United States Patent Office

3,389,064

Patented June 18, 1968

3,389,064

ELECTROLYTIC REFINING OF COPPER AND TANK HOUSE ELECTROLYTE USEFUL THEREIN

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No Drawing. Filed July 22, 1964, Ser. No. 384,519

6 Claims. (Cl. 204—108)

This invention relates to the electrolytic refining of copper. More particularly this invention relates to the use of an improved electrolyte in the electrolytic refining of copper.

In the electrolytic refining of copper, an electric current is passed between cast anodes of impure copper to be refined and cathodes of substantially pure copper, both the anodes and cathodes being immersed in an electrolyte comprising essentially an aqueous solution of cupric sulfate and sulfuric acid. Upon the passage of electric current between the anodes and the cathodes and through the electrolyte, copper is dissolved from the anodes into the electrolyte and is deposited from the electrolyte onto the cathode in purified form. Impurities present in the anode either dissolve in the electrolyte without being redeposited at the cathode or settle out of the electrolyte as an insoluble anode mud or anode slime. After the copper cathode deposit has built up to a substantial thickness (three-eighths to five-eighths inch or more), the copper cathodes are removed and melted for casting into marketable shapes.

Addition agents are incorporated in the electrolyte either continuously or from time to time during the refining operation to improve the refining operation and the physical characteristics of the cathode-deposited copper. These addition agents are often complex organic materials or mixtures of such materials and serve to insure the formation of a smooth, dense, uniform cathode copper deposit. If no addition agent is used, the cathode-deposited copper tends to grow irregularly and develops "sprouts" or "trees" which soon make contact with an adjacent and closely spaced anode and cause a short circuit. When this occurs, no further amount of copper deposits on the cathode until the short circuit is broken. Even if no short circuit develops, rough cathode-deposited copper favors entrainment or occlusion of pockets of electrolyte and of anode slime which cannot be washed out or otherwise removed. Because the electrolyte in such pockets contains impurities derived from the anode, it causes contamination of the cathode-deposited copper.

The manner in which addition agents function to produce a smooth and dense cathode deposit is not precisely and fully understood. Various theories have been formulated in attempting to explain the functions of addition agents in the electrolytic refining of copper. None of these theories are set forth herein as it is deemed sufficient to describe the practice of this invention in order to obtain the desired results and to set forth the character of the results which are attainable when operating in accordance with the invention.

It is an object of this invention to provide an improved electrolyte useful in the electrolytic refining of copper.

It is another object of this invention to provide an electrolytic refining operation useful for the production of high purity cathode-deposited copper and having improved productivity.

Another object of this invention is to provide an improved electrolytic refining operation useful for the production of high purity cathode-deposited copper, i.e. copper cathodes of increased purity and improved physical characteristics.

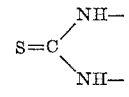
Still another object of this invention is to provide an improved operation for the electrolytic refining of copper wherein current efficiency is increased and operating costs and labor costs are decreased.

How these and other objects of this invention are achieved will become apparent in the light of the accompanying disclosure.

It has now been discovered that an improved electrolyte particularly useful for the electrolytic refining of copper is provided by incorporating in the electrolyte an admixture of glue, thiourea and a hydrolyzed sulfonated derivative of a paraffinic hydrocarbon, the above-identified components of the admixture being present in the electrolyte in particular amounts. Still more particularly, in accordance with this invention in the electrolytic refining of copper employing an electrolyte comprising essentially an aqueous solution of sulfuric acid and copper sulfate, i.e. cupric sulfate, improved results are obtainable by incorporating in the electrolyte an admixture of glue, thiourea and a hydrolyzed sulfonated derivative of paraffinic hydrocarbons.

The glue employed in the combination of special addition agents in the electrolyte in accordance with this invention is preferably a glue of animal origin. Particularly, satisfactory results have been obtained by employing a ground bone glue.

The thiourea addition agent employed in the special combination of addition agents in accordance with the practice of this invention may be commercially pure thiourea or commercial grade thiourea. Organic compounds containing a thiourea nucleus, viz.



also appear to be useful as the thiourea component in the special combination of addition agents in accordance with this invention.

Of the hydrolyzed sulfonated derivatives of paraffinic hydrocarbons employed as one of the addition agents in the special combination of additives, Avitone A, a hydrolyzed sulfonated derivative of paraffinic hydrocarbons, specifically a saturated hydrocarbons sodium sulfonate composition in the form of light tan paste generally used as a leather finishing agent or softener in paper coatings has been found to yield particularly satisfactory results. U.S. Patents 2,197,800 and 2,660,555 are of interest in connection with the preparation of materials of the Avitone A type.

