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ELECTROWINNING/ELECTROSTRIPPING AND ELECTRODIALYSIS PROCESSES FOR THE RECOVERY AND RECYCLE OF METALS FROM PLATING RINSE SOLUTIONS

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ABSTRACT

Two electrochemical-based methods have been evaluated to remove heavy metals from a tin/zinc electroplating rinse solution with subsequent recycle of the metals back into the original plating bath. The first method uses electrodialysis to move tin to the anolyte strip solution as an anionic citrato complex while zinc is distributed to both the anolyte and catholyte,showing it exists as both an anionic citrato complex and in free cationic form. Zinc can be recovered by scraping the loose deposit from the cathode and dissolving it in mineral acid.

The second method is a combined electrowinning/ electrostripping technique. The process involves continuously flowing the plating rinse solution through a porous graphite cathode and removing the metal ions via electrodeposition. When a sufficient quantity of metal has been deposited, the electrode is placed in a solution whose chemical composition is similar to that of the original plating bath and the metals ions are stripped from the electrode anodically. The resulting solution is then placed into the original plating bath.

Both methods were used to treat a surrogate rinse solution originally containing 100-300 parts per million of each metal and were successful in reducing the metal-ion concentrations to less than 15 parts per million each. Approximately 70% of the tin and 100% of the zinc are recoverable by either method.

INTRODUCTION

Cadmium and chromium are often electrodeposited over base metals to provide corrosion protection and provide other desirable properties that the base metal itself may not possess. For example, the plated metal may have a different coefficient of friction that can provide better adhesion between conjugate parts such as nuts and bolts. However, due to the toxicity of these metals and the cost associated with treating spent baths and rinse solutions prior to disposal, alternate coatings are being sought as replacements. Unfortunately, no single element has all of the desirable physical properties of cadmium or chromium, so bimetallic coatings are under investigation. Development work has thus far focused on nickel-zinc, nickel-tungsten(1), and tin-zinc binary systems.

The bimetallic replacement plating baths and associated rinse solutions will also have to be treated prior to disposal in order to remove the metal ions down to an acceptable discharge level. The most desirable option would be to concentrate the metals from the rinse solution into a form that could be reintroduced into the plating bath, approaching a closed-loop system. Recycling the metal would simultaneously lower the cost of reagents associated with extending the life of the plating bath and the costs associated with disposal of waste metal ion.

Two methods to achieve this goal are being evaluated. The first method is electrodialysis, in which a standard three-compartment electrodialysis cell is used to transfer the metal ions from the rinse solution to strip solutions where they are collected in concentrated form. The second method is a combined electrowinning/electrostripping process. In this process the metal ions are deposited on a cathode; and, when the metal-ion concentrations in solution have been diminished to an acceptable level, the water is then discharged and the metals recovered from the cathode, if desired.

One shortcoming to the electrowinning process is the relatively low current efficiencies that are characteristic of trying to remove low concentrations of ions from large volumes of solution. In the constant-current mode, current flows whether or not there is a metal ion present near the electrode surface; so a large fraction of the current is wasted. There are two ways to improve the current efficiency and lower the cost of this process. First, use a porous, flow-through cathode so that metal ions are never far from the electrode even in relatively dilute solution. Thus, the probability for deposition is significantly increased. Second, use a constant applied potential rather than a constant applied current. In the constant-potential mode only species with a less negative redox potential than the applied potential will be deposited, so little current is wasted. A constant-potential power supply (potentiostat) is somewhat more expensive than a constant-current power supply, but long-term cost savings should be realized.

To recycle the metals into the plating bath, the metal-coated electrode can be contacted with fresh electrolyte and polarized anodically to strip the metals in concentrated form back into solution.

Experimental results of applying these two electrochemical-based techniques to the recovery and recycle of tin and zinc from a plating bath rinse solution are presented in this paper.

EXPERIMENTAL

A commercially available tin-zinc plating bath (DGV SZ-240, Dipsol Gumm Ventures, Kearney, NJ) was used in this study. To simulate a rinse solution, the original bath was diluted 100-to-1 with deionized water.

