# EVALUATION OF AN ELECTRODIALYTIC PROCESS FOR PURIFICATION OF HEXAVALENT CHROMIUM SOLUTIONS

by

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## FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, Superfund-related activities, and pollution prevention. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

Passage of the Pollution Prevention Act of 1990 marked a significant change in U.S. policies concerning the generation of hazardous and nonhazardous wastes. This bill implements the national objective of pollution prevention by establishing a source reduction program at the EPA and by assisting states in providing information about and technical assistance for regarding source reduction. In support of the emphasis on pollution prevention, the "Waste Reduction Innovative Technology Evaluation (WRITE) Program" has been designed to identify, evaluate, and/or demonstrate new techniques and technologies that lead to waste reduction. The WRITE Program emphasizes source reduction and on-site recycling. These methods reduce or eliminate transportation, handling, treatment, and disposal of hazardous materials in the environment. The technology evaluation project discussed in this report describes the use of an electrodialytic process to purify hexavalent chromium solutions. The electrodialytic process reduces wastes by prolonging the use of the concentrated hexavalent chromium solution. The prolonged use reduces the need for solution replacement, treatment, and disposal.

E. Timothy Oppelt, Director
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## ABSTRACT

This evaluation addresses the waste reduction and economics of an electrodialytic process that can be used to selectively remove impurities that build up in chromic acid solutions with use. The removal of impurities extends the useful life of the chromic acid solution and avoids periodic replacement of the solution. The electrodialytic units tested in this evaluation were manufactured by Ionsep™. The units were tested at SL Modern Hard Chrome in Camden, New Jersey, for a hard chromium plating solution and at Paramax in St. Paul, Minnesota, for a chromic acid solution etching copper from printed wire boards.

The electrodialytic process was found to effectively remove the impurities that build up in chromic acid solutions. The rate of return on investment varied from being not cost effective to a payback of less than 5 years. The payback is a function of the rate of contaminant buildup in the solution — the more frequently a solution must be replaced when contaminants are not removed, the shorter the payback after an electrolytic process is installed. There was a waste reduction of 68.4 kg (151 lb) annually in chromium reaching the environment from the chromium plating operation and a projected reduction of 4,410 kg (9,700 lb) in chromium reaching the environment from the copper etching operation.

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# SECTION 1

# INTRODUCTION

## GENERAL OVERVIEW

The objective of the U.S. Environmental Protection Agency's (U.S. EPA's) Waste Reduction Innovative Technology Evaluation (WRITE) Program is to evaluate, in a typical workplace environment, prototype or innovative commercial technologies that have potential for reducing wastes at the source or for preventing pollution. In general, each technology is evaluated on three issues.

First, the impact of the new technology on waste generation is measured. The new technology is compared to the existing technology (baseline) or the process that it replaces. The waste generated from each technology is determined, and the values are compared.

Second, the economics of the new technology is quantified and compared with the economics of the existing technology. It should be noted that improved economics is not the only criterion for using a new technology. Justifications other than reduced costs would encourage implementing new approaches or technologies. Nevertheless, a measure of the economic impact of any potential change is useful.

Third, the effectiveness of the new technology is assessed. Waste reduction or pollution prevention technologies typically recycle or reuse materials or use alternative materials or techniques. Therefore, it is important to verify whether the quality of the feed materials and the quality of the product are acceptable for the intended purpose.

This study evaluated an electrodialytic process that selectively removes impurities from hexavalent chromium process solutions. The process uses a cation-selective membrane operated under an electrolytic potential. Removal of the impurities makes possible extended use of the chromium solution, thus reducing solution replacement and waste.

## DESCRIPTION OF THE TEST SITES AND PROCESS

Metal finishing industries and printed wire board manufacturers use chromium process solutions to plate chromium and to etch copper. The solutions contain hexavalent chromium, which is

in an anionic form in solution. During plating or etching, cations build up in the solution, making it less effective. The chromium solution must be replaced when product quality drops or the etch rate falls below an acceptable rate. This project estimated the increase in bath life by use of the Ionsep™* electrodialytic process for removal of contamination from both a chromium plating and a chromium etching solution.

## Test Sites

SL Modern Hard Chrome, located in Camden, New Jersey, was the site for testing the electrodialytic process on a hard chromium plating solution. SL Modern Hard Chrome has specialized in industrial hard chrome plating for over 35 years and plates a full spectrum of materials, ranging from aluminum through the copper, ferrous, and nickel base alloys to zinc. The thickness varies from 0.0001 inch to 0.030 inch or more on parts ranging in size from a few ounces to several tons. The company, which has 40 employees, had sales of up to $5 million in 1991.

Paramax (a Unisys company), located in St. Paul, Minnesota, was the site for testing the electrodialytic process on a chromic acid etching solution. Paramax manufactures multilayer printed wire boards at this facility. The boards have more than 10 layers and must meet military specifications. Paramax Midwest Operations has 3,000 employees and had sales over $100 million in 1991.

## Ionsep™ Electrodialytic Process

The aim of the technology is to reduce wastes by removing metals other than chromium from the process solution. This improves plating and etching product quality and extends process solution life. The Ionsep™ electrodialytic process uses a voltage gradient to separate salt in a solution into cations and anions. It also converts the anions to acids and cations to hydroxides using electricity and water. Anions and cations react with water to form acids and bases, respectively. Chromium is present in the anionic chromate form in the plating and etching solutions.

Figure 1 shows a two-compartment cell used for the purification of a chromium plating solution. Metal contaminants (cations) migrate across a semipermeable membrane, under the influence of the electric field. Conversion of the electroplatable metal cations to insoluble hydroxides occurs when

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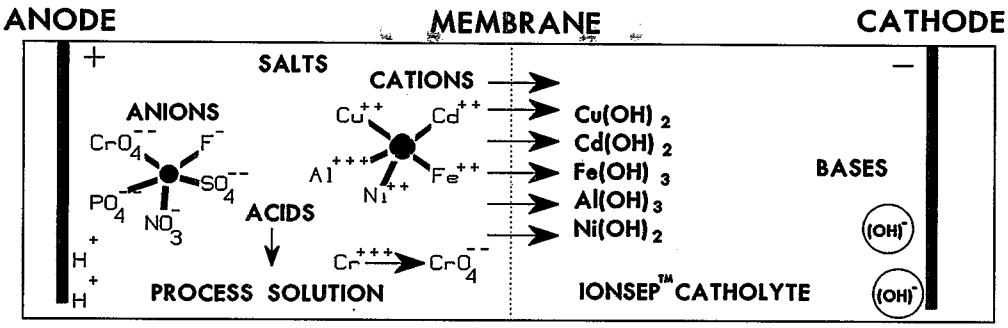
* Mention of trade names or products does not constitute endorsement for use.




