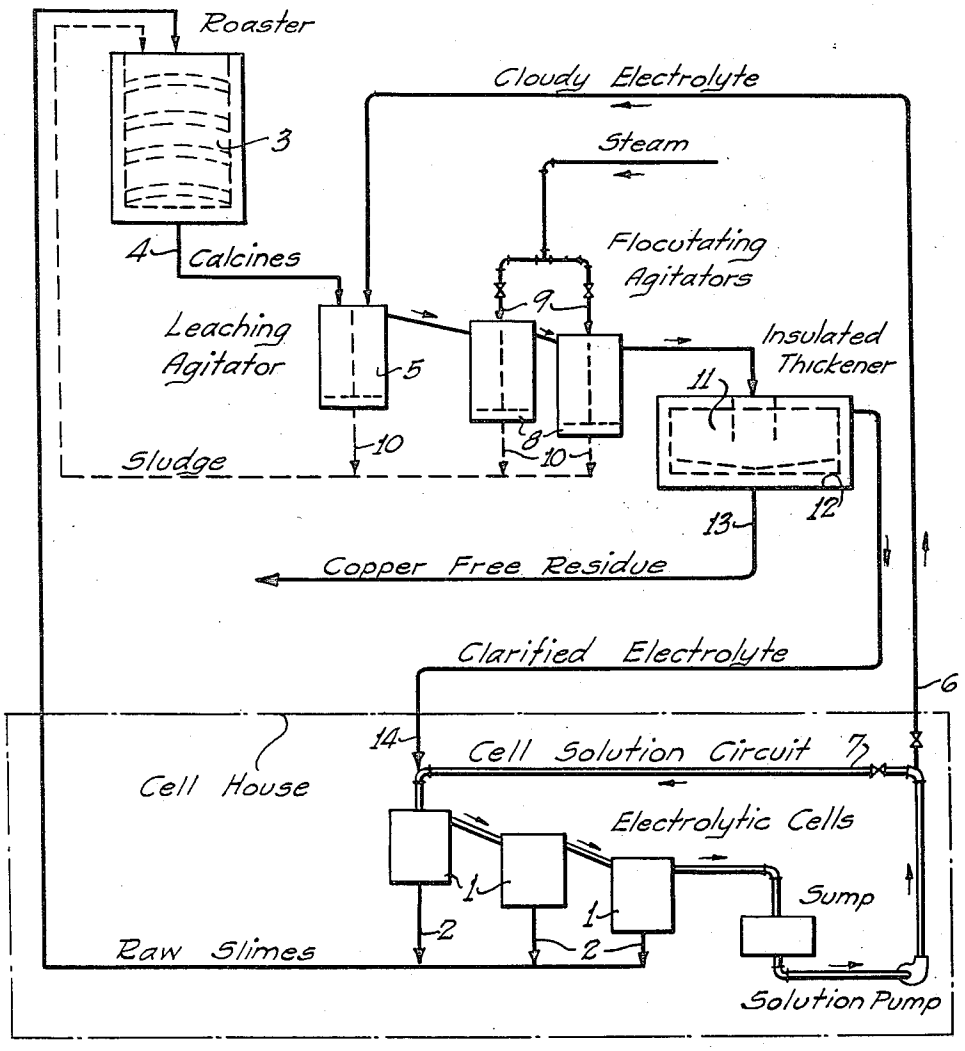
Dec. 13, 1932. T. LEWIN 1,890,856

PROCESS FOR THE CLARIFICATION OF ELECTROLYTE

Filed Aug. 17, 1931



INVENTOR
Tannie Lewin
BY Ralph Lewis
ATTORNEY

Patented Dec. 13, 1932

1,890,856

UNITED STATES PATENT OFFICE

TANNIE LEWIN, OF UNIVERSITY CITY, MISSOURI

PROCESS FOR THE CLARIFICATION OF ELECTROLYTE

Application filed August 17, 1931. Serial No. 557,493.

This invention relates generally to electrolysis and, more particularly, to a certain new and useful process for the clarification of impure and weakened electrolyte resulting from the electroyltic separation and recovery of the copper content of impure anodic materials, as brass, bronze, or copper, secondary metals and their residues.

