode compartment containing a plurality of cathode compartments. The cathode liquor flows from either of two tanks i (Fig. 3) into a lead lined trough k whence it flows through pipes k', having flexible extensions k^2 (Fig. 1), into each cathode compartment. In order to keep a constant head in the trough k the supply of liquor thereto is in excess of the flow of liquor therefrom, the excess draining through an overflow pipe k^3 to a trough l common to all the vats.

The liquor flowing into the cathode compartment being of higher specific gravity than that which has been electrolyzed in the compartment, tends to descend displacing the lighter liquor through the pipe m into trough m' which resembles the trough k and has an overflow pipe m^2. From this trough the liquor flows through pipe m^3 to the trough k of the next vat.

The liquor leaving the last trough m' flows into a well q whence it is raised by a pump q' to be returned through pipe q^2 to tank i. The well q also receives the liquor from trough l.

The anode liquor flows from tank o into the bottom of vat a by way of pipe o' displacing liquor which has undergone electrolysis through pipe o^2 which opens from the top of this vat and is carried to the bottom of the next. From the last vat the anode liquor flows into a well p, whence it is raised by a pump p' through pipe p^2 to the tank o.

The best temperature for the electrolysis being 60° C. the troughs k and the vats a are furnished with steam circulation pipes r and s respectively. Pipe t serves for emptying the vat when necessary for cleaning or repairing it.

The installation here represented is primarily intended for the treatment of liquor made by extracting nickel - copper matte which has first been calcined and then reduced. The most convenient strength of sulfuric acid for this purpose is 10 per cent. Accordingly the liquor in the well p is withdrawn wholly or in part when it has attained the said strength and is used for extracting nickel.

A suitable current density is 10 amperes per square foot and the drop of E. M. F. from vat to vat may be 3—3.5 volts.

What I claim as new and desire to secure by Letters Patent of the United States is:—

1. The continuous cyclic process for electrolytically producing nickel which consists in electrolyzing a slightly acid liquor containing nickel salt, obtained by treating nickel ore with an acid, and kept in continuous circulation through the cathode compartments of a series of electrolyzing vats in serial order, the insoluble-anode compartments of which vats are traversed by a similar circulating liquor, withdrawing part of said last named liquor as soon as its acidity has exceeded the optimum acidity in the catholyte, and treating fresh nickel ore with said withdrawn liquor to produce further quantities of the first liquor.

2. The continuous cyclic process for electrolytically producing nickel which consists in electrolyzing a slightly acid liquor containing nickel salt, obtained by treating nickel ore with an acid, and kept in continuous circulation through the cathode compartments of a series of electrolyzing vats in serial order, the insoluble-anode compartments of which vats are traversed by a similar circulating liquor, the diminishing acidity of the catholyte of the subsequent vats being restored to the optimum acidity by the partial transfusion of the progressively more acid anolyte into the catholyte, withdrawing part of said last named liquor as soon as its acidity has exceeded the optimum acidity in the catholyte, and treating fresh nickel ore with said withdrawn liquor to produce further quantities of the first liquor.

3. The continuous cyclic process for electrolytically producing nickel, which consists in electrolyzing a slightly acid liquor containing nickel salt, obtained by treating nickel ore with an acid, and kept in continuous circulation by being passed in parallel

through a plurality of stationary-cathode compartments separated by diaphragms from insoluble anode compartments, formed by the electrolyzing vats themselves, and traversed by a similar liquor, and thence in series to the next vat, withdrawing part of said last named liquor as soon as its acidity has exceeded the optimum acidity for electrolysis in the catholyte, and treating fresh nickel ore with said withdrawn liquor to produce further quantities of the first liquor.

4. The continuous cyclic process for electrolytically producing nickel, which consists in electrolyzing a slightly acid liquor containing nickel salt, obtained by treating nickel ore with an acid, and kept in continuous circulation by being passed in parallel through a plurality of stationary-cathode compartments separated by diaphragms from insoluble-anode compartments, formed by the electrolyzing vats themselves, and traversed by a similar liquor and thence in series to the next vat, the diminishing acidity of the catholyte of the subsequent vats being restored to the optimum acidity by the partial transfusion of the progressively more acid anolyte into the catholyte, withdrawing part of said last named liquor as soon as its acidity has exceeded the optimum acidity in the catholyte, and treating fresh nickel ore with said withdrawn liquor to produce further quantities of the first liquor.

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

CHRISTIAN HEBERLEIN.