TOXICS USE REDUCTION INSTITUTE

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TRI-STAR TECHNOLOGIES COMPANY INC.
METHUEN, MASSACHUSETTS

CUPRIC CHLORIDE ETCH REGENERATION

TOXICS USE REDUCTION INSTITUTE
CLEANER TECHNOLOGY
DEMONSTRATION SITES & MATCHING GRANTS
PROGRAM

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University of Massachusetts Lowell

Tri-Star Technologies Co., Inc.
Methuen, Massachusetts

Cupric Chloride Etch Regeneration

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The Toxics Use Reduction Institute
Cleaner Technology Demonstration Sites
and Matching Grants Program

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

Preface

In its 1997 fiscal year, the Massachusetts Toxics Use Reduction Institute combined the Cleaner Technology Demonstration Sites and Industry Matching Grants programs. The goal of the combined program is to provide companies with the opportunity to test and demonstrate new cleaner technologies as well as to promote the adoption of cleaner technologies by Massachusetts industry. Five companies were selected as demonstration sites to showcase the implementation of technologies that embrace the concepts and principles of toxics use reduction. The program, which included a series of visits to the facilities and related presentations and publications, allowed individuals and firms to observe and assess their value first-hand. Site visits were open to industry, environmental groups, community groups, the media and others.

Associate sponsors of the program included the Massachusetts Office of Technical Assistance for Toxics Use Reduction, the Executive Office of Environmental Affairs, the Department of Environmental Protection, the Environmental Protection Agency of New England, and the Associated Industries of Massachusetts.

This program will continue to provide grants to recognize the many companies across the Commonwealth that have used toxics use reduction and cleaner technologies while enhancing their firm's competitiveness.

The following report is an in-depth analysis of the cleaner technology demonstrated at Tri-Star Technologies Co., Inc., Methuen, Massachusetts.

We would like to express sincere thanks to John Raschko, Office of Technical Assistance, for his helpful comments and insights in the development of this report.

Notice

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1.0 INTRODUCTION

Tri-Star Technologies, located in Methuen, Massachusetts, has one of the world's largest facilities offering in-house printed circuit board design, fabrication and assembly, from prototype through production volumes. Their state-of-the-art, 120,000 square foot facility provides a "one-stop shop" for a full range of on-site services and expertise, providing the customer with the advantage needed in today's competitive marketplace.

In its continuous efforts to implement toxics use reduction (TUR) and pollution prevention, Tri-Star Technologies evaluated, adopted and installed an electrolytic regeneration technology to reduce the amount of spent cupric chloride etchant generated. By making electrolytic regeneration an integral part of the process, Tri-Star is able to reuse the etchant and sell the recovered copper. This technology replaces the chemical regeneration system previously used, while reducing costs, worker exposure to hazardous materials, and environmental impact. Tri-Star has achieved many prior successes with TUR, including an 86% reduction in volatile organic compounds through the addition of a double-sided solder mask screening unit, a reduction in sulfuric acid use on the auto pattern plate line, and the elimination of bath contamination on the copper deposition line.

2.0 DESCRIPTION OF TECHNOLOGIES

2.1 ETCHING AND ETCHANTS

In order to remove unwanted copper (Cu) from printed wiring boards (PWB's), discrete areas are etched away (areas of copper that are to remain are coated with photographic resist or tin plating to protect the copper from etching). Typical PWB's require the removal of 60 - 70% of the total copper surface area, although up to 90% of the copper may be removed from some panels.

A variety of chemicals are used to remove the copper from the PWB, three of which are commonly used. Ammonium hydroxide and ammonium sulfate are versatile, easy to use, and have relatively high etch rates. Cupric chloride etchants produce finer details than ammoniacal etchants, and can be regenerated using an electrolytic process. Cupric chloride etchants also have a "holding" capacity of 1.5 pounds of copper per gallon. Tri-Star made the decision to use two etchants: ammonium hydroxide for outer layer processes and cupric chloride etch to achieve the finer detail required for inner layer processes. Though the use of cupric chloride etchants required the installation of a bulk storage system and an increase in hydrogen peroxide and hydrochloric acid use, the benefits expected led the company to move in this direction.

