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RECLAMATION OF NITRIC ACID FROM SOLDER STRIP

PRINTED CIRCUIT CORPORATION

Technical Report No. 26 **1995**

University of Massachusetts Lowell

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The Toxics Use Reduction Institute FY 95 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.

Toxics Use Reduction Institute
Matching Grants Program

The Institute annually provides direct funding to Massachusetts industries on a matching basis for toxics use reduction (TUR) feasibility and technology studies. The Matching Grants Program was initiated in FY 93 to facilitate the development and use of innovative techniques that reduce the use of toxic chemicals or the generation of toxic by-products in Massachusetts businesses. Grants are awarded on a competitive basis for companies to conduct TUR studies at their facilities. Recipients prepare project reports which assist in transferring toxics use reduction technologies and methods to other companies.

Notice

Executive Summary

Printed Circuit Corporation (PCC), founded in 1961, is a contract printed circuit board manufacturer located in Woburn, Massachusetts (SIC Code 3672). PCC provides its products, primarily multilayer boards, to companies in the electronics, instrumentation, medical, telecommunications, and automotive industries.

The manufacture of printed circuit boards is a complex, multi-step process. As part of the process, a tin/lead solder coating is applied to copper circuitry in order to protect the pattern from the subsequent ammoniacal etching process. After the unwanted copper is etched from the surface of the printed circuit board, the solder coating is stripped from the remaining circuitry with a proprietary aqueous solution of nitric acid, iron salts, and various inhibitors and adjuncts. When the speed at which stripping occurs drops below the PCC specified limit, the solder strip solution is considered "spent" and the entire solution is replaced. However, if the metals can be separated from the stripping solution, it is possible that the solution could be reused continuously, with adds made only to replace dragout.

In order to reduce the nitric acid by-product generation PCC has implemented a diffusion dialysis acid recycling process developed by Pure Cycle Environmental Technologies, Inc. This proprietary design features an extended membrane area configuration that efficiently promotes the removal and concentration of the acid up to 95% of its original strength with very little power consumption. The purified acid is directed back to the process tank, while the contaminant-laden spent acid stream goes to metal recovery or waste treatment for further processing.

Unfortunately, diffusion dialysis will remove the necessary iron component and inhibitor and/or anti-tarnish components from the solder strip as well. Technical feasibility was evaluated by an off-line recycling of the solder strip solution. Based on the results from the sampling events, Alpha Metals (supplier of the original formula for the solder strip solution) should be able to determine the additive package which would replace the components lost from the diffusion dialysis process.

As of the date of this report, PCC has been able to reach the desired goal of being able to effectively process 1:1 (virgin:spent) solder strip. In-house testing results indicated nitric acid reclaim efficiencies of ≈ (87-89%), and metal rejection rates for Cu, Pb, and Sn of ≈ (75-90%). Samples were sent to the independent lab (Contest Laboratories) on March 9, 1995, and through the use of a dynamic recovery efficiency formula, rejection rates of 57% and 53% were determined for TOC and ammonia, respectively.

In September of 1995 PCC approved a design for an in-line recycling system which will incorporate a 50 gallon/day unit. At this point recovery rates of the organic and inorganic additives to the solder strip solution have not been determined. Alpha Metals is

working on an additive package that will guarantee high stripping rates, low copper etch rates, and non-sludging properties. A design of experiments has been developed to test potential packages and fresh acid make-up rates. When all parameters have been optimized, and the bath has been shown to perform successfully, the recycle unit will be installed in-line.

The use of nitric acid recycling produces several potential benefits. An analysis of total costs before and after nitric acid recycling indicate a first year saving of ≈$47,000, and current estimates indicate a decrease in nitric acid usage on this line of ≈74%. This spent solder strip is currently sent off-site for disposal. If PCC treats this material in-house, the sludge that is created will be sent off-site for metals recycling, therefore, showing a decrease in hazardous waste generation and an increase in total metals recycled. Should an operator detect solder or intermetallics that are not removed, it is a simple process to change the solder strip and have the line up and running in short order, while investigating the cause of the problem.