The special combination of addition agents including glue, thiourea and a saturated hydrocarbon sodium sulfinate composition, such as Avitone A, in specific amounts or proportions has been found to improve the performance of the electrolyte in commercial operations for the electrolytic refining of copper. The usual electrolyte employed in the electrolytic refining of copper comprises essentially an aqueous solution of sulfuric acid and copper sulfate. A commercial electrolyte useful in the electrolytic refining of copper and one whose performance is improved

when the combination of special additives in accordance with this invention is incorporated therein has the composition set forth in accompanying Table I:

TABLE I

Component:	Grams per liter
Copper	40–49
Sulfuric acid	182–192
Arsenic	0.44–0.56
Antimony	0.07–0.10
Nickel	8.0–10.3
Iron	0.13–0.20
Bismuth	0.10–0.14
Chlorine	0.014–0.024

An electrolyte of the type having the above-identified composition would exhibit a specific gravity in the range 1.24–1.27. In the electrolyte having the composition set forth in Table I the components arsenic, antimony, nickel, iron and bismuth are impurities therein, accordingly their presence in the electrolyte is undesirable. These impurities are not in the electrolyte when initially prepared but accumulate therein during the electrolytic refining operation. The impurities which are derived from the relatively impure copper anodes are, however, tolerated in the electrolyte in the concentrations up to about the upper limit of the concentration range indicated.

The exact composition of the electrolyte in the practice of this invention as applied to the electrolytic refining of copper is not critical and conventional electrolytes useful in the electrolytic refining of copper and comprising essentially an aqueous solution of sulfuric acid and copper sulfate are useful provided, of course, that in accordance with the practice of this invention there is incorporated therein the specific combination of special addition agents comprising glue, thiourea and a hydrolyzed sulfonated hydrocarbon.

By applying the practice of this invention to the electrolytic refining of copper it has been observed that copper quality is improved, ampere efficiency is increased, cathode production, i.e. copper production, is increased, labor as measured in man-hours per ton of copper produced is decreased, power consumption is decreased and consequently the current density is also decreased. In an actual commercial production trial of the practice of this invention extending over a period of six months it was observed that the practice of the invention permitted the operation of the entire tank house on two cathode pullings per anode loading instead of the usual three. Also, the practice of the invention permitted the release of two stripper sections and the conversion of these sections to cathode production. The stripper sections, comprising eighteen electrolytic tanks each, are used to make thin sheets of electrolytic copper which later serve in the commercial sections as starting sheets for the electrodeposition of commercial copper cathodes. The practice of the invention in this same commercial trial permitted a decrease in inspection requirements by about one-third and an overall decrease in labor of about 7%. The resulting improvement in tank house performance and quality of the resulting refined copper was reflected in decreased operating cost and decreased metal losses. On the basis of the production of about 260,000 tons of copper cathodes per year, the saving as a result of the practice of this invention was very substantial.

Set forth in accompanying Table II are data showing the improvements effected by carrying out the electrolytic refining of copper employing an electrolyte in accordance with this invention containing the special combination of addition agents glue, thiourea and a hydrolyzed sulfonated paraffinic hydrocarbon, such as Avitone A, as compared with another type of electrolyte, identified as old electrolyte, previously employed in commercial operations and containing only glue and Avitone A as addition agents in the amounts of about 0.046 and 0.043 pound respectively per ton of cathode deposited copper. The test data reported in accompanying Table II were

obtained from commercial scale tests carried out over a period of six months both for the old, previously commercially used electrolyte and for the new electrolyte composition in accordance with this invention.

TABLE II

	Old Electrolyte	New Electrolyte	Change, percent
Monthly cathode production, tons	22,036	22,273	+1
Average amps. (Powerhouse)	17,201	16,750	−2.5
Current density, amps./sq. ft.	18.72	18.20	−2.8
Current efficiency, percent	94.4	97.5	+3.2
Man-hours per ton cathode	1.86	1.73	−7
Svenska Elongation,[1] mm	[2] 157	251	[2] +60
Total cathode impurities, avg. p.p.m.*	261	252	−3.4
Tellurium, p.p.m.	1.9	1.2	−35
Arsenic, p.p.m.	1.8	1.7	−5.5
Antimony, p.p.m.	1.3	1.3	
Lead, p.p.m.	3.1	1.7	−45
Nickel, p.p.m.	3.7	4.3	+16.3
Iron, p.p.m.	10.1	10.3	+2
Silver, p.p.m.	9.0	7.9	−12
Bismuth, p.p.m.	0.17	0.13	−23.5
Selenium, p.p.m.	3.8	1.6	−58
Oxygen, p.p.m.	217	210	−3.2
Sulfur, p.p.m.	10	12	+20
Loss of silver, tr. ozs.	45,412	32,137	−29
Loss of gold, tr. ozs.	1,507	585	−61

[1] Svenska elongation is a measure of the annealability of copper and indicates its purity. Generally, the greater the Svenska elongation, the higher the copper purity.

[2] Due to refinement in the testing, indications are that the old value for Svenska elongation is probably low by about 25–30 mm. Thus, the change is closer to 35% than to the apparent 60%.

*Parts per million by weight.

In the tests reported in connection with Table II the amount of glue employed in the new electrolyte amounted to about 0.10 pound per ton of copper cathode produced. The amount of Avitone A in the new electrolyte amounted to about 0.03 pound per ton of copper cathode produced and the amount of thiourea in the new electrolyte amounted to about 0.05 pound per ton of copper cathode produced.

