REMOVAL OF METAL CATIONS FROM CHROMIUM PLATING SOLUTIONS

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ABSTRACT

This paper presents the results of a study which focused on the identification and testing of technologies for removing iron and copper from chromium plating solutions. Initially, a literature review was conducted to identify the most viable technologies. Two technologies were then selected for testing: an electrodialytic membrane unit and a porous pot. Tests were conducted on contrived baths with metal concentrations initially in the range of 10 to 15 g/l. The results showed a superior performance by the membrane technology in terms of iron and copper removal. Also, the membrane technology produced a much smaller volume of residual waste. These test results can be used to aid metal finishers in selecting and sizing chrome purification units. Several case studies are examined which document use of purification technologies.

BACKGROUND

Chromium plating solutions become contaminated with various metallic impurities including trivalent chromium, iron, copper, nickel, aluminum, and zinc. Trivalent chromium contamination results from the plating process when the anode surface area is insufficiently sized in comparison to the cathode area. Other metallic contaminants are introduced by drag-in, cathodic etching, and attack on racks, fixtures and bus bars (figure 1).

Various defects in chromium plated deposits are attributed to metallic impurities. However, researchers, experts, and quality control departments have differing opinions as to the tolerable levels of these contaminants.

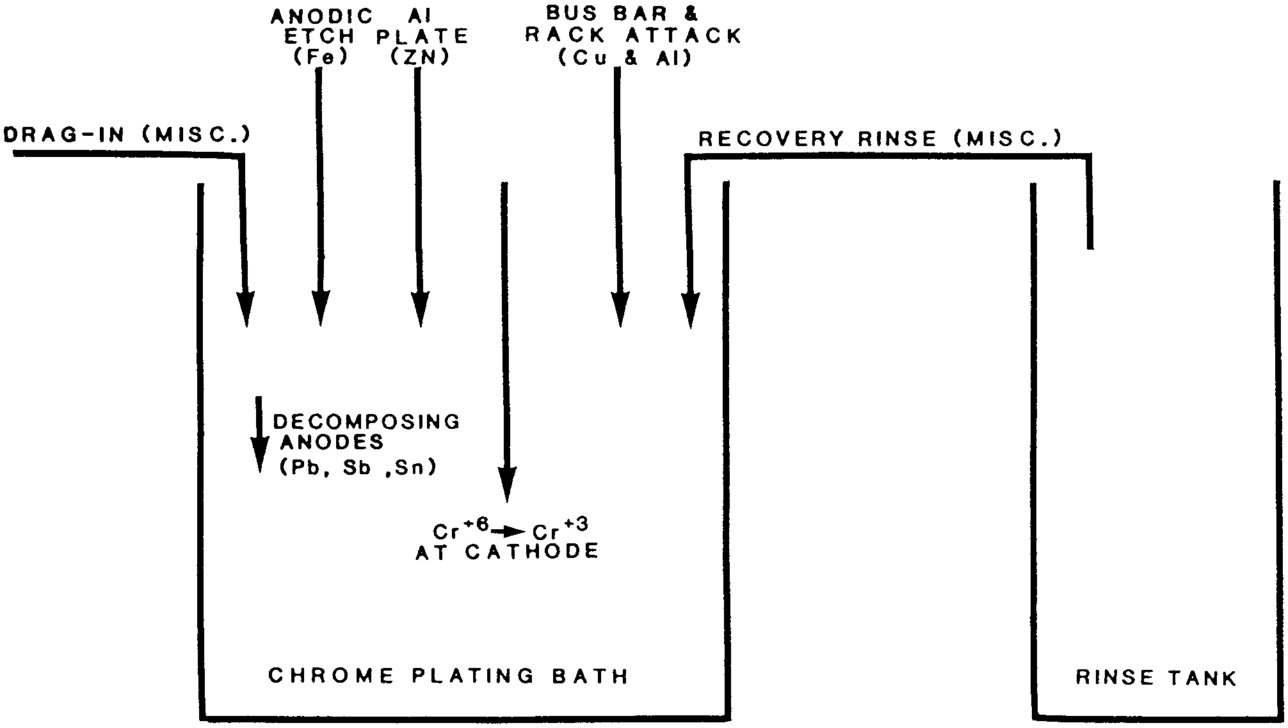

Figure 1. Sources of cation contaminants in chrome plating baths.

