THE FSL REGEN SYSTEM
for CUPRIC CHLORIDE ETCHANT

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DESCRIPTION – PROCESS
QUESTIONS AND ANSWERS
Description

The FSL 'Regen' System is a system designed for the ELECTROLYTIC regeneration of Cupric Chloride Etchant as used in the etching process of Printed Circuit Board production. The System provides an 'in situ' instantaneous regeneration of the etchant as it is being used in the etching machine with the ability to recover the etched/dissolved copper in a pure dendritic form in the Cathode compartment of the Electrolytic Regen Cell.

History

The initial development work was performed by the Electricity Council of Great Britain's Research Institute at Capenhurst, Cheshire, U.K. After successful laboratory trials, the Institute awarded FSL with the sole world-wide manufacturing rights to the 'Regen Cell'. At the same time a world-wide patent was passed and enforced.

The first full size industrial plant was commissioned for trials in Summer 1983 with the first commercial unit sold in Autumn 1984. This unit having a capacity of 4 kg/hr. This capacity referring to the maximum Copper Recovery Rate per hour that the Cell can cope with.

Since that first installation sixteen other units have been successfully installed with eleven different customers worldwide. However as the awareness to 'Clean Technology' heightens, FSL feel confident that the requirement for their Regeneration System will increase rather than decrease.
Process

The FSL Regen system can basically be seen as a direct replacement for the established method of Chemical Regeneration. Let us look at the etching reaction with respect to the CHEMICAL REGENERATION TECHNIQUE.

\[
\text{Cu}^{++} + \text{Cu} \rightarrow \text{Cu}^{+} + \text{Cu}^{+}
\]

Cupric Ions + Copper on Formation of Two inactive Cuprous Ions in Etchant PCB Ions in Etching Machine Sump

Add \( \text{H}_2\text{O}_2 \) or Cl

\( \text{HCl} \)

\( \text{H}_2\text{O} \)

Mixing of Additional Chemistry in Sump

Production of Two Cupric Ions

One Ion stays in Etching Machine for re-use

\[
\text{Cu}^{++} + \text{Cu}^{++}
\]

One Ion to Bulk storage

Storage/Transportation

Summary of Chemical Regeneration Technique

Basically as a result of the Etching Reaction the etching solution loses its etch effectiveness. To 'revive' this solution oxidising chemicals are dosed into the etching machine sump and regenerate the etchant. However as a result the equivalent volume of chemistry that is pumped in has to be pumped out to a Bulk Storage system.

The dosing of the oxidising chemicals is controlled by a Redox probe and meter. This system monitors the level of active Cupric ions in the etching machine and displays this as millivolt reading. Lower and Upper millivolt set points are used to determine the point at which the oxidising chemicals are dosed in and are switched off. The set points are typically in the range 500 mv to start dosing and 560 mv to stop the dosing.
Process continued

As a direct comparison let us look at the etching reaction with respect to the FSL ELECTROLYTIC REGEN SYSTEM.

\[ \text{Cu}^{++} + \text{Cu} \rightarrow \text{Cu}^{+} + \text{Cu}^{+} \]

Cupric Ions Copper on Formation of Two inactive Cuprous in Etchant PCB Ions in Etching Machine Sump

\[ \text{Cu}^{+} \rightarrow -e \rightarrow \text{Cu}^{++} \]

\[ \text{Cu}^{+} \rightarrow -e \rightarrow \text{Cu}^{++} \]

Both cuprous ions formed are oxidised to active Cupric Ions

Simultaneously: In the Cathode Compartment

One of the oxidised Cupric Ions formed at the Anode migrates through the membrane which separates the Anode and Cathode and performs the following Reaction

\[ \text{Cu}^{++} \rightarrow +2e \rightarrow \text{Cu} \]

