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N. V. HYBINETTE.

SEPARATION OF METALS.

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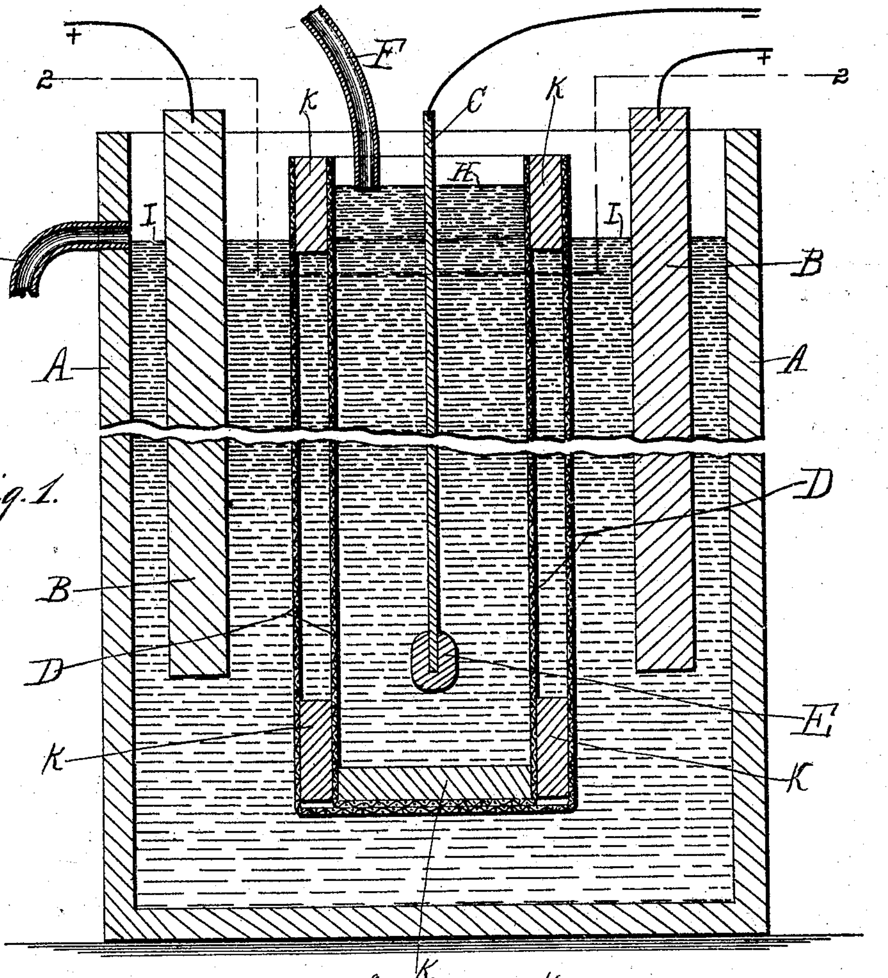

Fig. 1.

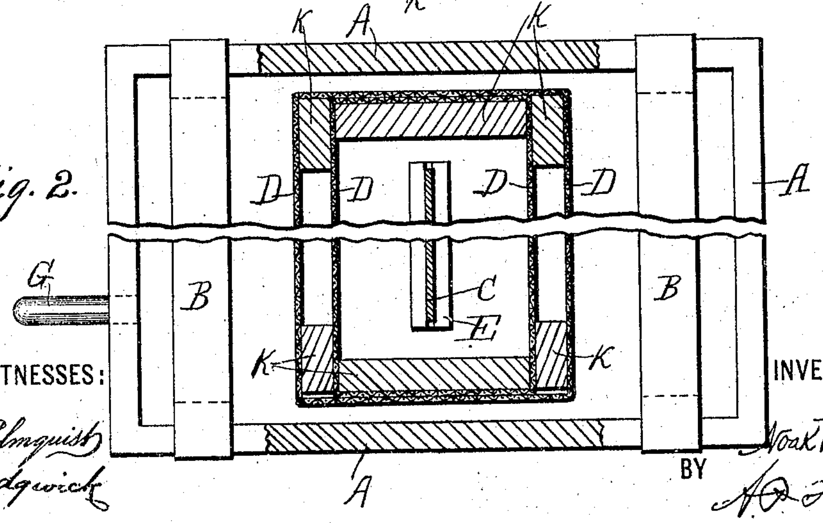

Fig. 2.