Chessin, Knill, and Seyb (reference 1) report that plating baths containing 10-15 g/l of iron plus trivalent chromium have been operated successfully, but for deposits greater than about 5 mil in thickness, differences in roughness may be perceptible when the combined concentration exceeds 4 g/l. Knill and Chessin (reference 2) indicate that copper has a greater detrimental effect on coverage than equivalent large amounts of iron, however no specific limits were suggested for copper or other nonferrous metals. As stated by Knill and Chessin, the harmful effects of an impurity depend on many factors including the overall chemistry of the bath, plating procedures used and the type of work being plated.

In addition to causing plating quality problems, chrome bath contamination increases plating shop operating costs. Dissolved metal impurities reduce bath conductivity. This increases bath resistance and requires higher plating voltages to maintain the correct current density on the parts (reference 3). In the case of dissolved iron, 7.5 g/l iron will require approximately 30 to 50 percent higher voltage to obtain the same amperage as compared to a new bath (reference 4).

For many shops the major cost with respect to bath contamination is the cost of replacement and disposal. The current price of bath makeup for a standard hard chrome solution is approximately $2.60 per gallon. Disposal costs vary by region and are generally increasing because of changing waste management and disposal practices. Prior to the adoption of stringent environmental laws, portions of contaminated baths were often decanted to the sewer or an empty tank and replaced with fresh solution. The contaminants remaining in the bath were then diluted, using fresh solution, below the concentration at which plating problems arise. Many shops retain excess solution in drums and unused tanks, imposing a significant liability.

Currently, shops disposing of chromic acid either treat it on-site or have it hauled to a permitted treatment/disposal contractor. On-site treatment is not always possible because treatment facilities may not be sized to handle the concentrated solution which produces high volumes of sludge (treatment of 1 gallon of chromic acid solution will produce 12 lbs. of sludge at 20% solids) (reference 5). Off site disposal is expensive. Current prices for hauling/treatment/sludge disposal range from $3 to $12 per gallon (reference 6). New landfilling restrictions are expected to increase these prices in the near future.

Technologies for the purification of chromium plating baths can be categorized into three major groups: 1) ion exchange, 2) electrolysis and 3) electrodialytic processes. The functions or applications of these technologies can be divided into two groups: 1) removal or conversion of trivalent chromium and 2) removal of other metallic impurities (i.e., iron, copper, etc.). Table 1 lists the available configurations and applications of commercial technologies. As shown, with the exception of "dummying", each technology has been applied for the control of both trivalent chromium and the other metal impurities.

Trivalent chromium build-up is a major problem at some shops, especially where the majoriety of work is inside diameter (ID) plating. ID plating always results in a low anode-to-cathode area ratio. The traditional method for trivalent control is simple electrolysis or dummying. This process involves the use of a high anode-to-cathode area ratio. It can be performed in the plating tank without loss of chromium solution. Although dummying remains a viable process, there are several negative aspects: 1) requires shutdown of tank; 2) causes sharp fluctuations in Cr^{+3}, and therefore hinders the predictability of the solution; 3) the process is labor intensive; 4) the process has no effect on iron, copper, and other tramp metals; and 5) the process is very inefficient.

Table 1
Chromium Solution Purification Technologies
Functions or Applications

Technology	Cr+3 Oxidation or Removal	Other Metal Removal
Ion exchange	Yes	Yes
Electrolysis		
W/out diffused barrier	Yes	No
W/ diffused barrier	Yes	Yes
Electrodialytic		
Acidic catholyte	Yes	Yes
"Caustic catholyte"	Yes	Yes

Iron, copper, and the other metal impurities present a more difficult problem than trivalent chromium and were the focus of this study. The objective of the project was to identify the most effective technology in terms of its ability to purify chrome baths. The initial focus of the project was a screening process during which the applicable technologies were identified and compared on a qualitative basis. Following screening, two representative technologies were selected and tested.

TECHNOLOGY REVIEW

Ion Exchange

Ion exchange (IX) has been applied to chromium solutions for the removal of trivalent chromium, iron, and miscellaneous metallic impurities. With this process, the plating bath is usually treated on a batch basis with a shutdown of the plating process being required. However, a continuous process has been used. Generally, the plating solution must be cooled and diluted prior to purification. One of the first applications of IX for hard chrome bath purification was installed at the Rock Island Arsenal in the early 1950s (reference 7). That unit was designed to treat 1,000 gallons of contaminated chromium solution. The trivalent chromium concentration was reduced from 5 g/l to 1 g/l and iron from 6 g/l to 1 g/l.

