Electrically Mediated Process For Functional Trivalent Chromium To Replace Hexavalent Chromium: Scale-up for Manufacturing Insertion

by R.P. Renz, J.J. Fortman, E.J. Taylor & M.E. Inman

This project work is investigating the various parameters affecting the plating of chromium from a trivalent chromium bath. Since the project is still active, this is an update on accomplishments to date involving the bath chemistry, diffusion layer and electrically mediated waveform parameters. This paper will report on the progress toward establishing a pilot-scale electroplating line for both shock absorber rods and pump augers. The pilot-scale line is a complete system, including waste management protocol relating to both air and effluent waste management considerations. The project is being funded by the U.S. EPA and a commercial partner.

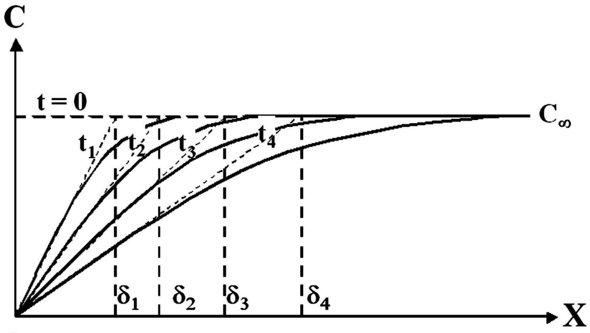


Fig. 2—Mass transfer in charge modulation by diffusion.

Chromium coatings are widely used in a variety of industries. Plating operations are used to fabricate two types of chromium coatings, functional and decorative. Functional chromium coatings consist of a thick layer of chromium [typically 1.3 to 760 μm (0.05 to 30 mil)[1]] to provide a surface with functional properties such as hardness, corrosion resistance, wear resistance and low coefficient of friction. Applications of functional chromium coatings include strut and shock absorber rods, hydraulic cylinders, crankshafts and industrial rolls. Carbon steel, cast iron, stainless steel, copper, aluminum and zinc are substrates commonly used with functional chromium. Decorative chromium coatings consist of a thin layer of chromium [typically 0.003 to 2.5 μm (0.12 to 98.4 μ-in.)[1]] to provide a bright surface with wear and tarnish resistance when plated over a nickel layer. It is used for plating automotive trim/bumpers, bath fixtures and small appliances.

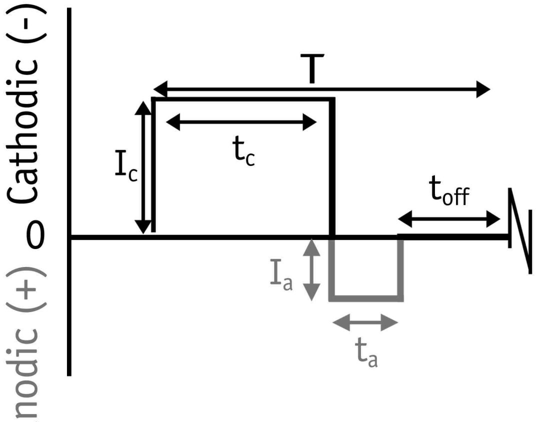


Fig. 1—Schematic of an electrically-mediated waveform.

Nuts & Bolts: What This Paper Means to You

Wouldn't it be great to plate hard chromium thicknesses with trivalent chemistry without excessive effort? This paper deals with just that. This paper is an update on work involving the bath chemistry, diffusion layer and electrically-mediated waveform (*i.e.,* non-DC) parameters. It also describes the development of a pilot-scale electroplating line for both shock absorber rods and pump augers. The pilot line is a complete system, including waste management protocol relating to both air and effluent waste management. This is an edited version of a paper presented at AESF SUR/FIN® 2002.

Hexavalent chromium (Cr(VI)) plating has been commercialized for many years. However, a Cr(VI) plating bath operates at an elevated temperature and produces a mist of chromic acid. Since worker exposure to (Cr(VI)) plating baths is regulated by OSHA, exhaust/scrubber systems must be installed for Cr(VI) plating operations and the exposure limit is 0.01 mg/m^3.[2] The Clean Air Act, as well as local constraints, regulates the emission of chromium to the air and water. Since Cr(VI) plating produces hazardous air emissions, all of the Cr(VI) platers must control and monitor the bath surface tension and report the results to the EPA. In contrast, trivalent chromium (Cr(III)) platers are not required to monitor bath surface tension.[2]

The USEPA has identified chromium as one of 17 "high-priority" toxic chemicals. The USEPA selected the high-priority chemicals based on their known health and