Background

Printed Circuit Corporation (PCC), founded in 1961, is a contract printed circuit board manufacturer located in Woburn, Ma. (SIC Code 3672). PCC provides its products to companies in the electronics, instrumentation, medical, telecommunication, and automotive industries. The majority of the boards produced are multilayer (4 or 6). Continuous improvement in customer service through improved quality, reduced cycle times, and ISO 9002 certification give PCC its competitive edge in today's market. In addition, PCC completely eliminated the releases and transfers of all 33/50 Program chemicals (dichloromethane and 1,1,1-trichloroethane) by 1993, exceeding its program goals two years ahead of schedule.

The manufacture of printed circuit boards is a complex, multi-step process. As part of the process, a tin/lead solder coating is applied to copper circuitry in order to protect the pattern from the subsequent ammoniacal etching process. After the unwanted copper is etched from the surface of the printed circuit board, the solder coating is stripped from the remaining circuitry with a proprietary aqueous solution of nitric acid, iron salts, and various inhibitors and adjuncts. The stripping solution becomes spent as metals concentration increases in the solution. When the speed at which stripping occurs drops below the PCC specified limit, the entire solution is changed. However, if the metals can be separated from the stripping solution, then it is possible that the solution could be reused continuously, with adds made only to replace dragout.

Process Description

A multi-stage process is required in the manufacture of printed circuit boards. A schematic of this process is shown in figure 1. First, in order to apply the circuit board pattern onto the inner layers, the copper surface is coated with a photo-sensitive polymer. The circuit pattern is then transposed onto the polymer-coated board using high-intensity ultraviolet (UV) light, then developed, exposing only the intended circuit pattern for the subsequent electroplating chemical process. The polymer is then stripped away and the board is subjected to a chemical etching process to remove unwanted copper, leaving only the designed pattern. The film is then stripped from the circuit trace exposing the copper underneath, and an oxide coating is put on the panel to protect it during the multilayer process.

Next, holes are drilled to precise specifications in order to communicate from one side of the board to another. Burrs are also removed. The electroless copper process then deposits a thin layer of copper in holes in order to later deposit a full layer thickness on the hole. The outer layers are then negatively exposed (everything not wanted is coated) with film (photoresist). The remaining circuit pattern and holes are then plated with copper, followed by plating with Sn/Pb or Sn. The film is then stripped off and the underlying copper is removed with the outer layer etch leaving the circuit traces which are protected by the metallic etch resist (Pb/Sn or Sn).

The Pb/Sn or Sn is then removed with the proprietary stripping solution leaving the exposed copper circuit pattern. A solder mask (organic coating) is then placed over the pattern, but not the holes or any other connective area. A Pb/Sn solder is put on the exposed copper (holes and other connective areas) in order to facilitate the connection of diodes, transistors, etc.. The fingers are then plated with gold in the microplate or tab plating step. Lastly, the board is then cut to final dimensions.

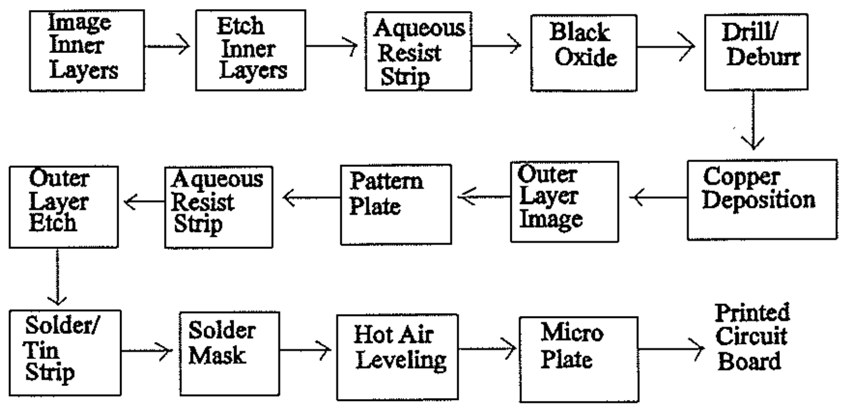

Fig.1. Printed Circuit Board Flow Diagram.