An IX system generally consists of an IX column, a feed tank, storage tank, regeneration system, and in some cases an evaporator. The column which contains the resin is sized for either batch or continuous use. Batch operations require much larger column sizes. Continous systems require additional controls. An IX column containing 8 $ft.^3$ of resin will typically treat 500 gallons of plating solution per cycle, removing 12.5 lbs. (as calcium carbonate) of metallic impurities. The solutions are diluted prior to treatment to minimize damage to the IX resins. Resin life is reportedly 6 to 12 months (reference 8). The evaporator is used to concentrate the plating solution after purification. Some installations are able to avoid dilution and the use of an evaporator. Also, some hard chrome applications simply make use of plating tank evaporative losses to "balance" the dilution.

Use of ion exchange will generate significant volumes of both concentrated and dilute wastes. Concentrated wastes are produced during regeneration of the IX column. This involves passing a solution of mineral acid through the column to remove the heavy-metal impurities from the IX resin. Dilute wastes are produced during the rinsing and backwash of the column. The total volume of waste generated by an IX system is typically equal to 4-6 times the volume of the IX column per cycle. Therefore, treating a 500 gallon bath with an 8 $ft.^3$ column will generate approximately 300 gallons of waste. This wastewater can be treated using neutralization/hydroxide precipitation. The resulting sludge would be a hazardous waste.

A case study of an IX chrome bath purification application was presented in the literature (reference 9). The system treats 500 gal of chromic acid per cycle. The chromic acid is diluted to 50 percent strength before purification. Results from the process are shown in Table 2. The study reported that a 13 percent productivity increase was observed. Furthermore, energy requirements were reduced by 25 percent. The analytical results indicate that chromium losses due to trivalent chromium removal were 6.8 g/l or approximately 28 pounds per 500 gallons of bath treated.

The advantages of IX are its proven capabilities and the relative speed of the process. The disadvantages are the high waste volumes, which require treatment; a loss of chromium due to trivalent chromium removal; and a limited life span for the resin.

Electrolysis

Electrolysis is one of the earliest methods used for chromium bath purification. In its simplist form, it consists of a plating cell with a large anode to cathode ratio (typically 30 to 1). Simple electrolysis or dummying, used to reoxidize Cr^{+3}, was employed over 40 years ago and is well documented (reference 10). Efforts to improve the process lead to the use of the porous ceramic pot which is perhaps today the most widely used method of chromium bath purification. The porous pot technology is designed to provide both the reoxidation of Cr^{+3} and the removal of foreign cation contaminants (reference

11). More recently, a membrane electrolysis technology has been commercialized (reference 12).

The purpose of the pot or the membrane is to separate the reactions and reaction products of the anolyte (plating bath) and catholyte (chromic acid or mineral acid). Catholyte solutions are usually chromic acid or sulfuric acid. Chromic acid is used with plating baths, since some catholyte is expected to migrate to the plating solution which cannot tolerate high sulfate concentrations. Sulfuric acid has been used as a catholyte in the purification of chromic acid etch baths (typically formulated with high sulfate).

Table 2. Analytical Results From Ion Exchange Case Study

Parameter	Untreated Bath, g/l	Treated Bath, g/l	Contaminant Removal, %
Chromic Acid	233	109	-
Sulfate	2.3	1.1	-
Iron	8.4	0.69	85
Nickel	2.23	0.11	90
Copper	6.03	0.29	90
Trivalent	6.90	0.17	95
Bath Vol.	500 gal	1050 gal	

Source: Reference 8.

When the porous pot is activated, the Cr^{+3} in the anolyte is reoxidized to the hexavalent state. The cations in the anolyte are electrically driven through the pores of the pot into the catholyte. Some cations are deposited on the cathode, most remain in solution. The chrome present in the catholyte is reduced to Cr^{+3}. As these changes occur, the effectiveness of the unit diminishes and eventually the catholyte is replaced. The frequency of catholyte replacement is usually in the range of 8 hrs. to 3 days.

Two basic design configurations exist for the porous pot technology. One type of unit consists of a tank holding 4 to 8 pots. Plating solution is pumped to the tank on a continuous basis and returned by gravity flow to the plating tank. The cells are powered by a rectifier (1,000 to 2,000 amps) dedicated to the purification unit. A second type of porous pot technology consists of a single pot which is suspended directly in the plating bath. This unit is powered by the tank rectifier and draws up to 240 amps. The advantage of the smaller unit is that it does not require redundant equipment needed by the larger unit, such as the rectifier, fume exhaust system, and an overhead hoist for removing pots. The disadvantages are its limited capacity and the fact that it only operates when the tank rectifier is energized.