The rate and quality of etching is dependent upon the specific gravity and normality of the etchant. The ideal range of specific gravity and normality ensures the optimum degree of etching and maintains the bath in proper balance. The cupric chloride solution should have a specific gravity of 1.28 or 32 degrees baume. If the specific gravity is too low, the resolution of the etching process is reduced, while a higher than optimum specific gravity tends to slow the etching rate below specified levels. The optimum normality of the etching bath is 2.75, and a higher than ideal normality has a tendency to increase the degree of etching beneath the protective layers.

The cupric chloride etching rate is indirectly proportional to the amount of cuprous salt dissolved in the etching solution. Etching proceeds rapidly with a clean solution and is reduced with an increase in dissolved cuprous salt. As seen in equation [1], the copper etching process converts the cupric ion (Cu^{++}) and metallic copper (Cu^0) to cuprous ion (Cu^+), changing the color of the cupric chloride solution from a bright green to a dark green or brown.

$$Cu^{++} + Cu^0 \rightarrow 2Cu^+ \qquad [1]$$

2.2 Etchant Regeneration

Spent cupric chloride etchant can be regenerated by chemical and electrolytic methods. By regenerating rather than disposing of the spent etchant, significant reductions in chemical purchases are realized. While chemical regeneration has been used for nearly 20 years, the first electrolytic regeneration unit became available in 1984. As seen in equation [2], the spent etchant is transformed from a solution containing cuprous ions (Cu^+), produced during normal etching, to one containing cupric ions (Cu^{++}), which are then available to etch the copper.

$$2Cu^+ \rightarrow 2Cu^{++} + 2e^- \qquad [2]$$

The oxidation/reduction potential of the etchant is used to quantify its optimum cuprous to cupric ratio. The ratio is measured in millivolts (mV) with a redox probe in the anolyte cooling box. The optimum reading ranges from 525 to 575 mV. A low mV reading implies a high cuprous ion concentration, and the regeneration rate of the etching solution must be increased. A high mV reading signifies a high cupric ion concentration, and the regeneration rate should be reduced. If the redox potential reaches 1000 - 1100 mV, chlorine gas may form, causing potentially lethal exposures.

Hydrogen peroxide and hydrochloric acid are used in the regeneration process to effect the transformation of the cuprous chloride (CuCl) back to cupric chloride ($CuCl_2$). The fully balanced equations relating to equations [1] and [2] are:

$$Cu + CuCl_2 \rightarrow 2CuCl \qquad [1a]$$

$$2CuCl + H_2O_2 + 2HCl \rightarrow 2CuCl_2 + 2H_2O \qquad [2a]$$

Hydrochloric acid is also used in electrolytic regeneration to maintain the conductivity and the etch activity of the solution, and to prevent the buildup of oxides in the system.

2.2.1 Electrolytic Regeneration

Electrolytic regeneration uses a cell, divided into two chambers (anode and cathode) by a permeable membrane. Cuprous ions are regenerated in the anode compartment, while cupric ions move into the cathode compartment. The permeable membrane is composed of a PVC-based ion exchange material and the anode and cathode are graphite. Tri-Star has purchased a Finishing Services Limited (FSL) electrolytic regeneration unit to replace the chemical regeneration unit used until now. The chemical regeneration unit is still being used as a backup when the new unit is off-line due to operational problems or maintenance (See Section 5.1). The unit consists of eight separate membranes and anodes working in tandem to regenerate the spent etching solution, while copper is plated on four cathodes. Metallic copper is removed at a maximum rate of 8 kg/hr at the cathodes of the system and sold as scrap. The power requirements of this system are 8,000 amps at 6-10 V DC. Figure 1 shows a schematic of the FSL system.