Source: Ionsep Corporation, 1989

**Figure 1. Ionsep™ electrodialytic process.**

the cations migrate through the membrane, eliminating the buildup of metals on the cathode. Membranes in the electrodialytic cells serve to physically separate the acidic, basic, and other process solutions. Figure 2 shows the incorporation of the Ionsep™ unit in a chromium process bath. The chromium anions remain in the process solution and are returned to the process bath.

At SL Modern Hard Chrome, contamination builds up in the chromium plating solution. The contaminants typically are in the form of cations, including iron, trivalent chromium, and lead. As the contaminants build up, the plating solution fails to produce the required product quality and must be

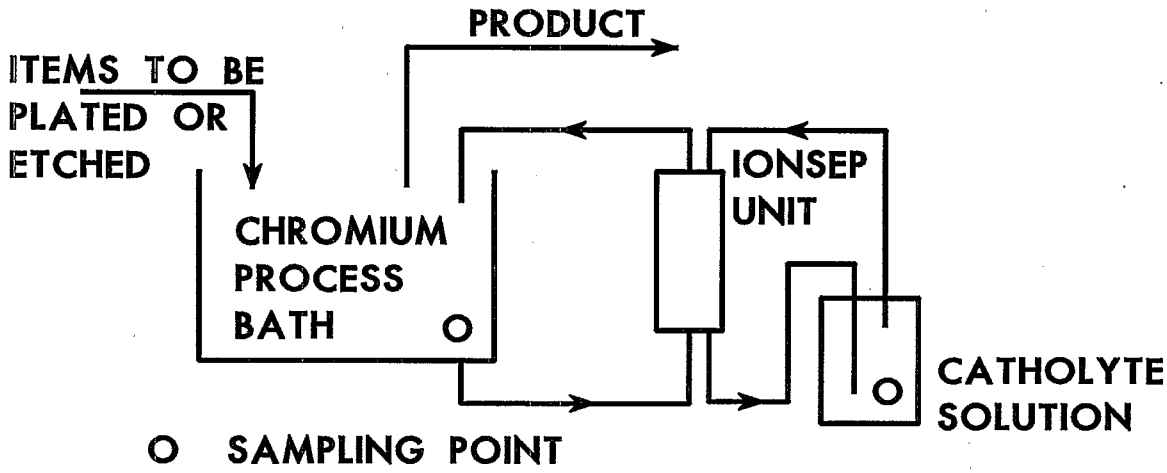



**Figure 2. Ionsep™ electrodialytic process system diagram.**

replaced. At SL Modern Hard Chrome, it has been more than 3 years since a chromium plating bath was replaced. The Ionsep™ electrodialytic process is used to remove the cations from the chromium plating solution, allowing it to be used longer. The electrodialytic process was installed in 1988.

At Paramax, a chromic acid solution is used to etch copper from printed wire boards (PWBs). As copper builds up in the etching solution, the etching rate becomes unacceptably slow. Before Ionsep™ was installed, the chromic acid solution was replaced with fresh solution from once a day to once a week, at the operator's discretion. The Ionsep™ electrodialytic process is used to remove copper from the etching solution and to convert some of the trivalent chromium back to hexavalent chromium electrolytically, extending the usefulness of the etching solution.

## LITERATURE REVIEW

A literature review found two general articles and two papers specific to the electrodialytic process. The two articles appeared in the July and August 1986 issues of *Plating and Surface Finishing*. In these articles, Knill and Chessin discuss the contamination and purification of hexavalent chromium plating baths. The first article, entitled "Contamination of Hexavalent Chromium Plating Baths," describes the sources of metal contaminants and their impact on the plating of chromium. It also describes anions and organic contaminants. According to the authors, cleanliness and good work habits, combined with standard filtration of the solution, can improve product quality more cost effectively than any other quality control investment. The second article, entitled "Purification of Hexavalent Chromium Plating Baths," details the methods that can be applied to remove contaminants from a hexavalent chromium plating bath. The article discusses filtration, oxidation of trivalent chromium to hexavalent by chemical and electrolytic means, ion exchange to remove contaminants, and electrolytic and electrodialytic processes to purify hexavalent chromium plating baths. The authors assert that the most valuable benefit from solution purification is the significant improvement in the quality of deposits and the attendant reduction in rejects.

In "Removal of Metal Cations from Chromium Plating Solution," a paper presented at the 10th AESF/EPA Conference on Environmental Control for the Metal Finishing Industry, January 23-25, 1989, Cushnie and Anderson presented the results of a study that identified and tested technologies for removing iron and copper from chromium plating solutions. The two technologies tested were an electrodialytic membrane unit and an electrolytic porous pot. The results showed that the membrane technology removed iron and copper better. In 16 days, the contaminant concentration dropped from

10.4 g/L to 4.0 g/L with a membrane, and from 10.4 g/L to only 9.0 g/L with a porous pot under test conditions.

Several papers and/or articles have been prepared by developers of the Ionsep™ electrodialytic process. One of these, "Closed-Loop Processing of Chromic Acid Solutions," also presented at the 10th AESF/EPA Conference, described how the electrodialytic process can be used to remove contaminants from a chromium plating solution. It also described the use of the electrodialytic process to recover regeneration solutions for ion exchange systems. The paper's authors found that the electrodialytic technology can maintain closed-loop processing for most chromic acid solutions. They also found that it was possible to maintain the rate of a metal-finishing operation and the quality of the product over a long period without discarding or decanting part or all of the chromic acid finishing solution.

## STATEMENT OF PROJECT OBJECTIVES

The purpose of this project was to evaluate the applicability of the Ionsep™ electrodialytic process as a means of removing cations from both a chromium plating solution and a chromic acid etching solution. This project had the following objectives:

- Evaluate the ability of the Ionsep™ electrodialytic process to remove cations from chromium solutions.
- Evaluate the waste reduction potential of the technology.
- Evaluate the cost effectiveness of this technology compared to that of current practice.
- Evaluate the effect of the Ionsep™ electrodialytic process on product quality.

The study compared the wastes generated and the life of the bath with and without use of the Ionsep™ electrodialytic process. The comparison was performed at a hard chrome plater and at a printed wire board manufacturer using a chromic acid etch bath, SL Modern Hard Chrome and Paramax, respectively.

## SECTION 2

## CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations from this study are presented in two subsections. The results of using the Ionsep™ electrodialytic process to treat hexavalent chromium plating solutions are discussed first, followed by the results of treating chromic acid etch solutions.

The tests conducted demonstrated that the Ionsep™ system removes impurities from the chromium plating and the chromic acid etch solutions. The rate of removal is 25 grams per day for a 250-amp unit, based on the buildup of metals in the catholyte solution.

### CHROMIUM PLATING SOLUTION

#### Waste Reduction Potential

This study evaluated the waste reduction potential of the Ionsep™ system used in a 1,400-gal hard chromium plating bath. SL Modern Hard Chrome purchased the Ionsep™ system as part of its plan to eliminate all industrial liquid waste discharges to the city. To achieve zero liquid discharge, SL Modern Hard Chrome initially rinses parts over the bath and performs a final rinse that is totally collected in a sump, filtered, and then returned to the bath to make up water lost to evaporation. Impurities build up in the plating bath because all rinse water is returned to it; the Ionsep™ system was purchased to reduce this buildup. The only resulting waste discharge is the sludge from the Ionsep™ catholyte solution. This catholyte sludge contains levels of chromium at 2,000 to 3,200 mg/L total chromium and 760 to 1,050 mg/L hexavalent chromium and therefore must be handled as a hazardous waste.