The design and use of a porous pot unit was recently documented (reference 13). That system was applied to a chromic acid etch bath. Results from the study (table 3) indicate that the unit was relatively effective in reoxidizing Cr^{+3}, but was ineffective in removing metal contaminants. Further, the unit generates a significant volume of chromium bearing waste.

The membrane electrolysis unit, termed an ion transfer membrane technology, has been commercialized since 1982 (reference 12). The unit employes a separate tank and power source rather than using the plating equipment. Plating solution is circulated through the unit which contains an anode compartment and 10 cathode modules. When the unit is energized, bath cations pass through the membranes and deposit on the cathodes. The membrane is not anion or cation selective, the selectivity is a result of the electrical driving force. This fact distinguishes the technology from the more recently developed electrodialytic units.

Table 3. Operational Data of Porous Pot Technology

PARAMETER	ANOLYTE (220 GAL) mg/l	CATHOLYTE (24.4 GAL) mg/l
Cr^{+3}	26,000	700
Cr^{+6}	420,000	140
Cu	8,400	40
Ni	4,000	600
Fe	30	23
Pb	240	1.0
Sn	250	<1.0

Notes:
1. Source: Reference 13.
2. Catholyte analysis is after one week of operation which was the normal operating period between catholyte changes.
3. Conversion efficeicny of Cr^{+3} to Cr^{+6} was 80%.
4. Total metal removal was 0.14 lbs.

Electrodialysis

Electrodialysis is the newest of the chromium bath purification technologies. These units generally consist of: 1) a tank containing an anode and cathode compartment separated by a selective membrane, and 2) a power source. The membranes are ion specific in a manner similar to ion exchange resin. They only allow the passage of positive or negative ions, depending on the type of membrane. Cation specific membranes are used for chromic acid purification. When current is applied to the cell, cations present in the anolyte flow through the cation permeable membrane. The anions in the catholyte are restricted by the membrane and remain in that compartment. As with electrolysis units, Cr^{+3} ions present in the anolyte (plating bath) are reoxidized to the hexavalent state and are mostly retained in the anolyte.

Some electrodialytic units use an acidic catholyte solution. Cations flow through the permeable membrane and into the acidic catholyte. The electroplatable cations deposit on the cathode and the non-electroplatable cations stay in that solution as salts. The metals deposited on the cathode must be removed frequently to prevent burn through of the membrane. The cell voltage must be increased as salts build up in the solution to maintain the needed current density. Eventually, a maximum operational voltage is reached where the unit could be damaged by further increases. At this point, the catholyte solution is discarded and replaced and the cathode is cleaned. The operational period can be as short as one day if the cation concentration in the anolyte is high.

One manufacturer has overcome the capacity problem associated with early versions of electrodialytic purification units. The more advanced unit uses a caustic catholyte[1]. This catholyte converts multivalent metal cations entering the catholyte solution into insoluble hydroxides. The hydroxyl ions needed to react with the metal cations are formed at the cathode of the cell. Precipitation of the cations prevents a loss of conductivity and eliminates the build up of a deposit on the cathode. The operational period is extended to two or more weeks and there is no need to clean the cathode. This same unit has a unique design which packages the anode, membrane and cathode into a small cylinder which is placed directly into the plating bath, thereby reducing floor space requirements.

TECHNOLOGY SUMMARY

A comparison of the various bath purification technologies is presented in table 4.

With the exception of ion exchange, bath purification is a relatively slow process. Commercial purification units are not designed for a rapid clean up of highly contaminated baths. Such baths may have been building up impurities over a ten year or more period. Rather, these technologies are intended more for continous bath maintenance. Larger or multiple bath purification units could be used to hasten the processes. However, the large units have excessive capacity for maintenance of the bath and represent a large capital investment. If the user selects a maintenance unit a time period of up to six months or more may be required to reach a given taget level.

