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ELECTROLYTIC REFINING OF COPPER

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This invention relates to the electrolytic refining of copper, and is particularly directed to the provision of an improved combination of addition agents in the electrolyte. The invention is based upon my discovery that when an acrylamide polymer hydrolyte is incorporated in the electrolyte in combination with an addition agent selected from the group consisting of glue and casein, a more satisfactory cathode deposit is formed than can be obtained using addition agents of the character and in the combination heretofore employed.

In the electrolytic refining of copper, an electric current is passed between cast anodes of copper to be refined and cathodes of pure electrolytically refined copper, both the anodes and cathodes being immersed in an electrolyte composed primarily of an aqueous solution of cupric sulfate acidified with sulfuric acid. Under the influence of the electric current, copper is dissolved from the anodes into the electrolyte, and is deposited from the electrolyte onto the cathodes in purified form. By adjusting the pH of the electrolyte as well as the current density, the impurities present in the anode are not deposited at the cathode, but rather remain in solution in the electrolyte or accumulate in an insoluble anode mud.

Addition agents, which generally are complex organic compounds or mixtures of such compounds, are incorporated in the electrolyte to insure the formation of a smooth and dense cathode deposit. Failure to use such an addition agent usually results in the development of substantial protuberances, known as "sprouts" or "trees," as the cathode deposit. Since the spacing between each anode and cathode in an electrolytic copper refining cell is usually about 1½ inches, it is easy for these "sprouts" or "trees," if they form, to make contact with the neighboring anode, thereby causing a short circuit. When this occurs, further deposit of copper on the cathode is hindered until the short circuit is broken, and both cell voltage and overall cathode current density in the cell are disturbed. Even if no short circuit develops, the formation of a rough cathode deposit is accompanied by entrainment of pockets of electrolyte which cannot be washed out. Because the entrained electrolyte in such pockets contains various impurities dissolved from the anode, the cathode copper is contaminated upon being melted.

A great number of addition agents have been tested for use in preventing the development of projections on the cathode surface. Unfortunately, many of these addition agents often promote undesirable properties, such as hardness and brittleness in cathode deposits, and their use generally leads to reduced current efficiencies. Consequently, a substantial amount of work has been done to find an addition agent, or combination of addition agents, that gives as smooth a deposit as possible with a minimum of undesirable effects.

In general, the addition of a proteinaceous electrophilic (positively charged) colloid to the electrolyte has been found effective to prevent the formation of "sprouts" or "trees." The use of animal glue, in particular, has found wide acceptance, either individually or in combination with casein or "Goulac" (a lignin pitch product obtained from paper mill waste) or both. Many refineries use animal glue in combination with "Goulac"

in electrolytic copper refining, but the major disadvantage of this combination is that the "Goulac" tends to form insoluble carbonaceous compounds in the electrolyte which precipitate in the tanks and the solution lines.

I have discovered that acrylamide polymer hydrolytes, when incorporated in the electrolyte in conjunction with one or more conventional addition agents, result in unusual advantages in the refining of copper electrolytically. In particular, when the acrylamide polymer hydrolyte is used in combination with animal glue or casein, or both, the quality of the cathode deposit is superior in smoothness and freedom from entrapped impurities, to that obtained with any previously used addition agents or combination. In addition, the formation of harmful carbonaceous deposits is substantially avoided. Elimination of these carbonaceous deposits, which are characteristic of the use of "Goulac," in turn facilitates the washing, leaching, filtering, and subsequent treatment of the anode slimes for recovery of their metal values.

Acrylamide polymer hydrolytes are high-molecular-weight polymers (and copolymers) of acrylamide in which from 0.8 to about 10 percent of carboxamide groups of the polymer are replaced by carboxyl groups. These polymer hydrolytes, which are marked by the Dow Chemical Company under the trade name "Separan," are characterized by a viscosity of at least 4 centipoises as determined with an Ostwald viscosimeter for an 0.5 percent by weight aqueous solution of the polymer hydrolyte at a pH of 3 to 3.5 and a temperature of 21.5° C. The term "acrylamide polymer hydrolyte," however, is inclusive of hydrolytes of polyacrylamide as well as copolymers of acrylamide with up to 15 percent by weight of other suitable monomers, such as alkyl acrylates, alkyl methacrylates, styrene, vinyl acetate, acrylonitrile, methacrylonitrile, vinyl alkyl ethers, vinyl chloride, and vinylidene chloride.