Copper plates out on the Cathode

Summary of FSL Regen Technique

As Etching occurs within the etching chamber so solution is pumped from the sump of the etching machine over the ANODES of the Regen Cell before returning to the etching machine sump. When inactive Cuprous ions, formed in the Etch Reaction, are present at the Anodes oxidation occurs, regenerating active Cupric ions. However in order to maintain an electrolytic balance within the cell a proportion of these regenerated Cupric Ions are "pulled" through the dividing membrane onto the Cathode where they are reduced to solid copper which plates out in a crystalline dendritic form on the Cathodes. A Redox measurement system, exactly of the kind found to control chemical regeneration, is used to signal the beginning and ending of electrolytic regeneration in the cell. This is marked by the supply and shut-off of electrical energy from the Transformer/Rectifier used to power the cells. Similar Redox set points to those used to control the chemical regeneration systems are employed.
The FSL Regen Cell

The cell itself, as already briefly described, consists of a series of Anode and Cathode compartments divided by a special membrane material. The type of membrane used allows the transfer of ions, when the system is under current load, but not that of solution. As a result it is possible to have two similar solutions but of different chemical percentages/concentration adjacent to one another divided only by the membrane.

Anode Compartment

Within the Anode compartments of the cell is where the OXIDATION of the inactive copper ions formed during the etching reaction occurs.

The Etching solution is pumped on a continuous basis from the Etching machine sump over the Anodes of the cell and back to the sump. This flow rate, typically, for a 6 kg/hr cell, lies in the region of 220-250 litres per min. This high flow rate ensures that there will be a very swift response by the Regen Cell to any changes which may occur in the etching machine sump.

As stated this flow loop is continuous, with the controlling redox measurement being taken at the return point of the etching solution to the etching machine sump.

The Redox set points employed ensure that the Oxidation reaction ends at around 560-580 mV, i.e. the electrical power supply to the cell is shut off. In this way the evolution of Chlorine gas cannot occur as this reaction is only possible at a Redox millivolt reading of 1000 - 1100 mV.

Cathode Compartment

Within the Cathode compartments of the cell is where the REDUCTION of copper ions occurs. This takes the form of reducing some of the active cupric ions formed at the ANODE to solid crystalline copper metal which is plated out on the CATHODES.
As already explained, as a direct result of applying the electrical energy to the cell, some of the regenerated cupric ions formed at the ANODE are pulled through the membrane where they are reduced and plate out as copper. The solution in the cathode compartment, the catholyte, is circulated within a closed loop through the Cathode compartments and involves a high liquid circulation rate with the solution being pumped over the Cathodes themselves. This solution is fundamentally the same solution as in the anolyte/etching solution, however it has a much lower copper concentration, typically 20g/ltr. As a result of this low copper concentration it is possible to plate out solid copper on the cathodes without the risk of re-etching the plated copper. This is because acidic copper etching solutions will not begin the etching process until the copper concentration in the solution lies in the region of 50 – 70 g/l.

The reaction at the cathodes occurs very rapidly and due to the nature of the membrane material used, a situation is soon reached whereby the proscribed copper concentration in the Catholyte begins to fall. This is due to the inability for sufficient cupric ions to pass through the membrane from the Anode into the Cathode compartment.

Therefore in order to maintain the required copper concentration of around 20 g/ltr in the catholyte it is necessary to have a direct solution bleed line from the Anolyte into the Catholyte. This bleed line allows high copper concentration Anolyte into the low copper concentration Catholyte. The rate of flow through this line is controlled by a metering valve and solenoid valve. The solenoid valve only opens when the electrolysis within the cell is occurring, i.e. when electrical power is being supplied from the Transformer/Rectifier to the cell, as controlled by the Redox control system. The rate of flow is controlled by the fine adjustment of the metering valve.

Regular analysis of the Catholyte solution, i.e. once per 8 hr shift, and subsequent manual adjustment of the metering valve is sufficient to ensure the correct Catholyte Chemistry is maintained.
Summary of Electrolytic Reactions occurring within the FSL Regen System.

