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ELECTROWINNING OF ZINC

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This invention relates to electrowinning of zinc and, more particularly, to means and methods of densifying the anode sludge in zinc electrowinning processes.

Zinc of high purity can be obtained by electrowinning with an acidic electrolyte containing dissolved zinc salts, for example, a solution of zinc sulfate. Solutions of this character contain some dissolved manganese, which plates out at the anode in the form of a loose, fluffy sludge of manganese dioxide. Periodic shutdown of the electrolytic cells, approximately monthly in commercial practice, is necessary to avoid excessive accumulation of this anode sludge. Accumulation of large quantities of this sludge results in clogging of the overflow pipes, and covering of the cooling coils, and may result in electrical shorts and other undesirable operating conditions.

An object of the present invention is to form the anode deposit as a dense, adherent scale.

A further object of this invention is to reduce the frequency of cell shutdowns for cleaning purposes by elimination or substantial reduction of the amount of loose sludge in the cell.

These and other objects will be apparent from the specification.

According to this invention it has been found that the addition of a small quantity of an aromatic sulfonic acid to the electrolyte in zinc electrowinning cells results in a dense scale which adheres to the anodes. Only a small portion of the total anode deposit is in the form of loose sludge. This materially reduces the necessary frequency of shutdowns for the purpose of cleaning out anode sludge.

Sulfonic acids which have been found particularly suitable for the purposes of the present invention are the halogenated sulfonic acids, especially the chlorinated sulfonic acids, of benzene, naphthalene, and the alkyl substituted benzenes and naphthalenes. Other aromatic sulfonic acids having no halogen, and in particular the sulfonic acids of benzene and naphthalene and the alkyl substituted derivatives of benzene and naphthalene have also been found to improve the adherence of manganese dioxide to the anode, although these are not as effective or as stable as the helogenated acids.

Specific acids which have been found to be effective according to this invention include 2,5-dichlorobenzenesulfonic acid and monochloronaphthalenesulfonic acid (probably 1-chloro-4-naphthalenesulfonic acid). Either the sulfonic acids or their alkali metal salts may be used interchangeably. Other halogenated aromatic sulfonic acids besides these particular compounds are also suitable. Other aromatic acids which are suitable according to the present invention include 2,7-naphthalenedisulfonic acid and 1,4-dimethylbenzenesulfonic acid.

The sulfonic acid additives according to the present invention are present only in minor amounts in the range of about 0.01 to 0.1 gram per liter. The permissible and the optimum concentrations both vary somewhat from acid to acid. For example, 2,5-dichlorobenzenesulfonic acid is used in small quantities, preferably 0.013 to 0.020 gram per liter, and seldom in concentrations exceeding 0.022 gram per liter. The optimum concentration of monochloronaphthalenesulfonic acid sodium salt, on the other hand, is from 0.022 to 0.044 gram per liter, and may be higher, up to about 0.09 gram per liter. The nonhalogenated sulfonic acids are generally used in somewhat higher concentrations. The optimum concentration of 2,7-naphthalenedisulfonic acid is from 0.022 to about 0.09 gram per liter. The sodium salt of 1,4-dimethylbenzenesulfonic acid is also used in concentrations of 0.022 to about 0.09 gram per liter. Additive concentrations higher than those specified cause a slight reduction in cathode efficiency.

The electrolyte in cells for zinc electrowinning is essentially a solution of zinc sulfate containing approximately 200 to 700 grams per liter of zinc sulfate. These concentrations are illustrative, and the present invention can be practiced with greater or lesser concentrations. About 10 to 15 percent (100 to 150 grams per liter) of free sulfuric acid is generally present in the electrolyte. Zinc sulfate solutions such as those used for the electrolyte of the present invention ordinarily contain about 1 to 6 grams per liter of manganous sulfate

$$(MnSO_4 \cdot H_2O)$$

The anodes in zinc electrowinning cells are preferably lead or a lead alloy. One example of suitable lead-alloy anode of low solubility is an alloy containing about 1 percent of silver, balance lead. The starting cathodes are generally of aluminum.

Cells according to the present invention are preferably operated continuously. In such cells, an inflowing solution of zinc sulfate containing about 500 to 700 grams per liter of zinc sulfate ($ZnSO_4 \cdot 7H_2O$) and having a pH of about 4.0 to 5.0 continuously flows into the cell. The zinc content of the solution is substantially all plated out on the cathodes, leaving an effluent solution of sulfuric acid containing a relatively small amount of zinc. In commercial operations, it is preferable to have a number of cells in cascade arrangement, in which each cell receives the effluent liquor from the previous cell. A solution of zinc sulfate is introduced into each cell, and a solution of sulfuric acid containing less than 60 grams per liter of zinc is withdrawn from the last cell.