These values of the amounts of the special addition agents were obtained by calculation based upon the amounts of these materials added to the electrolyte to make up the electrolyte in accordance with this invention and to maintain satisfactory electrolyte performance during the electrolytic refining operation. Generally, the various special addition agents, glue, thiourea and a hydrolyzed sulfonated hydrocarbon, such as Avitone A, are present in the electrolyte in an amount of concentration of about 3.0 p.p.m., 1.5 p.p.m., and 0.9 p.p.m., respectively. Expressed in other terms, in accordance with this invention, the glue is present in the electrolyte in an amount of about 0.0037 gram per liter (g./l), thiourea in an amount of about 0.0018 g./l and Avitone A in an amount of about 0.0011 g./l.

It is more satisfactory, and it is preferred in the practice of this invention, to specify the amounts of the addition agents which must be added during the electrolytic refining operation either on a per day basis or per ton of copper cathode production basis. In view of the fact that the addition agents appeared to be used up during the electrolytic refining operation the amounts of these special addition agents are incorporated in the electrolyte at a rate at which the special addition agents appear to be consumed. Usually in the practice of this invention glue is incorporated in the electrolyte at an amount in the range 0.101–0.108 pound per ton of copper cathode produced. The thiourea is incorporated in the electrolyte in an amount in the range 0.051–0.054 pound per ton of copper cathode produced and the hydrolyzed sulfonated paraffinic hydrocarbon, Avitone A, is incorporated in the electrolyte in an amount in the range 0.031–0.033 pound per ton of copper cathode produced.

Indicative of the practice of this invention and the benefits obtainable by incorporating the special combination of addition agents, glue, thiourea and a hydrolyzed sulfonated paraffinic hydrocarbon, such as Avitone A, in the electrolytic refining of copper in the amounts, 0.10, 0.05, 0.03 pound, respectively, per ton of copper cathode

production, Table III sets forth comparative test data wherein different amounts of these special addition agents were employed in an electrolyte used for the electrolytic refining of copper.

TABLE III

	Other	Invention
Glue, lbs./ton cathode	0.06–0.10	0.10
Avitone, lbs./ton cathode	0.1–0.2	0.03
Thiourea, lbs./ton cathode	0.01	0.05
Current efficiency, percent	96.8	97.5
Selenium in copper deposited, p.p.m.	2.3	1.5–1.6
Silver in copper deposited, p.p.m.	11.0–11.1	7.9–8.0
Svenska elong., mm.	197–227	238–268

The test data presented in Table III clearly show the superiority of employing the special combination of addition agents in the particular proportions, all in accordance with this invention.

As will be apparent to those skilled in the art in the light of the foregoing disclosures, many substitutions, alterations and changes are possible in the practice of this invention without departing from the spirit or scope thereof.

We claim:

1. An electrolyte suitable for use in the electrolytic refining of copper consisting essentially of an aqueous solution of sulfuric acid and copper sulfate and minor amounts by weight of glue, thiourea and a sulfonated hydrocarbon, said glue, said thiourea and said sulfonated hydrocarbon being present in said electrolyte in an amount of about 3.0, 1.5 and 0.9 parts per million by weight, respectively.

2. An electrolyte in accordance with claim 1 wherein said electrolyte has a specific gravity in the range 1.24–1.27.

3. An electrolyte suitable for use in the electrolytic refining of copper having the composition in grams per liter, respectively, copper 40–49, sulfuric acid 182–192, and having a specific gravity 1.24–1.27, said electrolyte additionally containing a bone glue, thiourea and a hydrolyzed sulfonated derivative of a paraffinic hydrocarbon in a concentration of about 3.0, 1.5 and about 0.9, parts per million by weight, respectively.

4. In the electrolytic refining of copper involving passing an electric current between anodes of copper to be refined and cathodes of substantially pure copper immersed in an electrolyte consisting essentially of an aqueous solution of sulfuric acid and copper sulfate, the improvement which comprises adding to said electrolyte about 0.10 pound of glue, about 0.05 pound of thiourea and about 0.03 pound of a hydrolyzed sulfonated hydrocarbon, respectively, per ton of cathode deposited copper.

5. A method in accordance with claim 4 wherein the amounts of glue, thiourea and hydrolyzed sulfonated hydrocarbon incorporated in said electrolyte are sufficient to maintain the concentration of said glue, thiourea and sulfonated hydrocarbon in the electrolyte at about 3.0, 1.5 and 0.9, parts per million by weight, respectively.

6. In the electrolytic refining of copper involving passing an electric current between anodes of copper to be refined and cathodes of pure copper immersed in an electrolyte consisting essentially of an aqueous solution of sulfuric acid and copper sulfate, the improvement which comprises maintaining in said electrolyte during the electrolytic refining operation an amount of bone glue of about 0.0037 gram per liter, an amount of thiourea of about 0.0018 gram per liter and an amount of a hydrolyzed sulfonated paraffinic hydrocarbon of about 0.0011 gram per liter.

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