---

For additional information, contact:
Phillip Miller
Faraday Technology, Inc.
315 Huls Drive
Clayton, OH 45315
Phone: (937)-836-7749
FAX: (937)-836-9498

environmental effects, production volume and potential for exposure.[3] Under former USEPA administrator William K. Reilly's Industrial Toxic Program, the high-priority toxic chemicals were targeted for 50% reduction by 1995.[4]

The chemistry of chromium provides a basis for understanding the toxicology. Chromium can exist in oxidation states ranging from II to VI. However, only Cr(III) and Cr(VI) are stable enough to actually be used. Cr(VI) is readily reduced to the more stable Cr(III) and in this process, substances in contact with the Cr(VI) are oxidized. Cr(VI) compounds are very soluble compared to Cr(III) compounds. Therefore, in the environment, Cr(VI) is much more likely, on release into a stream or an aquifer, to dissolve and move with the flow. In fact, one method that has been used to stabilize Cr(VI) (make it less mobile) in the environment is to reduce it to Cr(III).[5]

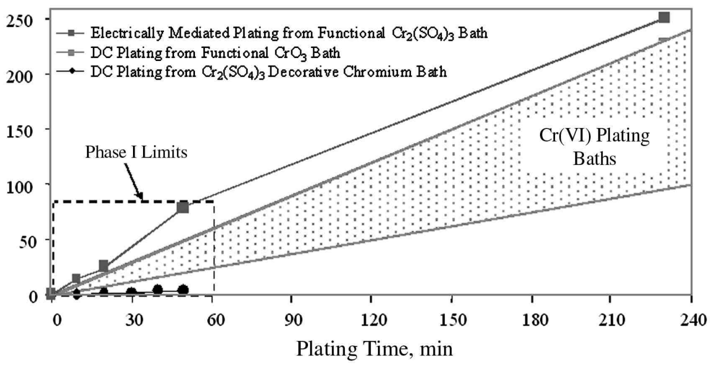


Fig. 3—Chromium plating thickness vs. plating time.

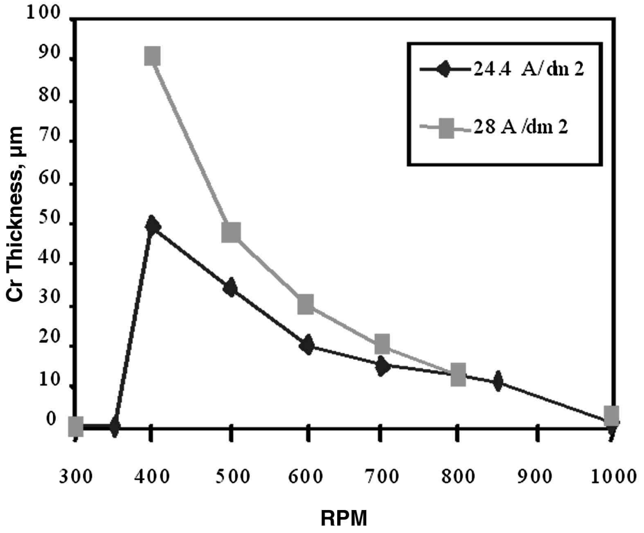


Fig. 4—Chromium thickness vs. RPM.

Cr(VI) is widely recognized as a human carcinogen. In a study recently published,[6] Cr(VI) was reported to cause increased incidences of lung cancer in a group of 2,357 workers at a chromate production plant. In the same study, the carcinogenic property of Cr(III) was also examined. The article reports, "Cumulative hexavalent chromium exposure was associated with an increased lung cancer risk; cumulative trivalent exposure was not." This study "offers the best quantitative evidence to date of the relationship between Cr(VI) and lung cancer." In previous studies, it was recognized that workers were exposed to a mixture of Cr(VI) and Cr(III). However, the relative contributions of each of the forms of chromium were not assessed. In the study cited here, the relative exposure levels were calculated and on the basis of their findings, the authors indicated that exposure of workers to Cr(III) did not result in an increase in lung cancer.

Another report has been published in the scientific literature that also implicates Cr(VI) as a human carcinogen.[7] This report states that the US Environmental Protection Agency has classified Cr(VI) as "a Group A known human carcinogen." This same publication states "Cr(III) is much less toxic and is recognized as an essential element in the human diet." EPA classifies Cr(III) as "a Group D carcinogen, not classifiable as to carcinogenicity in humans." The acute and chronic effects of exposure to Cr(VI) and Cr(III) are described in detail in this report.

