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Project Summary

Evaluation of an Electrodialytic Process for Purification of Hexavalent Chromium Solutions

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The evaluation summarized here 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 reduces 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, NJ, (a hard chromium plating solution) and at Paramax in St. Paul, MN, (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 was not cost effective for the hard chromium plating bath but was cost effective for the chromic acid etch bath, which had a payback of less than 5 yr. In these two examples, the payback was related to the rate of contaminant buildup in the solution — the more frequently a solution was replaced when contaminants were not removed, the shorter the payback after an electrodialytic process had been installed. The chromium plating operation annually reduced chromium needing disposal by 73 kg (161 lb), and the copper etching operation projected an annual reduction of 4,410 kg (9,700 lb).

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

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate Technology Evaluation Report of the same title (see Project Report ordering information at back).

Introduction

This study, performed under the U.S. Environmental Protection Agency's (EPA) Waste Reduction and Innovative Technology Evaluation (WRITE) Program, was a cooperative effort among EPA's Risk Reduction Engineering Laboratory (RREL), SL Modern Hard Chrome, and Paramax. The goal of the WRITE Program is to evaluate, in a typical workplace environment, examples of prototype or innovative commercial technologies that have potential for reducing wastes and then to provide this information to potential users. The objectives of the electrodialytic technology study were to evaluate (1) the waste reduction potential of the technology, (2) the economic feasibility of the technology, and (3) the impact on product quality.

SL Modern Hard Chrome 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 chromium thickness varies from 0.0001 in. to 0.030 in. or more on parts ranging in size from a few ounces to several tons. Paramax (a Unisys company) was the site for testing the electrodialytic process on a chromic acid etching solution. Paramax manufactures multilayer printed wire boards at this facility.

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 replaced. The Ionsep™ electrodialytic process removes the cations from the chromium plating solution and allows it to be used longer. At SL Modern Hard Chrome, it has been more than 3 yr since a chromium plating bath was replaced.

Paramax uses a chromic acid solution to etch copper from printed wire boards (PWB). As copper builds up in the etching solution, the etching rate becomes unacceptably slow. Before Ionsep™ installation, 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 extends the usefulness of the etching solution by removing copper from the etching solution and converting some of the trivalent chromium back to hexavalent chromium electrolytically.

Ionsep™ Electrodialytic Process

The aim of this 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.

Figure 1 shows a two-compartment cell used for the purification of a chromium plating solution. The Ionsep™ electrodialytic process uses a voltage gradient to separate salt in a solution into cations and anions. Chromium is present in the anionic chromate form in the plating and etching solutions. 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 the cations migrate through the membrane; this migration eliminates the buildup of metals on the cathode. Membranes in the electrodialytic cells serve to physically separate the acidic, basic, and other process solutions.

Materials and Methods

One test site uses a chromium plating solution and one a chromic acid for etching copper. At each site, metal analyses were performed on the chromium solution and the catholyte solution to determine contaminant levels in the process solution and the rate of metals buildup in the catholyte solution. From the analyses, the rate of metals buildup in the catholyte solution was determined. This corresponded with metals removal from the process solution, which in turn was used to determine the bath life-extending capabilities of the Ionsep™ process and the waste reduction potential. Operating costs with and without the Ionsep™ process were used along with installation costs to determine the economics of the process.

Results and Discussion

The results from the two sites 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.

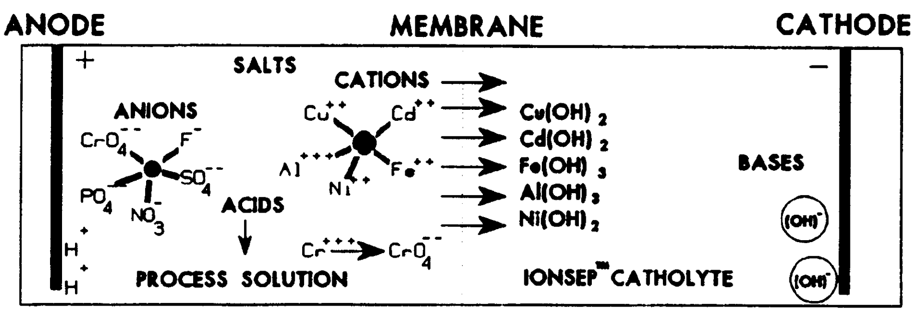

Figure 1. *Ionsep™ electrodialytic process. (Source: Ionsep™ Corporation, 1989)*

Chromium Plating

At SL Modern Hard Chrome's 1,400-gal hard chromium plating bath, 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

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; the final rinse 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. With use of Ionsep™, the only resulting waste discharge is the sludge from the Ionsep™ catholyte solution. This catholyte sludge contains levels of chromium at 2000 to 3200 mg/L total chromium and 760 to 1050 mg/L hexavalent chromium and therefore must be handled as a hazardous waste. With the catholyte solution replaced monthly, the annual discharge of total chromium is 6.5 kg (14.2 lb).