Electrowinning is started by charging a cell with a zinc sulfate solution, and electrolysis is continued until the zinc content of the electrolyte is reduced to some predetermined low level, say about 50 grams per liter. Thereafter, zinc sulfate solution is added continuously to compensate for the zinc metal being deposited on the cathodes.

It is desirable to electroplate high-purity zinc containing less than 0.003 percent by weight of lead. Such purities are difficult to attain, particularly in lead-lined cells. It has been found that the purity of cathode zinc is substantially increased in cells having the lead lining connected through a high resistance to the cathode so as to constitute a secondary cathode on which the greater portion of lead in solution is plated. The potential drop maintained between the secondary cathode and the anode is slightly less than the potential drop between the primary cathode and the anode. For example, when the potential difference between the anode and the zinc cathode is about 3 to 3.1 volts, there is a potential difference of about 2.3 to 2.7 volts between the anode and the secondary cathode. This secondary cathode reduces the amount of lead dissolved from the tank lining. The current consumption by the secondary cathode is quite small. For example, the current density on the tank lining is only about 0.07 to about 0.2 ampere

per square foot, while the cathode current density is about 30 to 40 amperes per square foot.

Various operating conditions may be used in the practice of this invention. It has been found advantageous, for example, to have approximately equal anode and cathode areas with current densities of about 30 to 40 amperes per square foot on both electrodes. Satisfactory operation has been attained at an electrolyte temperature of about 95 to 105° F. It is necessary to cool the electrolyte to maintain these temperatures, and this may be done by means of cooling coils submerged in the cell. These cooling coils, of course, form a surface on which anode sludge may collect, and the amount of sludge deposits on these cooling coils is substantially reduced by the present invention. Other methods of cooling may also be used, for example, evaporation towers.

The following examples are illustrative of specific embodiments of the present invention:

Example I

A solution of the following ingredients:

	G./l.
Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)	686
Manganous sulfate ($MnSO_4 \cdot H_2O$)	4.50
2,5-dichlorobenzenesulfonic acid	0.020
pH=4.0	

was continuously introduced into a 6-liter lead-lined electro-winning cell at the rate of 0.0975 cubic foot per day. A solution of the following composition:

	G./l.
Zinc sulfate	220
Sulfuric acid	150
Manganous sulfate	2.46

was continuously withdrawn from the cell. The cell was 9½ inches by 7 inches by 8 inches deep. The anodes were a lead alloy containing 1 percent silver, balance lead. The primary cathode was aluminum. The lead lining constituted a secondary cathode, and a resistance of about 40 ohms was placed in series with the lining. The primary cathode was in parallel with the lead lining and resistor. A voltage of 3.0 volts between the anode and the primary cathode was maintained, and a voltage of 2.7 volts between the secondary cathode and the anode was maintained. The anode and primary cathode current densities were both 35 amperes per square foot, and the current density on the lead cell lining was 0.2 ampere per square foot. Substantially pure zinc containing 0.0016 percent by weight of lead deposited on the cathode. A dense anode scale, of which more than 75 percent adhered to the anode, was also formed.

Example II

A solution of the following ingredients:

	G./l.
Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)	652
Manganous sulfate	4.56
2,7-naphthalenedisulfonic acid	0.022
pH=4.0	

was continuously added to a cell identical to that in Example I at a flow rate of 0.0975 cubic foot per day. The voltages and current densities were the same as in Example I. More than 75 percent of the anode scale adhered to the anode. Electrolytic zinc containing 0.0025 gram per liter of lead was deposited on the cathode.

Example III

The equipment, cell voltages, current densities, and flow rate were the same as in Example I. The composition of the feed solution was as follows:

	G./l.
Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)	686
Manganous sulfate ($MnSO_4 \cdot H_2O$)	4.56
Monochloronaphthalenesulfonic acid (probably 1-chloro-4-naphthalene-3-sulfonic acid)	0.044
pH=4.0	

Electrolytic zinc containing 0.0031 percent of lead was deposited. The anode scale was dense, and 65 percent of it adhered to the anode.

Example IV

The equipment, cell voltages, current densities, flow rates, and cell electrolyte were the same as in Example II, except that no organic additive was present. The zinc deposit contained 0.0018 percent by weight of lead. A loose, fluffy anode scale, less than 50 percent of which adhered to the anode, was formed.