Table 4. Comparison of Bath Purification Technologies

TECHNOLOGY	STATE OF TECHNOLOGY	APPROXIMATE INSTALLED COST (1988 $)	WASTE PRODUCTS	OTHER
Ion Exchange	First used in 1952. Limited use today for Cr bath purification.	35,000	Concentrated waste containing mineral acid and chromium (regenerate) and dilute waste (rinsewater).	Relatively fast process. Limited use today because of high waste volume. Cost does not include treatment system for waste products.
Electrolysis				
Separate Tank System	Frequently used for larger solution volumes (>2,000 gal).	20,000	Large volume of concentrated waste. Chrome content depends on type of catholyte used (chromic or mineral acid).	Requires exhaust system to remove chromic acid mist. Requires overhead hoist to remove pots for cleaning. Labor intensive due to frequent changing of catholyte and cleaning of anodes.
Single Cell Unit	Widly used for hard chrome tanks <2,000	650	Same as separate tank system.	Limited capacity, large tanks would require numerous units. Labor intensive, requires daily catholyte changing for most applications. Uses tank rectifier rather than separate power source.
Membrane	First commercial unit in 1982.	16,000	Relatively small volume of acid used to clean cathodes.	Limited capacity.
Electrodialytic Acid Catholyte	Original design for electrodialitic technology. In use prior to 1980.	16,000	Generates acid waste. Some units tend to have chrome carry over to catholyte due to design problems.	Capacity is limited due to buildup of cations in catholyte and metal deposits on the cathode.
Caustic Catholyte	First commercial unit in operation in 1985. Recent increase in use.	14,000	Generates metal hydroxide waste similar to pretreatment systems.	Requires minimal labor for operation. Has high metal removal rate.

The selection of a bath purification unit should be based on: 1) a target level for contaminants (g/l); 2) a reasonable time period for reaching the target level (months); 3) an estimate of the contaminant build up rate (g/day); 4) a current analysis of the bath; and 5) the removal capacity of the technology. As will be shown in the next section, removal capacity is related to the concentration of cation contaminants in the bath.

Although not discussed previously in this paper, bath purification can be performed on a batch basis by a service firm. Ion exchange has already been used in this manner. Plating shops ship contaminated solution to a central service facility where the solution is purified, then returned. Such services are rare and new hazardous waste regulations are making operation of their service more difficult (e.g., manifest requirements, liability questions with regard to residuals disposal).

Future services should consider performing the purification process at the metal finisher's location. Such a service would employ a mobil treatment system. The technologies could be sized to perform purification in a short time period (e.g., 3 to 5 days). On-site service would eliminate the need to transport the chromium solution. Electrodialysis would be a viable technology for a purification service. Its major advantage over other technologies is the smaller volume of residuals generated.

TECHNOLOGY SELECTION FOR TESTING

Two technologies were selected for testing: 1) the single unit porous pot, and 2) the caustic catholyte electrodialytic unit. The porous pot was selected because it is presently the most widely used technology and therefore would provide a baseline for comparison. Furthermore, although this technology is widely used there are very little data available that characterize its performance. Therefore, testing would aid in establishing the potential of this technology. For the evaluation, a single pot configuration was chosen because it lends itself to testing on a small scale. The electrodialytic technology was selected because it is the newest technology. The caustic catholyte unit was chosen because of its operational and size advantages. Furthermore, the electrodialytic technology appears to have an advantage over ion exchange and other technologies with respect to residuals generation. This is especially true with regard to chromium waste. IX produces a significant chromium waste volume due to the fact that most trivalent chromium is removed from the bath and is lost in the waste product. The electrodialytic technologies convert most Cr^{+3} to Cr^{+6} rather than remove it.

TESTING

Test Procedures

Three sets of tests were conducted which ranged in duration from 11 to 16 days. In the first test, both the porous pot and electrodialytic units were evaluated. The results indicated a far superior performance by the electrodialytic unit and in the subsequent two tests only that unit was used.

The tests were performed using a contrived plating bath. The standard 100:1 (32 oz/gal CrO_3 , 0.32 oz/gal SO_4) hard chrome bath was formulated. Metals (copper and iron) were then dissolved in the solution to achieve the desired contaminant starting levels. During the first test, metal drums (55 gal) were used to hold the anolyte (plating solution). The operating volumes of the two units were: porous pot, 40 gal; electrodialytic, 45 gal. For the second and third tests a plastic tank was used which was fabricated from a 12 in. diameter PVC pipe. This tank provided a smaller operating volume (17 gal), and therefore shortened the testing period.

During testing, the technologies were operated according to manufacturer's instructions. The anolyte solutions were not heated although each technology generated sufficient heat to maintain a temperature in the range of 100 to 105 ^{o}F. The instructions of both technologies indicate that such conditions are permissible for operation.