Under date of February 23, 1926, United States Letters Patent No. 1,574,043 were granted to me for a process for the separation and recovery of the copper, tin, and lead content of brass, bronze, or copper secondary metals or their residues. Reference is made to said Letters Patent for a full and complete disclosure and description of said process, which will be descriptively designated as the main process. Suffice it now, for present purposes, to state, as steps in such main process, the metals or their residues under treatment are cast into forms adapted for use, and then utilized, as anodes in an electrolytic bath in suitable electrolytic cells or tanks, where, by electrolysis, (*a*) the copper content of such anodes is electrolytically extracted and deposited upon the cathodes, (*b*) the tin and lead content or values of such anodes are, through dissolution or disintegration, removed or separated out and precipitated as slime upon the bottom of the electrolytic cells, and (*c*) the cell-deposited slimes are removed and retreated for the recovery of their tin and lead content.

In practicing and carrying on said main process, however, it has been found that a certain proportion of the copper separated from the anodes is precipitated with the slimes as metallic copper, and also some copper is lost from the electrolyte as copper sulphate and copper compounds more or less insoluble. Further, the electrolyte becomes contaminated with compounds of the anodic impurities of such nature and fineness that they remain in suspension indefinitely and cause the electrolyte to assume a characteristic cloudy appearance, the electrolytic deposition of copper in the cells when employing such an impure or cloudy electrolyte being attended with entrapment of these impurities in the cathode copper to a commercially unprofitable and impracticable extent.

Finally, the strength and efficacy of the electrolyte becomes impaired due, in part, to the loss of its copper content depleted by the cathodes by reason of the relatively low copper content of the anodes, and, in another part, to the entrapment of copper sulphate and other more or less insoluble copper compounds in the slimes.

It may be here stated that the anodic impurities additionally deplete the acid content of the electrolyte by forming sulphates in the slimes, the replenishment of the acid contact of the electrolyte being accomplished, however, by any convenient means not pertinent to my present invention.

My present invention has hence for its prime objects, and resides in, the provision of an auxiliary or supplemental process for the recovery of the copper content of the slimes, the enrichment of the copper content of the electrolyte, the clarification of the electrolyte, and the recovery of the copper-leeched slimes for further beneficiation thereof for the efficient, economical, and commercially profitable carrying on of my said main process.

According to, and in practicing, my present supplemental process, as illustrated in the accompanying diagrammatic or so-called flow-drawing, the raw slimes are suitably withdrawn from the electrolytic cells 1, as indicated at 2, and delivered to the top of a multiple hearth-roaster 3, where such slimes are roasted at a temperature up to approximately 1200-degrees F. for the oxidation of the anodic impurities or metals in the slimes. The roasting operation decomposes practically all of the sulphates present, except possibly some of the anhydrous copper sulphate,

and has the beneficial effect of destroying the colloidal properties, if any, of the slime material.

The roasted slimes or calcines are in due course withdrawn, as at 4, from the roaster 3 and introduced at suitable intervals and in suitable volumes into a leaching agitator 5, together with a certain volume of cloudy electrolyte preferably continuously withdrawn, as at 6, from the cell-solution circuit 7.

The electrolyte, when pure, is composed of from 8 to 12 percent of sulphuric acid and from 3 to 5 percent of copper sulphate, but during the carrying on of said main process, the content of copper sulphate of the electrolyte is depleted, as has been previously explained. I have found that most, if not all, of the deficiency of copper sulphate in the electrolyte may be supplied from the copper in the slimes, and since the roasting operation produces, among other oxidation products, those of the electrolyte-soluble copper-oxides, the leaching agitation of the calcines with the electrolyte is here carried on principally for the copper-sulphate enrichment of the electrolyte with the production of a copper leached residue, any anhydrous copper-sulphate present passing, of course, directly into solution with the electrolyte.

During the carrying on of said main process, however, the electrolyte becomes contaminated, as has been stated, with compounds of the anodic impurities including principally lead, tin, and antimony, as well as minor quantities of other metals, as iron, zinc, nickel, arsenic, etc. In part, these impurities will be in solution in the electrolyte, but, in other principal part, they appear as colloidal dispersions suspended in cloud-like manner in the electrolyte, having such dispersion persistent characteristics that, as far as I am aware, it is impracticable, if not impossible, to remove these clouds from the electrolyte by any of the filtering methods at present commercially available.

