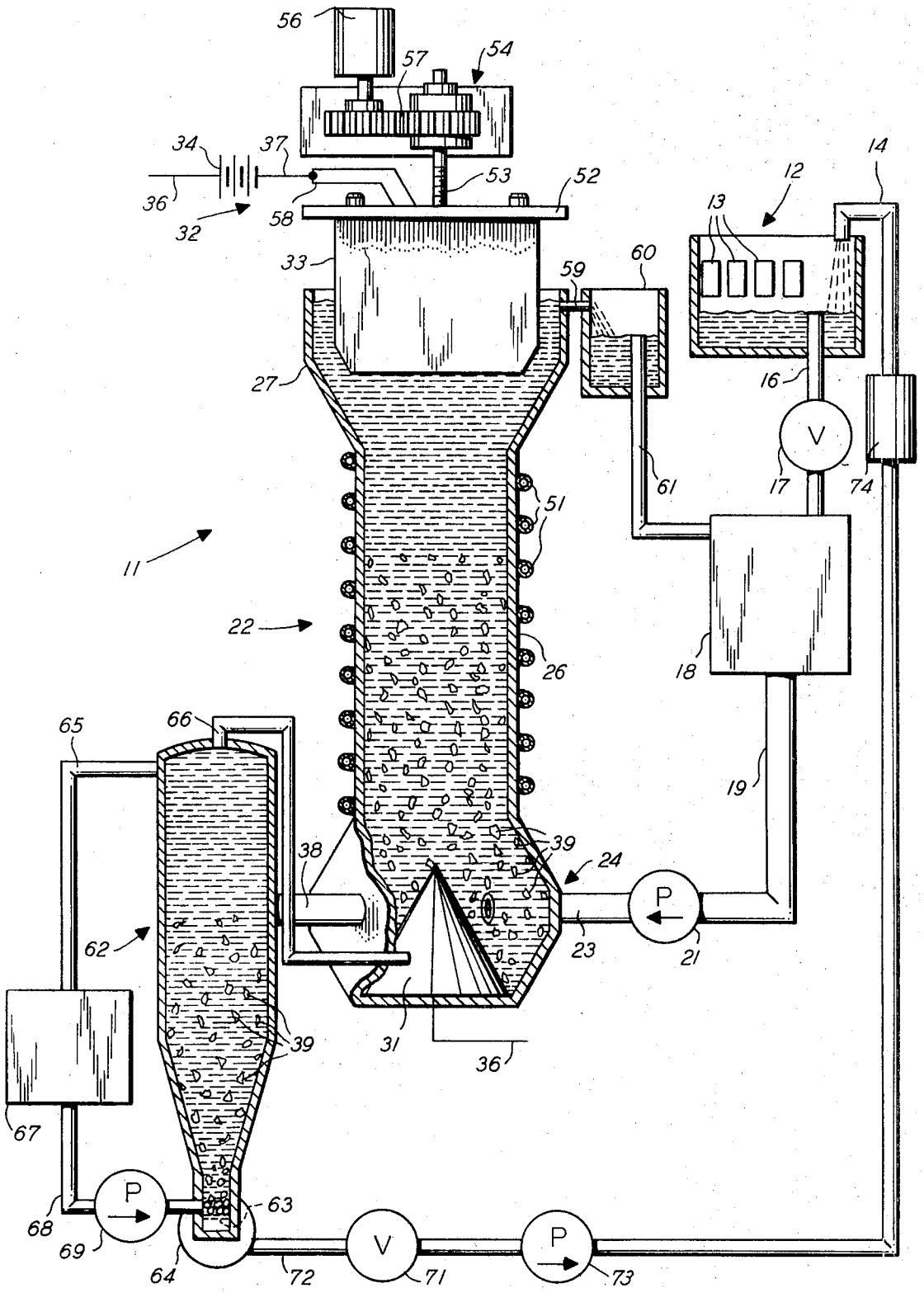
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METHOD OF CONTINUOUSLY REGENERATING AND RECYCLING A SPENT ETCHING SOLUTION

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METHOD OF CONTINUOUSLY REGENERATING AND RECYCLING A SPENT ETCHING SOLUTION