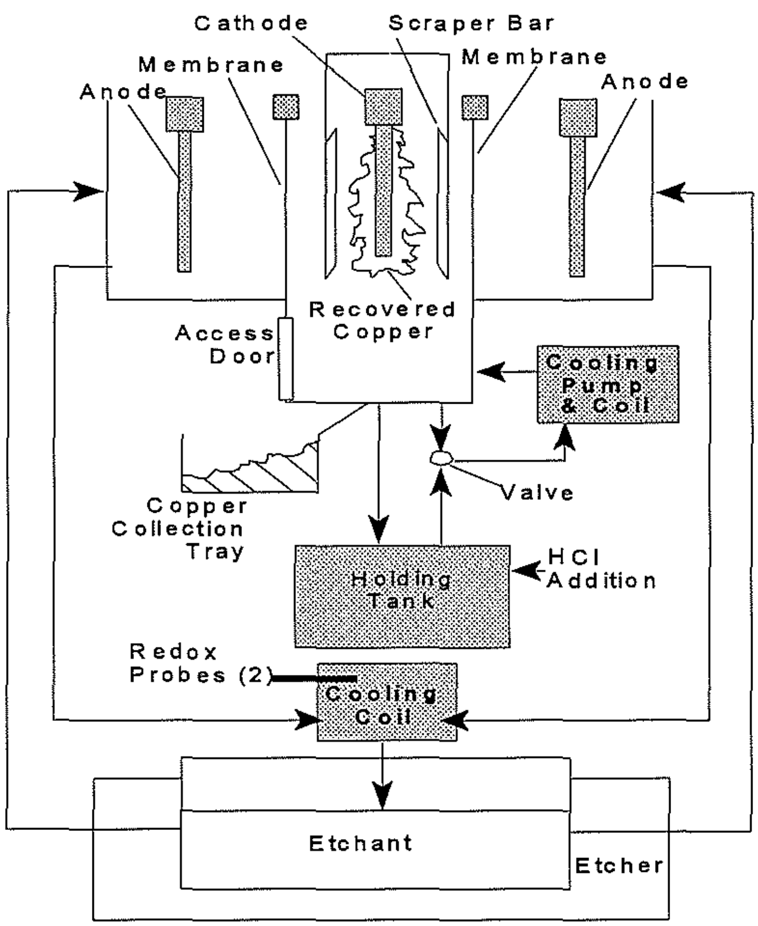

Figure 1: Cupric Chloride Electrolytic Regeneration Cell

The redox probe is connected to the unit's power source and registers the oxidation/reduction potential in the anolyte return loop. If the redox potential exceeds 560 mV, the power is shut off, allowing the increase of cuprous ions within the regeneration cell, and avoiding the formation of chlorine gas.

The spent etch undergoes a continuous, high cyclic flow rate of 350 - 400 L/min between the etching machine and the anode compartment. This high mixing rate, effected by the action of the cooling pumps, avoids large concentration gradients within the anode compartment and creates conditions for efficient regeneration of cuprous ions. Mixing within the cathode compartment helps to maintain a high copper plating efficiency.

The two compartments of the electrolytic regeneration unit need to be cooled due to the heat generated by the electrolytic reaction and the high volume pumping of solution. The temperature of the system should be maintained between 120°F and 132°F. Above 132°F, the PVC membrane will become unstable, and below 120°F, the etching process is slow. In order to keep the etchant within this temperature range, over 70 L/min of chilled water is pumped through the system. Despite this, the etchant temperature still rises too high on jobs in which greater than 75% of the copper is removed. This is less of a problem if the copper in the etch solution is held as low as possible, at around 15-17 ounces per gallon.

The overall copper concentration is maintained by a dual head metering pump which transfers etchant from the etch sump to the catholyte loop and returns an equal amount of catholyte to the etcher. The variable displacement pump is adjusted to maintain the optimum copper concentration in the anolyte and catholyte solutions. The excess cupric ions that are pumped into the catholyte solution are then electrolytically removed from the etchant and pure dendritic copper is collected in the copper collection chamber.