In the case of the two forms of chromium, one can say that the chemistry and toxicology of each form is markedly different. Perhaps the most important facts to remember are that Cr(III) is rather insoluble and does not oxidize organic material. Cr(III) is poorly absorbed from the gastrointestinal tract and is not considered to be a carcinogen. Cr(VI) is very soluble, penetrates cell walls and is a human carcinogen. Cr(VI) is very reactive and causes ulceration of the nasal septum and other tissues upon exposure as well as reproductive, gastrointestinal and dermal effects. However, Cr(III) is not without toxic effects and should be handled appropriately. To put this last statement in perspective, aluminum, for example, is not without toxic effects. Aluminum is ubiquitous in our society today. Cooking utensils are formed from aluminum as are soda cans. Nevertheless, aluminum is, depending on the route of exposure and dose, potentially toxic.[8]

The use of Cr(III) in industrial and commercial processes is preferred over Cr(VI) on the basis of the comparison of the toxicities. Cr(III), like other metals (*e.g.*, aluminum) must be handled appropriately since each of these metals is at some dose and via at least one route of exposure, capable of causing harm to humans.[5]

From an environmental perspective, plating from additive-free Cr(III) has several advantages relative to Cr(VI):

1. Cr(III) is non-toxic, non-hazardous and is not an oxidizer. Therefore, meeting air quality regulations is easier and working conditions are greatly improved. The exposure limit for Cr(III) is an order of magnitude higher than that for Cr(VI).
2. Disposal costs are significantly reduced for Cr(III) plating. Hydroxide sludge generation is reduced ten to twenty times because Cr(III) generally operates at a Cr(III) content of about 4 to 20 g/L (0.53 to 2.67 oz/gal) vs. 150-300 g/L (20.0 to 40.0 oz/gal) for a Cr(VI) bath.
3. Since there are no proprietary additives in the Cr(III) bath, the rinse water may be recycled.

In addition, Cr(III) has the following technical advantages:

1. The Cr(III) plating bath is not sensitive to current interruptions.[9] Therefore, the innovative modulated reverse current approach used in this program is more suitable for Cr(III) plating than for Cr(VI) plating.
2. Drag-in of chloride and sulfate from any previous nickel plating operations into the Cr(III) process is tolerated.[10] In contrast, chloride and sulfate drag-in upset the catalyst balance in a Cr(VI) process.
3. Throwing power for Cr(III) plating, which is poor in a Cr(VI) bath, is good and similar to other metals such as copper.[10]

As described above, Cr(III) plating has numerous environmental, health and technical advantages relative to Cr(VI) plating. Considerable research has been done to study Cr(III) plating, including the effects of the plating bath chemistry on plating thickness, brightness, hardness and corrosion resistance[11-13] and the effect of current waveforms on chromium deposit structure, distribution, brightness and hardness.[14,15] By including proprietary

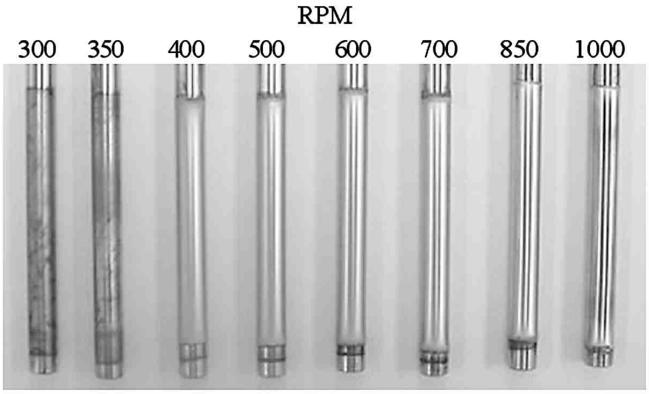


Fig. 5—Rods plated at 24.4 A/dm² (227 A/ft²) with rotational speed from 300 to 1000 RPM.

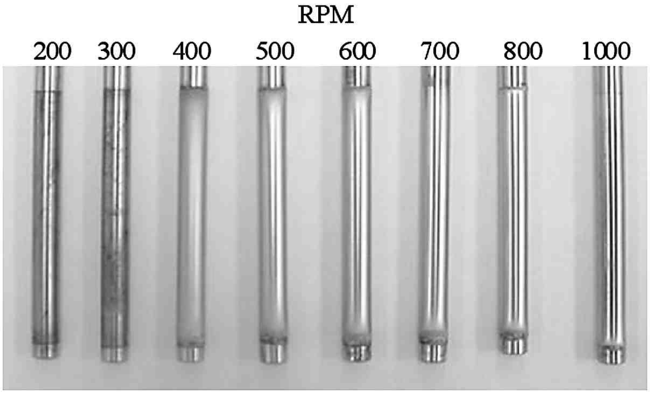


Fig. 6—Rods plated at 28.0 A/dm² (260 A/ft²) with rotational speed from 200 to 1000 RPM.

organic additives, Cr(III) plating baths are commercially available for decorative chromium coating applications. However, the additives are difficult to control because of their low concentration. Furthermore, the additives react and break down with time to form contaminants. Because of these contaminants, the used Cr(III) bath and rinse water cannot be replenished and recycled owing to the "drag-in" and buildup of these contaminants. Finally, decorative Cr(III) plating still suffers from low current efficiency.