The catholyte solution was analyzed after the solution had been in use for 1 to 2 months and immediately before disposal. The metals in the catholyte solution were removed from the plating bath. Analysis indicates a removal rate of approximately 25 g total contaminants/day for a 250-amp Ionsep™ unit. If the contaminants were not removed, levels would eventually reach the limit 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 x 3.79 L/gal x 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/yr (that would otherwise be disposed of), based on an operation schedule of 250 days/yr (1,400-gal bath/40 yr).

Hexavalent chromium is significantly reduced with the use of the 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 5% decrease in rejects experienced by SL Modern Hard Chrome corresponds to approximately 237 lb chromium/yr 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/yr, at a plating amount of 1.77 oz CrO_3 per ft^2, and a 5% savings (0.05 x 42,900 ft^2/yr x 1.77 oz/ft^2 x 1/16 oz/lb).

Table 1 summarizes the waste reduction potential of the new technology. The top part of Table 1 (without Ionsep™) lists the wastes from infrequent bath replacement and the estimated amount of chromium stripped from rejected parts. The bottom part of Table 1 (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. Barium carbonate is used to precipitate the sulfate as barium sulfate. The use of barium carbonate increased when the Ionsep™ was installed.

The total waste without the use of Ionsep™ amounts to 317 lb 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-yr 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.

Economic Evaluation

SL Modern Hard Chrome provided economic information for most aspects of its operations. The annual operating costs with and without the Ionsep™ unit are itemized in Table 2. Without the Ionsep™ system, the operation of a 1,400-gal bath costs $3,684/yr. The cost for the same bath with an electrodialytic unit is $3,578/yr.

According to SL Modern Hard Chrome personnel, a major incentive for installing the equipment was to improve product quality by reducing contaminant buildup in the plating bath. Fewer rejects result in economic savings (e.g., faster turnaround time, decreased need for stripping solution, and ease of operation). The costs for rejects and additional plating are included in the operation without Ionsep™.

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

Although economic considerations are important, they are not the only justification for installing waste reduction equipment. SL Modern Hard Chrome has zero discharge from its plating operations to the city water treatment system because all rinsewater is returned to the plating baths.

Product Quality Evaluation

Chemical analyses of the chromium plating solution were conducted to verify that the solution met operational specifications for hard chromium plating solutions. Analysis of the bath 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.

The products, chromium-plated 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). Since installation of the Ionsep™ unit, the number of rejects has decreased by about 5%, a key factor in its continued use. The improved chromium plating quality has produced more uniform chromium deposit and fewer pits.

Chromium Etching

At the second company, Paramax, chromium-based etchant was tested as a batch process. Eight of the six cells in the process line were used, and over a 2-day period, 200-gal etchant baths 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. The company is currently using 12 cells to keep up with the buildup of copper and has successfully recycled the etchant during production.

Waste Reduction Potential

Calculation of 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.

Experience at Paramax indicates that use of the Ionsep™ unit prevents disposal of approximately 7.5 baths/wk. Paramax currently disposes of 8.5 baths/wk and estimates that, with the Ionsep™ unit, disposal will be reduced to one bath/wk. Each bath contains 110 gal (the Ionsep™ unit can treat up to 500 gal, or about four 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 x 110 gal/bath x 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

Table 1. *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 yr would contain 14.2 lb Cr^{+6}.*

Table 2. *Economics of the Chromium Plating Line**

Description	Annual Use	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*

* *Wastewater discharge costs are not applicable. Analytical costs are assumed to be the same for both cases.*

needing disposal. This amount of etchant contains approximately 7,154 lb of chromium that would otherwise have gone to waste (80 g/L CrO_3 in etchant x 52 g Cr/ 100 g CrO_3 x 20,625 gal x 3.785 L/gal). Table 3 summarizes the items evaluated in the waste reduction analysis.

To recover the etched copper, Paramax acidifies the cake filtered from the catholyte solution. Water use at Paramax is increased to make up the catholyte solution. After acidification and copper recovery, the resulting solution is nonhazardous.

Economic Evaluation

Paramax provided economic information for its etching operations. Because the Ionsep™ unit at Paramax is still undergoing testing, most of the cost analysis was based on Paramax estimates derived from economic information in plant records and experience of Paramax personnel. These estimates indicate that the unit can prevent disposal of approximately seven etchant baths/wk and, thus, save 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. Table 4 compares costs with and without the Ionsep™ unit.

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

Table 3. *Waste Reduction of the Etching Line*

Description	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.*

Product Quality Evaluation

The Ionsep™ unit at Paramax was in the initial testing phases during this study. 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 whether bath quality was an indication of product quality. 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. 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 product quality had not been evaluated.

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.

The full report was submitted in partial fulfillment of Contract Number 68-CO-0003, Work Assignment 3-36, by Battelle (Columbus) under the sponsorship of the U.S. Environmental Protection Agency.

Table 4. 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.

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The complete report, entitled "Evaluation of an Electrodialytic Process for Purification of Hexavalent Chromium Solutions," (Order No. PB94-165214; Cost: $17.50, subject to change) will be available only from:
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