The rate at which impurities are removed from the chromium plating bath and collected in the catholyte solution leads to a projection that the plating bath would exceed permissible bath impurity levels in 40 years. Thus, every 40 years the bath would have to be replaced if the Ionsep™ unit were not used. Using the Ionsep™ system, SL Modern Hard Chrome generates one-third of a 55-gal drum of catholyte sludge every month, or 220 gal per year, from the 1,400-gal bath. In 6.4 years, a volume equal to that of the bath (1,400 gal) has been disposed of as sludge. Therefore, by volume alone, the Ionsep™

system generates more waste. Most of this sludge consists of metal hydroxides with a high concentration of water because it is only decanted. However, there is a net reduction of 12 kg (26.6 lb) annually in chromium reaching the environment. If the bath is replaced every 40 years, the total annual discharge is calculated at 18.5 kg (40.8 lb). With the catholyte solution replaced monthly (Ionsep™ is not used to reclaim catholyte solution), the annual discharge of chromium is 6.5 kg (14.2 lb).

## Economic Evaluation

The operating cost associated to the chromium plating bath without the Ionsep™ system is $3,684 annually. The operating cost with the Ionsep™ system is $3,578 annually. This is an annual savings of $106 in operating costs.

The cost savings from not having to strip and replate reject parts provides a major motivation for using the Ionsep™ system. This reduction in rejects resulted in annual cost savings of $3,218 because the company did not have to strip the defective chromium plating and replate. Economic data were not available for estimating cost savings resulting from not having to operate a wastewater treatment system. However, management of SL Modern Hard Chrome believes that the ability to avoid wastewater treatment plus the reduced reject rate more than offset the initial purchase cost. The savings for the 1,400-gal bath is $106 annually. This results in a long payback without allowing credit for wastewater treatment cost avoidance.

In general, the payback of an Ionsep™ unit is site specific and depends on how frequently the plating bath is replaced and the associated disposal costs. The use of the Ionsep™ system at other sites requires sizing the unit to the rate of contaminant buildup in the chromium plating solution.

## Product Quality Evaluation

SL Modern Hard Chrome measured product quality by visual inspection for pits, blisters, or any other plating deformity and thickness testing to ensure the desired chromium thickness and uniformity over the plated item. The company found that use of the Ionsep™ process resulted in a 5% decrease in rejected parts. Prior to introduction of the Ionsep™ process, SL Modern Hard Chrome employees waited for parts to be rejected before they performed a bath analysis to determine the reason for defective plating. The reduction in rejects corresponded with the implementation of frequent bath analysis and bath additions.

## CHROMIC ACID ETCHING SOLUTION

### Waste Reduction Potential

At a minimum, the etching solution at Paramax is replaced once a week, resulting in 200 gal of chromium and copper waste solution for disposal. In the past, Paramax blended the waste with other copper-containing wastestreams, and the copper was treated by electrowinning and sold for scrap. The solution then had to be treated for chromium and other metals before discharge. The Ionsep™ system at Paramax removes the copper and makes possible reuse of the etching solution, thus eliminating the discharge and replacement of the chromic acid etching solution. The sludge formed in the catholyte solution is collected in a filter press. The catholyte solution is reused, and the filter press is flushed with waste acid to remove the sludge by resolubilizing it. The flushed liquid is then treated by electrowinning to recover copper. The projected waste reduction of chromium is 9,700 lb per year.

### Economic Evaluation

The installed cost of the unit was $563,000 and the annual savings is approximately $126,000. The payback for the Ionsep™ system at Paramax is projected to be 5 years. The savings are the result of the reduced chromium disposal and chemical replacement costs provided by Paramax.

### Product Quality Evaluation

The copper concentration in the etching solution must not exceed 25 g/L. The testing during this evaluation reduced the copper concentration from 18.1 g/L to 10.8 g/L in the etching solution. The etchant can then be reused. At present, environmental personnel at Paramax are trying to convince production personnel that the Ionsep™ system can effectively regenerate the etching solution and not affect PWB quality. To do this, Paramax is collecting the etching solution when it is replaced and treating it with the Ionsep™ system. The regenerated/recovered etching solution then is used on test boards. The testing results were not available at the time of this report. However, the chemical analysis of the regenerated etching solution shows the solution to be within specifications.

## SECTION 3

## MATERIALS AND METHODS

### SITE 1 — CHROMIUM PLATING

#### Waste Reduction Potential

The catholyte solution was sampled over a 3-month period at SL Modern Hard Chrome, as shown in Table 1. The Ionsep™ system with sampling points at the first test site is shown in Figure 2. Any metals buildup in the catholyte solution represents what was removed from the plating bath by the Ionsep™ unit. Knowing the amount of metals in the catholyte solution and the duration of the solution use made it possible to calculate the metals removal rate, which was assumed to correlate to the rate at which metals would have built up in the plating bath had Ionsep™ not been installed. Grab samples from the catholyte tank were taken after the precipitated materials had been mixed well with the catholyte solution. The solution was sampled immediately before disposal so that the amount of contaminants removed from the chromium plating solution could be determined. The catholyte solutions usually were

**TABLE 1. SAMPLES COLLECTED FOR THE HARD CHROME LINE TESTING**

| Description | Sample I.D. No. | Type of Sample | Date | Time |
|---|---|---|---|---|
| Chromium Solution | CSL-1 | Grab | 4/6/92 | 12:35 |
| | CSL-4 | Grab | 4/7/92 | 9:15 |
| | CSL-6 | Grab | 4/7/92 | 13:45 |
| Catholyte Solution | CSL-2 | Grab | 4/6/92 | 12:45 |
| | CSL-8 | Grab | 3/6/92 | 9:15 |
| | CSL-9 | Grab | 2/6/92 | 10:30 |
| Catholyte Blank | CSL-3 | Grab | 4/6/92 | 13:15 |
| Water Blanks | CSL-5 | Grab | 4/7/92 | 10:00 |
| | CSL-7 | Grab | 4/7/92 | 14:15 |

disposed of monthly. At SL Modern Hard Chrome, the first sampling of catholyte was from a catholyte solution used for 2 months; the other two samples were both from catholyte solutions that were used 1 month. The samples were taken before disposal of the catholyte solution.

Metals analyses for chromium, iron, and lead were performed on the catholyte solution as described under the product quality evaluation section for the plating solution. The purpose of the analyses was to determine rate of metals buildup, which in turn was used to calculate the amount of use that could be obtained from the chromium bath before disposal without the Ionsep™ unit.

