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ELECTROWINNING OF METALS

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This invention is concerned with the electrowinning of metals and is particularly directed to an improved process and to a novel cell feed composition for electrowinning operations.

In recent years increasing amounts of metals, particularly copper and zinc, have been recovered by leaching the ore to extract the metal values in the form of soluble salts in solution. Thereafter such solution is submitted to electrolysis to separate the metal. Such electrowinning processes have encountered certain difficulties. For example, the deposit of metal on the cathode is frequently non-uniform and tends to build up irregular "trees" which may grow across the space between the cathode and anode causing a short circuit in the cell. Further, such non-uniform deposits frequently show poor adhesion to the cathode so that portions of the deposit break off and redissolve with a resultant loss in current efficiency.

It is an object of the present invention to provide an improved method for the electrowinning of metals. It is a further object to provide a method for the electrowinning of metals whereby uniformly adherent deposits of metal are obtained. Another object is to provide a method for minimizing the growth of "trees" in electrolytic deposits of metal. An additional object is to provide an improved and novel cell feed composition. Other objects will become apparent from the following specification and claims.

According to the present invention, it has been discovered that the incorporation of small amounts of polyethyleneimine in the cell feed employed in the electrowinning of metals from aqueous solution results in improved current efficiencies and in the formation of a smooth, dense, uniform deposit of metal.

The water-soluble polyethyleneimines are mildly alkaline, hydrophylic substances prepared as described in U. S. Patents Nos. 2,182,306 and 2,208,095. These materials are commercially available in the form of concentrated aqueous solutions. The particular polyethyleneimines employed in the present invention are characterized by viscosities in aqueous 25 percent by weight solution of at least 20 centistokes and preferably at least about 200 centistokes at a temperature of 25° C., as determined with an Ostwald viscosimeter. The term "viscosity," as employed in the following specification and claims, refers to the viscosity of an aqueous 25 percent solution under the conditions set forth above. Jones et al., Journal of Organic Chemistry, volume 9, pages 146–147 (1944), show that polyethyleneimines are linear poly-secondary-amines of degree of polymerization of 25 to 100 and Trout, Tappi, volume 34, pages 539–540 (1951), shows the formula of said polymer to be $H_2N—(CH_2CH_2NH)_n—H$ and that in commercial preparations, n is about 100.

In carrying out the invention, the polyethyleneimine is added to the cell feed in any suitable fashion. For convenience of operation, the polyethyleneimine is usually introduced into the cell feed in the form of a dilute aqueous solution. In general, it is desirable to meter the polyethyleneimine solution into the cell feed under conditions such as to provide for thorough mixing of the polymer with the feed before introducing the mixture into the electrolytic cells. However, if necessary, as, for example, in adjusting the concentration of polyethyleneimine, the latter may be added directly to the electrolytic cell while electrolysis is proceeding. Following the addition of the polyethyleneimine, the resulting cell feed composition is electrolyzed in conventional fashion to accomplish the deposition of the desired metal.

The cell feeds employed in the operations, as set forth above, are, in general, those obtained in conventional hydrometallurgical leaching operations followed by purification steps as required for the particular metal. Cell feeds for the electrowinning of zinc usually contain from about 100 to about 200 grams of zinc, chiefly in the form of zinc sulfate, per liter of cell feed. Such solutions are substantially free of iron and copper. For the electrowinning of copper, conventional cell feeds contain from about 20 to 70 grams of copper per liter of cell feed. In such operation, the cell feed electrolyte usually contains a substantial proportion of sulfuric acid and is essentially free of chlorides.

The amount of polyethyleneimine employed will vary depending upon such factors as the particular metal being recovered and the type and concentration of impurities in the electrolyte. In general, from about 25 to about 150 parts by weight of polyethyleneimine is employed for each million parts by weight of cell feed. The concentration of polyethyleneimine in the treating solution added to the cell feed is not critical, provided the treating solution is sufficiently fluid to allow for ease of mixing with the feed. Thus, for example, with polyethyleneimines having viscosities of from about 20 to 50 centistokes, treating solutions may conveniently contain up to about five percent by weight of polymer, while with polymers having higher viscosities, it is generally desirable to employ treating solutions containing not more than about two percent by weight of polymer.

In a representative operation, the cell feed electrolyte was found to have the following analysis.