Electrodialysis experiments were carried out using a standard plate-and-frame cell with a 100-cm^2 electrode surface area (EC Electro MP-Cell), Model 730 power supply, seal-less magnetic drive solution pumps, and rotameters (Electrosynthesis Co., Inc., Amherst, NY). The cell was fitted with a stainless steel cathode and a platinized titanium anode. Tosflex(2) DF34 and Nafion(3) 350 were used as the anion and cation exchange membranes, respectively. Approximately 2 L of the rinse solution was fed into the central compartment; the anolyte and catholyte solutions were approximately 1 L, made 0.1 M in sodium sulfate to increase the conductivity. Samples were extracted for chemical analysis periodically from all three solutions during the run.

The electrowinning experiments were carried out in an apparatus specially designed to accommodate the porous graphite electrode. The apparatus consisted of a rectangular box with slots along the inside walls for placement of working and counter electrodes and a frame assembly that held a Nafion cation exchange membrane. The box had a solution entry port at the bottom of one end and an exit port at the upper part between the working electrode and the membrane cell divider. The solution had to flow through the porous graphite electrode in order to exit the cell. The working electrode compartment had a total volume of approximately 2.3 L, and the counter electrode compartment had an approximate 0.9-L volume. The experiments were carried out on a batch basis.

Deposition of the metal ions was attained potentiostatically (constant applied potential) rather than galvanostatically (constant current). This was done to assure a high current efficiency. An EG&G Princeton Applied Research Model 173 Potentiostat fitted with a Model 179 digital coulometer was used to power the cell and track the progress of the electrodeposition. A double-junction reference electrode was placed adjacent to the working electrode to constantly monitor the applied potential. The cell used a 6 in. x 6 in. x 0.5 in., 80-pores-per-inch, porous graphite working electrode (Energy Research and Generation, Inc., Oakland, CA) and a solid graphite anode. A 0.1 M solution of sulfuric acid was used as an electrolyte in the counter electrode compartment. After winning the metals onto the porous graphite electrode, the rinse solution was removed and replaced with a fresh electrolyte solution. A positive potential was then applied to the electrode to strip the metals back into solution.

Tin and zinc were analyzed by anodic stripping voltammetry (EG&G PAR Model 384B) in 0.5 M citrate buffer. Citrate was analyzed by ion chromatography (Dionex Series 4500).

RESULTS

Electrodialysis

The composition of the tin-zinc plating bath used in this study is given in Table 1.

Using literature values for the acid dissociation constants of citric acid(4) and the formation constants for tin-citrate(5) and zinc-citrate(6) complexes, we were able to calculate the distribution of species in the solution under the concentration conditions and pH given. The results of these calculations are shown in Figure 1. Within the operating range of the bath, essentially all of the metal ions in solution are in the bis-citrato complex form, $Sn(Cit)_2^{4-}$ and $Zn(Cit)_2^{4-}$. Any excess citrate exists as the trianion, Cit^{3-}, or the mono-protonated dianion, $HCit^{2-}$. The only cationic species in solution is ammonium ion added as ammonium citrate and ammonium sulfate.

During electrodialysis, the ammonium ion is expected to migrate to the cathode compartment, where hydroxide ion is being generated at the cathode, to produce ammonium hydroxide. All of the other ions are expected to migrate to the anode compartment. Protons generated at the anode would compete with the metal ions for the citrate, freeing up the metal ions and forming citric acid (see, for example, pH values less than 2 in Figure 1). By using anolyte and catholyte volumes approximately 100 times less than the feed rinse solution, one could theoretically concentrate the ions into the strip solutions, then mix them together to give essentially a solution of the same makeup as the original plating bath. Results of a typical electrodialysis run are shown in Table 2.

As expected, the tin and citrate migrated to the anolyte strip solution. However, only some of the zinc migrated to the anolyte; the rest migrated to the catholyte where it deposited on the cathode as a fine black powder. Apparently the zinc exists in solution in uncomplexed cationic form. Zinc forms a weaker complex with citrate than tin, and a small fraction of zinc ion in solution exists as the mono-citrato complex. But the mono-citrato complex also has a net anionic charge and still should not migrate to the catholyte.

TABLE 1. COMPOSITION OF TIN-ZINC PLATING BATH.