Blanks also were sampled and analyzed. One was taken of the fresh catholyte solution, and two were taken of the tap water on site. The tap water was run several seconds before sampling.

## Economic Evaluation

SL Modern Hard Chrome provided economic information on its operations. The information provided included utility rates, chemical costs, disposal costs, and labor rates. A recent cost analysis of the Ionsep™ system was used. The savings were calculated on the difference between the operating costs with and without the system. The payback period is then the cost of the system divided by the annual savings.

## Product Quality Evaluation

Chemical analyses of the chromium plating solution were used to verify that the solution met their operational specifications for hard chromium plating solutions. These specifications are:

- Chromium oxide: 270 g/L (minimum)
- Chromium: 140 g/L (minimum)
- Total metals (cations): 52 g/L (maximum).

Over a 2-day period, three grab samples were taken from the well-mixed chromium plating solution at SL Modern Hard Chrome. Total chromium, lead, and iron were analyzed by EPA Method 6010 (inductively coupled plasma spectrometry), and hexavalent chromium by EPA Method 7196 (colorimetric method) by an outside contractor. Iron and lead were the only contaminant metals analyzed because they are known to be the major contributors to contamination of the baths at the test site.

Table 1 identifies the samples. SL Modern Hard Chrome also provided bath analysis data for total chromium, hexavalent chromium, and sulfite from December 3, 1991, through April 2, 1992.

The manufacturer routinely performed quality checks to determine product quality. Visual inspections of the items for pitting, blisters, and any other coating deformities were performed. The thickness of the chromium coating was checked, as was the uniformity of the coating thickness on the plated item. The numbers of rejected parts both before and after installation of the Ionsep™ system were based on estimates of plating shop personnel because no records were available.

## SITE 2 — CHROMIUM ETCHING

### Waste Reduction Potential

The waste reduction potential was based on the difference between the amount of chromic acid etch solution disposed without Ionsep™ treatment and the amount of chromic acid etch that can be reused after treatment with the Ionsep™ unit. Samples of catholyte were collected as shown in Table 2.

**TABLE 2. SAMPLES COLLECTED FROM THE ETCHING LINE**

| Description | Sample I.D. No. Date | Time | Type of Sample |
|---|---|---|---|
| Etchant | 5/19/92 | 12:35 | Grab |
| | 5/19/92 | 15:30 | Grab |
| | 5/20/92 | 10:00 | Grab |
| | 5/21/92 | 10:45 | Grab |
| | 5/21/92 | 16:00 | Grab |
| Catholyte | 5/19/92 | 11:45 | Grab |
| | 5/19/92 | 13:18 | Grab |
| | 5/19/92 | 15:20 | Grab |
| | 5/20/92 | 10:45 | Grab |
| | 5/21/92 | 10:45 | Grab |
| | 5/21/92 | 16:00 | Grab |
| Catholyte Sludge | 5/20/92 | 13:00 | Grab |
| | 5/21/92 | 16:30 | Grab |
| Water Blank (hot water makeup) | 5/21/92 | 16:00 | Grab |

The Ionsep™ system schematic at Paramax is shown in Figure 3 with sampling points. Samples of the sludge filtered from the catholyte tank also were collected. The processing time of 3 days was used to calculate the treatment rate of the Ionsep™ unit. From the treatment rate, the amount of etchant for reuse (per unit time) can be calculated.

## Economic Evaluation

Paramax provided economic information for its etching operations. The economic data provided included utility rates, chemical costs, and installed equipment costs. The annual cost savings is the difference in annual operating costs with and without the use of the Ionsep™ system. The method used to calculate the payback period is to divide the annual savings into the system installed cost.

## Product Quality Evaluation

Chemical analyses of the spent chromic acid etching solution during treatment by the Ionsep™ unit at Paramax were used to verify that the solution met operational specifications for PWB etching solutions. These specifications are as follows:

- Chromium oxide: 60 g/L (minimum)
- Chromium: 31 g/L (minimum)
- Total other metals (cations): 25 g/L (maximum)
- Copper: 0 to 25 g/L.

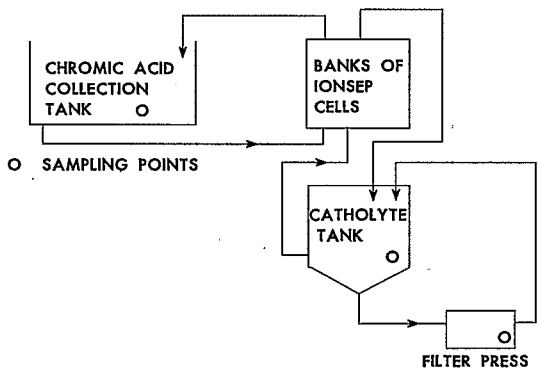



**Figure 3. Ionsep™ system schematic.**

Four grab samples were taken from the etching solution over a 3-day period. The final sample represents the etching solution that would be reused if Paramax returned the Ionsep™-treated spent etchant back to the etching line. Total chromium, copper, zinc, cadmium, lead, and iron were analyzed by EPA Method 6010 (inductively coupled plasma spectrometry), and hexavalent chromium by EPA Method 7196 (colorimetric method). Table 2 lists the samples taken at Paramax.

## SECTION 4

## RESULTS AND DISCUSSION

Testing was done on the electrodialytic process applied to two different operations at two distinct sites — a chromium plating solution at SL Modern Hard Chrome and a chromic acid etching solution at Paramax. The results are discussed separately for each site because the bath process and the Ionsep™ process used at the two sites were very different. For each site, the discussion is divided into the three project objectives: waste reduction potential, economic evaluation, and product quality evaluation.

### CHROMIUM PLATING

At SL Modern Hard Chrome, the chromium plating solution was recovered continuously by placing the Ionsep™ unit (cell) directly into the bath. The catholyte solution is contained in a plastic 55-gal drum outside the bath and is circulated through the Ionsep™ cell.

#### Waste Reduction Potential

The waste reduction potential of the Ionsep™ unit at SL Modern Hard Chrome is determined from the extended bath life and the reduced number of rejects that require stripping and replating. The actual contaminants are not broken out individually because the contaminants are disposed either with the bath in the old practice or with the catholyte in the new process.