Anode Compartment
The reoxidation of cuprous ions (Cu^{+}) formed during the etching process, occurs in the anode compartment. See equations [2] &[2a]. Initial electrolytic regeneration can proceed when the anode compartment copper concentration is between 130 - 140 g/L (17.3 - 18.7 oz/gal) and the free hydrochloric acid concentration ranges from 70 - 125 g/L (2 - 3.5 N). (The regeneration process will operate at almost any concentration - these are the recommended ranges.) Hydrochloric acid is added to maintain the chloride ions within the etching solution, allowing the reformation of the cupric chloride molecules (see equation 2a).

Cathode Compartment
The reduction of cupric ions (Cu^{++}) to copper metal (Cu^{0}) occurs within the cathode compartment, by the following reaction:

$$\mathbf{Cu^{++} \rightarrow Cu^{0} - 2e^{-}} \qquad [4]$$

Pure copper plates onto the cathode in dendritic form at approximately 1 gram/amp/hour. In order to ensure that re-etching of the copper metal doesn't occur at the cathode, a low copper concentration, approximately 20 g/L, is kept in the cathode solution, using the metering pump. Typically, the maximum efficiency of the copper plating operation is determined by the amount of cupric ions present in the cathode compartment. Control of this process maximizes the quantity and quality of copper which plates on the cathode.

The copper is continuously removed from the cathode with a scraper bar. Up to 130 kg of copper can collect at the bottom of the cathode compartment. To remove the copper through the access door, the solution in the cathode compartment is drained to a holding tank. The copper then is washed with water to remove the acid and improve its overall resale value, which can be up to 75% of the price of grade A copper.

2.2.2 Chemical Regeneration

Chemical regeneration of etchants uses an oxidizer, such as hydrogen peroxide, chlorine, or sodium chlorate, to increase the available positive charges in the spent etch, allowing the transformation of the cuprous (Cu^{+}) ion to the cupric (Cu^{++}) ion. During chemical regeneration, the oxidation/reduction potential is used to determine the addition rate of the oxidizer. Chlorine regeneration is notably less costly per pound of copper etched than the hydrogen peroxide/hydrochloric acid or sodium chlorate methods. When using a hydrogen peroxide (H_2O_2) regeneration system, hydrochloric acid (HCl) reacts with the H_2O_2 to manufacture chlorine ions. As etched copper is added to the system, more chlorine is required to form the cupric chloride molecules. HCl is also used to maintain the normality and etch rate of the chemical regeneration process and to prevent a buildup of oxides in the system.

Water is used to control the specific gravity of the etching solution. The sodium chlorate regeneration method requires the least amount of water per pound of copper etched, while the chlorine method requires much more water for adequate performance. A limitation of the hydrogen peroxide regeneration method is the relative lack of specific gravity control. The addition of peroxide and hydrochloric acid to regenerate the spent etching solution creates large amounts of water in the system. This leads to a relatively high volume of waste generated, approximately equal to the amount of regeneration chemicals added to the system.

3.0 ENVIRONMENTAL AND OCCUPATIONAL HEALTH ASSESSMENT

The use of electrolytic regeneration instead of chemical regeneration to recover cupric chloride at Tri-Star has eliminated the use of 50% hydrogen peroxide (except during electrolytic downtime) and reduced hydrochloric acid use by 90% while eliminating bulk hazardous waste shipped off site for recycling.

Hydrogen peroxide is a powerful oxidizing agent, causing severe burns on contact. If not properly ventilated, an explosion could result, potentially endangering workers. Hydrochloric acid is toxic by inhalation, and is a corrosive irritant to the skin, eyes, and mucous membranes. When heated, hydrochloric acid emits very toxic fumes of hydrochloric acid and chlorine. Accidental release of either of these chemicals would pose serious threats to the environment. The successful implementation of technologies which lead to the reduction or elimination of these chemicals has significantly reduced the risks they present.