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ABSTRACT OF THE DISCLOSURE

A spent alkaline metal persulfate etching solution containing alkaline metal sulfates, a metal sulfate and residual amounts of persulfate values is regenerated by first introducing the spent solution into an anode zone of an electrolytic cell. The spent solution is passed through a cooling zone which separates the anode zone from a cathode zone to precipitate the persulfate values from the spent solution with the precipitate moving into the anode zone. This results in a catholyte which is free of the persulfate values. The catholyte moves into the cathode zone where the metal sulfate is reduced to its corresponding metal with the metal plating out on a cathode and sulfate values reduced to bisulfate values. This results in an anolyte which is subsequently recirculated to the anode zone to oxidize the bisulfate values to persulfate values and thereafter the oxidized anolyte is mixed with the precipitate of the persulfate values to form a slurry. The slurry is then heated to dissolve the precipitate thereby regenerating the spent etching solution.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a method of continuously regenerating and recycling a spent etching solution and, in particular, to a method of removing metal ions from and increasing persulfate values of a spent alkaline metal persulfate etching solution.

(2) Description of the prior art

Peracids such as ammonium persulfate are commonly used as an etchant for metals such as copper, cobalt, iron, nickel, zinc, and alloys thereof. For example, in the production of printed circuit boards, a metal film may be selectively etched to form a desired circuit pattern. This is generally accomplished by immersing a metal laminated board in a persulfate etching solution. The metal areas not covered by a mask are exposed to the etching solution and dissolved while the metal covered by the mask remains to form a desired circuit pattern.

The persulfate etching solution may be used over and over as an etching solution until it becomes spent, that is, its rate of dissolution of the metals practically ceases. The spent solution is regenerated by removing the dissolved metal and exposing sulfate values, a reaction product of the etching, to a redox reaction to regenerate additional persulfate values.

In one method of regenerating spent ammonium persulfate etching solution, the spent solution is introduced as an anolyte into an anode section of an electrolytic cell and an electrolyte having an acidic sulfate or a bisulfate therein is introduced as a catholyte in a cathode section of the electrolytic cell. The cathode and anode sections of the electrolytic cell are separated by a cation exchange membrane which permits dissolved metal ions to pass from the anolyte to the catholyte but inhibits persulfate values in the anolyte from entering the catholyte. An electric current is passed through the catholyte and anolyte by way of a cathode in the catholyte and an anode in the

anolyte. The dissolved metal is plated from the solution at the cathode and the sulfate values are converted to persulfate values at the anode. The anolyte solution having increased persulfate values and decreased dissolved metal concentrations is now suitable for reuse as an etching solution.

While the above process regenerates a spent ammonium persulfate etching solution, the process requires that the catholyte and anolyte be separated by a cation membrane. Accordingly, the efficiency of the process depends upon the efficiency of the cation membrane in permitting metal ions to enter the catholyte from the anolyte while excluding persulfate ions from the catholyte. Also, as cation membranes are relatively fragile, there is always the danger that they will rupture. As a result, there is a need for a simple and economic method of regenerating spent persulfate etching solutions.

OBJECT OF THE INVENTION

An object of the invention is to provide a method of removing metal ions from a spent persulfate solution. Another object of the invention is to provide a method of increasing persulfate concentrations of a spent persulfate solution.

A further object of the invention is to provide a method of regenerating a spent persulfate solution.

With these and other objects in view, the method of this invention contemplates the reduction of a metal sulfate to its corresponding metal wherein the metal sulfate is in a solution of alkaline metal sulfates containing residual values of an alkaline metal persulfate and includes the steps of (1) cooling the solution to precipitate the persulfate thereby forming a catholyte containing the alkaline metal sulfates and the metal sulfate, and (2) exposing the catholyte to a reduction reaction to reduce the metal sulfate to its corresponding metal. In addition, the invention also contemplates increasing the persulfate concentrations of the solution and includes the additional steps of (1) reducing the alkaline metal sulfates to an anolyte containing alkaline metal bisulfates, and (2) exposing the anolyte to an oxidation reaction to oxidize the alkaline metal bisulfates to alkaline metal persulfates. Further, the invention contemplates regenerating the solution and includes the additional steps of (1) mixing the persulfate precipitate with the oxidized anolyte to form a slurry, and (2) dissolving the persulfate precipitate in the oxidized anolyte.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a front elevated view of a closed loop system suitable for practicing the method of the invention, which system is illustrated with portions cut away for purposes of clarity.

