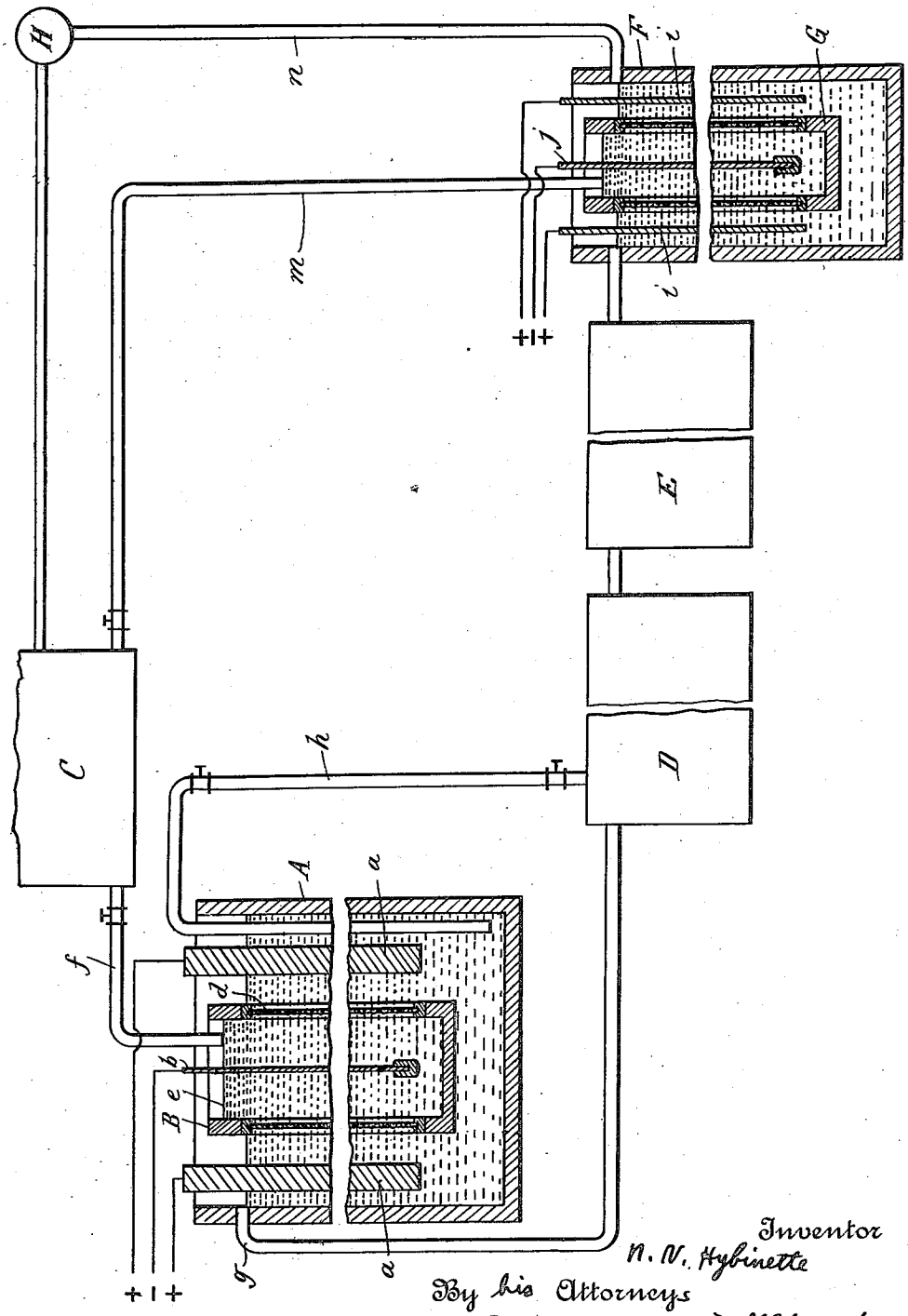
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SEPARATING METALS BY ELECTROLYSIS.

APPLICATION FILED FEB. 16, 1920.

1,395,827. Patented Nov. 1, 1921.



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SEPARATING METALS BY ELECTROLYSIS.

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To all whom it may concern:

Be it known that I, NOAK VICTOR HYBINETTE, a citizen of Norway, residing at Christiania, Norway, have invented certain new and useful Improvements in Separating Metals by Electrolysis; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

In Letters Patent of the United States of America No. 805,969, issued November 28, 1905, I have described and claimed a process for the separation of metals consisting mainly in smelting ore into more or less pure copper-nickel anodes, which are then electrolyzed in a cell or cells, having a so-called "filter" which separates the anode compartment from the cathode compartment, a stream of neutral nickel sulfate solution running into the cathode compartment continuously and thence through the filter, whereby the copper as it dissolves from the anode is prevented from entering the cathode compartment, and a pure nickel deposit is produced upon the cathode.