Currently, functional chromium plating from a Cr(III) bath is not commercially available because of the difficulty of plating thick chromium coatings with the appropriate properties. In addition, the low current efficiency and low plating rate of Cr(III) baths lead to unfavorable economics. Because of the rapid drop in current efficiency, the practical limit for existing conventional DC Cr(III) plating is 2.5 μm (0.1 mil).[16] The plating thickness increases quickly at the beginning of the electroplating process. As plating continues, the deposition rate diminishes and becomes negligible.

Electrically-mediated Plating

During Cr(III) plating, chromium is deposited and hydrogen is evolved at the cathode, as described in the following reactions:

$$Cr^{+3} + 3e^{-} \rightarrow Cr\ (\phi^{o} = -0.74V_{SHE}) \qquad (1)$$

$$2H^{+} + 2e^{-} \rightarrow H_2\ (\phi^{o} = 0\ V_{SHE}) \qquad (2)$$

The current efficiency for chromium plating from a Cr(III) bath is usually below 20%. Therefore, about 80% of the current is used for the hydrogen evolution reaction. As a result, the pH near the cathode surface increases dramatically and chromic hydroxide ($K_{sp} = 5.4 \times 10^{-31}$) precipitates in the high pH layer at the cathode. The sedimentation of chromic hydroxide covers the cathode surface and its thickness increases as the plating time and pH increase. This promotes an increase of cathode polarization, a further decrease of chromium plating efficiency (*i.e.*, increase in the hydrogen evolution reaction) and the increase of impurities in the plating film. All of these factors retard the normal growth of crystals in the plating film, leading to the prevention of further plating of chromium. The evolution of hydrogen continues as the only reaction. The precipitation of chromic hydroxide at the cathode also results in surface cracks and reduces the hardness and brightness of the chromium coating. Our approach deals with overcoming this hydrogen evolution problem by utilizing electrically-mediated plating.

The basis of electrically mediated plating is a charge modulated electric field, shown in Fig. 1. Essentially, it consists of a cathodic (forward) current modulation followed by an anodic (reverse) current modulation and a relaxation period. The cathodic peak current is I_c and the cathodic on-time is t_c. The anodic peak current is I_a and the anodic on-time is t_a. The relaxation time is t_{off}. The sum of the cathodic on-time, anodic on-time, and relaxation time is the period of the modulation ($T = t_c + t_a + t_{off}$) and the inverse of the period of the modulation is the frequency of the modulation. The ratio of the cathodic on-time to the period (t_c/T) is *the cathodic duty cycle* (D_c) and the ratio of the anodic on-time to the period (t_a/T) is *the anodic duty cycle* (D_a).

The current densities during the cathodic on-time and anodic on-time are known as the *cathodic peak modulation current density* and *anodic peak modulation current density*, respectively. *The average current density* (i_{ave}) is the average cathodic current density (D_cI_c) minus the average anodic current density (D_aI_a).

Once the average current density (i_{ave}), modulation frequency (*f*), cathodic duty cycle (D_c), anodic duty cycle (D_a) and the cathodic-to-anodic charge ratio (Q_c/Q_a) are given, the cathodic and anodic on-time and relaxation time (t_c, t_a, and t_{off}) and cathodic and anodic peak current density (i_c and i_a) are determined from the following equations:

$$T = \frac{1}{f} \qquad (3)$$

$$D_c = \frac{t_c}{T} \qquad (4)$$

$$D_a = \frac{t_a}{T} \qquad (5)$$

$$\frac{Q_c}{Q_a} = \frac{i_c t_c}{i_a t_a} \qquad (6)$$

$$i_{ave} = i_c D_c - i_a D_a \qquad (7)$$

$$T = t_c + t_a + t_{off} \qquad (8)$$

Another condition is:

$$D_c + D_a \leq 1 \qquad (9)$$

It should be noted that the cathodic on-time, anodic on-time, relaxation time and the cathodic and anodic peak modulated current densities are additional parameters available to control the electroplating process as compared to conventional DC plating. In DC plating, the cathodic current is turned on and held for the duration of the plating process.