Chemical regeneration produces large volumes of waste due to the addition of oxidizing and acidic chemicals. The implementation of the electrolytic regeneration process eliminates the 50% hydrogen peroxide (H_2O_2) used in chemical regeneration of cupric chloride etchants. The hydrochloric acid (HCl) used in the electrolytic regeneration process is used only to replace drag out and evaporation losses, compared to the large amount used in the chemical regeneration method. The generation of excess regenerant and on-site accumulation of spent etch is eliminated. SARA and TURA reporting for HCl will be eliminated because Tri-Star will drop below the reporting threshold.

At Tri-Star, approximately 40,280 pounds of copper per year is etched. In chemical regeneration, the copper is disposed of with the excess regenerant, whereas in the electrolytic regeneration process the etched copper is recovered in metallic form. The FSL system should recover 100% of the copper.

The elimination of hydrogen peroxide and the significant reduction in hydrochloric acid use results in decreased potential for worker exposure. Not only is worker handing reduced, but the elimination of spent etch shipments has reduced potential liabilities associated with surface transportation and off-site treatment/recycling.

4.0 ECONOMIC ASSESSMENT

The TUR and pollution prevention projects undertaken by Tri-Star have had a positive economic impact. The capital expense of $110,000 for the electrolytic regeneration system was justified through reduced operating costs. The capital expenditure includes the cost of the regeneration unit, power supply, bus bar, support structure, plumbing materials, and installation. The payback period is estimated to be less than two years. The operating costs used to determine the payback period incorporated electricity costs, annual rebuilding of the anodes, the resale price of copper, chemical purchases, waste disposal, and regulatory reporting fees, although minimal savings was realized from decreased regulatory fees.

The net savings between the electrolytic and chemical regeneration methods are directly related to the production levels and the percent of copper removed during the manufacturing process. Tables 2 & 3 show projected expense profiles at 800 versus 1,000 layers to illustrate this point.

TABLE 2
CHEMICAL VS. ELECTROLYTIC REGENERATION
COMPARISON OF YEARLY COSTS (IN $)

800 inner layers per day (3.30 oz. copper removed per layer*)		
Cost Factor	Chemical Regeneration	Electrolytic Regeneration
50% H_2O_2	$21,168	$0
32% HCl	$47,987	$2,392
Spent Etch Disposal	$12,830	$0
Copper Reclaim	$0	($30,075)
Maintenance**	$0	$5,000
Electrical (rectifier)***	$0	$22,948
Total	**$81,985**	**$265**

TABLE 3
CHEMICAL VS. ELECTROLYTIC REGENERATION
COMPARISON OF YEARLY COSTS

1,000 inner layers per day (3.30 oz. copper removed per layer*)		
Cost Factor	Chemical Regeneration	Electrolytic Regeneration
50% H_2O_2	$26,460	$0
32% HCl	$59,983	$3,588
Spent Etch Disposal	$16,037	$0
Copper Reclaim	$0	($37,594)
Maintenance**	$0	$5,000
Electrical (rectifier)***	$0	$28,685
Total	**$102,480**	**($321)**

* This is an average removal rate at Tri-Star

** Maintenance costs are expected to be $5,000 per year to cover the manufacturer's recommended maintenance schedule regardless of production.

*** Electrical costs are based on $0.08 per kilowatt hour

5.0 RESOURCES AND BARRIERS TO TUR IMPLEMENTATION

5.1 Installation and Start-Up Issues

Membrane Fouling
In the now closed-loop etchant system, the expectation is that organics leaching into the system may accumulate in the system and cause some fouling of the membranes. This would eventually cause inferior plating of copper onto the cathode. Based on the experience of other users of FSL regeneration units, carbon filters will be required to avoid membrane fouling.

Membrane Puncture
Malfunction of the scrapers could potentially allow the copper to plate onto the cathode thick enough to contact and thus puncture the membrane. Regular inspection of the scraper mechanism is indicated to avoid this problem.

Membrane Replacement
With the exception of the aforementioned issues, there is no vendor-recommended schedule for membrane replacement. One company replaces membranes annually to avoid any down-time, while others are still using the original membranes after 18-24 months.