Component	g/L	Moles/L
Sn2+	10	0.084
Zn2+	10	0.15
Citrate	130	0.54-0.68
$(NH_4)_2SO_4$	100	0.76
Brightener	8 mL/L	
pH	6-7	

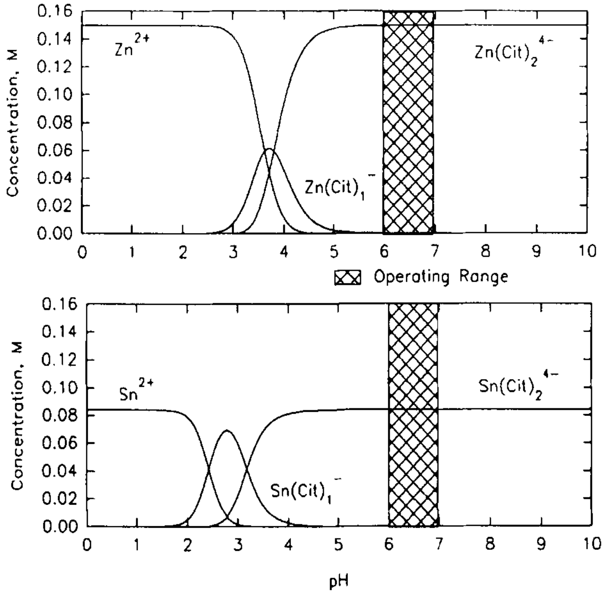

FIGURE 1. Distribution of species in original tin-zinc plating bath.

TABLE 2. RESULTS OF ELECTRODIALYSIS OF TIN-ZINC PLATING BATH RINSE SOLUTION

	Catholyte, 0.97 L		Feed, 1.97 L		Anolyte, 1.06 L	
Metal Ions	Sn	Zn	Sn	Zn	Sn	Zn
Initial Quantity, mg.	0	0	240	140	0	0
After 9400 Coulombs	0	90	100	40	140	10
pH	12.9		5.4		5.3	

The only plausible explanation for the results observed is that the citrate is more mobile than the larger metal-citrato complexes and is preferentially stripped from the feed solution. As the citrate concentration decreases, the metal-citrato complexes begin to dissociate. This equilibrium behavior for fixed metal-ion concentrations at varying citrate concentrations is shown in Figure 2.

The extreme right-hand side of the graph represents starting conditions for the rinse solution. There is a significant quantity of free citrate, and all metal ions exist as anionic citrato complexes. In moving to the left across the graph (i.e., as the total citrate concentration is decreased), free cationic zinc ion begins to appear rather soon and is the dominant species when approximately half of the citrate has been removed. However, because tin forms a much stronger series of complexes with citrate, a free cationic tin species does not dominate until almost 90% of the citrate has been removed.

In spite of the fact that the metal ions do not collect in the same strip solution, they are removed from the plating rinse solution. At the completion of the electrodialysis treatment the final concentration of each metal ion in the plating rinse solution is less than 15 ppm.

Electrowinning/Electrostripping

In order to use a constant-potential deposition mode, it is important to know the reduction potential of the ions in solution that are to be deposited. This is most easily

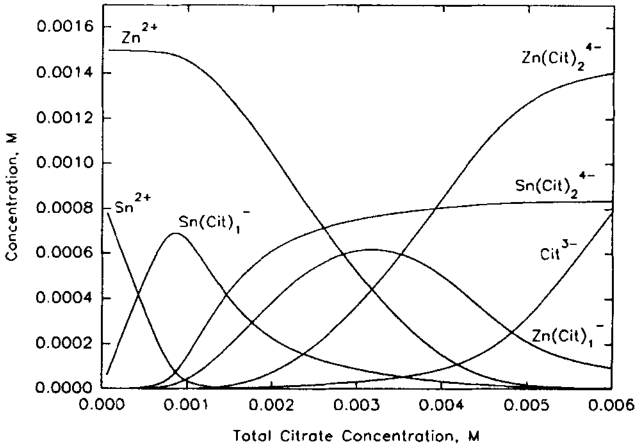

FIGURE 2. Distribution of species in 1:100-dilution plating bath as a function of total citrate concentration.

accomplished by cyclic voltammetry. In the presence of citrate the deposition of tin on graphite occurs at approximately -0.8 volts with a stripping wave close to -0.7 volts. The zinc deposition potential is very close to the cathodic solvent limit at approximately -1.3 volts with a corresponding stripping potential of -1.1 volt. Because the zinc deposition potential is so far negative it is impossible to deposit the metal at 100% current efficiency, even in the potentiostatic mode, due to simultaneous decomposition of water. Figure 3 shows the results of electrowinning zinc and tin from the plating rinse solution at an applied potential of -1.400 volts.