I have found, however, that such cloud-like dispersions may be readily flocculated and coagulated in the presence of finely divided or particulate metallic oxides especially treated under suitable thermal conditions, as, for example, the influence of a sufficiently elevated solution temperature up to approximately 150 to 212 degrees F. Most economically, for such purpose, the hot calcines from the roaster are preferably discharged directly from the roaster 3 into the agitator 5, the sensible heat of the calcines being additive to the heats of reaction of the acid with the oxides of copper and of the solution of the sulphate-copper in the electrolyte for causing rapid reaction-accelerating rise of the temperature thereof.

When the oxidized particulate material from the roaster 3 is caused to remain in suspension in the heated electrolyte by reason of the agitation carried on in the leaching-tank 5, there follows or ensues an initial coagulation or flocculation, as may be said, of the dispersed colloidal material in the electrolyte solution.

In practice, I have discovered that the degree and rate of such flocculation may be considerably increased and speeded up by the introduction of so-called "live" steam into the flocculation solution, for which purpose the electrolyte, with its partially flocculated colloids and suspended leached slimes or oxidized material, is caused to overflow from the agitator 5 into so-called flocculating-agitators 8, where the solution is treated with steam supplied, as at 9, from any source suitable for the purpose.

In the agitators 8, which are preferably arranged in a series or cascade, the process of solution of the calcine-borne copper as a sulphate in the electrolyte is completed, and at the same time, the heat-content of the solution being increased by the inflowing steam and its condensate, the flocculation of the colloidal material is carried on with hence increasing intensity in the presence of the agitated oxidized material until the former cloud-like dispersions are coagulated into flake-like bodies in suspension in the electrolyte-solution.

It may be here mentioned that it is not commercially practicable to completely dead-roast all of the cell-slimes, as there will always appear in the product of the roasting operation a proportion of nodulated material containing unroasted kernels and the like, which settle as a heavy sludge in the tanks 5 and 8. Such sludge, however, is from time to time withdrawn, as at 10, from the tanks 5, 8, and returned to the roaster 3 for retreatment.

It will be seen that the solution in the tanks 5 and 8 is under continual agitation for most effectively promoting the reactions desired, which latter being accomplished, the overflow from the last flocculating agitator, carrying the now flocculated colloids and suspended copper leached slimes, is suitably, for colloid coagulation and slimes-settling purposes, caused to flow into a settling device or thickener 11.

It is important that the temperature of the solution in the thickener 11 remain substantially constant during the coagulation process for iso-thermally carrying on the same, and it is likewise important to avoid heat-differential agitating currents in the solution for most efficient settling of the coagulated material. The tank 11 is, therefore, heat-insulated, as at 12, for conserving the heat-content of the solution and, at the same time, substantially preventing heat-differential eddy-currents therein.

As a result, the colloidal impurities of the electrolyte being treated are under iso-

thermal conditions coagulated and precipitated from the electrolyte-solution and settle together with the residue of the slimes-material to the bottom of the thickener 11 as an aggregated residue free, or substantially free, from insoluble copper compounds.

Such aggregated residue is withdrawn, as at 13, from the thickener 11 for delivery to the residue retreatment plant, not shown, and the treated, clarified electrolyte overflows from the thickener 11 and is sent to the head of the cell-house, as at 14, where it joins the cell-solution circuit 7 for reuse in practicing and carrying on my said main process.

In practice, preferably, the apparatus is arranged such that the clarified electrolyte will flow gently by gravity from the thickener-overflow to the cell-house solution feed-launder.

It will be seen that my present process provides for the efficient carrying on of said main process in the following particulars, to wit, (1) the recovery of the copper in the slimes, (2) the enrichment of the electrolyte, (3) the clarification of the electrolyte, and (4) the beneficiation of the slimes.

And it will be also seen that my process includes, among others, those steps or stages consisting in (1) the oxidation of the slimes, (2) the leaching of the slimes by the cloudy electrolyte for enrichment of its copper-sulphate content, (3) the flocculation of the colloidal impurities in the electrolyte under thermal conditions in the presence of oxidized anodic material, (4) the acceleration of the rate of said flocculation by means of steam in the presence of said oxidized material, and (5) the iso-thermal coagulation of the flocculated material, together with settling of the coagulated material in the presence of and with the oxidized slime-material, for (6) the production of a clarified electrolyte, and (7) a copper-leached residue highly suited by reason of its oxide-content for subsequent retreatment for recovery of its metal-values.

I am aware that changes in the several steps of my process may be made and substituted for those herein described without departing from the nature and principle of my invention.