Constituent:	Concentration, Grams per liter
Zn	129.6
S (total)	68.4
S (as sulfate ion)	68.2
Mg	3.34
Na	2.95
As	0.00003
Sb	0.00002
Co	0.0084
H_2O	967

This electrolyte solution was representative of solutions obtained by sulfuric acid leaching of oxidized zinc ore concentrates as employed for electrowinning operations. A portion of the above solution was mixed with an aqueous 0.8 percent by weight solution of a polyethyleneimine characterized by a viscosity of about 200 centistokes. The solutions were mixed in the proportions of 1000 parts by weight of electrolyte solution to 19 parts by weight of polyethyleneimine solution to provide a cell feed composition containing 150 parts by weight of polyethyleneimine per million parts of composition. This cell feed composition was placed in a electrolytic cell equipped with a stirrer and an aluminum cathode and lead anode. A portion of the unmodified electrolyte solution was placed in an exactly similar cell and current was passed through the two cells in series for a period of about 13 hours to accomplish electro-deposition of zinc on the cathode. The current density was about 45 amperes per square foot of

electrode surface and the voltage drop was about 3.6 volts per cell. On completion of the electrolysis the cathodes were removed from the cells, washed thoroughly with distilled water, dried and weighed. It was found that the cathode from the cell containing the unmodified electrolyte solution had a rough, dark, porous deposit with many "trees" sprouting from the surface. The current efficiency for this cell was 36 percent. The cathode deposit from the cell containing the electrolyte modified with polyethyleneimine was uniformly smooth, dense and bright with essentially no "tree" formation. The current efficiency for the latter cell was found to be 65 percent.

By operating in similar fashion with cell feed compositions containing from about 20 to 70 grams of copper per liter in the form of copper sulfate and from about 25 to 150 parts by weight of polyethyleneimine per million parts of composition and electrolyzing at a current density of about 16 amperes per square foot, uniform, smooth, bright cathode deposits of copper are obtained.

We claim:

1. A process for the electrowinning of zinc which comprises electrolyzing a zinc sulfate solution containing from about 25 to about 150 parts by weight of a polyethyleneimine per million parts by weight of said solution, said polyethyleneimine having the formula

$$H_2N—(CH_2CH_2NH)_n—H$$

where n is an integer and is at least 25.

2. A cell feed composition for the electrowinning of zinc which comprises an aqueous solution containing from about 100 to about 200 grams of zinc, chiefly as zinc sulfate, per liter of solution and from about 25 to about 150 parts by weight of a polyethyleneimine per million parts by weight of solution, said polyethyleneimine having the formula

$$H_2N—(CH_2CH_2NH)_n—H$$

where n is an integer and is at least 25.

3. A composition according to claim 2 wherein the polyethyleneimine is characterized by a viscosity of at least 200 centistokes for an aqueous 25 percent by weight solution thereof at a temperature of 25° C., as determined with an Ostwald viscosimeter.

4. A process for the electrowinning of a metal selected from the group consisting of copper and zinc which comprises electrolyzing an aqueous solution of a sulfate of said metal, said solution containing from about 25 to 150 parts by weight of a polyethyleneimine per million parts by weight of solution, said polyethyleneimine having the formula

$$H_2N—(CH_2CH_2NH)_n—H$$

where n is an integer and is at least 25.

5. A process according to claim 4 wherein the polyethyleneimine is characterized by a viscosity of at least 20 centistokes for an aqueous 25 percent by weight solution thereof at a temperature of 25 C. as determined with an Ostwald viscosimeter.

6. In a process for electrowinning of a metal from the group consisting of copper and zinc from an aqueous solution of the sulfate of said metal, the improvement which comprises the step of incorporating in the electrolytic cell feed from about 25 to 150 parts by weight of a polyethyleneimine per million parts by weight of cell feed, said polyethyleneimine being chaarcterized by a viscosity of at least 200 centistokes for an aqueous 25 percent by weight solution thereof at a temperature of 25° C., as determined with an Ostwald viscosimeter, said polyethyleneimine having the formula

$$H_2N—(CH_2CH_2NH)_n—H$$

where n is an integer and is at least 25.

7. A cell feed position adapted to be employed for the electrowinning of the metal therefrom which comprises an aqueous solution of a salt selected from the group consisting of copper sulfate and zinc sulfate and incorporated therein a polyethyleneimine in an amount sufficient to accomplish improved deposition of the metal upon electrolysis of the feed composition, said polyethyleneimine having the formula

$$H_2N—(CH_2CH_2NH)_n—H$$

where n is an integer and is at least 25.

8. A composition in accordance with claim 7 wherein the polyethyleneimine is characterized by a viscosity of at least 20 centistokes for an aqueous 25 percent by weight solution thereof at a temperature of 25° C. as determined with an Ostwald viscosimeter.

9. A composition according to claim 7 wherein the polyethyleneimine is employed in the amount of from about 25 to about 150 parts by weight per million parts by weight of the composition.

UNITED STATES PATENTS

References Cited in the file of this patent

2,182,306	Ulrich et al.	Dec. 5, 1939
2,245,086	Bray et al.	June 10, 1941
2,393,741	Bray et al.	Jan. 29, 1946

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Metal Industry, November 29, 1940, Bray et al., pp. 433–436.