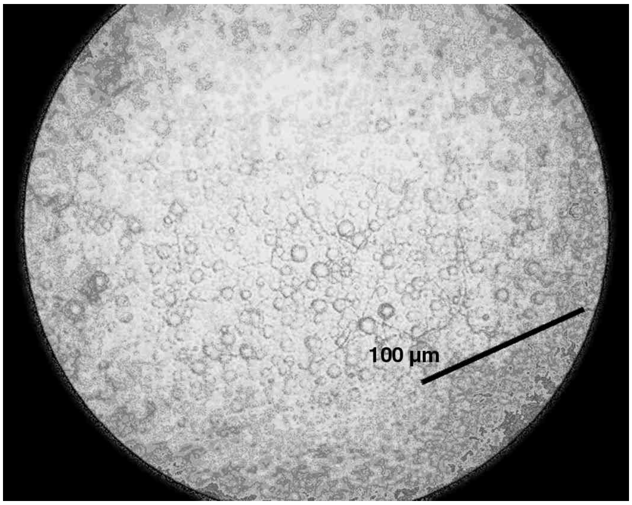


Fig. 7—Chromium surface after replate with short dry interval.

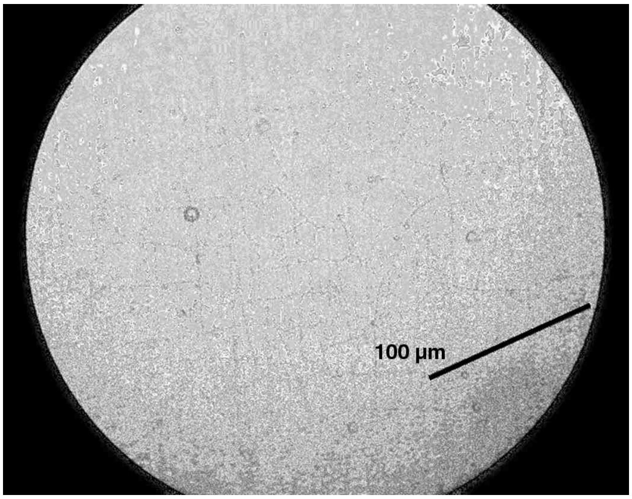


Fig. 8—Chromium surface after replate with 60-min dry interval.

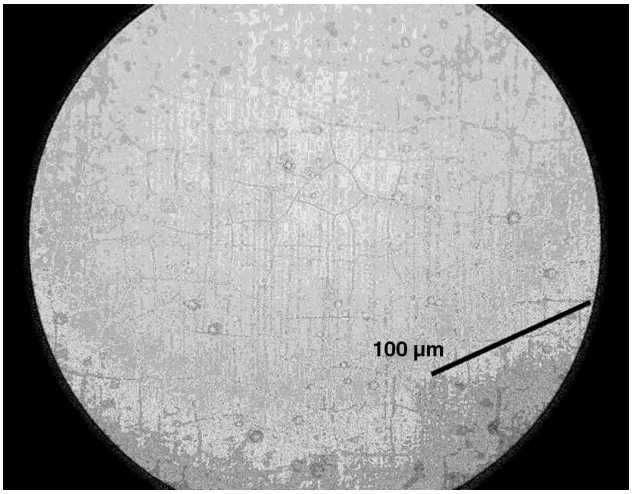


Fig. 9—Chromium surface after replate with overnight dry interval.

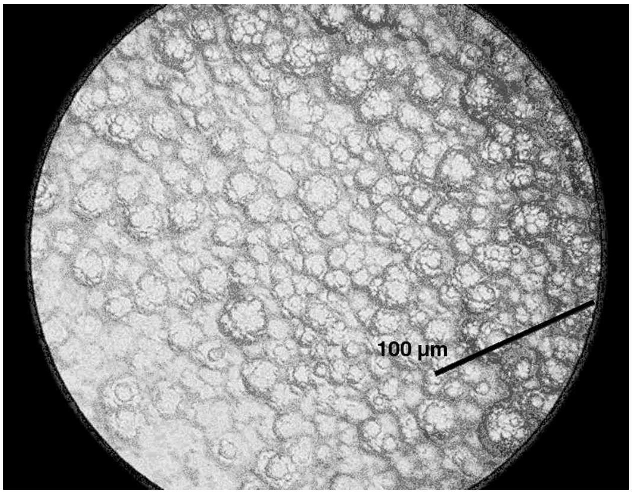


Fig. 10—Chromium surface after replate with polish.

For chromium plating from a Cr(III) bath, we use a cathodic modulation with either a long duty cycle or a large modulated current to deposit chromium, followed by an anodic modulation with either a short duty cycle or a small modulated current to convert the nascent hydrogen gas formed during the cathodic cycle to H^+, and a relaxation period to allow the Cr(III) ions to diffuse to the cathode surface and be available for subsequent deposition. During the cathodic portion of the modulation, chromium is deposited and hydrogen is evolved, analogous to conventional chromium plating. During the anodic portion of the modulation, we can selectively consume the nascent hydrogen according to the following reaction:

$$H_2 \rightarrow 2\ H^+ + 2e^- \tag{10}$$

In this manner, a low pH is maintained and chromic hydroxide precipitation is avoided. By properly adjusting the anodic and cathodic peak currents, the anodic and cathodic duty cycles and the frequency, nascent hydrogen can be consumed. In addition, we can constrain the above parameters so that the net plating rate for the Cr(III) process is equivalent to that currently used in the Cr(VI) process.