The porous pot was operated at a voltage of 5.0 v with an initial corresponding current of 70 amps. The amperage diminished during operation. The porous pot instructions indicated that the catholyte (approximately 8.25 oz/gal CrO_3) should be changed when the amperage drop is 60%. This occurred after approximately 12 hours of operation throughout the testing period (i.e., changed twice per day). Whenever the porous pot catholyte was changed, the unit was disassembled, the cathode was removed and it was wire brushed to remove the metal deposits.

The electrodialytic unit was operated at 130 amps with a corresponding voltage of 4.5 v. During the first day of operation the amperage tended to increase and it was adjusted back to 130 amps. After the first day, no adjustments were necessary as the unit maintained the correct amperage. The electrodialytic catholyte was changed after two weeks of operation according to manufacturer's instructions.

Samples were taken from the anolyte tank on a daily basis and analyzed for the contaminant metals. Records were kept on the volume of waste catholyte generated. The waste catholyte was analyzed to determine the mass of lost chromium.

Test Results

The results of the daily anolyte analysis are shown graphically in figures 2, 3, and 4.

During the first test, the porous pot removed 0.58 lbs. of copper and the electrodialytic unit removed 2.82 lbs. of copper. The porous pot generated 15 gal of waste catholyte containing 7.7 lbs. of chrome. The electrodialytic unit generated 5 gal of metal hydroxides containing less than 0.01 lbs. of chome.

These initial results indicated that the porous pot would generate 13.3 lbs. of waste chrome for each pound of contaminant metal removed assuming a constant removal rate. Therefore, to treat the bath from say 10.4 g/l to 4.0

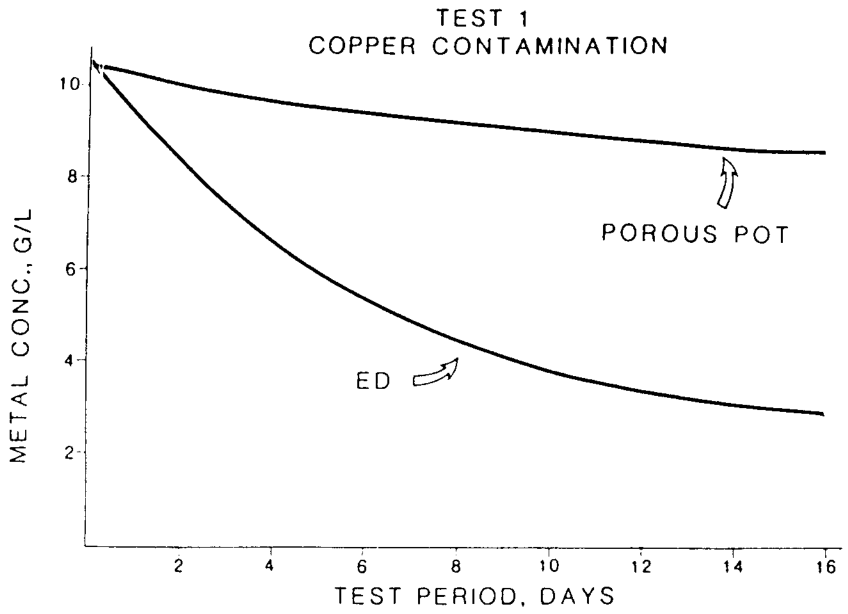

Figure 2. Reduction in metal concentration during purification (test 1).

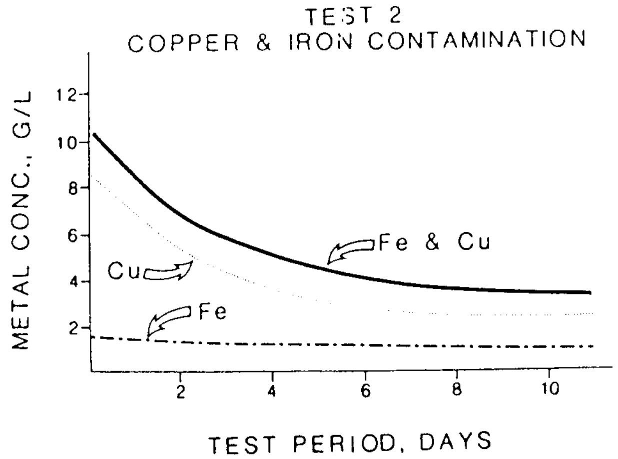

Figure 3. Reduction in metal concentration during purification (test 2).

