

UNITED STATES PATENT OFFICE.

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ART OF SEPARATING COPPER FROM OTHER METALS.

1,050,630.

Specification of Letters Patent.

Patented Jan. 14, 1913.

No Drawing.

Application filed May 18, 1911. Serial No. 627,993.

To all whom it may concern:

Be it known that I, THOMAS A. EDISON, a citizen of the United States, and a resident of Llewellyn Park, West Orange, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in the Art of Separating Copper from other Metals, of which the following is a description.

In Letters Patent of the United States No. 936,525, dated October 12, 1909, and Nos. 865,687 and 865,688, dated September 10, 1907, I have described processes for making metallic films or flakes, and particularly films or flakes of metallic nickel for use in the makeup of the positive electrodes of storage batteries of the Edison type. These processes consist generally in forming composite sheets composed of alternating layers of electrolytically deposited copper and nickel, cutting up the sheets into strips or other small portions, and dissolving out the copper. In the hereinbefore mentioned Patent No. 865,687, I have described the use of an ammoniacal copper sulfate solution for dissolving the copper without affecting the nickel, and in my application Serial No. 626,298, filed May 9th, 1911, I have described and claimed a method for accomplishing this result, in which I treat the associated metals with a solution of ammonium sulfate containing a small quantity of a reducible haloid, such as cupric chlorid, and simultaneously stir, heat, and supply air to the mixture.

My present invention relates generally to an improved process for separating copper from another metal or metals associated therewith, by dissolving out the copper and leaving the other metal or metals unaffected.

More specifically, my invention relates to an improved process for separating copper and nickel which are associated together in their metallic states by dissolving out the copper and leaving the nickel unaffected.

My improved process is particularly adapted to the manufacture of films or flakes of metallic nickel for use in the makeup of the positive electrodes of storage batteries of the Edison type.

I have discovered that metallic copper is dissolved by a solution of copper sulfate containing a small quantity of a reducible haloid, such as cupric chlorid; that the rapidity of the dissolving action is increased

very considerably by stirring and heating; that the reducible chlorid may be regenerated by supplying the solution with air, oxygen, or other oxygen containing gas, and the operation thereby rendered continuous without the necessity of adding additional quantities of reducible chlorid; and that the by-product is a pure basic sulfate of copper which can be made into pure sulfate of copper by adding the proper amount of sulfuric acid.

In the practice of my invention as applied to the manufacture of films or flakes of metallic nickel, I proceed substantially as follows:—Composite sheets each composed of a thin layer of copper and a thin layer of nickel, or of a number of such layers with copper and nickel alternating, are prepared by any of the methods described in the hereinbefore mentioned patents, or in any other suitable manner. Each of these sheets is then cut into strips or into small portions corresponding to the size of the flake desired, in the manner described in any of the hereinbefore mentioned patents. These strips or other small portions, each consisting of copper and nickel associated together in their metallic states, are then put into a solution of copper sulfate containing a small quantity of a reducible chlorid or other haloid, such as cupric chlorid. I have found that excellent results are obtained by using a 25% solution of sulfate of copper and about 15 grams of cupric chlorid per liter of solution. These proportions may be varied within certain limits. The solution is preferably kept near the boiling point, and air blown into it from any suitable source, such as an air compressor. The air itself may be heated before being blown into the solution. The solution is also stirred, and the stirring may be accomplished by any suitable stirring apparatus, such as rotating vanes, or by the air forced in, or by both. As a result of the reaction, the copper is separated out as a basic sulfate of copper, which is insoluble in the solution used, and which is held in suspension during the stirring. The nickel flake collects at the bottom of the solution, and the solution, together with the suspended basic sulfate may be poured or siphoned off. The basic sulfate is then separated from the solution by subsidence or filtration. In the reaction which takes

place, the cupric chlorid apparently acts merely as a transferring agent for conveying an oxidizing element to the copper, first forming mono-chlorid of copper, which reacts with the other substances present to form a basic copper sulfate. The oxygen contained in the air which is blown into the mixture serves to regenerate the cupric chlorid.

Ferric chlorid may be employed instead of cupric chlorid, but the results are less satisfactory. Other reducible haloids may be used to take the place of the cupric or ferric chlorid, such as cupric bromid and ferric bromid, but these salts are more costly than the chlorids.