Elimination of Hydrogen

The evolution of hydrogen during a metal deposition process results in a low current efficiency and high power consumption. In addition, hydrogen evolution during metal deposition leads to hydrogen embrittlement of the substrate or hydrogen bubble inclusion in the metal deposit. This adversely affects the electrodeposit in terms of (1) low corrosion resistance, (2) poor adhesion to the substrate, (3) high internal stress and (4) excess porosity. By properly adjusting the electrically-mediated process parameters, one can alter the kinetics of both the metal deposition and hydrogen evolution reactions. While reaction kinetics can be modified using a process with a forward modulation only, hydrogen bubbles adsorbed on the electrode surface can be released during the off-time period. By adding an anodic modulation, one can “tune” the anodic or reverse part of the waveform to consume the nascent hydrogen according to the following reaction:

$$H_2 \rightarrow 2\ H^+ + 2e^- \tag{11}$$

In this manner, a low pH is maintained and chromic hydroxide precipitation is avoided. Furthermore, hydrogen is not permitted to diffuse into the substrate or be incorporated in the deposit. Finally, by compensating for the anodic current with an increased cathodic current, the overall electrodeposition rate is maintained and the net current efficiency is improved.

Mass Transfer

Unlike DC electrolysis, the mass transfer characteristics of charge modulation are a time dependent process. Charge modulation causes concentration fluctuations near the electrode surface and reduces the effective Nernst diffusion layer thickness.

Table
Relative Costs of Chromium

	Constituent	%Cr	$/kg	$/kg of Cr	$/lb.	$/lb. of Cr
#1	CrO_3	52.0%	$5.51	$10.60	$2.50	$4.81
#2	$CrCl_3 \times 6H_2O^*$	19.5%	$5.80	$29.72	$2.63	$13.48
#3	$Cr_2(SO_4)_3 \times 7.5H_2O^*$	19.7%	$1.54	$11.75	$0.70	$5.33

**$/lb. [or kg] /% chromium*

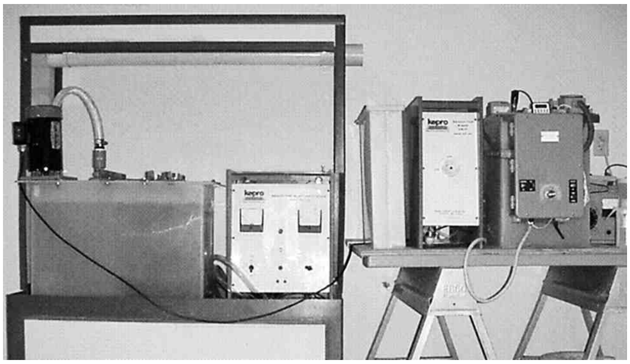


Fig. 11—Pilot line set-up.

Consequently, very high instantaneous limiting current densities can be obtained with electrically-mediated electrolysis as compared to DC electrolysis. To qualitatively illustrate how electrical mediation enhances the instantaneous mass transfer rate, consider the case of a single rectangular cathodic current modulation. Before the current is turned on, the concentration of the diffusing ion is equal to the bulk concentration, C_b. After the current is turned on, the concentration near the cathode drops and a diffusion layer builds up. Using the non-steady-state Fick's law of diffusion, this concentration profile as a function of the distance from the electrode surface, X, is depicted in Fig. 2. The corresponding thickness of the Nernst diffusion layer, δ, is also shown in Fig. 2 for various time periods. The mass transfer limited current density is related to the concentration gradient at the electrode surface and to the thickness of the Nernst diffusion layer by:

$$i = nFD[dC/dx]_{x=0} = - nFD[(C_b - C_s)/\delta] \qquad (12)$$

In steady state DC electrolysis, δ is a time-invariant quantity for given electrode geometry and hydrodynamics. This quantity is represented by δ_∞. In electrically-mediated electrolysis, however, δ varies from 0 at the beginning of a current modulation to a value of δ_∞ when the steady state Nernst diffusion layer is fully established. The corresponding diffusion current density would then be equal to an infinite value at $t = 0$ and decreases to a steady state value of the DC limiting current density at $t = t_\infty$. The advantage of electrically mediated electrolysis is that the current can be interrupted (*e.g.*, at $t = t_a$) before δ has a chance to reach the steady-state value. This allows the reacting ions to diffuse back to the electrode surface and replenish the surface concentration to its original value before the next current modulation. In this way, one obtains a diffusion-controlled modulated current density greater than the steady state limiting current density. This diffusion-controlled modulated current density can be made very large if one employs a current modulation of very short duration followed by very long relaxation time to permit the surface concentration to recover to the bulk value. Modeling work by Chin[17] indicates that limiting current densities obtained under the pulse reverse current (PRC) conditions of low duty cycle and high frequency, can be two to three orders of magnitude greater than the DC limiting current density. Vilambi and Chin[18] confirmed the earlier modeling work with experimental studies for a copper sulfate bath for selected pulse periods and duty cycles in PRC electrolysis. They reported peak current densities as high as several hundred A/cm^2 for PRC electrolysis, while the corresponding values for DC electrolysis were less than 1.0 A/cm^2.

Prior Work

In previously reported work,[19,20] we accomplished the following milestones:

- *Plated from a trivalent chromium sulfate bath where the consumable was in the price range of chromic acid.*

We are continuing the development of a trivalent chromium plating process, using chromium sulfate as the consumable. In earlier work we used a chromium chloride bath but the consumable, chromium chloride was much more expensive than chromium sulfate. Using chromium sulfate brings the cost of the consumable into the range of chromic acid currently in wide use for producing chromium deposits. The table illustrates the relative costs of chromic acid, chromium chloride, and chromium sulfate.

- Simplified bath chemistry using an electrically mediated waveform.

During our prior work, we realized that the bath chemistry was not understood, so we directed initial efforts toward modifying the plating bath components and understanding their purpose. This led to simplifying the bath. To understand the effects of the bath components, we used a rotating electrode set-up to accurately control the diffusion layer. The bath components originally consisted of:

1. Chromium sulfate
2. Chromium potassium sulfate
3. Ammonium sulfamate
4. Ammonium sulfate
5. Boric acid
6. Formic acid
7. Potassium hydroxide
8. Surfactant

Potassium hydroxide was used to adjust the pH of the bath to 2.5 and a surfactant was used to lower the surface tension. ϕ9.525 mm hardened and ground steel rods were used for the substrate and a nickel strike was applied before chromium plating to enhance adhesion. Since we were still adjusting the bath chemistry, we held the electrically-mediated process parameters to small variations necessary to achieve smooth surfaces and adequate deposition rates. The following parameters were used:

1.Current density: 25-35 A/dm^2 (232-325 A/ft^2)
2.Cathodic duty cycle: 80-90%
3.Anodic duty cycle: 3-5%
4.Charge ratio: 20-40
5.Diffusion layer thickness: 38 μm (1.5 mil)
6.Temperature: 25-35°C (77-95°F)

Originally, either a thermal treatment or dummying with a nickel-plated part was used to produce divalent chromium in the bath needed to initiate plating. However, we are now using chromium chloride ($CrCl_2$) to serve the same purpose. This considerably shortened the bath preparation time and quantified the amount of Cr(II) in the bath before plating. We soon realized that chromium potassium sulfate was not necessary for good deposits and it has been removed as a component. It may have been in the original bath to increase the ionic strength of the bath. Ammonium sulfamate was also eliminated.

- *Increased chromium plating thickness to 250 µm (9.84 mil).*
- *Maintained plating rate similar to hexavalent chromium.*

In our earlier efforts we were limited to approximately 75-μm (3-mil) thick deposits as shown in Fig. 3. However, in this work, we have achieved 250-μm (10-mil) thick deposits. Also, the plating rate is similar to the rate used in hexavalent chromium plating.

- Determined maximum diffusion layer thickness for plating from trivalent chromium sulfate bath.
- Determined acceptable range for achieving bright plating.

Rotating rod tests were run to determine the effect of rotation speed (RPM), and the corresponding diffusion layer, on the plating rate and appearance. The rotation rate had a definite effect on the deposition rate at any speed less than 400 RPM failing to deposit chromium. However, the highest deposition rate also occurred at 400 RPM, corresponding to a diffusion layer thickness of 44 μm (1.7 mil). As expected, the higher current density produced a slightly higher deposition rate but the surface was dull at 400 RPM and 28.0 A/dm^2 (260 A/ft^2). However, the deposit, at these conditions, tended to be irregular (rough, dull) indicating that the current density was too high for the other parameters. As the rotation speed increased, the deposit became brighter and thinner. This “bright” range is the acceptable area of deposition. As the rotation speed approached 1000 RPM, the thickness decreased to a flash of chromium. Figure 4 illustrates the effect of rotational speed at two current densities. Figures 5 and 6 show the appearance of the rods at current densities of 24.4 and 28.0 A/dm^2 (227 and 260 A/ft^2), respectively.