The invention contemplates the improvement, in the electrolytic refining of copper, of establishing and maintaining in the electrolyte from ¼ to 5 ounces of an addition agent selected from the group consisting of glue and casein and from 1/10 to 5 ounces of an acrylamide polymer hydrolyte for each ton of copper deposited on the cathodes, the acrylamide polymer hydrolyte having from about 0.8 to about 10 percent of the carboxamide groups of the polymer replaced by carboxyl groups. The actual concentrations of addition agents which are most advantageous are, of course, dependent upon several factors, including the current density, the impurity content of the anodes, and the temperature and pH of the electrolyte. Although there appears to be no critical upper limit to the concentration of the acrylamide polymer hydrolyte, since this compound apparently functions as a flocculant, there is no great advantage in using more than about 2 ounces per ton of copper deposited on the cathodes. In most electrolytes, substantially the full benefit of the presence of an acrylamide polymer hydrolyte may be achieved by adding not more than 1½ ounces for each ton of copper deposited on the cathodes.

The acrylamide polymer hydrolyte appears to function best when used in the electrolyte in combination with animal glue or casein. Surprisingly enough, casein and glue produce hard, brittle cathode deposits when either is used alone as the addition agent, but when either agent is combined with the acrylamide polymer hydrolyte, the resultant cathode deposit is fine-grained, dense, and desirably soft. By adding to the electrolyte animal glue in quantities as low as ¼ to 5 ounces together with 1/10 to 5 ounces of the acrylamide polymer hydrolyte per ton of copper deposited on the cathodes, the surface of the deposit is smooth and completely free from any objectionable trees or sprouts. Similar results

are obtained when ¾ to 5 ounces of casein are substituted in the electrolyte for the animal glue.

To illustrate the improvements obtained in electrolytic refining of copper when an acrylamide polymer hydrolyte is added to the electrolyte in conjunction with animal glue, a preferred embodiment of the invention is described below:

A typical electrolytic copper refinery comprises a large number of electrolytic cells, each of which is in the form of a tank holding a considerable number of cast anodes of copper to be refined, arranged alternately with cathodes of pure electrolytically refined copper. The anodes and cathodes are hung vertically in the cell tank and are spaced apart by only a little over an inch. An electrolyte comprising an aqueous solution of cupric sulfate and sulfuric acid is introduced continuously into each cell tank at one end and is continuously withdrawn at the other. The electrolyte fills the tank almost to the tops of the anodes and cathodes. Although cupric sulfate and sulfuric acid are the main ingredients of the electrolyte solution, it generally also contains other substances, such as a small amount of sodium chloride, added to prevent antimony and bismuth impurities from accumulating in the solution, and soluble compounds of such anode impurities as arsenic, nickel and iron. The electrolyte flowing from the electrolytic cell passes through a circulation system including a sump where make-up amounts of required reagents (including the addition agents) are added; and a part of the electrolyte is continuously withdrawn for treatment to remove accumulations of arsenic, nickel and other impurities. The electrolyte is pumped back again from the sump to the electrolytic cell tank. It is most convenient to add the combination of addition agents contemplated by the invention to the electrolyte in the sump tank or well, the addition agents being added continuously in an amount calculated to maintain them in desired concentrations in the electrolyte.

Since both animal glue and the acrylamide polymer hydrolyte (e.g. "Separan 2610") are quite readily soluble in water and in acid solution, the combination of addition agents is introduced in the electrolyte by preparing a dilute solution which can be measured continuously into the circulating electrolyte. By suitably adjusting the ratio of the acrylamide polymer hydrolyte to animal glue in this addition solution, it is possible to introduce into the electrolyte from 1/10 to 2 ounces of the hydrolyte and from ¼ to 5 ounces of the glue for each ton of cathode copper produced. Particularly satisfactory results have been obtained by adding glue in an amount from 1 to 2 ounces and "Separan 2610" in an amount from ⅛ to 1½ ounces for each ton of copper deposited on the cathodes.

If casein is to be used in the electrolyte in combination with both glue and "Separan 2610," a separate dilute solution of casein may be prepared and run continuously in a measured amount into the electrolyte in the sump. The casein solution should be freshly prepared each day, since casein undergoes extensive decomposition if allowed to remain in contact with acid solution. When casein is used, however, the amount of glue added to the electrolyte may be correspondingly reduced.