1) **Etching Reaction**

\[
Cu^{2+} + Cu \rightarrow Cu^{+} + Cu^+ 
\]

- active cupric copper on PCB
- two inactive cuprous ions formed

ii) **At the ANODE**

Both Cuprous ions re-oxidised

\[
2 \times Cu^+ \xrightarrow{-2e} 2 \times Cu^{2+} \quad 2 \text{ electrons removed}
\]

- cuprous ion
- cupric ion

iii) **At the Cathode**

One of the Cupric ions formed at the ANODE migrates through membrane or via bleed valve to CATHODE where following reaction occurs.

\[
Cu^{2+} \xrightarrow{+2e} Cu \quad 2 \text{ electrons added}
\]

- cupric ion
- pure dendritic copper

As can be seen the ionic balance between ANODE and CATHODE reactions is maintained.
QUESTIONS AND ANSWERS

Q: How is the process controlled?
A: By a Redox Measurement System which is interfaced to switch ON/OFF the electrical power to the Regen Cell.

Q: What Current/Voltage is required to power the cell?
A: For every 1 Kg of Copper plated out per Hour at the anode, the system requires 1000A at 6-7 V DC. i.e. for a cell of capacity 6 Kg/Hr, Electrical supply would be 6000A, 6-7 V DC.

Q: What is the Current Density on the Electrodes?
A: 40 A/dm²

Q: What are the Anodes and Cathodes made from?
A: Graphite sheet.

Q: Do the Electrodes wear away/self destruct?
A: No, they don’t. This is due to the fact that no gas is formed at either the Anode or Cathode. It is only gas formation which weakens the structure of graphite which eventually leads to it wearing away. In the FSL Regen Cell the Anode and Cathode reactions concern themselves only with the oxidation and reduction of metal ions.

Q: What is the life span of Anodes and Cathodes?
A: Since the first commercial systems became available in 1984, FSL have never found it necessary to replace Anodes or Cathodes in any of their operating systems.

Q: Is Chlorine evolved at the Anode?
A: No, this is because the electrolytic cell reactions are controlled by a Redox measurement system, which uses set points of typically 500 mV and say 560 mV to switch on and switch off the electrical power to the cell. In this way the Redox potential of 1000 mV, at which Chlorine gas is normally evolved, is never reached.

Q: Is Hydrogen evolved at the Cathode?
A: When the cell is operating normally the Cathode reaction concerns itself with the reduction of Copper ions to solid copper, plated out in a dendritic form. As long as Copper ions are present in the Catholyte solution there is no risk of evolving Hydrogen. The maintenance of the copper concentration in the Catholyte is described under the section headed 'Catholyte Compartment'.
Questions and Answers continued

Q: How is the Copper concentration maintained in the Catholyte?

A: Via a direct bleed line from the Anolyte into the Catholyte, which incorporates a metering valve and solenoid valve system. This bleed line system is more comprehensibly described under the section headed 'Cathode Compartment'.

Q: What is the Current Yield?

A: In answering this question we must remember that within the FSL Regen Cell there are basically two separate reactions occurring. These can be clearly seen as an ANODE and a CATHODE reaction.

Firstly ANODE reaction:

\[ \text{Cu}^+ \rightarrow \text{Cu}^{++} \]

Secondly CATHODE reaction:

\[ \text{Cu}^{++} \rightarrow \text{Cu} \quad \text{solid copper} \]

It is therefore difficult to give an accurate overall Current Yield as the two reactions differ. However it may be considered that the ANODE reaction is 100% whereas the CATHODE reaction is slightly less in accordance with the literature.

i.e. at 100% Current Yield for Copper plating on to a Cathode we have: 1.18 g/A/Hr

or: 1.18 kg/1000A/Hr

However, with the FSL Regen Cell the plate out rate is:

\[ 1.0 \ \text{g/A/Hr} \]

or: \[ 1.0 \ \text{kg/1000A/Hr} \]

Therefore we can calculate the Current Yield in comparison to value given in the literature.

\[ 1.0 \times 100 = 85\% \]

\[ 1.18 \]

Therefore the current yield at the Cathode of Cell is 85%.
Questions and Answers continued

Q: What is the Membrane material made from?
A: Suffice to say a PVC based ion exchange material

Q: What is the average life span of the Membrane material?
A: 2 - 3 years. Longer if carefully looked after.

