United States Patent Office

3,389,063

Patented June 18, 1968

3,389,063

PROCESS FOR ELECTROLYTIC RECOVERY AND REFINING OF METALS

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No Drawing. Filed Mar. 18, 1965, Ser. No. 440,950
Claims priority, application Germany, Mar. 19, 1964, N 24,652
6 Claims. (Cl. 204—106)

The invention relates to an improved process for recovery and refining of metals electrolytically employing improved depositing electrodes.

The invention more particularly relates to a process for electrolytically recovering and refining metals, especially heavy metals, as, for example, copper, using cells or baths having a so-called cold liquid electrolyte. Cells using electrolytes of this kind for the most part have thin cathode plates, sheets or films as so-called "starting sheets" or "bases" inserted or mounted between the anode plates to be electrolyzed. The so-called "starting surface" is chosen according to the properties of the metal to be separated on the one hand and according to the aspect of efficiency on the other. It can be produced according to various methods. Thus, for example, a copper base, produced electrolytically, suitable for the electrolysis of copper, is removed or taken off a specially treated rolled plate or sheet, a so-called mother or parent sheet, of copper. For the electrolysis of lead thin cast lead plates or sheets have been demonstrated as suitable cathode surfaces, and for gold electrolysis rolled gold film or foil is suitable. The cathodic metal separation begins on each of these suitable plates, sheets or films.

The type of electrocrystallization of the metal to be separated also depends on or influences whether cathode surfaces of like or different materials are chosen. Thus, for example, if copper or nickel is bonded together firmly with the base or substrate in the usual manner, the base or substrate must likewise consist of copper or nickel. On the other hand, if silver, as an example of a material which is easily stripped or scaled off the solid base, is employed a steel surface or sheet is suitable. Naturally other factors effect the type of separation, as, for example, the current density, the composition of the electrolyte or the temperature.

It is recognized in practice that use of large electrolysis apparatus which requires the customary production of the base in an electrolytic manner, for example, a copper refining plant using electrolysis, involves large expenditures for space and operating lines and accordingly large costs. Replacement of the base in such apparatus by rolled sheets or surfaces has been shown to be uneconomical. Thus up to the present time no usable method or means has been found which provides a so-called starting surface by means of a material which is produced in a more simple manner and which is easily transportable.

Also, the thickness of the starting surface plays an important roll, especially in the case of electrolysis tanks or baths having large dimensions since under otherwise identical conditions the electrodes suspended in the electrolysis tank each can be kept closer to the precipitating or depositing electrode.

In an old patent, British Patent 2,898/1906 (page 3, lines 12–16), reference is made to use of a precipitating or depositing electrode having a thickness of 0.2 mm. as the cathode in recovery of copper from copper waste, ore and the like. This reference indicates that in order to avoid throwing or rejecting these films in the bath, the edges should be put in grooves of wood strips or frames. Disregarding the fact that production of these thin sheets is relatively cumbersome and highly costly, enclosure in the wood frame is obviously undesired. Thus for a long time

thicker metal sheets have been used in practice as the precipitating or depositing electrode.

It has also been proposed, in Belgian Patent 369,624, issued Apr. 18, 1930, that the metallic cathode made of sheet metal be stiffened or made more rigid by making it in corrugated form. Even if the problem of throwing or rejecting such metal films in the electrolysis bath was solved thereby, special apparatus and several operating steps are still required for production of such films or foils in an electrolytic manner, and a relatively high cost factor in electrolytic refining is still present.

The use of cathodes of sheets of materials similar to the materials to be electrolytically deposited thereon was avoided by using an electrode carrier of a material neutral to the electrolyte and the metal to be deposited, as, for example, vinyl polymers or other organic or inorganic artificial materials or plastics. This material is made conductive by applying a layer of metal thereto similar to that to be electrolytically recovered and which is removed from the electrode carrier and the electrolytic bath or tank in order to use the carrier again. This type of precipitating or depositing electrode, however, must be essentially thicker than the metal sheets or metal films used. Moreover, separation of the recovered metal from the carrier material involves additional work as set out, for example, in German Patent 878,107.

The invention accordingly comprises a process for electrolytic recovery or refining of metals, especially copper in which the precipitating or depositing electrode (the cathode) used is made of paper or analogous electrolytic nonconductive material, which has no detrimental impurities, and which is made conductive by application thereto of an electrically conductive material, as, for example, a metal of the same type to be deposited or separated, this conductive material preferably being applied as an extremely thin layer. The cathode in cooperation with this depositing electrode is suspended or mounted in the cell or bath. Current is applied thereto resulting in deposition of the desired metal.

The metal deposited or separated according to the invention is of good electrolytic quality.

Various and different types of paper, felt from wood fiber and the like can be used as the non-conductive component of the depositing electrode which simplifies production of the depositing electrode very much and effects significant cost reduction. Production of the electrolytic conductive layer can similarly be effected in a simplified manner. Metallizing processes are especially suitable for this purpose. The conductive layer may be provided by spraying metal powder onto the surface or by mixing the metal powder into the paper mass which is then used for production of the cathode film. Metallizing of the nonconductive carrier layer can also be carried out by applying a thin metal layer by means of vacuum vaporization processes, cathodic spraying processes, metal spraying processes, and chemically depositing the metal from solution. Application of the metal to the paper or equivalent material by electrolytic deposition of the metals before suspension of the depositing electrode in the refining bath or tank provides advantages in addition to the usual production of the cathode films electrolytically because the metal layer used in the depositing electrode according to the invention is extremely thin, for example, 1μ to 1 mm. thick, preferably 0.1 mm. This results in significant saving of time and the operation of dissolving the formed metal layer from the base is dropped.