Table 3 shows analytical results for the catholyte solution and the chromium plating solution. The catholyte solution was analyzed after the solution had been in use for 1 to 2 months and immediately before disposal. Metals in the catholyte solution are metals that were removed from the plating bath. Analysis indicates a removal rate of approximately 25 g total contaminant per day for a 250-amp Ionsep™ unit. The rate is calculated by adding the mass of metals in the catholyte solution divided by the days of catholyte solution use: CSl-8 (2,030 + 740 + 760 + 28 mg/L) × 3.785 L/gal × 55 gal/29 days/ 1,000 mg/g = 25.5 g/day. If the contaminants were not removed, levels eventually would reach the limit

**TABLE 3. ANALYTICAL RESULTS FOR THE CHROMIUM PLATING BATH**

| Sample ID | Cr mg/L | Fe mg/L | $Cr^6$ mg/L | Pb mg/L | Date | Days Use |
|---|---|---|---|---|---|---|
| Catholyte | | | | | | |
| CSL-9 | 3,230 | 1,100 | 1,050 | 48.6 | 2/6/92 | 56 |
| CSL-8 | 2,030 | 740 | 760 | 27.5 | 3/6/92 | 29 |
| CSL-2 | 2,500 | 717 | 860 | 27.6 | 4/6/92 | 31 |
| Process Bath | | | | | | Time |
| CSL-1 | 153,000 | 1,710 | 150,000 | 7.71 | 4/6/92 | 12:35 |
| CSL-4 | 151,000 | 2,740 | 160,000 | 89.8 | 4/7/92 | 9:15 |
| CSL-6 | 155,000 | 1,760 | 160,000 | 70.4 | 4/7/92 | 13:45 |
| Blanks | | | | | | |
| CSL-3 | 0.07 | 0.26 | 0.02 | 0.034 | 4/6/92 | 13:15 |
| CSL-5 | 0.03 | 0.15 | 0.02 | < 0.03 | 4/7/92 | 10:00 |
| CSL-7 | 0.05 | 0.15 | 0.02 | < 0.03 | 4/7/92 | 14:15 |

of 52 g/L in the plating bath. The time estimated from these data for a 1,400-gal bath to reach that limit is 52 g/L × 3.79 L/gal × 1,400 gal/25 g/day, or 11,036 days. Therefore, the use of Ionsep™ extends bath life beyond 40 years, which results in approximately 35 gal of solution saved per year (that would otherwise go to the environment without Ionsep™), based on an operation schedule of 250 days per year (1,400-gal bath/40 year).

There is a significant reduction of chromium with the use of Ionsep™ unit – from 165 lb to 14.2 lb. The 14.2 lb of chromium is the small amount lost to the catholyte solution. The reduction is the result of not having to replace the bath periodically and of having all rinse water returned to the plating bath to make up evaporative water losses.

Chromium is saved not only through reduced replacement of plating solution, but also through the reduced number of rejects. For every reject, the company must strip and replate the part. The reject data are based on estimates of plant personnel because no records were maintained. The reject reduction also corresponds to the company's implementation of regular bath analysis and chemical additions, which would also contribute to fewer rejects. The 5% decrease in rejects experienced by SL Modern Hard Chrome corresponds to approximately 237 pounds of chromium per year that is not disposed of with the stripper and that need not be purchased for addition to the plating solution. The 237 lb of chromium oxide is calculated from the company's plating rate from this bath of 42,900 $ft^2$ per

year, at a plating amount of 1.77 oz $CrO_3$ per $ft^2$, and a 5% savings ($0.05 \times 42{,}900\ ft^2/yr \times 1.77\ oz/ft^2 \times 1/16\ oz/lb$).

Table 4 summarizes the waste reduction potential of the new technology. The top part of Table 4 ("without Ionsep™") lists the wastes from infrequent bath replacement and the chromium stripped from rejected parts. The bottom part of Table 4 ("with Ionsep™") lists the chemicals used to make the Ionsep™ catholytic solution and the additional barium carbonate used to adjust the sulfate levels of the chromium plating bath by precipitating the sulfate as barium sulfate. The use of barium carbonate increased when Ionsep™ was installed. The total waste without the use of Ionsep™ amounts to 317 pounds of $CrO_3$ (165 lb Cr). The total waste with the use of Ionsep™ increases to 451 lb. This increase is the result of the catholyte salts and sludge and the increased use of barium carbonate to reduce sulfate in the bath. The sulfate concentration builds up faster in the bath because rinse water is reused in the bath when the Ionsep™ unit is used. In a 1-year period, 36 lb of barium carbonate was used to form barium sulfate, which precipitates out in the bath. The precipitate is either filtered out or allowed to collect at the bottom of the plating bath. The 36 lb of barium carbonate would react to form 43 lb of barium sulfate.

**TABLE 4. WASTE REDUCTION OF THE CHROMIUM PLATING LINE**

| Waste | Annual Generation |
|---|---|
| Without Ionsep™ | |
| $CrO_3$ in bath solution | 80 lb **(41.6 lb Cr)** |
| $CrO_3$ due to rejects | 237 lb **(123 lb Cr)** |
| **Total $CrO_3$** | 317 lb **(165 lb Cr)** |
| With Ionsep™* | |
| Catholyte solution | |
| Sodium sulfate | 120 lb |
| Sodium carbonate | 288 lb |
| Additional barium sulfate from sulfate reduction w/$BaCO_3$ | 43 lb |
| **Total†** | 451 lb **(14.2 lb $Cr^{+6}$)** |

* Sludge from Ionsep™ not included because it should equal the amount of metal contaminants disposed of with the chromium plating solution without Ionsep™.

† The sludge for 1 year would contain 14.2 lb $Cr^{+6}$.

## Economic Evaluation

The annual operating costs with and without the Ionsep™ unit are itemized in Table 5. Without the Ionsep™ system, the operation of a 1,400-gal bath costs $3,534 per year. The cost for the same bath with an electrodialytic unit is $3,973 per year. According to SL Modern Hard Chrome personnel, a major incentive for installing the equipment was to improve product quality. The reduction in rejects results in economic savings (e.g., faster turnaround time, decreased need for stripping solution, and ease of operation). These costs were included in the operation without Ionsep™.

The factors involved in the economic analysis are summarized in Table 5. Operating costs include costs for labor, maintenance, chemicals, utilities (water and electricity), and waste treatment/disposal.

**TABLE 5. ECONOMICS OF THE CHROMIUM PLATING LINE**

| Description | Annual Usage | Rate | Annual Cost |
|---|---|---|---|
| Without Ionsep™ | | | |
| Cr bath | 35 gal | $11.30/gal | $396 |
| Bath disposal | 35 gal | $2/gal | 70 |
| $CrO_3$ due to rejects | 237 lb | $1.13/lb | 268 |
| Labor due to rejects | 140 hr | $20/hr | 2,800 |
| Strip solution replacement and disposal | 100 gal | $1.50/gal | 150 |
| **Total without Ionsep™** | | | **$3,684** |
| With Ionsep™ | | | |
| Catholyte solution | | | |
| Sodium sulfate | 120 lb | $18/100 lb | $22 |
| Sodium carbonate | 288 lb | $18/100 lb | 52 |
| Water | 660 gal | $2.66/1000 gal | 2 |
| Barium carbonate | 36 lb | $1.22/lb | 44 |
| Sludge disposal | 4 drums | $205/drum | 820 |
| Labor | 41 hr | $20/hr | 827 |
| Maintenance | — | — | 1,080 |
| Power | 8,100 kWh | $.0902/kWh | 731 |
| **Total with Ionsep™** | | | **$3,578** |
| | | Annual savings | **$106** |

- Labor for the Ionsep™ unit is for a weekly check on the system of ⅓ hour per week and 2 hours per month to change the solution. The labor rate is calculated at $20 per hour.