Q: How long does it take to change a complete set of membranes in a 6 kg/hr Cell?
A: 1 working day for two engineers

Q: Do the membranes have to be changed complete with their frames or is it possible to change just the membrane material?
A: Normally we recommend that membranes be changed complete with their frames, and then the old membranes be sent to FSL to have new membrane material fitted. This refitting of new material being a cheaper option than completely replacing the original membrane frames and material with new ones.

Q: How is the Copper removed from the Cell?
A: The copper plated out on the Cathodes falls to the bottom of the cell where it collects, when the copper collection compartment is full, then catholyte solution is drained into the sump of the machine, the copper remains where it has settled. The porthole doors are then opened and the copper shovelled out into a collecting vessel, i.e. barrel etc.

Q: What condition is the Copper in when removed from the cell?
A: The copper is in a dendritic crystalline form although it is damp, as it has been lying in the copper collection part of the cell under Catholyte solution. Therefore it is also acidic.

Q: Is it necessary to wash the Copper?
A: If the copper remains un-washed although it will eventually dry, there will be a green copper chloride crust to it as the acid has not been washed away. If washed the copper will look cleaner and should probably obtain a higher price at resale.
Questions and Answers continued

Q: Can the copper be washed in the cell prior to removal?
A: Yes as an option a water rinse system can be built into the cell which allows copper washing and has separate drainage for the rinse water.

Q: What is the weight of Copper collected in the Cell?
A: Up to 300 Kg in a 6 Kg/Hr unit and up to 200 Kg in a 4 Kg/Hr unit.

Q: What time is required to empty the Copper from the cell and refill the Catholyte side?
A: From the beginning of the drain-down process thorough copper removal and Catholyte re-fill would take a trained operator 45 minutes for a 6 kg/hr Cell.

Q: What is the Copper purity?
A: The dendritic crystalline copper plated out is 99.9% pure copper.

Q: What is the resale value of the recovered copper?
A: This very much depends on the efforts of the seller to find a customer willing to pay a good price. Obviously if the copper is sold in its raw - un-washed - state to say a scrap metal merchant it will obviously not realise as much value as say a customer who has washed the copper and stored up a large amount for sale to a smelting plant for instance.

Typically one would expect a value in the region of 60 - 75% of that stated for Grade A copper metal as listed on the International Metal Exchanges.

Q: Does the recovered Copper re-dissolve back into the Catholyte solution if it left in the cell for an extended period, whilst the cell is not functioning?
A: No, the recovered copper will not re-dissolve as the Catholyte solution is typically in the range 15 - 25 g/l in copper, at which concentration it will not re-etch/re-dissolve copper metal.

Q: What is the Anolyte solution flow rate between the etching machine and the Regen Cell?
A: 200 - 250 ltr per min. for a 6 kg/hr Cell
Questions and Answers continued

Q: What is the Anolyte/Etching solution recipe?
A: The FSL regen system can operate with a wide range of chemical concentrations in the Anolyte solution. This allows the customer to use their normal etching solution specification. The typical acceptable ranges for the various etching solution components are shown below.

Anolyte/Etching solution:

Copper Concentration: 80 - 130 g/l
Hydrochloric Acid Concentration: 80 - 180 g/l

Q: What is the free acid concentration in the Anolyte/Etching solution?
A: This concentration will not be affected by the Regeneration process and therefore can be regarded as the same as when a chemical regeneration process is being employed with the particular Etching solution composition in question.