In this process, the metals dissolved at the anode make the nickel sulfate solution passing from the cathode compartment into the anode compartment impure, and it is regenerated by cementation of copper on nickel, and, eventually, by precipitating iron by means of nickel oxid. The liquid thus regenerated and purified is again supplied to the electrolytic tank.

It is well known that a good cathode deposit of nickel is dependent upon the employment of an absolutely neutral plating solution, with or without the addition of a number of "dopes" known to the art and which are referred to in the patent as "weak acids." If, however, free sulfuric acid in the solution should rise to a content of more than a few hundredths of one per cent., or if, on the other hand, the solution should become slightly basic, the nickel deposit will be immediately injuriously affected,—in the first instance becoming hard and brittle, and, in the latter instance, being soft, porous and mixed with basis precipitate.

It is, therefore, of the greatest importance to keep the solution of the correct acidity. Accordingly, in my U. S. patent above referred to, I have specified that the filter should be very porous so that it would not act as a dialytic diaphragm, that is to say, that it would not cause dialysis of the cathode solution by the migration of any notable amount of acid ions through the filter; in other words, the provisions made in my patent were such that the acidity of the solution would be very slight on both sides of the filter.

I have found, however, that the use of filters of the very porous type contemplated by the patent involves the circulation of a large quantity of solution and that, accordingly, the operation of the process is correspondingly more expensive than if a smaller quantity of solution could be circulated. I have also found that, in certain instances, it is necessary to maintain a greater degree of acidity of the solution on the anode side than on the cathode side of the filter. Thus, the anode efficiency of the current, in neutral solution, is considerably less than the cathode efficiency in those instances where use is made of a less easily soluble anode, such as hereinafter described to increase the anode efficiency, under such conditions, it is desirable to have a greater acidity in the anode compartment than that permissible for good plating on the cathode.

The present invention is intended to correct the defects hereinbefore noted. In carrying the invention into effect, instead of supplying to the cathode compartment a neutral solution (with or without the addition of the dopes or weak acids, sometimes employed) I make use of a nickel sulfate solution, continually flowing into the cathode compartment, and containing a notable proportion of free sulfuric acid. In fact, in the preferred practice of the invention the solution as it enters the cathode compartment, is so acid that commercially good nickel cannot normally be plated from it; nevertheless, in accordance with the present invention, such commercial plating is absolutely assured.

The way in which I accomplish this apparent paradox is by using a dense diaphragm instead of the porous filter partition of the patent, thereby correspondingly cutting down the amount of solution circulated per unit of time, while, at the same time, the dense diaphragm acts not merely as a filter to direct the circulation, as set forth in the patent, but partly as a diaphragm and partly as a filter. Furthermore,

the mode of operation of the process is such that the migration of the acid ions through the diaphragm is so rapid that the excess acidity of the cathode solution is progressively removed, and good plating is obtained upon the cathode, although the solution which enters the cathode compartment is *per se* entirely too acid for commercial plating purposes. In order to operate to the best advantage for the attainment of this result, it is necessary to bring into harmony seven variable factors, to wit, the hydrostatic pressure in the cathode compartment, the speed of filtration flow through the diaphragm, the acidity and the nickel content of the ingoing electrolytic solution, the dialytic capacity of the diaphragm, the temperature of the electrolyte, and finally, the current density.

For instance, for good plating, I use a solution of nickel sulfate containing about 50 grams of metallic nickel per liter continually flowing into the cathode compartment with a temperature of about 55° C. and with an acidity of about two grams of free sulfuric acid per liter. A sample of the solution, taken near the cathode, during the plating operation, will then show about 0.2 grams of free sulfuric acid per liter, an amount small enough to be suitable for good commercial plating. These results are obtained when using a diaphragm of heavy cotton cloth which lets through only about one liter per square foot of surface per hour, with a hydrostatic pressure in the cathode compartment ranging from about one-half inch to one inch, while the density of the current is about ten amperes per square foot. Under these circumstances, the migration of the acid ions is so much more rapid than the filtration flow that technically valuable results are obtainable, as noted. It also appears that the speed of migration of the acid ions in one direction is enormously greater than that of the copper ions in the other direction, and that this difference in migration, together with the flow of the electrolyte through the filter, results in exclusion of the copper ions from the cathode solution. The diaphragm alone will not exclude the copper ions from migrating to the cathode compartment, but the combined flow through the diaphragm filter and the removal of the electrolyte from the anode compartment, together with proper regulation of the process, enables contamination of the cathode solution with copper to be avoided.