DETAILED DESCRIPTION

In the following detailed description of the invention, the process is described with reference to a spent alkaline metal persulfate such as a spent potassium persulfate solution and a spent solution of potassium persulfate and sodium persulfate. However, as will be appreciated by those skilled in the art, a spent potassium persulfate solution and a spent solution of potassium persulfate and sodium persulfate is only illustrative of two spent alkaline metal persulfate solutions that can be regenerated by the method of this invention and that other spent alkaline metal persulfate solutions can be regenerated practicing the method of this invention.

An initial, conventional etching is first carried out with a fresh alkaline metal persulfate solution having a persulfate molar concentration of greater than 0.45 at temperatures of from about 35–45 degrees centigrade. This

etching solution can be used to etch unmasked portions of a metal such as copper either by conventional immersion etching or spray etching. Etching is normally continued until the solution is depleted of persulfate values to a molar concentration of about 0.45. At this point, the solution is capable of further etching, but the etch rate and quality of etch is unsatisfactory, and such solutions are normally discarded as spent solutions. Although the specific example given is copper, it will be appreciated by one skilled in the art that copper is only illustrative of one metal that an etching solution of alkaline metal persulfate will etch and that other metals such as cobalt, iron, nickel, zinc and alloys thereof are also etchable thereby.

The spent solution containing metal sulfates, alkaline metal sulfates and residual amounts of persulfate values is then passed into an anode zone of an electrolytic cell. The spent solution is then passed through a cooling zone which separates the anode zone from a cathode zone and then into the cathode zone of the electrolytic cell. In the cooling zone the persulfate values are precipitated out of the spent solution so that the solution entering the cathode zone is essentially free of persulfate values. In the cathode zone, the metal sulfate in the spent solution is reduced to its corresponding metal with the metal plating out on a cathode and the sulfate values are reduced to bisulfate values. This results in an anolyte which is subsequently recirculated to the anode zone to oxidize the bisulfate values to persulfate. By removing the persulfate values from the spent solution prior to reducing the metal sulfates to their corresponding metal, it is possible to regenerate the spent solution without the necessity of a cation membrane to separate the anode from the cathode and without the need of preparing separate catholyte to operate the electrolytic cell. The terms "anolyte" and "catholyte," as used in the context of this invention, not only refer to the electrolyte immediately adjacent to the anode and cathode respectively, but also refer to an electrolyte destined for exposure to an anode and cathode respectively.

Although it is desirable to precipitate all the persulfate values out of the spent solution prior to reducing the metal sulfate to its corresponding metal, it is not essential that this be done. As will be appreciated, the metal sulfate may be reduced to its corresponding metal in the presence of persulfate values if the potential at which the cathode is operated reduces the metal sulfate in the spent solution at a faster rate than the persulfate values can dissolve the metal plating onto the cathode. For example, it is possible to reduce metal sulfate from a spent solution having 0.20 molar persulfate concentration when the cathode is operated at 400–600 amps per square foot. Therefore for purposes of this invention, a spent solution having persulfate values therein which etch metal at a slower rate than metal sulfate in the spent solution is reduced to its corresponding metal are considered spent solutions essentially free of persulfate values.

Generally, the method of this invention is practiced with a peracid which precipitates from solution at low temperatures so that the solution is essentially free of persulfate values. However, such a peracid usually has a relatively low solubility at normal etching temperatures. As a result the persulfate molar concentration at normal etching temperatures is not satisfactory for etching. For example, potassium persulfate precipitates from a solution as the solution is cooled to a temperature of about 10 degrees centigrade leaving a molar persulfate concentration in solution of about 0.10. As discussed above, at this concentration the metal may be plated out from such a solution without the peracid attacking the metal at an undesirable rate. However, as potassium persulfate has a solubility of 108 grams per liter of solution at a temperature of 40 degrees centigrade the resulting persulfate molar concentration of 0.40 is insufficient to permit satisfactory etching of a metal from printed circuit boards. Although the method of the invention could be practiced with a potassium persulfate solution, potassium persulfate is not considered a preferred etchant due to the low molar concentration of persulfate at normal etching temperatures. It is therefore highly desirable to increase the persulfate molar concentration above 0.45 so that etch rate and quality of etch is acceptable at normal etching temperatures.