Q: How is the Copper removed from the Cathodes?
A: The cell is fitted with an automatic copper removal system. This takes the form of a scraper bar which fits around the Cathodes, but not actually touching it. The stand off distance being 25 mm. As the crystalline copper dendrites form on the Cathode surface, they grow outwards. The scraper, linked to a timer, moves back and forth across the Cathode face, knocking off the heavy copper dendrites which then fall to the floor of the Cathode compartment where they accumulate.

Q: At what temperature does the cell operate?
A: 48 - 52 degrees Celsius (125 - 134 degrees Fahrenheit).

Q: Why is a Cooling System required?
A: A cooling system is fitted to the Regen System to compensate for the heat energy put into the circulating Anolyte and Catholyte loops by the electrolytic reactions and also the action of high volume pumping.
Questions and Answers continued

Q: What level of Cooling is required?
A: As a result of operating the cell the Anolyte and Catholyte solutions rise in temperature by 1 or 2 degrees C above that of the etching machine temperature. This then requires to be cooled by passing the solutions through separate cooling towers. Each cooling tower requires 8 - 10 ltr per min. of water when operational. The solutions in the cell are thus maintained at the same temperature as the etching solution in the etching machine.

Q: What control system is used to operate the cooling system on the cells?
A: Both Anolyte and Catholyte solutions are monitored by temperature probes linked to a display unit which also, via a set point, control the operation of solenoid valves which control the flow of cooling water into the cooling towers.

Q: What are the Cooling Towers made from?
A: Glass body with integral glass cooling coils.

Q: What amount of cooling water is required?
A: For a 6 kg/hr unit, when cooling is required, 15 ltr/min
For a 4 kg/hr unit, when cooling is required, 10 ltr/min

Q: What is the cooling water pressure requirement?
A: Not higher than 14 psi/1 bar

Q: What maintenance is required for the Redox probe?
A: The type of redox probe employed uses a reference solution of 300 g/l KC1, potassium chloride, at ambient temperature. This must be added on a weekly basis just to ensure that the level is topped up. Apart from this a 6 weekly check of the redox meter reading can be made by using a zero calibration switch fitted on the redox meter itself.

Q: What is the life of the Redox probe?
A: This cannot be specifically defined, we recommend however that they be automatically scrapped and replaced after a working period of 18 months.

Q: How often is the Catholyte Analysis required?
A: Once per 8 hour shift, with total copper and Hydrochloric acid levels being analysed and recorded.
Questions and Answers continued

Q: What chemical additions need to be made to the cell chemistry?

A: The only additions that need to be made are to the etching machine sump to compensate for drag-out and evaporative losses. This takes the form of Hydrochloric Acid + water, diluted to give the acid concentration required. This addition can either be made in one "go" at the end of each shift, or can be dosed continually from a tank using a metering pump.

Q: What Air Extraction rate is required for the cell?

A: The cell is fitted with ventilation points which are connected typically to a 110 mm ventilation pipe. The rate of extraction is typically in the range of 100 c.f.m./70m³ per hour.

Q: What Safety Features are built into the Cell?

A: Apart from the standard electrical features, including overload protection, earth leakage, etc., the equipment is fitted with pressure sensors on solution pipe lines as well as a system for monitoring the cathode scraper mechanism. In the case of a high temperature situation, the cell will cease to function except for the cooling system and pumps which remain on and continue to cool the overheated solution until the correct operating temperature is reached. Another standard feature of the cell is to incorporate, via a direct interface, the alarm system of the Transformer/Rectifier unit.

Q: Is the cell fitted with a chlorine gas alarm?

A: The standard cell is supplied without a chlorine gas alarm. However if the customer feels it necessary then a unit can be fitted which will automatically shut down the operation of the cell if chlorine gas is generated to a level of 1 p.p.m. The only way in which this gas can occur is if the Redox measurement system is either improperly maintained, and subsequently fails, or incorrectly calibrated, which could possibly cause chlorine evolution. However should this occur then, as already stated, at a level of 1 p.p.m. the machine is shut down automatically.