It will be understood that the specific conditions mentioned above are capable of some variation, although these conditions are the ones that I have found most advantageous. For example, if a diaphragm is used which permits the solution to filter through faster, the acidity should be decreased. If the current density is increased, the acidity can be somewhat increased, while if the current density is decreased, the acidity should be decreased. Similarly, the acidity should be reduced with reduction in temperature, while increase in temperature permits somewhat increased acidity. The various conditions are thus interdependent and to a certain extent capable of variation, but they should be so correlated, for example, as above described, that the desired result will be obtained.

In the practical operation of the process, it becomes necessary to see to it that the acid solution from the anode side is purified so that the acidity remains substantially the same before and after such purification. Copper may be removed from the anode solution without disturbing the acidity. If, however, the anodes contain iron in such amount that it is necessary to precipitate iron out of the solution by nickel oxid (hydrated or carbonated, as the case may be) so that the solution becomes neutralized, it will then be necessary to acidify the solution after separating out the iron precipitate. So also, such acidification will be necessary in case the removal of the copper is effected by agents which neutralize the acidity.

If, therefore, for any reason, the solution has been neutralized, I find it most convenient to restore the acidity by plating out nickel from the solution, in an electrolytic tank, using insoluble anodes; because, if the acidity were to be produced by merely adding acid the equilibrium of ingoing and outgoing acid and nickel in the constantly circulating electrolyte would be disturbed. Inasmuch as the solution going out of the acidifying electrolytic tank is to contain more acid than is required for good nickel plating, I locate the cathode of the acidifying electrolytic tank within a cathode compartment provided with porous diaphragm walls and obtain the desired plating upon said cathode by circulating my ordinary pure cathode solution through said diaphragm walls, exactly as in the main plating tanks, and at the same time that the main supply of said pure solution to be acidified passes through the acidifying electrolytic tank on the anode side thereof only.

In the use of the present invention, the amount of electrolyte in circulation is so small as compared with the older practice that it has been found important to provide for a more perfect circulation in the soluble anode cell, and I have, therefore, found it desirable to draw off the solution, in part at least, at the bottom of the cell. In so doing, I find that the foul or impure electrolyte may, in this way, be separated into two parts, one running off at the top of the anode compartment and containing comparatively

little copper, and the other running out at the bottom with considerably more copper. This is of considerable advantage in the purification by cementation of the copper on nickel, and I wish, therefore, to be understood as claiming its use in this connection.

Another feature of the present invention which is of importance is the use of dense, hard copper-nickel anodes made of a copper-nickel alloy produced in an electric furnace. In the production of such anodes, the copper-nickel matte may be roasted and leached to remove the greater portion of its copper, and the roasted and leached matte, containing from 3 to 4 parts of nickel to 1 of copper, then mixed with about 10% of powdered coke and subjected to an electric furnace operation with a suitable flux which promotes the removal of iron therefrom in the form of a slag. The iron content of the nickel-copper alloy can thus be reduced to a small fraction of 1%, while the alloy can likewise be freed from the greater portion of its sulfur and from occluded gases. So also the alloy can be heated above its melting point to such a temperature that it is thinly fluid. The alloy is therefore of a different and improved composition as compared with an alloy produce in a blast furnace; and the anodes cast from such alloy are likewise distinguished from anodes cast from alloys produced in a blast furnace, in that they are dense and hard and relatively more insoluble, and relatively free from the impurities which are present in anodes made from blast furnace alloys. The use of the improved anodes, in the process of the present invention, results in an improved operation of the process. Accordingly, while the process is capable of operation with anodes made from blast furnace alloys it is more advantageous when practised with the improved anodes made of electric furnace alloy, and I wish, therefore, to be understood as claiming the use of these improved anodes in this connection, as well as the process when such anodes are not employed.

In the drawing hereunto attached, I have indicated, more or less diagrammatically, the apparatus employed in the carrying out of the process.

Referring to the drawing, A indicates the anode compartment of the main cell containing the anodes *a*. B indicates the cathode compartment containing the cathode *b* and having the dense diaphragm partitions of heavy cotton cloth or its equivalent *d*, all as hereinbefore described. The hydrostatic head in the cathode compartment is indicated by the line *e*.