WITNESSES:

L. Almquist

C. Sedgwick

INVENTOR

Noah V. Hybinette

BY

A. D. Thayer.

ATTORNEY

UNITED STATES PATENT OFFICE.

NOAK VICTOR HYBINETTE, OF WESTFIELD, NEW JERSEY.

SEPARATION OF METALS.

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To all whom it may concern:

Be it known that I, NOAK VICTOR HYBINETTE, a citizen of the United States of America, and a resident of Westfield, in the county of Union and State of New Jersey, have invented certain new and useful Improvements in the Separation of Metals, of which the following is a specification.

I have discovered a process for the economical separation of alloys into their constituents by electrolysis. It has been designed specially for the separation of nickel and copper from alloys of these metals, which are generally also associated with iron; but it may be employed for the treatment of other alloys.

The fundamental principles on which the process is built are as follows:

First. If copper-nickel alloy is electrolyzed, the nickel will dissolve more rapidly from the anode and the result will be that the anode-slimes falling to the bottom of the tank will consist mainly of copper compounds. If at the same time sulfur is present in the anode, sulfid of copper is separated as anode-slime. This reaction is one of the means used in my process for separating copper from nickel. I find in practice that about one-half of the copper which I take into the process is recovered as such slimes.

Second. There are at present in use several well-known processes for removing large proportions of copper from copper-nickel mattes. For instance, if a copper-nickel matte is roasted and leached with sulfuric acid, practically only copper is removed until the residue contains nickel and copper in the proportion of three to one. I have therefore in my power to produce an anode containing three parts of nickel and one part copper, and by the selective action of the electric current I have only to handle one part of copper to every six parts of nickel through my electrolytic solution.

Third. By this combination of processes I therefore come down to such proportions between copper and nickel that it becomes commercially possible to eliminate the copper by allowing it to pass off as an impurity through a solution of nickel, which is regenerated or purified as soon as the copper has accumulated in the solution to such an extent as to make the nickel deposit contain more copper than is allowed in the market.

Fourth. To be able to circulate a nickel solution in the way now mentioned, it has been necessary to invent a ready way to purify the same without in the least disturbing its plating qualities and return it in its original condition. Several electrolytic nickel processes have been proposed in the past; but all of them have had to make up new solution from time to time by an outside and independent process. Not all nickel-plating solutions would be suitable for such a process of constant regeneration; but I have now found a solution which will lend itself to my purpose in a weak neutral solution of nickel sulfate to which a weak acid—such as phosphoric, boric, acetic, or lactic acid is added. That nickel can be plated in such solution is not new; but it has never been used for this purpose before.

Fifth. Means by which such solution can be purified from copper will readily suggest themselves to the trained metallurgist; but for the best results commercially I want to make use of one particular way—namely, cementation—and in this connection I have discovered certain conditions under which the cementation of copper on nickel and even on copper-nickel alloy will take place as readily as to make the reaction available for commercial purposes, as will be further described below. With this system of circulation and purification the quality of the nickel produced to a certain extent will only be a question of how fast the solution is circulated; but the process would not be so economical had I not introduced means by which a pure nickel could be produced at the same time, as the solution passing form the plating-tanks contains a considerable quantity of copper.

Sixth. I accomplish this end by separating anode from cathode in a novel way. It is done by inserting between the two poles a filtering-diaphragm directing the current of solution perpendicularly from the surface of the cathode to that of the anode. Such diaphragms have been used before, but never for the purpose of separating metals from an alloy constituting the anode. I believe also that I am the first one to use such diaphragm in a case where the least decomposition of the solution would prevent the plating of the metal on the cathode. Furthermore, I do not know that anybody has succeeded in giving to such diaphragm a mechanical construction which will allow of its being used in an ordinary electrolytic plating-tank where the anode and cathode are hung vertically.