- Maintenance costs for the unit are for labor of 2 hours per month ($20/hr) to clean lines and replace parts for each cell and materials costs of $300 for a pump that lasts 2 years and $450 annually to replace the Ionsep™ membrane.

- Chemical costs for the unit are for the components of the catholyte solution as shown in Table 5.

- The water cost is based on just the additional water that is used in Ionsep™ catholyte solution.

- The decrease in rejects results in savings of the labor needed to reprocess the rejects and the additional chromium that would be used to replate the part and replacement and disposal of the strip solution. The replacement and disposal cost is estimated at $1.50/gal. The additional strip solution replacement due to rejects is estimated at 100 gal annually.

- Waste disposal costs are based on a waste disposal company's quote of $2/gal for chromium bath disposal and an actual sludge disposal cost of $205 per drum.

The capital cost of a 250-amp Ionsep™ unit in the fall of 1991 was $20,000. With the savings of $106 in annual costs using the Ionsep™ unit, there is a payback on the unit of 189 years.

The firm is planning to add an Ionsep™ unit to the caustic strip tanks to recover chromic acid for recycle back to the plating baths and to recover the sodium hydroxide. This additional system, along with the current practice of decanting the catholyte solution and adding the solution to the caustic strip tanks, may eliminate the need for additional stripping solution and result in greater savings.

Although economic considerations are important, they are not the only justification for installing waste reduction equipment. Because all rinsewater is returned to the plating baths, the electrodialytic system allows SL Modern Hard Chrome to have zero discharge from its plating operations to the city water treatment system. SL Modern Hard Chrome decided to purchase Ionsep™ to avoid the problems and costs of water discharge to the city.

## Product Quality Evaluation

The products at SL Modern Hard Chrome are the chromium-plated parts. The parts are inspected for pits, blisters, other deformities, and chromium thickness. The product quality is the plated

part quality, which correlates with the plating bath quality (specifications). Based on discussions with plant personnel, the number of rejects has decreased by about 5% since installation of the Ionsep™ unit. The fact that SL Modern Hard Chrome has experienced a drop in the number of rejects is a key factor in its continued use of the Ionsep™ unit. There are fewer rejects because the chromium plating quality has improved, producing more uniform chromium deposit and fewer pits.

Analysis of the bath (Table 3) showed it was within specifications — the contaminant level was below the maximum of 52 g/L and the chromium level was above the minimum of 140 g/L.

## Quality Assurance

A Quality Assurance Project Plan (QAPP) (Battelle, 1992) was prepared at the outset of the project to describe testing, sampling, and analysis procedures. Testing and sampling were carried out at SL Modern Hard Chrome according to the QAPP. Tables 6 and 7 give the accuracy and precision, respectively, of the analytical results.

Matrix spike recoveries (Table 6) were within 75% to 125% for all parameters except lead in the process bath solution. Therefore, levels of lead measured in the process bath should be considered as minimum levels present because recovery from the spike is low. Precision (Table 7) was within ±25% for all parameters except total chromium in the catholyte, for which precision was measured close

**TABLE 6. ACCURACY OF THE CHROMIUM PLATING LINE ANALYSIS**

| Parameter | Sample No. | Regular Sample µg/L | Matrix Spike Level µg | Matrix Spike Measured µg/L | % Recovery | Dilution Factor |
|---|---|---|---|---|---|---|
| Catholyte | | | | | | |
| Cr | CSL-8 | 1,014 | 1,000 | 2,031 | 102% | - |
| Fe | CSL-8 | 740 | 1,000 | 1,198 | 90% | - |
| Cr + 6 | CSL-3 | 19 | 2,000 | 1,735 | 86% | - |
| Pb | CSL-8 | 550 | 1,000 | 1,308 | 76% | - |
| Process Bath | | | | | | |
| Cr | CSL-4 | 1,513 | 1,000 | 2,469 | 96% | 100,000 |
| Fe | CSL-4 | 548 | 1,000 | 1,365 | 82% | 5,000 |
| Cr + 6 | CSL-4 | 1,600 | 1,000 | 2,636 | 104% | 100,000 |
| Pb | CSL-4 | 898 | 1,000 | 1,504 | 61% | 100 |

**TABLE 7. PRECISION OF THE CHROMIUM PLATING LINE ANALYSIS**

| Parameter | Sample No. | Regular Sample mg/L | Duplicate mg/L | Precision % |
|---|---|---|---|---|
| Catholyte | | | | |
| Cr | CSL-5 | 0.03 | 0.04 | 28.6 |
| Fe | CSL-5 | 0.15 | 0.17 | 12.5 |
| Cr + 6 | CSL-3 | 0.019 | 0.021 | 10 |
| Pb | CSL-5 | < 30 | < 30 | |
| Process | | | | |
| Cr | CSL-4 | 151,000 | 156,000 | 3.3 |
| Fe | CSL-4 | 2,740 | 3,110 | 12.6 |
| Cr + 6 | CSL-4 | 160,000 | 161,000 | 0.6 |
| Pb | CSL-4 | 89,800 | 77,900 | 14.2 |

to the detection limit and fell slightly out of range. Completeness, accuracy, and precision data quality objectives (DQOs) were met for this project.

## CHROMIUM ETCHING

At Paramax, the etchant was recovered as a batch process in the following way for these tests. Over a two-day period, etchant baths totalling 200 gal were removed from the process line to a treatment tank and pumped through the Ionsep™ unit. The unit ran continuously for 3 days. Paramax has since established that the recovered etchant meets its stringent requirements for etching solutions.

### Waste Reduction Potential

The waste reduction potential of the Ionsep™ unit at Paramax was calculated based on how many etchant bath disposals this process can prevent. The number prevented depends on how fast contaminants build up in the etchant bath and the extent of contaminant removal through the Ionsep™ unit.

Experience at Paramax indicates that use of the Ionsep™ unit prevents disposal of approximately 7.5 baths per week. The facility currently disposes of 8.5 baths per week and estimates that, with the Ionsep™ unit, disposal will be reduced to 1 bath per week. The rate of contaminant buildup in the etchant is slightly higher than the rate of removal by the Ionsep™ system. Each bath contains

110 gal (the Ionsep™ unit can treat up to 500 gal, or about 4 baths in 4 days), which means that 41,250 gal of etchant bath solution would not be disposed of per year (7.5 bath/wk × 110 gal/bath × 50 wk/yr). The etchant concentrate is diluted 50% to make up the bath. Therefore, the Ionsep™ unit could reduce 20,625 gal of etchant concentrate per year going to the environment. This amount of etchant contains approximately 7,154 pounds of chromium that would have otherwise gone to waste (80 g/L $CrO_3$ in etchant × 52 g Cr/100 g $CrO_3$ × 20,625 gal × 3.785 L/gal). Table 8 summarizes the items evaluated in the waste reduction analysis.