Solder Stripping

As part of the printed circuit board manufacturing process, tin/lead solder coatings are applied to copper circuitry to protect the circuits from the subsequent ammoniacal etching process. After the unwanted copper is etched from the surface of the printed circuit board, the solder coating is stripped from the remaining circuitry. A one-stage solder stripping chemistry is then used. One-stage chemistry integrates all the functions of the solder strip into a one step process. The functions are:

1. The nitric acid base strips the majority of the tin-lead solder from the printed circuit board.
2. The proprietary iron salt component (ferric nitrate and ferric chloride) adds additional oxidizing power to strip the intermetallic layer that forms the interface between the solder and the copper, and is composed of both copper and solder.
3. An inhibitor prevents significant attack on the copper traces.
4. Copper anti-tarnish prevents oxidation prior to subsequent processing.

When the solution is initially made up, it contains no metals other than iron. As work (solder coated boards) is passed through the solder strip machine, the metal concentration builds. As the metal concentration builds, the rate at which stripping occurs slows down, which results in a slowing of the line speed. When the line speed drops below the specified limit of 4.5-5.0 fpm, the solution is drummed for off-site disposal, and fresh solution is placed in the solder stripping unit.

Technology Background

In order to reduce the nitric acid by-product generation PCC has implemented a diffusion dialysis acid recycling process developed by Pure Cycle Environmental Technologies, Inc.. This proprietary design features an extended membrane area configuration that efficiently promotes the removal and concentration of the acid up to 95% of its original strength. The efficiency of a

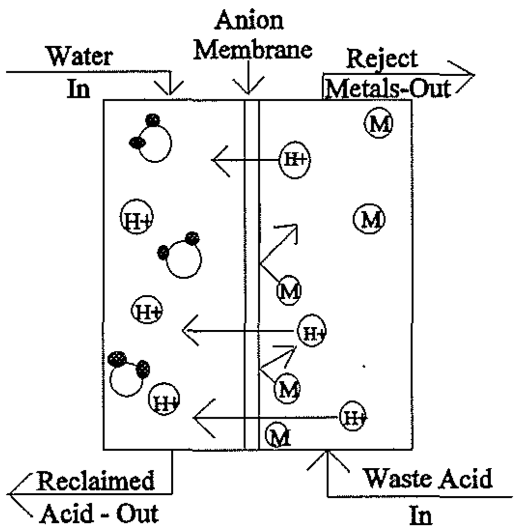

Fig. 2. Diffusion dialysis cell pair.

membrane to concentrate dilute acids in solution depends on the available surface area. Ion exchange membranes are sandwiched between spacers to form a series of cells (fig.2). The spacers, in addition to supporting the membranes, provide the flow path and the hydraulic interconnection between the cells. Each membrane may be arranged hydraulically in a series configuration providing for an extremely long flow path with enhanced membrane surface area. This extended membrane area combined with very low flow rates, results in a system that is capable of efficiently removing acids to extremely low concentrations with almost no power consumption.

In the Pure Cycle Acid recycling system, acid is metered through the system in contact with one side of an anion exchange membrane (fig.3). Water is metered in a counter-current fashion on the recovery side of the membrane. The majority of the acid migrates through the membrane into the water leaving contaminants, such as heavy metals, behind. The purified acid is directed back to the process tank, while the contaminant-laden spent acid stream goes to metal recovery or waste treatment for further processing. Fresh acid in proportion to the unrecovered amount is added to the bath to maintain the concentration within the correct operating window.