Example V

The equipment in this example was identical to that used in Examples I to IV except that there was no secondary cathode. A solution of the following composition:

	G./l.
Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)	594
Manganous sulfate ($MnSO_4 \cdot H_2O$)	3.85
2,5-dichlorobenzenesulfonic acid	0.026
pH=4.0	

was fed to the cell at the rate of 0.0975 cubic foot per day. A voltage of 3.0 volts between the anode and cathode was maintained, and the anode and cathode current densities were both 35 amperes per square foot. The zinc deposit contained 0.0034 percent by weight of lead. The anode scale was dense, and 91 percent of it adhered to the anode.

Example VI

The procedure, equipment, cell voltages, current densities, and flow rate were the same as in Example V. The solution flowing into the cell had the following composition:

	G./l.
Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)	562
Manganous sulfate ($MnSO_4 \cdot H_2O$)	5.82
Sodium salt of 1,4-dimethylbenzenesulfonic acid	0.088
pH=4.0	

More than 60 percent of the anode scale formed remained on the anode. The lead content was not determined.

Example VII

The procedure, equipment, voltage, current densities, and flow rate were the same as in Example V. The composition of the feed solution was as follows:

	G./l.
Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)	608
Manganous sulfate ($MnSO_4 \cdot H_2O$)	3.72
pH=4.0	

No organic additive was present. The zinc deposit contained 0.0116 percent by weight of lead. The anode scale was loose and fluffy, and only 48 percent of it remained on the anode.

While the foregoing invention has been illustrated with respect to the specific embodiments, it is understood that the scope is limited only by the scope of the appended claims.

What is claimed is:

1. In a process for electrowinning zinc by electrolyzing an acidic aqueous solution of zinc containing dissolved manganese, employing an anode of a material selected from the group consisting of lead and lead-base alloys, a method of densifying anode scale and causing a substantial portion of said scale to adhere to said anode that comprises maintaining in said solution about 0.01 to 0.1 gram per liter of an aromatic sulfonic acid selected from the group consisting of the benzene and naphthalene sulfonic acids, alkyl substituted benzene and naphthalene sulfonic acids, and halogenated derivatives thereof.

2. In a process for electrowinning zinc by electrolyzing an acidic aqueous solution of zinc containing dis-

solved manganese, employing an anode of a material selected from the group consisting of lead and lead-base alloys, a method according to claim 1 wherein said halogenated derivatives are chlorinated derivatives.

3. In a process for electrowinning zinc by electrolyzing an acidic aqueous solution of zinc containing dissolved manganese, employing an anode of a material selected from the group consisting of lead and lead-base alloys, a method of densifying anode scale and causing a substantial portion of said scale to adhere to said anode that comprises maintaining in said solution about 0.01 to 0.1 gram per liter of a chlorinated benzene sulfonic acid.

4. In a process for electrowinning zinc by electrolyzing an acidic aqueous solution of zinc containing dissolved manganese, employing an anode of a material selected from the group consisting of lead and lead-base alloys, a method of densifying anode scale and causing a substantial portion of said scale to adhere to said anode that comprises maintaining in said solution about 0.013 to 0.022 gram per liter of 2,5-dichlorobenzenesulfonic acid.

5. In a process for electrowinning zinc by electrolyzing an acidic aqueous solution of zinc containing dissolved manganese, employing an anode of a material selected from the group consisting of lead and lead-base alloys, a method of densifying anode scale and causing a substantial portion of said scale to adhere to said anode that comprises maintaining in said solution about 0.01 to 0.1 gram per liter of a chlorinated naphthalene sulfonic acid.

6. In a process for electrowinning zinc by electrolyzing an acidic aqueous solution of zinc containing dissolved manganese, employing an anode of a material selected from the group consisting of lead and lead-base alloys, a method of densifying anode scale and causing a substantial portion of said scale to adhere to said anode that comprises maintaining in said solution about 0.022 to 0.09 gram per liter of a monochloronaphthalenesulfonic acid.

7. In a process for electrowinning zinc by electrolyzing an acidic aqueous solution of zinc containing dissolved manganese, employing an anode of a material selected from the group consisting of lead and lead-base alloys, a method of densifying anode scale and causing a substantial portion of said scale to adhere to said anode that comprises maintaining in said solution about 0.022 to 0.09 gram per liter of 2,7-naphthalenedisulfonic acid.

8. In a process for electrowinning zinc by electrolyzing an acidic aqueous solution of zinc containing dissolved manganese, employing an anode of a material selected from the group consisting of lead and lead-base alloys, a method of densifying anode scale and causing a substantial portion of said scale to adhere to said anode that comprises maintaining in said solution about 0.022 to 0.09 gram per liter of the sodium salt of 1,4-dimethylbenzenesulfonic acid.

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