**TABLE 8. WASTE REDUCTION OF THE ETCHING LINE**

| | Amount Discarded Per Year |
|---|---|
| Without Ionsep™ | |
| Etchant | 20,625 gal |
| Water | 20,625 gal |
| Chromium | 7,100 lb |
| With Ionsep™ | |
| Catholyte solution | |
| Sodium chloride | 10,000 lb |
| Sodium sulfate | 5,000 lb |
| Soda ash | 1,000 lb |
| Water | 25,000 gal |
| Chromium | 42 lb* |

* estimated

## Economic Evaluation

The Ionsep™ unit at Paramax is still in the testing phase. Therefore, most of the cost analysis was based on Paramax estimates derived from economic information in plant records and experience of the Paramax personnel. These estimates indicate that the unit can prevent the disposal of approximately seven etchant baths per week, resulting in savings in disposal and replacement chemical costs.

Operating cost factors involved in the economic analysis for Paramax include labor, maintenance, chemicals, utilities (water and electricity), and waste treatment/disposal.

- Labor for operating the Ionsep™ unit is based on an estimate of one full-time technician at $20.00 per hour.

- Paramax estimates maintenance for the unit will cost $30,000 per year. This figure is mostly for replacement parts, including 4 membranes per year, and recoating the anodes. Maintenance labor also is included in Paramax's estimate.

- Chemical costs for the unit are calculated from the estimated usage of catholyte solution, the components of the solution, and their actual costs obtained from Paramax.

- The water cost is for the additional water that is used in the catholyte solution for the Ionsep™ unit and cost of water for Paramax.

- The power cost for the unit is for the power actually used during the test run and the unit cost of electricity for Paramax.

- Waste disposal costs are for the actual costs at Paramax. Minimal disposal costs are anticipated with the Ionsep™, because most of the waste is recovered (i.e., both the chromium bath and the copper are recovered).

Table 9 compares costs with and without the Ionsep™ unit.

**TABLE 9. ECONOMICS OF THE ETCHING LINE**

| Description | Annual Use | Rate $ | Annual Cost $ |
|---|---|---|---|
| Without Ionsep™ | | | |
| Etchant (concentrate) | 20,625 gal | 4.85/gal | 100,031 |
| Etchant disposal | 41,250 gal | 2.31/gal | 95,288 |
| Labor for disposal | 150 hr | 20.00/hr | 3,000 |
| Water* | 20,625 gal | 2.66/1000 gal | 55 |
| **Total** | | | **$198,374** |
| With Ionsep™ | | | |
| Catholyte solution | | | |
| Sodium chloride | 10,000 lb | 3.50/50 lb | 700 |
| Sodium sulfate | 5,000 lb | 17.50/100 lb | 875 |
| Soda ash | 1,000 lb | 0.23/lb | 230 |
| Water* | 25,000 gal | 2.66/1000 gal | 66 |
| Labor | 2,000 hr | 20.00/hr | 40,000 |
| Maintenance | — | — | 30,000 |
| Power | 1,430 kWh | 0.045/kWh | 65 |
| **Total** | | | **$ 71,936** |

* Water costs include sewage fee.

Without the unit, costs of approximately $198,000 are incurred for replacement and disposal of the etchant baths. Operating the unit costs approximately $72,000, mostly for added labor and maintenance on the unit. Thus, with the Ionsep™ system, an approximate annual savings of $126,000 is realized. The capital cost of the unit (specific to Paramax), including installation and modifications, was $563,000. Dividing this by the annual savings results in a payback period of approximately 4.5 years.

## Product Quality Evaluation

The Ionsep™ unit at Paramax was in the initial testing phases. The etchant was sampled and analyzed for both chromium and contaminants at the end of the 3-day treatment/recovery process. These analyses were used to determine whether the renovated bath was within specifications, and bath quality was an indication of product quality. The analytical results are shown in Table 10. Although total chromium in the etchant remained constant, hexavalent chromium increased. The hexavalent chromium started at approximately 74% of the total and increased to about 99%. It is believed that oxidation of the trivalent chromium back to the hexavalent form caused the increase in hexavalent chromium concentration. The resulting hexavalent chromium concentration of 30.3 g/L in the etchant over the 3-day sampling period approached the minimum specification level of 31 g/L, as given in Section 3. This could be increased further by longer treatment or by adding etchant concentrate. At the time this study was conducted, the etchant had not been reused and the effect of recovered solution on in-house printed wire board quality had not been evaluated.

As shown in Table 10, the cationic contaminants were within specification. The 10.8 g/L (mostly copper) was below the maximum level of 25 g/L. Because the chromium and the contaminant levels are both near specification levels, the etchant should be acceptable.

## Quality Assurance

Testing and sampling at Paramax were carried out according to the QAPP with the following exceptions. The initial plan for sample collection was for sampling at three locations: (1) chromium etching bath, (2) Ionsep™ return, and (3) catholyte solution. On site, it was realized that the Ionsep™ return line was a continuous recirculation of the chromium process fluid at a flowrate of about 10 gpm. Therefore, it was not necessary to sample both the process bath and the return line. The return line was representative of the process bath and was sampled.

## TABLE 10. ANALYTICAL RESULTS FOR THE ETCHING LINE AT PARAMAX

| ID | Cd µg/L | Cr mg/L | Cu mg/L | Fe mg/L | Pb µg/L | Zn µg/L | $Cr^{+6}$ mg/L | Date | Time |
|---|---|---|---|---|---|---|---|---|---|
| Etchant | | | | | | | | | |
| | 438 | 30,400 | 18,080 | 6.28 | 78,800 | 23,200 | 22,400 | 5/19 | 12:30 |
| | 437 | 32,600 | 18,000 | 7.32 | 35,600 | 22,700 | 23,700 | 5/19 | 15:30 |
| | 406 | 32,600 | 17,000 | 7.25 | 28,700 | 17,300 | 25,100 | 5/20 | 10:10 |
| | 376 | 29,000 | 11,600 | 6.62 | 15,700 | 13,300 | 26,300 | 5/21 | 10:45 |
| | 379 | 30,300 | 10,800 | 5.84 | 14,500 | 13,100 | 30,000 | 5/21 | 16:00 |
| Catholyte | | | | | | | | | |
| | 14 | 0.905 | 4.24 | 0.16 | 154 | 56 | 0.175 | 5/19 | 11:45 |
| | 11 | 5.61 | 22.8 | 0.14 | 326 | 73 | 0.378 | 5/19 | 13:18 |
| | 14 | 31.2 | 129.9 | 0.43 | 529 | 158 | 0.292 | 5/19 | 15:20 |
| | 24 | 220 | 775 | 0.24 | 1,100 | 767 | 9.74 | 5/20 | 10:45 |
| | 45 | 325 | 1,830 | 0.56 | 1,990 | 1,660 | 28.5 | 5/21 | 10:45 |
| | 36 | 196 | 1,220 | 0.31 | 1,340 | 1,240 | 27.7 | 5/21 | 16:00 |
| Sludge | | | | | | | | | |
| mg/kg | 3.5 | 7,000 | 7,000 | 32.3 | 182 | 140 | 788 | 5/20 | 13:00 |
| | 122 | 1,330 | 18,000 | 1.10 | 8,020 | 5,590 | 1.1 | 5/21 | 16:30 |
| Water | | | | | | | | | |
| | 1 | 0.378 | 0.377 | 0.20 | | 35 | | 5/21 | 16:00 |

Tables 11 and 12 give the analytical accuracy and precision, respectively, of the laboratory testing. Matrix spike recoveries and precision for all parameters were within acceptable ranges except for the precision of the iron results for the etchant samples which was slightly out of range. This implies that the values for iron in the etchant samples (Table 10) are not significantly different from each other. Completeness, accuracy, and precision data quality objectives in the QAPP were met.