After now having given an outline of the different means which I employ for obtaining my results I will give a more detailed account of the different steps which constitute the process.

Referring to the drawings, Figure 1 is a vertical section of the apparatus which I use, and Fig. 2 is a plan view.

A is the tank in which the electrolysis is carried out. It is preferably a wooden tank with or without lead lining. It has the overflow G, which always keeps the level of the solution at I and contains a filtering-bag D. The filtering-bag is made up of the wooden frame K and the two thicknesses of cotton cloth D, separated by the wooden frame K.

C is the cathode-plate with the wooden rib E, which is shown in the drawings to extend over the bottom edge of the cathode; but it may for still better protection extend all around the plate.

B represents the anodes.

F is the inflow, which is regulated in such a way that the solution in the bag stands at the level H, which is about one inch above the level I.

The rib E prevents the cathode from warping and making contact with the bag.

In separating copper and nickel I preferably employ as electrolyte a dilute solution of sulfate of nickel with a small proportion of weak acid—such as phosphoric acid, boric acid, lactic acid, or other organic acid well known to those conversant with the trade—and I particularly prefer a solution of nickel sulfate and weak acid so diluted that it will not crystallize at ordinary temperature. Other solutions—such as a very concentrated solution of sulfate or chlorid of nickel with or without inactive salts, such as sulfate or chlorid of aluminium or magnesium, used at comparatively high temperature and with high current density as means of making a coherent nickel deposit—are not well adapted to my process, and I therefore intend to make a specific claim to the employment in this process of a solution of weak acid with the sulfate of nickel which will give good results at low temperature and with low current density. My other claims, however, are not limited to the use of that particular solution.

The first step of my invention consists in placing in the electrolytic solution an anode composed of the alloy to be separated and a cathode-plate upon which the metal is to be deposited and separating the electrodes by a pervious diaphragm, such as filter-cloth or filter-paper. This is done, preferably, by inclosing one of the electrodes, preferably the cathode, in a bag of such cloth or paper. In that it has a decided filtering capacity my diaphragm is of a different nature from those porous diaphragms ordinarily employed in electrolytic processes, which diaphragms allow one reaction to take place on one side and a different reaction on the other side. My diaphragm is so porous that if it were alone relied upon to separate the anode side from the cathode side the solutions would mix and become homogeneous in a short time. Its action is therefore supplemented by keeping the solution in motion, causing it to flow from the cathode to the anode through the porous material, and thus preventing the metal which has been dissolved at the anode from coming into contact with the cathode. The diaphragm-bag is, in other words, only a convenient mechanical device for directing the circulation of the liquid in a direction from cathode to anode.

The anode may consist either of a pure alloy of copper and nickel, containing, say, equal parts of these metals or containing them in other proportions, or it may contain considerable proportions of sulfur, iron, carbon, silicon, oxygen, &c., its composition in this regard being determined by the conditions prevailing at the works where the process is employed. When the copper contents are high, I prefer to remove part of it by some well-known process before making my anode. I have also found that an anode containing less than one per cent. of sulfur is preferable on account of the smaller percentage of scrap which remains after the solution of the anode. On the other hand, a higher percentage of sulfur will leave more copper in the anode-slimes. I have also found that it is best to have not more than three or four per cent. of iron in the anode, as it is cheaper to remove iron by furnace treatment when it is in excess of that amount.

The cathodes preferably consist of copper plates, which should be greased or otherwise treated, so as to prevent the deposited nickel from adhering thereto, and each cathode made of heavy metal—say .10 to .15 inch thick—is held by a non-conducting, preferably wooden, frame. These thick metal plates when held in the frame will not warp and come into contact with the bags, which would interfere with the process. To make the bags more reliable, I prefer to employ two thicknesses of cloth at a distance from each other of about one-half inch, and this improvement I consider most important. The anodes described above are placed in the bath with the cloth-incased cathodes in vertical position. A solution of the metal desired to be plated on the cathode is caused to flow into the bag and through the filter-cloth at right angles to the surfaces of the electrodes to the anode side of the tank.