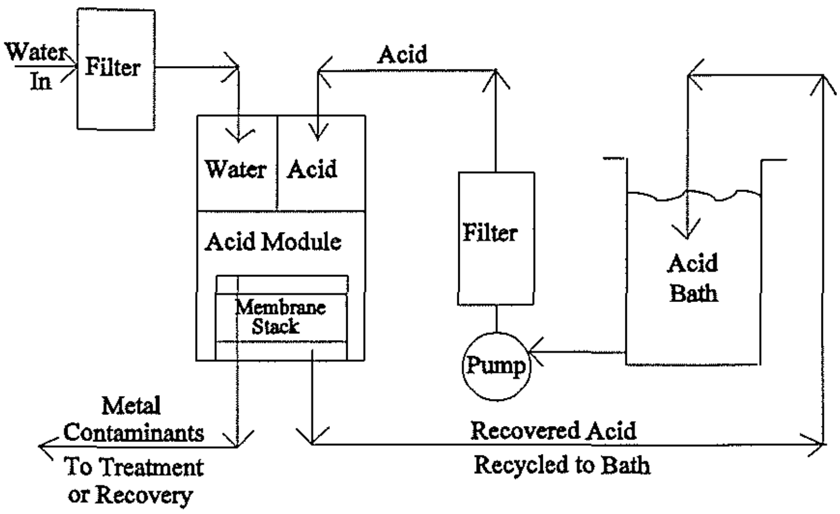

Fig. 3. Acid Recycling Flow Diagram

Solder Strip Recycling: Project Methodology

In this process metals are separated from the stripping solution and nitric acid is reclaimed and reused continuously. If the stripped, dissolved metal ions can be removed from the solution at a rate equal to or slightly faster than they are stripped from the work, then the only loss of nitric acid will be from dragout, rather than from wholesale solution changes. The diffusion dialysis unit will remove the metal ions while returning the nitric acid to the solder strip chamber. Unfortunately, it will also remove the necessary iron component from the solder strip as well. Another potential problem is the removal of the inhibitor and/or anti-tarnish components of the solder strip.

Technical feasibility is evaluated by an off-line recycling of the solder strip solution. Various mixtures of virgin:spent chemistry are recycled. Beginning with 100% virgin material, virgin:spent ratios of (5:1, 4:1, 3:1, 2:1, 1:1) are analyzed. At each ratio level, internal testing is performed to check acid recovery and metal rejection rates. When the final ratio of (1:1) is reached, outside testing is performed for the following parameters; Fe, Pb, Cu, Sn, ammonia, and TOC. The goal of 1:1 (50% spent) is chosen because it is felt that operation of the solder strip process unit is best optimized by running the chemistry at ~ 50% spent. The solder strip, when spent, is extremely high in metal concentration, ~18 oz./gal. at a specific gravity (s.g.) of 1.4. There is concern that if the acid reclaim is too efficient, there is not enough acid in the reject to keep the metals in solution. If the concentration of metals is too high, then the excess metals would precipitate on the surface of the membrane. This would have disastrous results. By coating the membrane surface, solution transfer would be effectively halted, and no recovery would occur.

In this preliminary evaluation, spent solder strip is recycled, and the chemical parameters are analyzed before and after recycling, as described below. These results are used to make three determinations:

1. The quantity of solder strip solution that is lost to process dragout, and therefore how much must be added to the system;
2. Any other individual components besides the metals that are being separated from the solder strip solution;
3. The quantity of iron salt that is removed by the recycling process, and therefore how much needs to be added back.

After the solder strip solution is recycled, analyzed, and adjusted to proper concentration, the solution is used to strip test panels to determine stripping rate and attack on base copper. If the initial evaluation is successful, then a full scale trial will be instituted and the recycle unit directly hard-piped to the solder strip unit to continuously receive solder strip solution. The recycled acid is piped back to the solder strip machine for continuous reuse. The reject is plumbed to waste treatment (W/T) to be treated. The chemical and physical parameters outlined below are evaluated, and a set schedule to ensure quality and optimum process efficiency is developed.

Chemical: The stripping solution is evaluated by standard wet analysis for acid components, and by atomic absorption spectrophotometry for metallic components.

Physical: The inhibitor component is tested for by thickness-testing of the copper plate prior and subsequent to the solder strip process. These values indicate if inordinate attack on the copper plate occurs.

