UNITED STATES PATENT OFFICE.

THOMAS A. EDISON, OF LLEWELLYN PARK, ORANGE, NEW JERSEY, ASSIGNOR TO EDISON STORAGE BATTERY COMPANY, OF WEST ORANGE, NEW JERSEY, A CORPORATION OF NEW JERSEY.

PROCESS OF MAKING NICKEL FILMS.

No. 865,687. Specification of Letters Patent. Patented Sept. 10, 1907.

Application filed January 19, 1907. Serial No. 353,060.

To all whom it may concern:

Be it known that I, THOMAS ALVA EDISON, a citizen of the United States, residing at Llewellyn Park, Orange, in the county of Essex and State of New Jersey, have invented certain new and useful Improvements in Processes of Making Nickel Films, of which the following is a description.

In an application for Letters Patent filed concurrently herewith, I describe an improved process for making films of metallic cobalt or metallic nickel, or of both metals, consisting generally in applying to a suitable cathode a film of chemically deposited copper and in then applying upon the cathode, as so prepared, alternating layers of electrolytically deposited copper and of the metal or combination of metals desired, after which the composite sheet so formed is stripped from the cathode (which operation is readily effected owing to the presence of the preliminary film of chemically deposited copper) and cut up into long filaments, which are then immersed and preferably agitated within a bath in which copper is soluble but which does not attack the cobalt or nickel.

I have discovered that when the process is used in connection with the manufacture of nickel films the final dissolution of the copper can be very readily effected in an ammoniacal solution of copper sulfate which is cheap, effects a ready and clean dissolution of the copper, and does not appear to have the slightest effect upon the nickel films.

I propose in the present application to claim the specific process used in connection with the manufacture of nickel films. To this end I practice the invention preferably as follows: The cathode is preferably a copper cylinder, having a polished nickel-plated surface. The cathode is first immersed in a suitable cobalt plating bath, preferably a concentrated solution of cobalt chlorid with cobalt anodes and while the cathode is rotating, an exceedingly thin film or blush of cobalt, say—.0001 of an inch, or less in thickness, is plated on the cathode. The cathode is now washed and is then immersed, preferably without being rotated, in a solution of copper sulfate, causing the cobalt to go into the solution and the copper to be deposited as "cement copper" in a granular, but slightly adhesive, form. Preferably, the immersion is continued only long enough to result in the covering of the cobalt film with a perfect layer of "cement copper", so as to leave a part of the cobalt film still intact. This permits the subsequent films to more perfectly retain their position on the cathode and enables a very large number of films to be deposited. If all the cobalt were dissolved in the copper sulfate bath, there would be danger of the subsequent films becoming detached during the plating, since they are deposited under a condition of tension. Instead of first depositing on the cathode a thin blush of cobalt, any other metal might be used in connection with which substantially the same reactions take place, for instance, iron, but this is not so desirable as cobalt, since the films will be liable to contamination by the iron, which would be objectionable in battery work. Great care should be taken in keeping the acidity of the copper sulfate bath in the neighborhood of two per cent by volume of free sulfuric acid. A substantial decrease in acidity would result in the deposit of a film of "cement copper" that would be totally lacking in adhesive properties, while, on the other hand, a substantial increase in acidity would make the deposit too tenacious and difficult to remove.

I now introduce the cathode in a copper plating bath, using preferably a copper sulfate solution with copper anodes, and I plate a film of copper on the chemically deposited film of "cement copper." The electrodeposited film is preferably somewhat thicker than the subsequent copper films, preferably between .003 and .0035 of an inch, in order to secure a firm support or basis for the subsequent films. During this deposit, the cathode is preferably rotated. The cathode is now washed and is then introduced into the nickel bath preferably employing a concentrated solution of nickel chlorid with nickel anodes. In this bath a film of nickel of the desired thickness is deposited on the previously deposited copper film. In practice I make use of nickel films of about .0002 of an inch in thickness, but obviously they may be of any desired thickness. Good results are secured with a cathode of about 12″ in diameter, when the latter is rotated at from sixty to one-hundred revolutions per minute in the nickel bath. The cathode is again washed, the wash water being preserved if desired, from which the nickel can be precipitated by suitable reagents, and a second film of copper is electrolytically deposited thereon as before. Preferably, this copper film, as well as the succeeding copper films, are made just thick enough to insure complete separation of the nickel layers and permit the ready access of the solution, for which purpose a thickness of about .0001 of an inch will be sufficient. The operations described are repeated, alternating layers of copper and nickel being deposited on the cathode until a composite sheet of the desired thickness is secured. This sheet is then cut longitudinally of the cathode, care being taken not to injure the nickel plated surface thereof, and the sheet is then cut up into long strips, say 10″ or more in length and about 1-16″ in width. The resulting long filaments are now placed in a suitable open work receptacle, for instance, a wicker basket, and introduced in an ammoniacal copper sulfate solution in which the copper will be dissolved without affecting the nickel. The preferred proportions of this solution

are 80% ammonium hydrate or aqua-ammonia, 5% copper sulfate crystals, 5% ammonium chlorid or sal-ammoniac, and 10% of water. In this bath the containing vessel or basket is moved up and down, either by hand or suitable mechanism, until the copper is dissolved and the nickel films are freed. I find that by thus agitating the composite strips in the bath the time required to dissolve the copper is only about one-half that necessary if the films are allowed to remain quiescent, while the circulation of liquid through the metallic mass serves to separate the nickel films from one another.

After the copper has been completely dissolved, the nickel films are then washed and dried, preferably in a centrifuge, until all traces of the solution are removed. The films are then annealed in hydrogen, care being taken not to have the temperature high enough to weld or "freeze" the films, after which they are cut up into small pieces, in any suitable machine.

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

1. The process for making films of metallic nickel which consists in electrolytically depositing a copper film on a suitable cathode, in then electrolytically depositing on the latter film a film of nickel, in then stripping the composite sheet from the cathode, and in finally dissolving the copper in an ammoniacal copper sulfate solution, substantially as set forth.

2. The process for making films of metallic nickel which consists in depositing upon a suitable cathode alternating films of copper and nickel, in then stripping the composite sheet from the cathode, and in finally dissolving the copper in an ammoniacal copper sulfate solution, substantially as set forth.

3. The process for making a film of metallic nickel which consists in first chemically depositing on a suitable cathode a film of metallic copper, in then electrolytically depositing a copper film thereon, in then depositing on the latter film a film of nickel, in then stripping the composite sheet from the cathode, and in finally dissolving the copper in an ammoniacal copper sulfate solution, substantially as set forth.

4. The process of making films of metallic nickel which consists in depositing on a suitable cathode alternating layers of copper and nickel, in removing the composite strip so secured, in cutting the same into long strips or filaments, and in finally subjecting the filaments to an ammoniacal copper sulfate solution, substantially as set forth.

5. The process of making films of metallic nickel which consists in depositing on a suitable cathode alternating layers of copper and nickel, in removing the composite strip so secured, in cutting the same into long strips or filaments, in subjecting the filaments to an ammoniacal copper sulfate solution, in drying the resulting filamentary filaments, and in finally reducing the same to pieces of the desired size, substantially as set forth.

This specification signed and witnessed this 18th day of January 1907.

THOS. A. EDISON.

Witnesses:
FRANK L. DYER,
ANNA R. KLEHM.