

UNITED STATES PATENT OFFICE.

TITUS ULKE, OF SAULT STE. MARIE, CANADA.

ART OF REFINING COMPOSITE METALS.

SPECIFICATION forming part of Letters Patent No. 694,699, dated March 4, 1902.

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To all whom it may concern:

Be it known that I, TITUS ULKE, a citizen of the United States, and a resident of Sault Ste. Marie, Province of Ontario, Dominion of Canada, have invented certain new and useful Improvements in the Art of Refining Composite Metals, of which the following is a specification.

My invention has reference to improvements in the art of refining composite metals, and is particularly designed to extract copper and nickel of commercial purity from nickeliferous-copper material.

In the electrolytic processes of refining composite metals, and especially nickeliferous-copper material, heretofore attempted or suggested it was the invariable practice or attempt to dissolve the composite metals and use the complex solutions thus obtained as an electrolyte, to use an insoluble anode for depositing one of the metals—say the copper—so that the electrolyte eventually became so greatly impoverished in copper as to require a considerable increase of the electromotive force for further depositing the copper, and in order to extract all or nearly all of the copper the electromotive force had to be increased to an inconvenient degree. In this manner the conditions of depositing the copper varied theoretically from moment to moment and practically so frequently as to require constant attention and readjustment of the electrical condition to meet the varying chemical conditions. The next step in such old processes would then be to deposit the nickel under variable and therefore commercially-impracticable chemical and electrical conditions again by the use of an insoluble anode, and this carries with it the same inconveniences as the use of such anode in depositing copper. In some cases it has been suggested to use a soluble anode, such as zinc, in the deposition of nickel; but this resulted of necessity in the contamination of the deposited metal with zinc or other metal of the soluble anode. By my improved process I avoid these inconveniences and render the deposition of both the copper and the nickel practically uniform and continuous, notwithstanding the fact that for the electrolytic deposition of the nickel I also use an insoluble anode. The uniform continuity of my process is secured

in a measure by utilizing in the deposition of the copper some of the material yielded in the extraction of the nickel, while the extraction of the nickel becomes uniformly continuous by utilizing in the same some of the material rejected or withdrawn in the process of the deposition of the copper. Thus in my process the depositions of the two metals are operatively connected and are in a manner dependent upon each other.

The uniform continuity of the refining process is secured not only with nickeliferous-copper material, but with other composite metals when the same are composed of two metals, one of which yields a compact deposit from an acid solution with a relatively low voltage and current density and the other a like deposit from a non-acid solution with a relatively high voltage and current density. The most important metals of the first order are copper and cadmium, and the most important metals of the second order are nickel, cobalt, and zinc. The composite metals, therefore, which may be treated with particular advantage by my refining process are copper-nickel, copper-cobalt, copper-zinc, and cadmium-zinc; but the most important of these composite metals is nickeliferous-copper material, and in the following description I shall treat of this material specifically, with the understanding that in the more important steps of the refining process cadmium would be the equivalent of copper and either cobalt or zinc would be the equivalent of nickel.

While all nickeliferous materials can be treated by my process, it is of advantage to employ a material that contains not more than twenty per cent. of nickel and not less than eighty per cent. of copper. Such nickeliferous-copper material I cast into plates, suspend the latter as anodes in a suitably-heated electrolyte—a solution of sulfate of copper and nickel or of the nickeliferous-copper material and which contains free sulfuric acid—and I use sheets of copper as cathodes. By passing an electric current from the anodes to the cathodes through the electrolyte the anodes are gradually dissolved, and commercially-pure copper is deposited upon the cathodes. The electrolyte is kept in circulation, as usual, in any well-known or improved manner.

Since the anodes are not made of pure copper, the electrolyte, if not renewed, would soon become appreciably poorer in copper and richer in nickel. In order, therefore, to prevent or diminish this undue enrichment in nickel and impoverishment in copper and in order to make the recovery of these metals commercially profitable, I regularly withdraw a certain amount of the solution for treatment in the manner which I shall describe farther on. The amount of solution to be withdrawn at any one time should be such that the amount of nickel it contains is equal to the amount of nickel dissolved from the anode since the last withdrawal. Guided by this rule, the volume of the solution to be withdrawn periodically is readily computed by a person skilled in the art. If, for example, the anode contains ten per cent. and the electrolyte 0.5 per cent. of nickel and the anode is completely dissolved in ten days and if the total volume of solution in circulation is six times the volume of the electrolyte in the depositing-tanks, it is found that about twenty-five per cent. of the solution should be withdrawn daily. Again, if the percentage of nickel in the electrolyte is maintained at four per cent. or five per cent. under otherwise identical conditions only three per cent. or 2.5 per cent, respectively, of the total volume of solution need be withdrawn daily. The amount of electrolyte thus withdrawn is replaced by a sufficient amount of acid solution of copper sulfate, so as to reestablish the original condition of the electrolyte. A portion of the sulfate of copper needed for replenishing the electrolyte is obtained as a residue or by-product in the extraction of the nickel, as will appear farther on. This withdrawal and replenishment would ordinarily be done periodically; but the periods may under some conditions be so frequent as to make the withdrawal of a portion of the electrolyte relatively poorer in copper and the replacement of it by an equal amount of normal solution practically continuous.