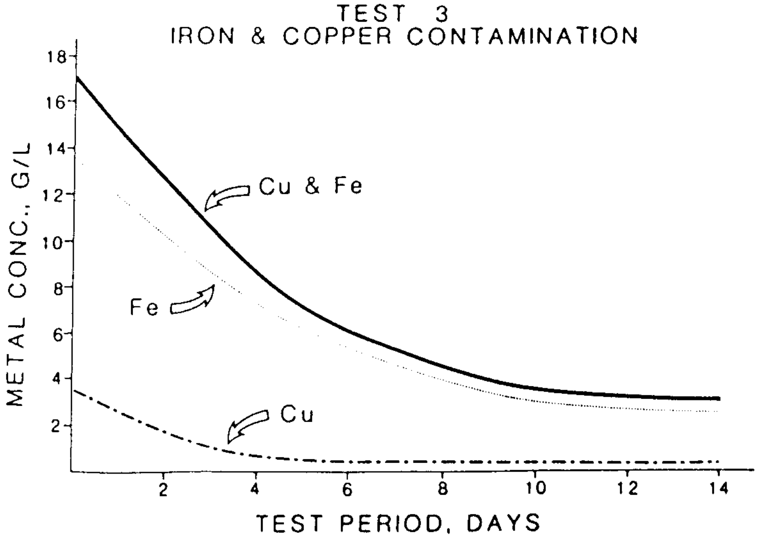

Figure 4. Reduction in metal concentration during purification (test 3).

g/l, the unit would generate 54.8 gal of waste containing 28.3 lbs. of chrome, while only removing 2.13 lbs. of metal contaminants. This assumes a linear removal rate which very much overstates the expected rate. More likely, the removal rate would diminish considerably as the concentration of the anolyte approached 4 g/l.

The initial bath contained only 82.5 lbs. of chromium (40 gal at 33 oz/gal). If decanting were used in place of the porous pot, 62% of the solution would need to be discarded to reach a 4.0 g/l target level. For a 40 gal bath, the decanted portion would be 24.8 gal containing 51.5 lbs. of chromium.

For the second and third test runs, both copper and iron removal were investigated. The second test run simulated a bath condition where copper is the major contaminant and iron is a minor contaminant. In the third test run, opposite conditions were investigated.

Data from each of the test runs show similar results for the electrodialytic unit. The removal rate of metal contaminants is initially high, then as the concentration of contaminants in the bath is reduced, the removal rate is lower. For example, in test 3 it took 0.38 days to reduce the combined concentration of iron and copper from 16 g/l to 15 g/l. From 11 g/l to 10 g/l it took 0.5 days and from 7 g/l to 6 g/l it took 0.88 days. This data emphasizes the need to consider a target level of contamination when sizing a bath purification process. Lower target levels will increase the capital cost of the system or extend the time needed to reach the target level.

Application of Results

It should be possible to apply these results to a full scale operation, since use of the electrodialytic unit is not effected by solution volume. The removal rate is only dependant on the concentration of contaminants and the current applied. For example, a plating bath with a volume of 500 gal (30 times greater than the volume used in tests 2 and 3) and similar contamination levels, would take 30 times longer to produce the same results. If the time period for purification is too long, then a higher amperage unit would be needed.

CASE STUDIES

Case studies for ion exchange and electrolysis (porous pot) were found in the literature and reported elsewhere in this report. The following are case studies, primarily of electrodialytic technologies, that are from shops familiar to the authors. The information and data were provided by technical individuals that worked directly with the purification units. These case studies were developed through interviews.

Generally, quantitative data were not available concerning performance or costs of the technologies. However, these experiences will be usefull to platers seeking relative comparisons of technologies.

Case Study 1

This facility is a job shop located in the Northeast. Both hard and decorative chrome are present. A standard chromic acid/sulfate bath is used with each process. The decorative process includes nickel/chrome deposites on brass. Two chrome tanks are used for decorative work (1,000 gal and 500 gal). Twenty hard chrome tanks (500 gal each) are present.

Prior to the enforcement of wastewater regulations, this shop made a policy decision to move toward zero discharge of chromium wastewaters. Recycling of rinsewaters was then performed, which resulted in an impurity buildup in the chromium baths.

The shop employed three different bath purification technologies: 1) dummying, 2) multicell porous pot, and 3) caustic catholyte electrodialysis.