The persulfate molar concentration of a peracid solution having a low persulfate molar concentration at normal etching temperatures, e.g., below 0.45 molar at 40 degrees centigrade, may be increased to an acceptable concentration level by adding one or more peracids to the solution which have a greater solubility at the desired temperature. For example, sodium persulfate has a solubility of 618.5 grams per liter of solution at a temperature of 40 degrees centigrade and may be added to the potassium persulfate solution in sufficient quantities to raise the persulfate concentration above 0.45 molar normal etching temperatures.

Typically, peracids having a high solubility at normal etching temperatures also have a relatively high solubility at lower temperatures. As a result, sufficient peracid can not be precipitated at lower temperatures to reduce the peracid concentration to a level which will permit the plating of a metal from the solution without the peracid attacking the metal at an unacceptable rate. For example, sodium persulfate has a solubility of 540 grams per liter of solution (2.29 molar persulfate) at a temperature of 10 degrees centigrade. As will be appreciated, this is well above the peracid concentration level at which a metal can be plated from the solution without the peracid attacking the metal at an unacceptable rate. However, it has been found that using the method of this invention the concentration of sodium persulfate is reduced to acceptable levels in the cathode zone.

For example, a spent etching solution of potassium persulfate and sodium persulfate contains reaction products of sodium sulfate, potassium sulfate and metal sulfate as well as residual amounts of potassium persulfate and sodium persulfate. As will be appreciated, the reaction products as well as the residual amounts of potassium persulfate and sodium persulfate are ionized in solution, i.e., break up into positive ions of potassium, sodium and the metal and into negative ions of persulfate and sulfate. These ions remain in solution until they combine to form an insoluble compound. For example, if the solution is cooled to 10 degrees centigrade, potassium ions which combine with persulfate ions form insoluble potassium persulfate and precipitate out of the spent solution as potassium persulfate crystals. This continues as long as the concentration of potassium persulfate in solution at 10 degrees centigrade is greater than 0.10 molar (29 grams per liter of solution). A reaction of this type, i.e., where the positive radical of one polar compound reacts with the negative radical of another polar compound and vice versa, is known as a methathesis.

As the sodium persulfate in solution contributes a persulfate ion and the potassium sulfate in solution contributes a potassium ion, insoluble potassium persulfate is precipitated leaving sodium sulfate in solution. In this manner, sodium persulfate in solution is converted to sodium sulfate thereby reducing the persulfate concentrations in the cathode zone to acceptable levels. The reaction is represented by the following reaction:

(1)

$$Na_2^+S_2O_8^{=}(aq) + K_2^+S_2O_8^{=}(aq) + K_2^+SO_4 \xrightarrow{-\text{temp}\downarrow} K_2S_2O_8(s) + Na_2^+SO_4^{=}(aq) + K_2^+S_2O_8^{=}(aq)$$

In order to convert sufficient sodium persulfate to sodium sulfate to reduce the sodium persulfate concentration to desired levels, it is only necessary for sufficient potassium ions to be present in solution to combine with the persulfate ions. If the original etching solution contains 80 to 108 grams of potassium persulfate and 72 to

110 grams of sodium persulfate per liter of solution, the spent etching solution will contain sufficient potassium ions in solution to convert sufficient sodium persulfate to sodium sulfate to reduce the persulfate values to acceptable levels. In this manner, by maintaining the spent solution at 10 degrees centigrade, the potassium persulfate is precipitated from the solution, the sodium persulfate is converted to sodium sulfate, and the persulfate values in solution are reduced to acceptable levels in the cathode zone.

Referring now to the drawing there is shown a closed-loop system **11** for regenerating a spent etching solution of potassium persulfate and sodium persulfate. The spent etching solution exits from an etching chamber **12**, is regenerated and then recycled back to the etching chamber.

A plurality of copper articles **13—13**, for example, a non-metallic substrate having a copper foil laminated to a surface thereof wherein areas of the surface are suitably masked to define a desired circuit pattern, are positioned in the etching chamber **12** to expose unmasked areas of the copper surfaces to an etching solution of potassium persulfate and sodium persulfate. Etching of the exposed copper surfaces is satisfactorily accomplished with a fresh aqueous solution of 0.40 molar potassium persulfate and 0.35 molar sodium persulfate (108 grams of potassium persulfate and 85 grams of sodium persulfate in a liter of solution). The etching solution is preferably heated to a temperature of about 35 to 45 degrees centigrade. This etching solution may be used to etch unmasked portions of the copper by any conventional etching technique such as immersion etching or spray etching. The etching of the copper, that is, the removal of the unmasked copper film, occurs as a result of a chemical reaction between the copper and the potassium persulfate and sodium persulfate. This reaction forms in solution potassium sulfate, sodium, sulfate and copper sulfate. The reaction is represented by the following chemical reaction:

(2) $K_2S_2O_8(aq)+Na_2S_2O_8(aq)+2Cu(s)\rightarrow 2CuSO_4(aq)+K_2SO_4(sq)+Na_2SO_4(aq)$

Etching is preferably discontinued when the concentration of persulfate values in the etching solution falls to about 0.45 molar. At this point the solution is capable of further etching, but as the etch rate and quality of the etch is greatly diminished, the solutions are normally considered to be spent etching solutions.

The concentration of the potassium persulfate and sodium persulfate of the etching solution in the chamber **12** is maintained at desired levels by introducing an etching solution into the chamber **12** having the desired concentrations via a connecting inlet line **14**. The flow of the etching solution through the line **14** into the chamber **12** can be adjusted in any conventional manner as a function of the amount of copper etched per given time interval or as a function of the copper or persulfate ion concentration of the etching solution in the chamber. Correspondingly, the spent etching solution, which has been exposed to copper and consists of the reaction products in equation (2) and any unreacted potassium persulfate and sodium persulfate, is displaced from the chamber **12** via a connecting outlet line **16**.

The spent etching solution emerging from the etching chamber **12** by way of the outlet line **16** passes through an open valve **17** into a conventional cooling chamber **18**. As the spent etching solution passes through the cooling chamber **18**, the spent etching solution is cooled from its etching temperature range of about 35 to 45 degrees centigrade to a temperature range of about 20 to 30 degrees centigrade to increase the efficiency of the subsequent regeneration steps. The cooled spent etching solution is pumped from the cooling chamber **18** through exit line **19** by way of pump **21** into a vessel **22** through inlet line **23**.

The vessel **22** has a generally bulb-shaped anode zone **24** connected to a cylindrically shaped cooling zone **26** which widens at the top as shown in the drawing into an open ended cylindrically shaped cathode zone **27**. Mounted in the anode zone **24** is a conically shaped anode **31** and mounted in the cathode zone is a moveable cathode assembly **32** having a stainless steel or copper cathode **33**. The anode **31** and cathode assembly **32** are connected to a suitable power supply such as a battery **34** by way of wires **36** and **37** respectively thereby forming an electrolytic cell in the vessel **22**.

The spent etching solution is introduced tangentially into the anode zone **24** through the inlet line **23** to flow circularly about the anode **31**. As the spent etching solution flows about the anode **31**, a portion of the spent etching solution flows out of the anode zone **24** by way of outlet line **38** as the remaining spent etching solution flows upward into the cooling zone **26**. The end of the outlet line **38** is mounted in the anode zone **24** opposite to the inlet line **23** and with the end of the outlet line **38** divergent to the circular flow of the spent etching solution in the anode zone **24**. The pump **21** moves the spent etching solution into the anode zone **24** at a velocity sufficient to eject subsequently formed potassium persulfate crystals **39** into the outlet line **38**. It has been determined that spent etching solution pumped into the anode zone through a line having a 24-inch inside diameter under 40 p.s.i.g. will eject potassium persulfate crystals through an outlet line having an inside diameter of 3 inches while moving a greater portion of the spent etching solution through the cooling zone **26**.

The cooling zone **26** is provided with cooling coils **51—51** to cool the spent solution to a temperature below 20 degrees centigrade. At temperatures below 20 degrees centigrade e.g. 10 degrees centigrade the solubility of potassium persulfate in solution is less than 29 grams per liter of solution. The potassium persulfate in the spent etching solution formed by the combining potassium ions and persulfate ions in excess of the solubility precipitate out of the spent etching solution as previously discussed. As a result of the precipitation of potassium persulfate, the spent etching solution has a decreased concentration of potassium ions and has a persulfate molar concentration of less than about 0.10. For purposes of this invention the spent etching solution is considered substantially free of all persulfate values. The reaction is represented in equation (1).