**TABLE 11. ACCURACY OF THE ETCHING LINE ANALYSIS**

| Parameter | Sample Date | Sample Time | Regular Sample | Matrix Spike Level | Matrix Spike Measured | % Recovery | Dilution Factors |
|---|---|---|---|---|---|---|---|
| Etchant | | | | | | | |
| Cr, μg/L | 5/21 | 16:00 | 1,515 | 1,000 | 2,542 | 103 | 20,000 |
| Cu, μg/L | " | | 646 | 1,000 | 1,714 | 107 | 20 |
| Fe, μg/L | " | | 1,168 | 1,000 | 1,939 | 77 | 5 |
| Zn, μg/L | 5/21 | 16:00 | 1,340 | 1,000 | 2,207 | 87 | 10 |
| $Cr^{+6}$, μg/L | " | | 300 | 2,000 | 2,416 | 106 | 100,000 |
| Catholyte | | | | | | | |
| Cd, μg/L | 5/19 | 15:20 | 14 | 1,000 | 987 | 97 | - |
| Cr, μg/L | 5/21 | 16:00 | 391 | 1,000 | 1,445 | 105 | - |
| Fe, μg/L | 5/21 | 16:00 | 237 | 1,000 | 968 | 73 | - |
| Pb, μg/L | 5/19 | 15:20 | 529 | 1,000 | 1,532 | 100 | - |
| Zn, μg/L | 5/21 | 16:00 | 1,245 | 1,000 | 2,141 | 90 | - |
| $Cr^{+6}$, μg/L | 5/21 | 16:00 | 300 | 2,000 | 2,416 | 106 | - |

Tables 11 and 12 give the analytical accuracy and precision, respectively, of the laboratory testing. Matrix spike recoveries and precision for all parameters were within acceptable ranges except for the precision of the iron results for the etchant samples which was slightly out of range. This implies that the values for iron in the etchant samples (Table 10) are not significantly different from each other. Completeness, accuracy, and precision data quality objectives in the QAPP were met.

**TABLE 11. ACCURACY OF THE ETCHING LINE ANALYSIS**

| Parameter | Sample Date | Sample Time | Regular Sample | Matrix Spike Level | Matrix Spike Measured | % Recovery | Dilution Factors |
|---|---|---|---|---|---|---|---|
| Etchant | | | | | | | |
| Cr, μg/L | 5/21 | 16:00 | 1,515 | 1,000 | 2,542 | 103 | 20,000 |
| Cu, μg/L | " | | 646 | 1,000 | 1,714 | 107 | 20 |
| Fe, μg/L | " | | 1,168 | 1,000 | 1,939 | 77 | 5 |
| Zn, μg/L | 5/21 | 16:00 | 1,340 | 1,000 | 2,207 | 87 | 10 |
| $Cr^{+6}$, μg/L | " | | 300 | 2,000 | 2,416 | 106 | 100,000 |
| Catholyte | | | | | | | |
| Cd, μg/L | 5/19 | 15:20 | 14 | 1,000 | 987 | 97 | - |
| Cr, μg/L | 5/21 | 16:00 | 391 | 1,000 | 1,445 | 105 | - |
| Fe, μg/L | 5/21 | 16:00 | 237 | 1,000 | 968 | 73 | - |
| Pb, μg/L | 5/19 | 15:20 | 529 | 1,000 | 1,532 | 100 | - |
| Zn, μg/L | 5/21 | 16:00 | 1,245 | 1,000 | 2,141 | 90 | - |
| $Cr^{+6}$, μg/L | 5/21 | 16:00 | 300 | 2,000 | 2,416 | 106 | - |

## TABLE 12. PRECISION OF THE ETCHING LINE ANALYSIS

| Parameter | Sample Date | Sample Time | Regular Sample | Duplicate | Precision % |
|---|---|---|---|---|---|
| Etchant | | | | | |
| Cd, μg/L | 5/21 | 16:00 | 379 | 382 | 0.8 |
| Cr, mg/L | | " | 30,300 | 29,000 | 4.4 |
| Cu, mg/L | | " | 10,800 | 10,600 | 1.9 |
| Fe, mg/L | | " | 5.84 | 7.66 | 27 |
| Pb, μg/l | | " | 14,500 | 14,900 | 2.7 |
| Zn, mg/L | | " | 13,100 | 13,000 | 0.8 |
| $Cr^{+6}$, mg/L | | " | 30,000 | 30,000 | 0.0 |
| Catholyte | | | | | |
| Cd μg/L | 5/19 | 11:45 | 14 | 13 | 7.2 |
| Cr mg/L | 5/19 | 15:20 | 31.2 | 31.9 | 2.2 |
| Cu mg/L | 5/19 | 15:20 | 129.9 | 140.0 | 7.5 |
| Fe mg/L | 5/19 | 15:20 | 0.43 | 0.44 | 2.3 |
| Pb μg/L | 5/19 | 15:20 | 0.529 | 0.515 | 2.7 |
| Zn mg/L | 5/19 | 15:20 | 158 | 162 | 2.5 |
| $Cr^{+6}$ mg/L | 5/19 | 13:18 | 378 | 381 | 0.8 |

## SECTION 5

## REFERENCES


Battelle. 1992. *Quality Assurance Project Plan for the Ionsep™ Electrodialytic Process Evaluation*, February. Prepared for the U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH.

Cushnie, G. C., Jr., and W. Anderson. 1989. "Removal of Metal Cations from Chromium Plating Solution." Paper presented at the 10th AESF/EPA Conference on Environmental Control for the Metal Finishing Industry, January 23-25, 1989.

Ionsep Corporation, Inc. 1989. "Closed-Loop Processing of Chromic Acid Solutions." Paper presented at the 10th AESF/EPA Conference on Environmental Control for the Metal Finishing Industry, January 23-25, 1989.

Knill, E. C., and H. Chessin. 1986a. "Contamination of Hexavalent Chromium Plating Baths." *Plating and Surface Finishing*, July.

Knill, E. C., and H. Chessin. 1986b. "Purification of Hexavalent Chromium Plating Baths." *Plating and Surface Finishing*, August.