The pure nickel sulfate solution, containing preferably two grams of free sulfuric acid to the liter may be conveniently contained in a storage receptacle *c* at a temperature of about 55° C. and discharges continuously, during the operation of the process, through the valve-controlled inlet pipe *f*. One of the outlets for the foul or impure solution from the anode compartment A is by means of the overflow pipe *g*, and the other outlet therefrom is the siphon or like discharge *h* leading from near the bottom of said anode compartment. These two outlets may conveniently discharge into the same cementation tank D wherein the copper is deposited out on nickel. From the cementation tank the solution passes to the tank E wherein any iron present is precipitated by nickel oxid, or the like, thereby neutralizing the solution. The neutralized solution then passes into the acidifying electrolytic tank, whose cathode compartment G is of the same construction as the like cathode compartment B of the main cell. The acidifying electrolytic tank is provided with insoluble anodes *i*, and a suitable cathode *j* for the precipitation of nickel is provided in the cathode compartment. The pure nickel acidified solution for the cathode cell G is supplied continuously from the storage reservoir C through the valved pipe *m*. A suitable pump H located in a return conduit *n* from the acidifying electrolytic tank F conveys the circulating solution back to the storage receptacle C.

From the foregoing description of the mode of operation of the invention, it will be understood that its main characteristic or basic principle consists in introducing into the cathode compartment of the depositing cell a solution containing an excess of free acid over the amount that would be tolerated for good commercial plating, and bringing about such a migration of acid ions through the diaphragm partition as to introduce and maintain proper plating conditions. Insofar as I am aware, this characteristic feature is broadly new in the art of electrolytic separation of metals. Accordingly, I wish to be understood as intending, in the appended claims, to protect its use in the plating, separating or refining of not only nickel, but also such metals as ferro-nickel, cobalt, zinc, and the like. So also, it will be apparent that the invention may be applied not only to operations wherein the anode is a soluble alloy, but also to other combinations; as, for instance, in the production of nickel by continuously dissolving nickel carbonate in the electrolyte and employing in connection therewith, an insoluble anode, and returning an only partly neutralized electrolyte to the cathode compartment.

I claim:

1. The process of plating metals upon a cathode which is separated from the anode by a filtering diaphragm, which comprises effecting a flow from the cathode to the anode of an electrolyte which enters the cathode compartment with an excess of free

sulfuric acid beyond the amount to be tolerated at the depositing surfaces of the cathode; sustantially as described.

2. The process of plating metals upon a cathode which is separated from the anode by a filtering diaphragm, which comprises effecting a flow from the cathode to the anode of an electrolyte which enters the cathode compartment with an excess of free sulfuric acid beyond the amount to be tolerated at the depositing surfaces of the cathode, and obtaining the desired condition of the electrolyte at said surfaces by the migration of acid ions through the diaphragm; substantially as described.

3. The process of plating metals upon a cathode which is separated from the anode by a filtering diaphragm, which comprises effecting a flow from the cathode to the anode of an electrolyte which enters the cathode compartment with an excess of free sulfuric acid beyond the amount to be tolerated at the depositing surfaces of the cathode, and obtaining a nearly neutral condition of the electrolyte at the depositing surfaces of the cathode suitable for commercial metal deposits thereon by the migration of acid ions through said diaphragm; substantially as described.

4. The process of separating nickel from other metals by electrolysis of an anode containing an alloy of nickel, and plating nickel at the cathode, which comprises separating the cathode from the anode by a filtering diaphragm and effecting a flow from the cathode to the anode of an electrolyte which, at its entrance into the cathode compartment, contains more free sulfuric acid than is appropriate for producing a deposit of nickel of commercial quality upon the cathode; substantially as described.

5. The process of separating nickel from other metals by electrolysis of an anode containing an alloy of nickel, and plating nickel at the cathode, which comprises separating the cathode from the anode by a filtering diaphragm and effecting a flow from the cathode to the anode of an electrolyte which, at its entrance into the cathode compartment, contains more free sulfuric acid than is appropriate for producing a deposit of nickel of commercial quality upon the cathode, regenerating the anode solution and acidifying the regenerated solution by causing it to flow through an electrolytic tank with insoluble anodes, in which tank the desired amount of acid to regenerate it is set free, and a corresponding amount of nickel is plated; substantially as described.

6. The process of separating nickel from other metals by electrolysis of an anode containing an alloy of nickel, and plating nickel at the cathode, which comprises separating the cathode from the anode by a filtering diaphragm and effecting a flow from the cathode to the anode of an electrolyte which, at its entrance into the cathode compartment, contains more free sulfuric acid than is appropriate for producing a deposit of nickel of commercial quality upon the cathode, regenerating the anode solution and acidifying the regenerated solution by causing it to flow through the anode compartment only of an electrolytic tank having insoluble anodes and equipped with filtering diaphragms around its cathodes and maintaining a flow of plating electrolyte from the cathode compartment into the anode compartment of said acidifying electrolytic tank; substantially as described.