The potassium persulfate crystals **39—39** formed in the cooling zone **26** are precipitated back into the anode zone **24**. As the potassium persulfate crystals enter the anode zone **24**, the crystals are urged outwardly by the centrifugal force resulting from the swirling spent etching solution and exit the anode zone through the outlet line **38**. The spent etching solution as it flows upwardly through the cooling zone **26** is converted to the catholyte, i.e., a solution essentially free of persulfate values and consisting essentially of potassium sulfate, sodium sulfate and copper sulfate. As can be appreciated, lowering the temperature in the cooling zone reduces the solubility of potassium persulfate and as previously discussed lowers the concentration of persulfate values in the catholyte. Satisfactory results have been obtained by operating the cooling zone **26** at 10 degrees centigrade.

The catholyte thereafter flows into the cathode zone **27** about the cathode **33**. The copper ions are then reduced to copper metal which plates out on the cathode **33** while the catholyte is reduced to an anolyte containing potassium bisulfate and sodium bisulfate. As will be appreciated, by one skilled in the art, this process will work with any suitable metal sulfate such as copper, cobalt, iron, nickel, zinc, and alloys thereof. As is well known, these metals will plate onto a cathode from a catholyte of potassium sulfate, sodium sulfate, and a metal sulfate while reducing the potassium sulfate and sodium sulfate to potassium bisulfate and sodium bisulfate respectively. The reaction at the cathode is as follows:

(3) $K_2SO_4\ (aq)+Na_2SO_4\ (aq)+2CuSO_4\ (aq)+4H^+\rightarrow 2Cu\ (s)+2KHSO_4\ (aq)+2NaHSO_4\ (aq)$

In general, a cathode having a large surface area is used to facilitate copper deposition. In typical operations, a current density from 25 to 50 amps per square foot is maintained at the cathode. As can be appreciated, as copper is plated onto the cathode **33**, the surface area increases thereby reducing the current density. In order to provide a constant current density, a moveable cathode is recommended. For example, as copper is plated onto the cathode, the cathode surface exposed to the free solution may be decreased by displacing the cathode out of the catholyte.

The cathode assembly **32** shown in the drawing is suitable for maintaining a constant current density at the cathode. The cathode **33** is securely mounted to a plate **52** having a threaded shaft **53**. The shaft is threaded into an elevator mechanism **54** which is driven by a motor **56** by way of a non-conductive belt **57**. When the motor **56** is energized the elevator mechanism **54** rotates and displaces the cathode **33** out of the cathode zone to decrease the surface area of the cathode in the solution. Current passes to the cathode **33** from the battery **34** by connecting the wire **37** to a brush contact **58**. The cathode **33** having copper plated thereon may be replaced when necessary by removing the cathode from the plate **52** and replacing it with a new cathode.

The anolyte flows from the cathode zone **27** by way of overflow pipe **59** into an overflow tank **60** which is connected by way of pipe **61** to the cooling chamber **18**. The anolyte from the overflow tank **60** flows into the cooling chamber and exits from the cooling chamber **18** by way of the outlet line **19** and is pumped into the anode zone **24** of the vessel **22** by way of the line **23** as previously discussed. When the spent etching solution exits from the etching chamber **12** into the cooling chamber, the anolyte is mixed with the spent etching solution in the cooling chamber **18** so that a mixture of the anolyte and the spent etching solution is introduced into the anode zone **24**.

As the anolyte passes over the anode **31**, the sodium bisulfate and potassium bisulfate is oxidized to sodium persulfate and potassium persulfate respectively. The reaction at the anode is as follows:

(4) $2KHSO_4\ (aq)+2NaHSO_4\ (aq)\rightarrow K_2S_2O_8+Na_2S_2O_8+4H^+$

The combined reaction at the cathode and the anode is as follows:

(5) $K_2SO_4\ (aq)+Na_2SO_4\ (aq)+2CuSO_4\ (aq)\rightarrow 2Cu\ (s)+K_2S_2O_8\ (aq)+Na_2S_2O_8\ (aq)$

In general, noble metals such as platinum or gold are preferred as the anode. A current density at the anode of 200–600 amps per square foot has been found to give satisfactory results in oxidizing bisulfate values to persulfate values.

As the potassium persulfate and sodium persulfate generated in the anode zone **24** flows upwardly through the cooling zone **26**, the potassium persulfate is precipitated from the solution and the sodium persulfate is converted to sodium sulfate as previously discussed. The precipitated potassium persulfate crystals **39—39** are centrifically ejected from the anode zone **24** as a slurry by way of the outlet line **38** into a separator **62**. This slurry consists of the potassium persulfate crystals suspended in the solution as constituted in the zone **24** at the time the crystals are ejected. The solution remaining in the zone **24** is passed upwardly through the vessel **22** as previously discussed.