By causing the solution to flow in a regular stream into the cathode-bag it may be made to stand therein at a level of, say, about one inch above the level of the solution outside the bag, thus imparting to the entire body of the solution within the cathode-bag a uniform hydrostatic pressure of one inch of liquid, causing it to flow outwardly through the pores of the entire bag in a direction perpendicular to the surfaces of the electrodes and at a uniform rate. The rate of flow is easily regulated by maintaining a desired difference of level between inside and outside the bag—for example, by having an overflow at a proper level outside the bag and an inlet-pipe admitting the sulfate-of-nickel solution in a regulated stream inside the bag. I can thus maintain such a flow of the solution as will prevent any of the ions dissolved at the anode from penetrating the bag to the cathode side. After the bag has been in use some time the pores become filled up with slimes of basic salts. This feature, far from being harmful, is a very desirable one. The electrical resistance of the diaphragm or bag is insignificant and the plating process goes on apparently as if no diaphragm were employed. There is, however, this important difference—namely, that an equivalent of nickel is deposited on the cathode within the bag and an ion of sulfuric acid is left free. This ion decomposes the molecule nearest to it, and so on throughout the bath, so that the final exchange will cause an ion of sulfuric acid to be liberated at the anode and at the same moment an ion of nickel to be deposited at the cathode. The ion of sulfuric acid at the anode immediately causes an ion of copper or nickel to be dissolved in the solution. As the exchange of ions goes on the newly-dissolved atoms of copper and nickel are traveling in a direction toward the cathode; but this movement is counteracted by the current through the porous bag, and the dissolved ions cannot pass to the cathode. Thus if I introduce into the cathode-bag a solution of nickel sulfate containing forty grams of nickel per liter the reaction will leave in the solution outside of the bag on the anode side of the tank, say, thirty-nine grams of nickel and one gram of copper per liter, the atomic weight of copper and nickel being approximately the same. A constant flow of the nickel sulfate is supplied to the cathode-bag, and although plating is going on the solution standing in the bag does not become deprived of its nickel, and thereby acidulated, but it contains at all times the same forty grams of nickel per liter. This process does therefore illustrate the theory for the wandering of the ions in a way that to my knowledge has never been done before. The operation thus goes on continually, nickel being deposited at the cathode until a sufficiently thick plating has been made, when the cathode-plates are removed and the nickel stripped therefrom, and there is a corresponding simultaneous solution of the copper, nickel, and iron at the anode until the anode is dissolved, when it is replaced by a fresh anode of impure alloy. The insoluble constituents of the anode—such as platinum, palladium, gold, &c., together with considerable copper—are deposited as a slime on the bottom of the tank. Copper, and specially sulfid of copper, is thus deposited as a slime, because the nickel of the anode being more electropositive is dissolved at a more rapid rate.

If desired, the anodes may be set in the porous bags and the solution drawn off from inside the bags. I prefer, however, to employ the arrangement above described.

It is evident from what I have said above that the process can be worked under the claims without the porous diaphragm and that still by far the greater part of the copper can be separated, partly as slime and partly through the regeneration of the solution; but nickel produced in such a way will always be very impure and can either be sold as such for special purposes or else will have to be refined.