The additional cost of the Chlorine gas alarm being £1,500.00 approximately.
Questions and Answers continued

Q: What does the maintenance routine involve?

A: Basically the cell requires to be kept clean and tidy. This would involve a weekly exterior wipe over with a damp cloth, ensuring all pipe connections remain tightened. Chemical analysis is done on a shift basis. Redox system maintained weekly. Occasionally especially during factory shut downs it is recommended to drain the cell of solution and leave it full with a mild Hydrochloric Acid solution.

Obviously any moving parts such as the scraper system and pumps should be monitored to check that they are not being fouled or are running abnormally.
COST JUSTIFICATION FOR CUPRIC CHLORIDE REGENERATION SYSTEM.

1. How much square footage per year.
   e.g. 1 sq. meter = 10.8 sq. ft
   if 540,000 sq. ft per year - 50,000 sq. meters.

2. How is the work broken down.
   e.g. 60% = 1 oz double/sided
        30% = 1/2 oz double/sided
        10% = 2 oz double/sided

   Now 1 oz = 35 (micron thick) copper = 0.305 Kg/sq meter
       1/2 oz = 17 (micron thick) copper = 0.152 Kg/sq meter
       2 oz = 70 (micron thick) copper = 0.610 Kg/sq meter

   Therefore, total copper on all laminate before etching weighs
   0.6 (60%) x 50,000 sq. m x 2 (double sided) x 0.305 Kg (1 oz/35)
   0.3 (30%) x 50,000 sq. m x 2 (double sided) x 0.152 Kg (1/2 oz/17)
   0.1 (10%) x 50,000 sq. m x 2 (double sided) x 0.610 Kg (2 oz/35)

   Total Weight - 28,960 Kg

3. How much copper is etched off the surface area of the panel as an average percentage.
   Let's say 70%.

   Therefore, total copper actually etched per year =
   28,960 x 0.7 - 20,272 Kg

4. Production time.
   i.e. 8 hours per day, 5 days per week, 40 weeks per year =
       1,920 hours per year.

5. Therefore, average hourly etch rate = 20,272 / 1,920 = 10.55 Kg.

6. We would therefore recommend 2 x 6 Kg/Hr cells giving 12 Kg/Hr Regen Capacity.
   This gives an over capacity of about 15%, which is acceptable.
Cost Justification.

These are the costs you have to consider in determining the payback period.


2. Cost of electricity to drive the system : Z

Calculate as follows :-

Every Kg of Copper recovered requires 7 x Y $ to recover

where 7 = 7 volts
and Y = Electrical cost per unit in customer's factory.

Therefore, having calculated total copper etched per year i.e. 20,272

Electrical cost : Z = 7 x Y x 20,272

So negative costs are X and Z

Savings are as follows:-

1. Chemical costs for Hydrochloric Acid per year
   Hydrogen Peroxide per year

   We will call this Cost : A

2. Disposal cost for old spent solution, Cost : B

3. Handling Cost i.e. Man hours in factory, if any, Cost : C

Additional Savings.

1. This comes from the resale value of the reclaimed copper - weight of copper
   etched per year i.e. 20,272 = 20.3 metric tonnes of copper

   Resale value of reclaimed copper = Cost : D

Summary

Cost of Cells : X
Cost of Electricity : Z
Cost of Chemicals : A
Cost of Disposal : B
Cost of Handling : C
Resale of Copper : D

Cost to install and operate F.S.L. System in first year :

X + Z

Savings made during first year:

A + B + C + D
From this you can work out how long it will take before

\[ A + B + C + D = X + Z \]  i.e. payback time

after which Annual Savings to you the customer will be

\[ A + B + C + D \]