7. In the electrolysis of metals, regenerating an acid anode electrolyte containing in solution nickel and another metal by depositing out the other metal by a precipitant which neutralizes the solution, and thereupon restoring the electrolyte to its original condition of acidity by plating out a portion of the nickel therefrom; substantially as described.

8. The process of plating nickel upon a cathode which is separated from the anode by a filtering diaphragm, which comprises supplying to the cathode compartment at a temperature of about 55° C. a nickel sulfate electrolyte containing about 50 grams of nickel per liter and having an acidity of about 2 grams of free sulfuric acid per liter, and effecting a flow of the electrolyte from the cathode compartment to the anode compartment through the filtering diaphragm, the current density, the rate of flow, and the diaphragm being such that the acidity of the electrolyte near the cathode will be reduced to about 0.2 grams of free sulfuric acid per liter substantially as described.

9. The process of plating nickel upon a cathode which is separated from the anode by a filtering diaphragm, which comprises supplying to the cathode compartment at a temperature of about 55° C. a nickel sulfate electrolyte containing about 50 grams of nickel per liter and having an acidity of about 2 grams of free sulfuric acid per liter, effecting a flow of the electrolyte from the cathode compartment to the anode compartment through the filtering diaphragm at the rate of about 1 liter per square foot of surface per hour, and maintaining a current density of about 10 amperes per square foot, the nature of the diaphragm and the regulation of the process being such that the acidity of the electrolyte near the cathode will be reduced to about 0.2 grams of free sulfuric acid per liter; substantially as described.

10. The process of plating nickel upon a cathode which is separated from a copper nickel anode by a filtering diaphragm, which comprises effecting a flow from the anode to

the cathode of a nickel sulfate electrolyte which enters the cathode compartment with an excess of free sulfuric acid beyond the amount to be tolerated at the depositing surfaces of the cathode, and drawing off a part at least of the impure electrolyte from the bottom of the anode compartment; substantially as described.

11. The process of plating nickel upon a cathode which is separated from a copper nickel anode by a filtering diaphragm, which comprises effecting a flow from the anode to the cathode of a nickel sulfate electrolyte which enters the cathode compartment with an excess of free sulfuric acid beyond the amount to be tolerated at the depositing surfaces of the cathode, and drawing off a part of the impure anode electrolyte from the top of the anode compartment and a part from the bottom of the anode compartment; substantially as described.

12. The process of plating nickel upon a cathode which is separated from a nickel copper anode by a filtering diaphragm, which comprises effecting a flow from the cathode to the anode of an electrolyte which enters the cathode compartment with an excess of free sulfuric acid beyond the amount to be tolerated at the depositing surfaces of the cathode, the copper nickel anode being made of an alloy produced in an electric furnace; substantially as described.

13. Electrolytic apparatus, comprising an anode compartment and a cathode compartment, provided respectively with anode and cathode, and separated from each other by a filtering diaphragm, and means for supplying a flow of the electrolyte to the cathode compartment and from the anode compartment, said filtering diaphragm being of such permeability that it acts partly as a filter and partly as a diaphragm to deplete the solution in the cathode compartment in acid ions; substantially as described.

14. Electrolytic apparatus, comprising an anode compartment and a cathode compartment, provided respectively with a copper nickel anode and a cathode for the deposit of nickel thereon, and separated from each other by a filtering diaphragm, means for supplying to the cathode compartment a flow of nickel sulfate electrolyte and for removing from the anode compartment the copper-nickel electrolyte, said filtering diaphragm being of such permeability that it acts partly as a filter and partly as a diaphragm to deplete the solution in the cathode compartment in acid ions; substantially as described.

15. Electrolytic apparatus, comprising an anode compartment and a cathode compartment, provided respectively with a copper-nickel anode and a cathode for the deposit of nickel thereon, and separated from each other by a filtering diaphragm, means for supplying a flow of nickel sulfate electrolyte containing an excess of acid to the cathode compartment, means for drawing off a part at least of the impure nickel-copper electrolyte from the anode compartment, said filtering diaphragm being of such permeability that it acts partly as a filter and partly as a diaphragm to deplete the solution in the cathode compartment in acid ions; substantially as described.

In testimony whereof I affix my signature.

NOAK VICTOR HYBINETTE.