The second step of the operation is to remove the dissolved iron and copper from the liquid which flows from the electrolytic tank. I may do this in various ways—for instance, by electrodeposition; but I derive great advantages by cementing the copper on nickel or an alloy of nickel and copper. Copper has been cemented heretofore on metallic nickel, but the reaction has always been slow, and complete cementation has only been obtained by applying the nickel in the form of a fine powder, fresh portions of which are added to the solution from time to time. Ordinary nickel in the form of grains, shots, or sheets, such as are obtainable in the market, has been so slow in its cementing action that it is practically impossible to use it when it is desired to free the solution substantially from copper. I have discovered that the slowness of the cementing action which has attended such use of nickel is due to the fact that it has contained a small percentage of carbon, silicon, or sulfur. If these impurities are removed, there is no trouble in cementing all the copper out of a solution, especially when it is kept at a boiling temperature, and it is a remarkable fact that complete separation takes place even when the nickel, which is conveniently cast in slabs, becomes covered by a hard layer of cemented copper as much as an inch in thickness. I have also discovered that I can not only use pure-nickel slabs in this process of cementation, but I may employ efficiently slabs of copper and nickel alloy containing as much as thirty per cent. of copper, the alloy being free from sulfur, silicon, and carbon, as above explained. This novel use for such alloy is a very important step in my process, inasmuch as the metal can be produced cheaply by roasting and smelting of copper-nickel matte. Therefore after drawing the solution from the electrolytic tank I first heat it and then regenerate it with nickel by passing it into a vessel in which it is maintained at a boiling temperature and is brought into contact with suspended slabs of nickel and copper alloy containing, say, thirty per cent. of copper. In this tank copper is very largely cemented out of the solution upon the slabs, its place in the solution being taken by an equivalent of nickel dissolved from the slabs, so that if on entering it contains thirty-nine grams nickel and one gram copper per liter it will contain after cementation, say, 39.9 grams of nickel and 0.1 gram of copper, together with some iron dissolved from the anodes. I then prefer to complete the cementation by transferring the solution into a second tank, where it is also maintained at a boiling temperature in contact with pure nickel slabs, which, being more efficient in cementing action than the copper-nickel alloy, will more rapidly remove every trace of copper, leaving the solution containing forty grams nickel per liter, as it originally did, minus the iron dissolved from the anodes, as well as from the slabs of nickel and copper alloy. The nickel slabs should be free from the impurities above stated.

The next step of the process is to remove the iron. This I do, preferably, by passing the solution through an electrolytic tank containing insoluble anodes of platinum, lead, or carbon, by which the iron compound is converted by oxidation from $FeOSO_3$ to $Fe_2O_33SO_3$. The solution is then passed into a tank where nickel carbonate is added to it in excess. This precipitates the iron as iron carbonate, and it is then removed from the solution by filtering. The solution which then contains the original forty grams per liter of nickel as sulfate is delivered into a tank or reservoir from which it is supplied to the porous cathode-bags, as explained above. The process is therefore a continuous one, the nickel electrolyte being supplied to the porous bags in a continuous stream, so as to maintain an outward current from the cathode, the equivalent of copper, nickel, and iron being dissolved in the liquid on the anode side. The liquid thus treated is regenerated by cementation on slabs or plates of nickel or nickel-copper free from carbon, silicon, and sulfur. The iron is then extracted from the solution, preferably by oxidation and precipitation, and the liquid thus regenerated and purified is again supplied to the electrolytic tank.

I have found that a current density at the cathode of ten amperes per square foot is suitable; but my invention is not limited in this respect.

My invention may be employed for the separation of other metals. For example, in separating an alloy of copper, zinc, and lead I introduce a pure solution of zinc-salt into the cathode-bags and regenerate the solution when drawn from the anode side of the bags by cementing it on zinc or zinc alloy. My invention lessens very greatly the cost of separating the constituents of alloys of this nature and it enables me to effect great economy in the treatment of complex ores which hitherto have been separated by furnace treatment at very much greater expense. In some cases the expense has been so great as to be prohibitive, and as a consequence large bodies of such ores remain undeveloped.

The various steps of the process may be modified and the individual steps covered in the claims may be employed separately or in other combinations.

The process of circulation by means of the porous bag, particularly in combination with cementation, is applicable to the separation of alloys in general. The particular cementation of copper on nickel and copper-nickel alloy is of great value in all processes of electrolytic refining of nickel and also in those cases where electrolysis is not used.

What I claim as my invention is—

1. The process of separating nickel from copper consisting in electrolyzing an anode containing substantially an alloy of copper and nickel in a solution consisting of nickel sulfate and a weak acid, regenerating the solution and returning the same.