Dummying was performed as a means of trivalent chromium oxidation. The process was marginally effective prior to the recycling efforts. Approximately 50 to 60 hours of electrolysis was needed to bring a 500 gal chromium bath back to usable condition. However, after recycling was instituted and bath impurity concentrations quickly increased, the ability to dummy the bath decreased and the process was eventually ineffective.

A caustic catholyte unit was installed on the hard chrome line approximately 18 months ago and has remained in operation. One additional unit has been installed on the hard chrome line and another on the decorative line. Use of the units has significantly improved plating quality. The catholyte solutions are changed every two weeks. The spent solutions are stored until a sufficient volume is accumulated, then they are pumped through a filter press to remove metal hydroxides.

Case Study 2

This facility is a job shop located in the Northeast. Various electroplating processes are used. All chromium plating is decorative. Chrome plating is performed in a 600 gal tank containing a mixed catalyst bath. The majoriety of the work is die castings, however, both steel and copper bearing alloys are also chrome plated. The estimated work load is 8,000 ft^2/day.

Plating quality problems were experienced due to cation buildup. The primary problem was lack of coverage in the low current density areas. A porous pot (4 cell unit) was used on a trial basis. This effort was abandoned due to operational and performance problems. A caustic catholyte electrodialytic unit was installed two years ago and remains in service. Testing was performed during the first six months of operation. The following analytical results were provided:

	Zn, g/l	Ni, g/l	Fe, g/l
Prior to Installation	18	10	2
After Six Months Operation	6	3	<.5

Plating problems due to cations have not reoccured since installation of the electrodialytic unit.

Some costs of operation were provided. Chemical costs were estimated to be $4 per week. Operational labor was estimated at 0.5 hr/week plus the time needed for sludge dewatering. The spent catholyte is dewatered on a filter press and the sludge is disposed along with wastewater treatment sludges.

Case Study 3

This facility is a captive shop which manufactures small engines. They operate a single 4,600 gal chrome bath for plating pistons. Approximately 16,000 pistons are plated per day. The bath is a standard chromic acid/sulfate solution.

The pistons are aluminum die castings. The plating process includes: zincate, watts nickel, and chrome plate. Prior to the use of bath purification, the aluminum concentration in the bath would increase to levels which caused a black burn on low current density areas. To minimize the problem, the shop would decant 50 percent of the bath to waste treatment every 6 months and replace it with fresh solution.

The firm installed two caustic catholyte electrodiaysis units (max. capacity 3,500 amps each) for bath purification. Analytical data collected over the first six months of operation have shown a decrease in aluminum contamination from 18.0 g/l to 8.3 g/l. Operational labor for the two units was estimated at 2 hrs/wk. The catholyte solution is changed each week. It is dumped to the floor drain, which conveys it to a batch treatment system that services the remainder of the shop.

Use of the bath purification technology has eliminated plating quality problems.

Case Study 4

Harper Thiel, Inc. is a job shop located in Wilmington, Delaware. There are six chrome tanks present; four hard chrome tanks and one copper etch. The baths range in volume from 90 to 1,700 gal. All solutions are formulated with chromic acid and sulfuric acid.

Harper Thiel instituted a policy of closed loop rinsing to help meet local discharge standards. After a period of 2.5 years the hard chrome baths reached unsatisfactory levels of iron (approximately 10 g/l). Problems associated with the high iron levels included peeling, pitting, and incomplete coverage. Approximately five years ago, an electrodialytic bath purification unit was purchased. The unit is able to maintain 1 to 3 g/l iron in the hard chrome baths.

Testing is performed at Harper Thiel to assure that the purified hard chrome baths are able to maintain a quality deposit. Recent hardness test data indicate an average hardness of approximately 1,000 K.H.N.

The electrodialytic unit has also been applied to the copper etch unit. That bath is formulated with 4 lb/gal chromic acid and 4 fl. oz./gal sulfuric acid. Use of the bath purification unit has allowed continuous use of the same bath for a period of five years, which previously was discarded on a regular basis. During that time period, seven 55 gal drums of cupric oxide/hydroxide have been recovered. Base on previous experience, it was estimated that the bath purification unit has saved 30,000 lbs. of chromic acid over a five year period.

The operating cost of the unit was estimated to be approximately $1,800 annually (includes labor, chemicals, electricity, and waste disposal).

Footnotes:

1. "Caustic" or Ionsep catholyte is covered in U.S. patents 4,325,792; 4,439,293; and 4,636,288.

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