Chilled Water
The FSL literature states that "...for an 8 kg/hr unit...20 L/min [water] at ambient temperature..." are required. This is actually enough volume for the catholyte cooling chamber only - an additional 25-30 L/min are required for the anolyte cooling chamber and 20 L/min for the rectifier. Furthermore, the water must be approximately 50°F, not at ambient temperature.

Other Observations
The process used to replenish the catholyte loop with the small amount of HCl lost from dragout and evaporation is neither convenient nor efficient. Currently, the add is made to the holding tank by draining one or all of the cells, mixing the solution with the transfer pump and then refilling the cells. Direct injection of acid into the catholyte loop should be established either by modifying the anolyte/catholyte metering pump or by introducing the HCl at a different injection point.

The establishment and maintenance of the proper etch sump level has been difficult and needs to be monitored.

5.2 Management Support

Tri-Star Technologies Co., Inc. believes that sound environmental, safety and health practices are essential to an efficient operation. The corporate policy is to be sensitive to the legitimate concerns of employees, customers, and the community which hosts the Methuen facility. To achieve these goals, Tri-Star has implemented a company-wide program which accepts full compliance with environmental health and safety laws and regulations as minimum acceptable standards. The company is committed to systematically reducing toxic chemical use and the generation of wastes, thereby minimizing environmental impact and enhancing workplace safety. Management has encouraged and provided financial support for efforts made to minimize environmental impact and occupational exposures.

5.3 INVOLVEMENT OF PLANT PERSONNEL

In order to gain maximum involvement of employees, Tri-Star implemented a multi-faceted program which addresses chemical, material and energy use throughout the facility. Participation is encouraged through project teams, organizational interaction, and individual contributors. All implemented projects result in a pollution prevention profile which is posted in a prominent location within the facility.

5.4 PREVIOUS SUCCESSES WITH TOXICS USE REDUCTION

Tri-Star's broad-based Pollution Prevention Program has generated significant dollar savings through the implementation of several TUR projects. The success of these low cost/low tech solutions built the confidence to invest in more capital intensive projects like the cupric chloride etch regeneration system. Four examples of these projects are presented here:

The height of the rinse tanks on the Copper Deposition line was raised to just below the overflow point to insure that they would always be higher than the chemical tanks. This modification eliminated the major source of copper contamination of the Predip and Activator baths resulting in an annual savings of $20,669.

Evaluation of sulfuric acid baths throughout the PCB manufacturing process has resulted in the reduction of acid concentration of selected baths. The surface square feet processed per gallon (ssf/gal) in several baths has also been extended. For example, on the Pattern Plate Line, the sulfuric dip bath concentration was reduced from 10% by volume to 5% by weight, as well as an increase from 250 to 675 ssf/gal, yielding an annual savings of $2,500.

In May of 1996, a Circuit Automation DP1500 2X double-sided coater eliminated the existing curtain coat process for solder mask. While the curtain coat process satisfied production needs, it was apparent that future production would be limited by the existing VOC permit. By switching to the double-sided coater, VOC emissions were reduced by 86%. Several additional benefits were realized with the installation of this coater. The amount of solder mask used was reduced by 66% due to reduced mask thickness, and the new unit also significantly reduced scrap. This project resulted in savings of over $100,000 per year.

The implementation of closed loop cleaning, smart rinsing and water reuse have reduced water use by 28.8% and in some cases, have reduced the amount of chemistry required for chemical additions by 25%. Annual savings amount to $21,445 in water and waste water costs.

6.0 TRANSFERABILITY

Traditionally, vendors of this type of cupric chloride regeneration system have focused their marketing on the unit's process control capability. By recognizing electrolytic regeneration as a technology that lowers operational costs while reducing the use of toxic chemicals, many companies should be able to justify the purchase of an electrolytic regeneration unit. The units are available in multiples of 2 kg modules, making the technology flexible to meet the needs of different size companies.