Based on the results from the sampling events, Alpha Metals should be able to determine the additive package which would replace the components lost from the diffusion dialysis process. The project will proceed with PCC analyzing the solution and adding back the additive package prepared by Alpha Metals. Stripping rate and copper etch rate will be monitored along with nitric acid reclaim efficiency and metals rejection.

Results

As of the date of this report, PCC has been able to reach the desired goal of being able to effectively process 1:1 solder strip. In-house testing results indicate nitric acid reclaim efficiencies of ~(87-89%), and metal rejection rates for Cu, Pb, and Sn of ~(75-90%) at each level of solder strip ratio. Samples were sent to the independent lab (Contest Laboratories) on March 9, 1995 and through the use of a dynamic recovery efficiency formula, rejection rates of 57% and 53% were determined for TOC and ammonia respectively. The initial 5 gallons/day recycling unit that was used had a problem with the LMI pumps losing their prime during processing. They were concerned about metals precipitation on the membrane. After struggling with this unit for weeks, they noticed that the loss of prime was occurring only in the reclaim pump, which is inconsistent with precipitation on the membranes. Therefore, they replaced the unit with a 10 gallon/day unit, this gave them a greater static head pressure to force solution through the membrane stack. The new unit enabled them to proceed with the testing of each solder strip ratio.

In September of 1995 PCC approved a design for an in-line recycling system which will incorporate a 50 gallon/day unit. At this point the recovery rates of the organic and inorganic additives to the solder strip solution have not been determined. Alpha Metals is working on an additive package that will guarantee high stripping rates, low copper etch rates, and non-sludging properties. The additive package and acid make-up were determined as follows.

Recycling of 110 gallons of solder strip should yield an 80% recovery of nitric acid, and an 80% rejection of metals from the strip solution. In order to reconstitute the strip solution:

1. The nitric acid concentration of the solder strip is 30% by weight, so an 80% recovery should yield a 24% acid solution. Therefore, ~10 gallons of concentrated nitric acid needs to be added back.

2. The additive package (LT-5126A) is basically the original solder strip solution (PC 1115) minus the nitric acid. In order to reconstitute the total solution, 22 gallons of the package will need to be added (20% of total). The addition of 32 gallons of solution will increase the solution volume by ~29%. However, there is evaporation of water during the life of each solder strip bath due to heat (process temp. = 90°C) and ventilation, in addition to some solution loss due to dragout. Also, the diffusion dialysis unit can be set to recover a smaller volume than is rejected, however this may result in less efficiency. In order to test this package (and other potential packages at lower costs), the following design of experiments was suggested:

a. 110 gallons of solder strip that is 50% spent (s.g.~1.28) will be recycled off-line in the diffusion dialysis unit. Samples will be sent to Alpha Metals for analysis (including organics), and the additive package (LT-5126A), which is 20% of the volume of the original solution (PC 1115) (i.e., all chemical components except acid), and nitric acid to 30% by weight will be added back to the recycled material to make it reusable.

b. This will continue for several cycles, with strip rates, metal loadings, copper etch rates, etc. being tested continuously. If this is successful, after a re-evaluation of the project, then the recycle unit will go in-line.

c. The recycled material will be used only in the first chamber, and the second chamber will contain fresh material. This should insure that solder stripping will be complete.

Through the use of nitric acid recycling several potential benefits have developed.

1. Total Cost Assessment

Table 1 provides a comparison of current and projected costs on a monthly basis. An analysis of total costs before and after nitric acid recycling indicate a first year savings of ~\$.47,000. Neglecting the \$10,000 from the TURI Grant, the savings would be ~\$37,000. For additional information on some of the individual costs refer to the appendix.

2. Process Improvements

Due to the constant rejection of metal ions from the solution and the constant addition of nitric acid and the additive package, the specific gravity of the solution should vary within a fairly narrow range as compared to the current system. Currently, when the solution is fresh, the specific gravity is ~1.1. As metal content increases the line speed drops, and the solution is changed when the bath reaches a s.g. of 1.35 or the line speed drops below acceptable limits. When this change occurs, the s.g. starts all over again at 1.1. Through the use of in-line acid recycling, the specific gravity will vary from slightly above 1.1 to ~1.28.