2. The process of separating nickel from copper consisting in electrolyzing an anode containing substantially an alloy of copper and nickel in a solution consisting of nickel sulfate and a weak acid, removing the copper partly at least from such solution by cementation on a metal containing nickel and returning the regenerated solution.

3. The process of separating nickel from copper consisting in electrolyzing an anode containing substantially an alloy of copper and nickel in a solution consisting of nickel sulfate and a weak acid, removing the copper partly at least from such solution by cementation on a metal containing copper-nickel alloy and returning the regenerated solution.

4. The process of separating nickel from copper consisting in electrolyzing an anode containing substantially an alloy of copper and nickel in a solution consisting of nickel sulfate and a weak acid, circulating such solution in a direction from cathode to anode, regenerating the solution and returning the same to the cathode.

5. The process of separating metals consisting in electrolyzing an alloy, circulating the solution from cathode to anode, causing the solution surrounding the cathode to contain only one of the metals constituting the anode, regenerating the solution partly at least by cementation on the metal produced in the electrolytic bath.

6. The process of separating metals consisting in electrolyzing an alloy, circulating the solution from cathode to anode, causing

the solution surrounding the cathode to contain only one of the metals constituting the anode, regenerating the solution partly at least by cementation on an alloy consisting mainly of the metal produced in the electrolytic bath.

7. The process of separating nickel from copper consisting in electrolyzing an alloy and removing the copper from the solution partly at least by cementation on slabs of metal consisting mainly of nickel and refined at least to a point at which carbon, silicon, and sulfur are practically eliminated.

8. The process of separating nickel from copper consisting in electrolyzing an alloy and removing the copper from the solution partly at least by cementation on slabs of metal consisting mainly of copper-nickel alloy refined at least to a point at which carbon, silicon, and sulfur are practically eliminated.

9. The process of separating nickel from copper consisting in electrolyzing an alloy circulating the solution from cathode to anode, causing the solution surrounding the cathode to contain nickel only, and removing the copper from the solution partly at least by cementation on slabs or metal consisting mainly of nickel and refined at least to a point at which carbon, silicon, and sulfur are practically eliminated.

10. The process of separating nickel from copper consisting in electrolyzing an alloy, circulating the solution from cathode to anode, causing the solution surrounding the cathode to contain nickel only, and removing the copper from the solution partly at least by cementation on slabs of copper-nickel alloy refined at least to a point at which carbon, silicon, and sulfur are practically eliminated.

11. The process of separating nickel from copper consisting in electrolyzing an alloy, circulating the solution from cathode to anode through a porous diaphragm, causing the solution surrounding the cathode to contain nickel only, the solution on the other side of the diaphragm and surrounding the anode containing copper and nickel, preventing the passing of the copper through the diaphragm by maintaining a pressure on the cathode side of said diaphragm and by circulating the solution from cathode to anode, regenerating the anode solution by substituting nickel for copper and returning said regenerated solution to the cathode-compartment.

12. The process of separating metals, consisting in electrolyzing an alloy, circulating the solution from cathode to anode through a porous diaphragm, causing the solution surrounding the cathode to contain only one of the metals constituting the alloy, and the solution surrounding the anode containing all the metals dissolved from the anode, preventing the passage of the metals contained in the anode solution into the cathode-compartment by maintaining a pressure on the cathode side, and circulating the solution through said diaphragm.

13. The process of separating nickel from copper by electrolysis of an alloy in an electrolyte of nickel sulfate and a weak acid, circulating the solution from cathode to anode through a porous diaphragm and maintaining a pressure on the cathode side and regenerating the solution partly at least by cementation on nickel.

14. The process of separating nickel from copper by electrolysis of an alloy in a solution of nickel sulfate and a weak acid, circulating the solution from cathode to anode through a porous diaphragm, maintaining a pressure on the cathode side and regenerating the solution partly at least by cementation on copper-nickel alloy.

Signed at New York, this 22d day of November, 1904.

NOAK VICTOR HYBINETTE.

Witnesses:
C. SEDGWICK,
J. M. HOWARD.