The use of animal glue and "Separan 2610" as addition agents, in accordance with the invention, has resulted in a number of improvements in operating economy and efficiency. Not only is the current efficiency increased, when compared with the use of a glue-"Goulac" combination in the electrolyte, but the amount of organic deposits in the electrolyte is reduced. This in turn results in a more easily handled anode mud than is the case when other addition agents are used. Since both the glue and "Separan 2610" are soluble in water and in acid solution, the addition agents may be easily and effectively disseminated in the electrolyte.

I claim:

1. In the electrolytic refining of copper, in which anodes of copper to be refined are electrolytically dissolved in an aqueous electrolyte of cupric sulfate and sulfuric acid and copper is deposited from the electrolyte on cathodes of pure copper, the improvement which comprises adding to the electrolyte from ¼ to 5 ounces of an addition agent selected from the group consisting of glue and casein and from 1/10 to 5 ounces of an acrylamide polymer hydrolyte for each ton of copper deposited on the cathodes, said acrylamide polymer hydrolyte having from about 0.8 to about 10 percent of the carboxamide groups of the polymer replaced by carboxyl groups and being further characterized by a viscosity of at least 4 centipoises as determined for a 0.5 percent by weight aqueous solution of the polymer hydrolyte.

2. In the electrolytic refining of copper, in which anodes of copper to be refined are electrolytically dissolved in an aqueous electrolyte of cupric sulfate and sulfuric acid and copper is deposited from the electrolyte on cathodes of pure copper, the improvement which comprises adding to the electrolyte from ¼ to 2 ounces of glue, from ¾ to 2 ounces of casein, and from about 1/10 to 2 ounces of an acrylamide polymer hydrolyte for each ton of copper deposited on the cathodes, said acrylamide polymer hydrolyte having from about 0.8 to about 10 percent of the carboxamide groups of the polymer replaced by carboxyl groups and being further characterized by a viscosity of at least 4 centipoises as determined for a 0.5 percent by weight aqueous solution of the polymer hydrolyte.

3. In the electrolytic refining of copper, in which anodes of copper to be refined are electrolytically dissolved in an aqueous electrolyte of cupric sulfate and sulfuric acid and copper is deposited from the electrolyte on cathodes of pure copper, the improvement which comprises adding to the electrolyte from ¼ to 5 ounces of glue and from 1/10 to 2 ounces of an acrylamide polymer hydrolyte for each ton of copper deposited on the cathodes, said acrylamide polymer hydrolyte having from about 0.8 to about 10 percent of the carboxamide groups of the polymer replaced by carboxyl groups and being further characterized by a viscosity of at least 4 centipoises as determined for 0.5 percent by weight aqueous solution of the polymer hydrolyte.

4. In the electrolytic refining of copper, in which anodes of copper to be refined are electrolytically dissolved in an aqueous electrolyte of cupric sulfate and sulfuric acid and copper is deposited from the electrolyte on cathodes of pure copper, the improvement which comprises adding to the electrolyte from 1 to 2 ounces of glue and from ⅛ to 1½ ounces of an acrylamide polymer hydrolyte for each ton of copper deposited on the cathodes, said acrylamide polymer hydrolyte having from about 0.8 to about 10 percent of the carboxamide groups of the polymer replaced by carboxyl groups and being further characterized by a viscosity of at least 4 centipoises as determined for a 0.5 percent by weight aqueous solution of the polymer hydrolyte.

5. In the electrolytic refining of copper, in which anodes of copper to be refined are electrolytically dissolved in an aqueous electrolyte of cupric sulfate and sulfuric acid and copper is deposited from the electrolyte on cathodes of pure copper, the improvement which comprises adding to the electrolyte from ¾ to 5 ounces of casein and from 1/10 to 2 ounces of an acrylamide polymer hydrolyte for each ton of copper deposited on the cathodes, said acrylamide polymer hydrolyte having from about 0.8 to about 10 percent of the carboxamide groups of the polymer replaced by carboxyl groups and being further characterized by a viscosity of at least 4 centipoises as determined for a 0.5 percent by weight aqueous solution of the polymer hydrolyte.

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