Ideally, it is desired to operate the vessel **22** until all of the dissolved copper is removed and all of the sodium sulfate and potassium sulfate are converted to sodium persulfate and potassium persulfate respectively. However, as previously discussed, satisfactory etching results are obtainable when the persulfate molar concentration is above 0.45. Therefore, it is only necessary to operate the vessel **22** to produce a slurry having sufficient persulfate values in the form of potassium persulfate crystals and sodium persulfate and potassium persulfate in solution to yield a solution having greater than 0.45 persulfate molar concentration. The potassium persulfate crystals formed in the cooling chamber are dependent on temperature and the residual amount of potassium persulfate in the spent solution as well as the potassium persulfate formed as a result of the reaction between potassium ions of the potassium sulfate and persulfate ions of the sodium persulfate in the spent etching solution. The concentration of the sodium persulfate and potassium persulfate in solution exiting from the anode zone through the outlet line **38** is controlled by the amount of anolyte passed into the anode zone from the cooling chamber and the efficiency of the anode **31**.

As was previously discussed, spent etching solution in the etching chamber **12** is only removed therefrom and introduced into the cooling chamber **18** when the persulfate molar concentration in the etching chamber is below 0.45. However, the anolyte from the cathode zone **27** of the vessel **22** continuously passes through the cooling chamber **18** into the anode zone **24** when the vessel is operated. Therefore as spent etching solution is only periodically mixed with the anolyte the ratio of anolyte to spent solution entering the anode zone **24** is greater than 1 to 1. Accordingly, the slurry exiting from the anode zone **24** by way of the outlet line **38** is on the average richer in oxidized anolyte than spent etching solution.

By providing more potassium ions than sodium ions in a fresh etching solution of potassium persulfate and sodium persulfate there will be a sufficient amount of potassium ions in the spent solution to convert the sodium persulfate to potassium persulfate as the spent etching solution moves through the cooling zone **26**. An initial etching solution having 108 grams of potassium persulfate and 80 grams of sodium persulfate in a liter of solution has approximately twice as many potassium ions as sodium ions. At the start of the regeneration of spent etching solution, the initial spent etching solution converted to the catholyte has a decreased concentration of potassium sulfate and an increase concentration of sodium sulfate. This is due to the fact that the potassium sulfate interacts with the sodium persulfate in the cooling zone **26** to form sodium sulfate and potassium persulfate. Accordingly, the oxidized anolyte which mixes with the potassium persulfate precipitate to form the slurry has a higher concentration of sodium persulfate than potassium persulfate and the slurry exiting the anode zone **24** has a persulfate molar concentration greater than 0.45.

An alternate method of increasing the persulfate values as well as increasing the efficiency of the anode **31** is to add sulfuric acid to the spent etching solution. The sulfuric acid provides additional sulfate values in solution which are oxidized at the anode to persulfate thereby increasing the efficiency of the anode. Molar concentrations of sulfuric acid of from 0.1 to 2.0 have been found to increase the anode efficiency.

The slurry is ejected by centrifugal force out of the anode zone **24** through line **38** into the separator **62**. As the slurry passes downward through the separator **62**, as shown in the drawing, the potassium persulfate crystals collect on a screen **63** and the solution passes through the screen into a collector **64**. The solution at the top of the separator **62** flows through two exit lines **65** and **66**. The solution in exit line **65** flows into a heating chamber **67** where the solution is heated to a temperature of about 40 to 70 degrees centigrade. The heated solution is thereafter moved from the heating chamber through line **68** by a pump **69** which thereafter moves the heated solution over the potassium persulfate crystals collected on the screen **63**. The heated solution dissolves the potassium persulfate crystals on the screen and the now dissolved crystals pass through the screen into the collector **64**. The solution in the collector has essentially the same constituents as the solution in the anode zone **24** at the time the

potassium persulfate crystals were ejected and has been enriched with potassium persulfate values by dissolving the potassium persulfate crystals therein.