Having thus described my invention, what I claim and desire to secure by Letters Patent is,—

1. Those steps supplemental to the electrolytic treatment of brass or bronze secondary metals or their residues for the recovery of their copper-content, which consist in roasting cell-slimes for oxidation thereof, treating under thermally-elevated conditions cell-removed cloudy electrolytic solution with the oxidized slimes for flocculation of dispersed impurities in the solution, and then by coagulation and settling separating the slimes-residue and flocculated matter from the solution for return of the treated solution to the cells.

2. Those steps supplemental to the electrolytic treatment of brass or bronze secondary metals or their residues for the recovery of their copper-content, which consist in roasting copper-bearing cell-slimes for oxidation thereof, leaching under thermally elevated conditions the oxidized slimes with cell-removed cloudy electrolytic solution for flocculation of dispersed impurities in the solution and for removal of the copper-content of the slimes, and then by coagulation and settling separating the copper-leached slimes-residues and the flocculated matter from the solution for return of the enriched and clarified solution to the cells.

3. Those steps supplemental to the electrolytic treatment of brass or bronze secondary metals or their residues for the recovery of their copper-content, which consist in roasting copper-bearing cell-slimes for oxidation thereof, leaching under thermally elevated conditions the oxidized slimes with cell-removed cloudy electrolytic solution for flocculation of dispersed impurities in the solution and for removal of the copper-content of the slimes, then subjecting the solution to live steam in the presence of the oxidized slimes for accelerating the flocculation of the dispersed material, and then by coagulation and settling separating the copper-leached slimes-residues and the flocculated matter from the solution for return of the enriched and clarified solution to the cells.

4. Those steps supplemental to the electrolytic treatment of brass or bronze secondary metals or their residues for the recovery of their copper-content, which consist in roasting copper-bearing cell-slimes for oxidation thereof, agitating under thermally elevated conditions the oxidized slimes with cell-removed cloudy electrolytic solution for flocculation of dispersed impurities in the solution and for removal of the copper-content of the slimes, then subjecting the solution to live steam in the presence of the oxidized slimes for accelerating the flocculation of the dispersed material, and then by coagulation and settling under iso-thermal conditions separating the copper-leached slimes-residues and the flocculated matter from the solution for return of the enriched and clarified solution to the cells.

5. Those steps supplemental to the electrolytic treatment of brass or bronze secondary metals or their residues for the recovery of their copper content, which consist in removing slimes from the cells, then roasting the removed slimes for production of an oxidized particulate material, then removing a portion of cloudy electrolyte containing colloidally-dispersed impurities from the cell-solution circuit, then leaching the oxidized slimes in the electrolyte solution for enrich-

ment of the sulphate-copper content thereof and concurrently raising the temperature of the electrolyte by means of the resulting heats of reaction and solution for initiating flocculation of the colloidally-dispersed impurities, then treating the resulting solution with steam in the presence of the oxidized particulate material for accelerating the rate of flocculation of the colloidally-dispersed impurities, then coagulating and settling the flocculated impurities under iso-thermal conditions in the presence of, and also at the same time settling, the oxidized particulate material, and then separating the settled material as a copper-leached residue and returning the clarified solution to the cell-solution circuit.

6. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, and then employing the roasted slime as an oxide agent for effecting flocculation of anodic impurities colloidally suspended in the electrolyte-solution.

7. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, then employing the roasted slime an an oxide agent for effecting flocculation of anodic impurities colloidally suspended in the electrolyte-solution, and then coagulating and settling the flocculated matter from the electrolyte-solution.

8. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, and then employing the roasted slime as an oxide agent for effecting precipitation of anodic impurities colloidally suspended in the electrolyte-solution.

9. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, agitating the electrolyte-solution in the presence of the roasted slime for effecting flocculation of anodic impurities colloidally suspended in the electrolyte-solution, and then coagulating and settling the flocculated matter from the electrolyte-solution.

10. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, agitating the electrolyte-solution in the presence of the roasted slime under thermally elevated conditions for effecting flocculation of anodic impurities colloidally suspended in the electrolyte-solution, and then coagulating and settling the flocculated matter from the electrolyte-solution.

11. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, agitating the electrolyte-solution in the presence of the roasted slime under thermally elevated conditions for effecting flocculation of anodic impurities colloidally suspended in the electrolyte-solution, and then coagulating and settling the flocculated matter from the electrolyte-solution under iso-thermal conditions.

12. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, treating the electrolyte-solution with the roasted slime under thermally elevated conditions for effecting flocculation of anodic impurities colloidally suspended in the solution, and then coagulating and settling the flocculated matter from the solution.

13. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, treating the electrolyte-solution with the roasted slime under thermally elevated conditions for effecting flocculation of anodic impurities colloidally suspended in the solution, and then coagulating and settling the flocculated matter from the solution under iso-thermal conditions.

14. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, then subjecting the electrolyte-solution to steam in the presence of the roasted slime

for effecting flocculation of anodic impurities colloidally suspended in the solution, and then coagulating and settling the flocculated matter from the solution.

15. Those steps, supplemental to the electrolyte deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, employing the roasted slime as an oxide agent for effecting flocculation of anodic impurities colloidally suspended in the electrolyte-solution, introducing live steam and its condensate into the solution for accelerating the flocculation of said colloidally suspended matter, and then coagulating and settling the flocculated matter from the solution.

16. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, employing the roasted slime as an oxide agent for effecting flocculation of anodic impurities colloidally suspended in the electrolyte-solution, introducing live steam and its condensate into the solution for accelerating the flocculation of said colloidally suspended matter, and then coagulating and settling the flocculated matter from the solution under iso-thermal conditions.

17. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, employing the roasted slime as an oxide agent for effecting flocculation of anodic impurities colloidally suspended in the electrolyte-solution, and then coagulating and settling the flocculated matter together with the oxidized cell slime for removal thereof from the solution.

18. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, agitating the solution in the presence of steam and the roasted slime for effecting flocculation of anodic impurities colloidally suspended in the electrolyte-solution, and then coagulating and settling the flocculated matter from the solution.

19. Those steps, supplemental to the electrolytic deposition of copper from anodes of secondary metals, in which deposition anodic impurities are disseminated both into the electrolyte-solution and into the cell-slime, which consist in roasting the cell-slime for oxidation of contained anodic impurities, agitating the solution in the presence of steam and the roasted slime for effecting flocculation of anodic impurities colloidally suspended in the electrolyte-solution, and then under iso-thermal conditions coagulating and settling the flocculated matter together with the oxidized cell slime for removal thereof from the solution.

20. Those steps, supplemental to the electrolytic recovery of copper from anodes of secondary metals, in which anodic impurities are disseminated into both the electrolyte-solution and into the cell-slime, and in which also a portion of the anodic copper is deposited in the cell-slime, which consist in roasting the cell slime for oxidation of contained copper and anodic impurities, and then employing the roasted slime as an oxide agent for effecting precipitation of anodic impurities colloidally suspended in the electrolyte-solution and concurrently enriching the electrolyte-solution with sulphate copper derived from the soluble copper oxides of the roasted slime.

21. Those steps, supplemental to the electrolytic recovery of copper from anodes of secondary metals, in which anodic impurities are disseminated into both the electrolyte-solution and into the cell-slime, and in which also a portion of the anodic copper is deposited in the cell-slime, which consist in roasting the cell-slime for oxidation of contained copper and anodic impurities, continuously withdrawing a portion of the electrolyte-solution from the cell solution-circuit, employing the roasted slime as an oxide agent for effecting precipitation of anodic impurities colloidally suspended in the electrolyte-solution and concurrently enriching the solution with sulphate-copper derived from the soluble copper oxides of the roasted slime, and then returning to the solution circuit the clarified and enriched electrolyte.

22. Those steps, supplemental to the electrolytic recovery of copper from anodes of secondary metals, in which anodic impurities are disseminated into both the electrolyte-solution and into the cell-slime, and in which also a portion of the anodic copper is deposited in the cell-slime, which consist in roasting the cell-slime for oxidation of contained copper and anodic impurities, continuously withdrawing a portion of the electrolyte-solution from the cell-solution-circuit, employing the roasted slime as an oxide agent for effecting flocculation of anodic impurities colloidally suspended in the solution and concurrently enriching the solution with sulphate-copper derived from the soluble copper oxides of the roasted slime, then introducing live steam and its condensate into the

treated solution for accelerating the flocculation of said colloidally suspended matter, then coagulating and settling the flocculated matter together with the copper-leached slime for removal thereof from the electrolyte-solution, and then returning the clarified and enriched electrolyte to the cell-solution-circuit.

In testimony whereof, I have signed my name to this specification.

TANNIE LEWIN.