The next step in my process is the separation of the two metallic constituents from the withdrawn acid electrolyte, which, as stated, is impoverished in copper, but rich in nickel. This may be done by any of the well-known or improved methods; but I prefer to do it by adding ammonia (or ammonia sulfate) obtained by the last step of my process, as will appear farther on, to the heated solution, but still keeping the latter acid, and then cooling the solution. In this manner the nickel salt is both precipitated and crystallized from the solution. The salt thus obtained will contain a small percentage of copper, and in order to remove all copper it is again dissolved, and the process of precipitation and crystallization is repeated until the nickel salt is obtained practically free from copper. The copper contained in the mother-liquor is used for replacing in part the copper deposited from the original electrolyte. The nickel

salt obtained constitutes by itself an article of manufacture.

The next and final step of my refining process is the electrolytic deposition of the nickel. If the nickel salt is obtained as specifically described, it is dissolved in water and sufficient ammonia is added to make the solution ammoniacal. If the nickel salt is obtained by another process already in solution, this solution is likewise made ammoniacal. The ammoniacal-nickel-salt solution constitutes the electrolyte for the electrolytic deposition of the nickel. It is preferably used hot.

In depositing the nickel I preferably use anode-plates of lead and cathode-plates of any suitable material, but preferably one having a nickel surface.

The use of lead as the material for the anodes would at first glance seem to be impracticable, because of the formation in the process of electrolysis of sulfate and peroxid of lead on the surface of the anode, which former compound is soluble in ammonium sulfate. It would thus seem that the anode would gradually be consumed by sulfatization and solution and that the deposited nickel would become so impure by codeposited lead as to be of little value. I have found, however, that this is not the case. I have found that the lead anode remains practically intact and that only a very small percentage of lead goes into the solution and barely a trace of it is deposited with the nickel. The nickel obtained in this manner is commercially pure.

While I have described the use of lead as the material for the anodes in depositing nickel, I do not mean to restrict myself to the use of this material, since I have also obtained good results with insoluble anodes of passive iron.

As the nickel electrolyte would eventually become impoverished in nickel unless this metal is replaced in the solution and in order to prevent the saturation of the solution with sulfate of ammonia, I periodically withdraw a portion of the electrolyte from the nickel-depositing system and recover the contained nickel salt and the ammonium sulfate or ammonia, the latter being used to make the regular nickel electrolyte ammoniacal. Nickel sulfate obtained from both the solutions withdrawn from the copper-depositing system and the nickel-depositing system is added to the regular nickel electrolyte periodically to replace the nickel deposited from the latter and to keep the solution of normal strength.

I do not propose to restrict myself necessarily to the use of an ammoniacal nickel electrolyte, since I have obtained good results by the use of a heated neutral nickel electrolyte.

Having now fully described my invention, I claim and desire to secure by Letters Patent—

1. The process of refining nickeliferous-cop-

per material which consists in electrolytically depositing the copper from an acid solution of such material with an anode of the same material; periodically withdrawing a portion
5 of the electrolyte as it becomes poorer in copper and richer in nickel; separating the copper and nickel salts contained in the withdrawn electrolyte; electrolytically depositing the nickel from a non-acid bath of the
10 nickel salt by the use of an insoluble anode; periodically withdrawing and concentrating portions of the impoverishing nickel-bath, and periodically restoring to the copper and nickel baths respectively, the copper and
15 nickel salts obtained from the withdrawn solutions, substantially as described.

2. The circular process of electrolytically refining nickeliferous-copper material, which consists in depositing copper from an acid solution of that material with an anode of the same; periodically withdrawing from circulation an amount of the electrolyte containing the same amount of nickel as is dissolved at the anode; replacing that amount by copper
25 per by adding copper sulfate, so as to keep up the normal strength of the copper electrolyte, and recovering by electrodeposition the nickel from the solution thus withdrawn by passing a suitable current from anodes of
30 lead to suitable cathodes through a heated non-acid solution of the nickel sulfate first recovered from the withdrawn solution.

3. The process of recovering the copper from nickeliferous-copper material, consisting in dissolving such material, cast into anodes, simultaneously electrodepositing copper and regularly withdrawing a portion of the copper electrolyte containing an amount of nickel substantially equal to the amount
40 of nickel dissolved at the anode, and regularly replacing the withdrawn solution by a copper-sulfate solution, free from nickel, containing copper in the same proportion as the original electrolyte, obtained from the with-

drawn solution, so as to maintain the electrical and chemical conditions of the copper deposition substantially constant.

4. The process of electrorefining nickeliferous-copper material consisting in bringing this material into solution, electrolytically recovering copper from such solution while substantially maintaining the normal composition of the electrolyte, withdrawing a portion of such electrolyte for the separation of its
50 contained metals, recovering from it the nickel, and adding the remaining copper salt or solution, now free from nickel, to the original copper electrolyte, so as to substantially maintain its normal strength.

5. The process of refining nickeliferous-copper material consisting in bringing such material into solution, electrolytically recovering the contained copper while maintaining substantially constant conditions, withdrawing a portion of the electrolyte, separating
65 the metals contained in the latter, returning the copper thus obtained as salt or solution to the original copper electrolyte, and electrolytically depositing the nickel separated as salt or solution, from its solution, while
70 maintaining substantially the normal composition of the nickel electrolyte by the regular addition of nickel salt or solution obtained from the above withdrawn copper electrolyte and from the withdrawn nickel electrolyte.

6. The process of electrodepositing nickel with anodes of lead from a non-acid solution of nickel.

7. The process of electrodepositing nickel with anodes of lead from an ammoniacal solution of nickel.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

TITUS ULKE.

Witnesses:

F. T. CHAPMAN,
EDWIN S. CLARKSON.