3. Environmental Impacts

a. Nitric Acid Recycling

The impetus for this project is to recycle the nitric acid portion of the solder strip in such a way as to improve the environment and be economically beneficial to PCC. Current estimates indicate a decrease in nitric acid usage on this line of ~74% (~32,800 lbs or ~4,200 gallons/yr).

b. Metals Recycling

The spent solder strip is currently sent off-site for disposal. If they treat the material in-house, the sludge that is created will be sent off-site for metals recycling. Therefore, they will be able to show a decrease in hazardous waste generation and an increase in total metals recycled.

Table 1.

Category	**Current Costs**	**Projected Costs**	**Difference**
Chemical Costs			
PC 1115	1,250 gal. X $6.50/gal. = $8,125/mo.	N/A	
LT-5126A	N/A	250 gal. X $8.00/gal. = $2,000.00/mo.	
Nitric Acid	N/A	114 gal X $2.50/gal. = $284.09/mo.	
			$5,841.00/mo.
Waste Treatment Costs			
Off-Site Disposal	$1,980.00/mo.	N/A	
W/T Chemistry	N/A	$1,436.00/mo.	
			$545.00/mo.
Operating Costs			
Membrane Replacement	N/A	$292.00/mo.	($292.00/mo.)
Capital Costs			
50 GPD DD Unit	N/A	Down Payment: $12,000 Monthly Payment: $2,000/mo. for 1 year	

4. Potential Challenges

a. Quality Issues

If the operator should see solder or intermetallics that are not removed, it is a simple process to change the solder strip solution and have the line up and running in short order. Of course, for evaluation purposes they will try to find the cause for each problem and rectify it in-line, but if that can't be done, it will be necessary to change the solution.

b. Waste Treatment

Until they are 100% solder mask over bare copper (SMOBC), there will be an introduction of greater amounts of lead into the W/T system than usual. However, if the concentrated material from the dialysis unit can be batch treated, it should represent no threat to the compliance record of PCC, because they have complete control over the treatment levels of the solution (i.e., raise the pH or add dithiocarbamate to increase metal precipitation). Additional testing will be performed to see if the treated liquid has an adverse effect on the flow-through W/T system, but a review of the components of the solution suggests that this will not be the case.

APPENDIX

A. Waste Treatment Costs

For 1995, PCC will ship off-site (for disposal) 7,920 gallons of solder strip at a cost of $165.00/55 gallon drum (including taxes) resulting in a total cost of $23,760. At a concentration of 16 oz./gal. total metals, this equates to 7,920 lbs. of metals shipped off-site. Using a factor of 5 times the total metal weight as the weight of sludge produced by the metals, this will result in 17 tons of sludge. At $423.00/ton (including packaging), the cost is $7,191.00. The best W/T methodology for this process would be to batch treat this material. At an average process rate of 32 gallons/day, this would require the treatment of 176 gallons/5.5 day week. A conservative estimated cost for caustic soda is $10,000/yr.

B. Equipment and Operating Costs

In order to be prepared for future growth, a 50 gallon/day unit will be required, at a capital cost of $36,000. They have $10,000 on account with Pure Cycle Environmental as a result of the TURI Grant. One third down payment of $8,667 is required, and the $17,333 remaining can be paid over the course of a year. Neglecting the $10,000 on account, the down payment would be $12,000, and the balance would be paid over one year. Operating costs are based on the membrane life. In this case, they can conservatively estimate $3,600/yr average in membrane replacement costs.

C. Labor Costs

Complete changeouts of the solution will not be required with the diffusion dialysis system. This task currently takes 1.5 manhours/week. However, there will be an increase in analytical testing for nitric acid concentration and adds. How often this is required is unknown, but should be less than once a day. It is anticipated that the additive will be added on a square-footage basis, simplifying the add process. If required, analyses for iron can be performed to track the additive level. Based on these factors, weekly labor will remain the same or increase slightly.