Two aspects are specially considered for practical embodiments of the electrolysis according to the present invention, namely, alignment of the base and its suspension.

The first point is important in order to maintain a clear current density ratio and especially to avoid short circuits. Parallel alignment of the base with the adjacent anode causes greater difficulties according to the process the thinner they are, under otherwise similar conditions.

Increasing the stiffness or rigidity of such metallized papers or films is achieved in a known manner by making them in rolled form with the channels or spaces preferably running perpendicular. This is the optimum direction for increasing rigidity on the one hand and does not hinder removal of sediment particles on the other.

The risk of rejecting the paper electrode or the like in the electrolysis bath or tank emanates mainly from the flow or circulation of the electrolyte. Therefore to avoid this, the electrodes may be provided in roll form and then the electrolyte circulated when the cathode has achieved a determined thickness. Thus possible movement by current or flow effects are avoided.

The paper or film, made electrically conductive, for the purpose of suspension, is connected or attached in a known manner, for example, to straps or flaps, or clamped between sheets or plates. Both methods or means may be used in combination.

It is essential that the carrier element (bands, strips, sheets or the like) be sufficiently resistant and strong to carry the total weight of the final cathode. Therefore regard must be taken in beginning the electrolysis that a solid bond is formed between the carrier parts and the base. This is accomplished best if the electrolytic deposition of the metals is carried out at least at the beginning such that the level of the electrolyte covers the junction of the depositing electrode and the carrier piece.

One advantage of the process according to the invention is that, despite the use, the non-conductive carrier for the depositing electrode can be paper thin and accordingly the space in the electrolytic bath or tank can be used more favorably and efficiently. Another advantage of the invention is that a cheaper material is used for the non-conductive cathode carrier.

The process and apparatus according to the invention are illustrated in the following examples.

EXAMPLE 1

Paper having a copper layer 1.1 microns thick vapor deposited thereon was used as the cathode base in a copper refining electrolysis using an otherwise customary apparatus and method. The cathode had an area of 125 mm. x 130 mm. It was suspended on two lugs or handles of copper sheet and arranged in the electrolyte. In the course of the electrolysis a cathodic deposit grew thereon. Circulation of the electrolyte was avoided during the first 6 hours in order to avoid too strong a rejection of the cathode or short circuits.

Using a current density of 190 amperes per square meter each cathode at about 1200 ampere hours separated or refined 1415 grams of copper which corresponded to a current yield approaching 100%. The cell voltage fell from an initial 200 millivolts to 130 millivolts.

Analysis of the cathodic deposit corresponded to the usual quality of electrolytic copper.

EXAMPLE 2

In a procedure identical with Example 1 a paper base was used as the cathode having a layer of copper applied by flame spraying.

The superimposed copper correspond to 1.2 kilograms

per square meter. The cathode was 15 centimeters x 15.5 centimeters and was suspended in the cell or tank as in Example 1. Each cathode separated 2270.5 grams of copper using a current density of 194 amperes per square meter in 216 hours which corresponded to a current yield of 98.5%. The cell current similarly dropped about 200 millivolts.

EXAMPLE 3

Paper was overlayed on both sides with zinc totalling 440 grams per square meter. This was used as the cathode base for zinc electrolysis.

The cathode paper was suspended in the tank on two lugs or handles made of fine zinc sheet by means of copper carrier rods. The starting electrolyte contained 95 grams of zinc per liter, 40 grams of free H_2SO_4 per liter and an added amount of 250 milligrams of sizing per liter. The surface of each cathode was 3.65 square decimeters. 443 grams of zinc, corresponding to a current yield of 84%, was separated in 24 hours in dense form using a current density of about 495 amperes per square meter.

The zinc sheet lugs or handles used for suspension of the cathode had grown together with the cathodic deposit.

I claim:

1. In a process for electrolytic refining of a metal using a cold liquid electrolyte and a depositing electrode supported on a non-conductive carrier, the steps comprising suspending a depositing electrode consisting of paperlike non-conductive material having a conductive metal thereon in an electrolyte in an electrolysis cell, applying electric current thereto and recovering the deposited metal.

2. A process as in claim 1 also comprising suspending said depositing electrode in rolled form in said cell.

3. A process as in claim 1 also comprising maintaining said electrolyte still under a predetermined thickness of metal has been deposited on said electrode, then circulating said electrolyte around the cell.

4. A process as in claim 1 also comprising suspending said depositing electrode by carrier means joined to said electrode and maintaining the level of the electrolyte over the junction of the carrier means and said electrode at the beginning of the electrolysis to form a strong bond therebetween.

5. A process as in claim 1 wherein the non-conductive material is paper.

6. In a process for electrolytically refining copper using a cold liquid electrolyte, the steps comprising suspending a depositing electrode consisting of paper having a coating of copper about 1.1 microns thick thereon in an electrolyte in an electrolysis cell, applying electric current thereto and recovering the deposited copper essentially free of impurities.

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