In the process employed heretofore, in which the copper is dissolved in an ammoniacal solution of copper sulfate, it is necessary to use a large quantity of free ammonia. The ammonia is expensive, and even though it may be recovered afterward from the solution, the process of recovering it requires complicated apparatus and is expensive. The operation of dissolving the copper in the ammoniacal solution must be carried on where air can reach the solution to insure the dissolving of the copper. As a result, the solution cannot be heated to hasten the reaction, because, if heated, too much ammonia would be driven off. Even when carried on without heating, fumes of ammonia are given off, which fill the building and produce disagreeable and irritating effects. Furthermore, in this process, the copper is converted into a soluble salt, and its recovery in a useful form is expensive. In my improved process, ammonia and compounds of ammonia are entirely absent, and the copper is automatically thrown out as an insoluble compound, that is, as a basic copper sulfate which is practically pure and free from undesirable salts of ammonia, and which can be readily converted into copper sulfate by adding sulfuric acid. The copper sulfate may be used in the further practice of this process, or for any other purpose. Furthermore, the solution can be used continuously by filtering off the basic salt and adding a quantity of copper sulfate corresponding to the amount of sulfate removed from the basic salt. As the cupric chlorid is regenerated during the reaction and remains in the liquid, it is only necessary to add a little from time to time to replace what is lost in the operation of filtering.

My improved process has the following advantages over the process described and claimed in my application Serial No. 626,298, filed May 9th, 1911:—First: The solution of the metallic copper is accomplished more rapidly than by using ammonium sulfate and cupric chlorid. Second: My improved process is cheaper because in the

process described in my prior application, ammonium sulfate must be supplied, whereas, in my improved process, sulfuric acid, which is cheaper than ammonium sulfate, is used. Third: The basic copper sulfate is more completely insoluble in the solution described in this application than in that described in my prior application, apparently because of the entire absence of ammonia and compounds of ammonia.

My improved process is applicable generally to the separation of copper from such other metals as are not affected by the treatment hereinbefore described.

Having now described my invention, what I claim as new and desire to protect by Letters Patent is as follows:—

1. The process of separating metallic copper from another metal or metals associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid of a metal of variable valence, substantially as described.
2. The process of separating metallic copper from another metal or metals associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid of a metal of variable valence, and heating the mixture, substantially as described.
3. The process of separating metallic copper from another metal or metals associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid of a metal of variable valence, and stirring the mixture, substantially as described.
4. The process of separating metallic copper from another metal or metals associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid of a metal of variable valence, and heating and stirring the mixture, substantially as described.
5. The process of separating metallic copper from another metal or metals associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid of a metal of variable valence, and supplying oxygen containing gas to the mixture, substantially as described.
6. The process of separating metallic copper from another metal or metals associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid of a metal of variable valence, heating the mixture and supplying oxygen containing gas thereto, substantially as described.
7. The process of separating metallic copper from another metal or metals associated therewith, which consists in treating the as-

sociated metals with a solution of copper sulfate containing a reducible haloid of a metal of variable valence, and simultaneously stirring, heating, and supplying oxygen containing gas to the mixture, substantially as described.

8. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid, substantially as described.

9. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid, and heating the mixture, substantially as described.

10. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid, and stirring the mixture, substantially as described.

11. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid, and heating and stirring the mixture, substantially as described.

12. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid, and supplying oxygen containing gas to the mixture, substantially as described.

13. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid, heating the mixture and supplying oxygen containing gas thereto, substantially as described.

14. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing a reducible haloid, and simultaneously stirring, heating, and supplying oxygen containing gas to the mixture, substantially as described.

15. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper

sulfate containing cupric chlorid, substantially as described.

16. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing cupric chlorid, and heating the mixture, substantially as described.

17. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing cupric chlorid, and stirring the mixture, substantially as described.

18. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing cupric chlorid, and heating and stirring the mixture, substantially as described.

19. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing cupric chlorid, and supplying oxygen containing gas to the mixture, substantially as described.

20. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing cupric chlorid, heating the mixture and supplying oxygen containing gas thereto, substantially as described.

21. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing cupric chlorid, and simultaneously stirring, heating, and supplying oxygen containing gas to the mixture, substantially as described.

22. The process of separating metallic copper from metallic nickel associated therewith, which consists in treating the associated metals with a solution of copper sulfate containing cupric chlorid, stirring, heating, and supplying air to the mixture, whereby the copper is converted into an insoluble salt, and then removing the said salt, substantially as described.

This specification signed and witnessed this 12th day of May, 1911.

THOS. A. EDISON.

Witnesses:

HENRY LANAHAN,
ANNA R. KLEHM.