Interestingly, tin deposits first; and zinc deposits only after a significant fraction of the tin has been removed from the solution, even though the applied potential should be sufficient to deposit both metals simultaneously. Ultimately, both metals are deposited on the porous graphite cathode until the residual solution concentrations are less than 15 ppm.

Stripping the metals from the cathode back into solution was somewhat more difficult. Several different stripping solution compositions were investigated, but each met with only marginal success. The most desirable stripping solution would have been one with a

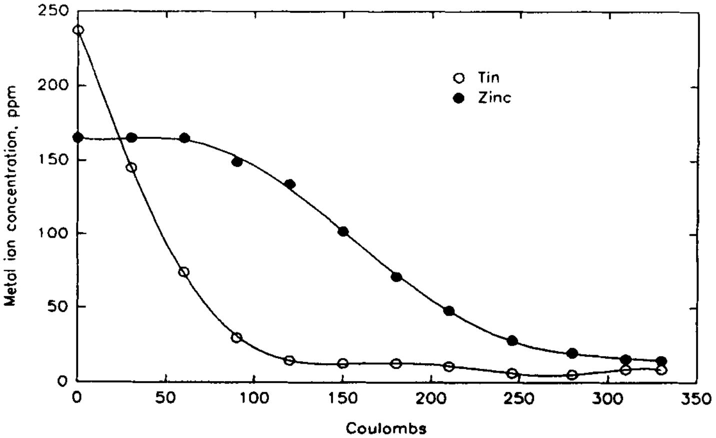

FIGURE 3. Concentration profile of tin and zinc in plating rinse solution during electrowinning as a function of total quantity of electricity passed.

composition similar to the plating bath. Then that solution could be added to the bath once the metals had been reintroduced during the stripping operation. However, while essentially all of the zinc was stripped back into solution by imposition of a positive potential, most of the tin remained on the electrode. The metallic coating turned a dull white color, suggesting the formation of tin oxide. More success at stripping the tin from the electrode occurred in acid rather than in neutral or basic media. For example in 0.5 M citrate adjusted to a pH of 3.0 all of the zinc and approximately 70% of the tin were reintroduced into solution. Following dissolution of the metals, adjustment of the solution pH to 6-7 with concentrated ammonium hydroxide would then yield a solution composition similar to that of the original plating bath. It is possible to redissolve all of the plated metals by soaking the graphite electrode in dilute mineral acid. But, that would add an additional ion to the bath which could ultimately shorten the bath life or alter the plating characteristics.

CONCLUSIONS

Both electrodialysis and electrowinning/electrostripping are viable methods for the removal and recycle of metals from a tin-zinc plating bath rinse solution. In the electrodialysis procedure, zinc powder that forms on the cathode must be scraped off and redissolved in dilute mineral acid before being recycled to the bath. The shortcoming of the electrowinning/electrostripping procedure lies in the electrostripping portion. Tin has a tendency to form an insoluble oxide on electrochemical oxidation rather than go into solution as a complex ion. However, both of the metals are won successfully from the solution down to an acceptable level, and at least 70% of the tin and 100% of the zinc can be recycled back to the original plating bath by using a slightly acidic stripping solution.

It is also possible to lower the metal ion concentration in the rinse solution to below 15 ppm by simply continuing either unit process for a longer period of time. But, because the intention is to use a closed-loop system, the steady-state concentrations of the metal ions in the rinse solution are not important as long as they are removed at approximately the same rate they are introduced during the rinse operation. This would allow the same rinse solution to be used continuously with minimal discharge to a wastewater treatment facility.

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REFERENCES

1. G. Purdy, C. Zawodzinski, B. Smith and W. H. Smith, Sep. Sci. and Tech., 30, (7-9), 1951 (1995).

2. Tosflex is a registered trademark of the Tosah Corporation, Tokyo, Japan.

3. Nafion is a registered trademark of E. I. du Pont de Nemours and Co.

4. L. Meites, ed., Handbook of Analytical Chemistry. McGraw-Hill Book Company, New York (1963).

5. T. D. Smith, J. Chem. Soc., Part II, 2145-2150 (1964).

6. T. Ya Vrublevskaya and O. P. Skovrinok, Zhur. Neorg. Khim., 34, 798-800 (1989).