The regenerated etching solution remains in the collector **64** until such time as needed to replace the volume of etching solution in the etching chamber **12** which is lowered as the spent etching solution exits from the etching chamber. At this time, valve **71** is opened and the regenerated etching solution emerges from the collector **64** through line **72** and is pumped by pump **73** into the etching chamber **12** by way of the line **14**. To assure that the regenerated etching solution is at the proper etching temperature, the regenerated etching solution may be passed through a heating chamber **74** as it flows through the line **14**.

At the start of the regeneration process, the initial solution in the anode zone **24** is the spent etching solution from the cooling chamber **18**. Only after, the anolyte is generated in the cathode zone **27** and introduced into the anode zone, does the anode zone begin to generate potassium persulfate and sodium persulfate. Accordingly, the slurry initially introduced into the separator **62** is relatively poor in potassium persulfate and sodium persulfate.

It is therefore advantageous to place potassium persulfate crystals on the screen **63** of the separator to insure sufficient persulfate values in the solution initially collected in collector **64**.

The solution in the separator **62** exiting through the line **65** flows into the anode zone **24** of the vessel **22** where it is mixed with anolyte in the anode zone. The solution is moved through the exit line **65** by vacuum generated by the centrifugal action of the swirling anolyte in the anode zone **24**. In this manner, the efficiency of the closed-looped regeneration system **11** may be increased.

As can be appreciated, the method of the invention provides a simple and economical method of regenerating a spent persulfate etching solution by removing dissolved metals and increasing persulfate values of the spent persulfate etching solution.

What is claimed is:

1. A method of reducing a metal sulfate to its corresponding metal wherein the metal sulfate is selected from the group consisting of copper sulfate, cobalt sulfate, iron sulfate, nickel sulfate and zinc sulfate and is in a solution comprising sodium persulfate and potassium sulfate in a molar concentration in excess of the persulfate concentration, comprising the steps of:

cooling the solution to a temperature below about 20° to precipitate potassium persulfate, thereby forming a solution essentially free of persulfate values; and

exposing the essentially persulfate free solution to an electrolytic reaction to reduce the metal in the metal sulfate to its corresponding metal.

2. The method of claim **1** wherein the persulfate concentration of the solution is increased by oxidizing lower oxidation state sulfur containing ions to persulfate to form a solution having an increased persulfate concentration.

3. The method of claim **2**, comprising in addition the steps of:

precipitating the potassium persulfate into the solution exposed to the oxidation reaction;

removing the potassium persulfate precipitates as a slurry containing the solution having an increased persulfate concentration; and

heating the slurry to dissolve the potassium persulfate precipitate so as to further increase the potassium persulfate concentration.

4. A method of reducing a metal sulfate to its corresponding metal wherein the metal sulfate is selected from the group consisting of copper sulfate, cobalt sulfate, iron sulfate, nickel sulfate and zinc sulfate and is in a spent persulfate solution of sodium sulfate and potassium sulfate containing residual values of potassium persulfate and sodium persulfate wherein the molar concentration of persulfate is less than 0.45, comprising the steps of:

cooling the spent solution to a temperature below about 20° C. to precipitate potassium persulfate without precipitating the potassium sulfate, sodium sulfate, metal sulfate or sodium persulfate, the precipitation of potassium persulfate converting the sodium persulfate to sodium sulfate thereby forming a first electrolyte containing potassium sulfate, sodium sulfate and the metal sulfate, said first electrolyte being essentially free of persulfate values; and

exposing the first electrolyte to an electrolytic reaction to reduce the metal of the metal sulfate thereby removing the metal from the solution.

5. The method of claim **4** wherein the electrolytic reaction generates a second electrolyte containing lower oxidation state sulfur ions and wherein the persulfate concentration of the spent persulfate solution is increased, comprising the additional step of:

exposing the second electrolyte to an oxidation reaction to oxidize the lower oxidation state sulfur ions to persulfate thereby forming a solution having an increased persulfate concentration.

6. The method of claim **5**, comprising in addition the steps of:

precipitating the potassium persulfate into the solution exposed to the oxidation reaction;

removing the potassium persulfate precipitate as a slurry containing the solution having an increased persulfate concentration; and

heating the slurry to dissolve the potassium persulfate precipitate so as to further increase the potassium persulfate concentration.

7. The method as set forth in claim **6** wherein spent persulfate solution is mixed with the second electrolyte prior to exposing the second electrolyte to the oxidation reaction.

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