Experimental

Replating Chromium on Chromium

In the process of running the experiments, we found it useful to be able to continue to plate on previously plated surfaces. This is necessary if the part needs to be examined during plating, interruptions occur during the plating cycle or the smoothness of the surface needs to be maintained. In order to do this we ran several experiments that interrupted the plating sequence. For each experiment new ϕ9.525 mm rods were cleaned in an alkaline cleaner and plated with a thin layer of nickel in a nickel strike bath to improve adhesion. In the first experiment we plated a rod for 20 minutes generating a plating thickness of 17 μm (0.67 mil). After rinsing, we allowed the surface to dry. When the rod was dry, it was returned to the chromium plating bath where plating continued for an additional 20 minutes producing an additional 17 μm (0.67 mil) of chromium. The surface is shown in Fig. 7. The surface was somewhat rougher than normal since the plating bath had been rejuvenated. In the second experiment we allowed the rod to dry for 60 minutes after rinsing. A fresher bath was used that produced a smoother surface. Each plating cycle produced 17 μm (0.67 mil). The surface is shown in Fig. 8. The third experiment had an overnight dry interval between the chromium plating cycles. However, there were some circular depressions on the surface that extended down to the first plated surface. They appeared to be small areas where gas evolved preventing the further deposition of chromium. The surface is shown in Fig. 9. The as-plated crack pattern is clearly apparent in Fig. 8 and 9. A surface was then plated for 8 hr to 200 μm (7.9 mil) and polished back to ~100 μm (3.9 mil). Following an alkaline clean and rinse, it was then replated for an additional 8 hr to a total thickness of 375 μm (14.8 mil) with good adhesion. This surface is shown in Fig. 10. We have encountered no problems in replating chromium over chromium using our process.

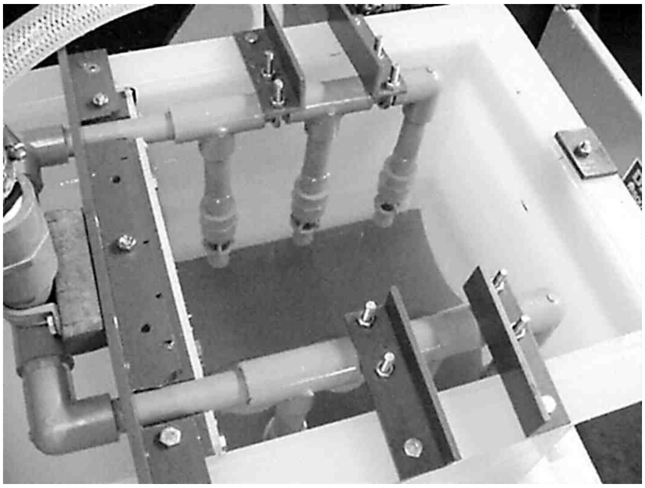


Fig. 12—Top view of plating tank.

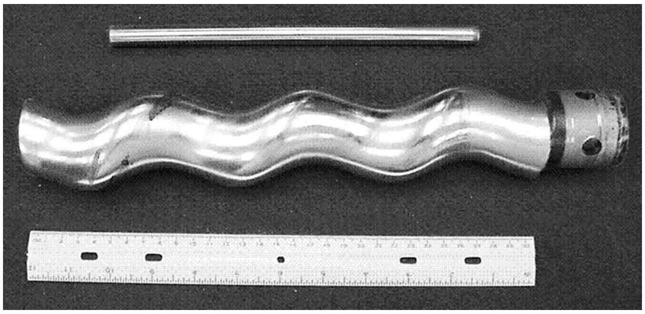


Fig. 13—Parts to be chromium-plated.

Pilot Line Scale-Up

In order to plate actual production parts using our trivalent chromium process we are constructing a plating set-up to accommodate shock absorber rods and a pump auger. The set-up is still under construction. When it is complete, we will be able to demonstrate trivalent chromium plating that will be evaluated by vendors using their standard qualification tests used to verify their production capabilities. Figure 11 shows the pilot line set-up. From left to right is the chromium plating tank, the nickel strike tank, the stagnant rinse tank, the spray rinse tank and the alkaline clean tank. The stagnant rinse tank will be connected to an electrolytic ion-exchange cell to purify the rinse water. An air quality monitor will be used to measure the air quality over the chromium plating tank.

The plating tank contains a pump and eductor to provide uniform flow past the work surfaces. Figure 12 is an overhead view of the chromium plating tank showing the eductors that move the solution downward where it is deflected up past the work that will be placed in the center of the tank. Shock absorber rods and pump augers, shown in Fig. 13, will be chromium-plated and then evaluated by standard tests performed on production parts at their respective vendors.

Conclusions

In summary, we are still varying the bath components to determine their effects on the deposit. However, we have established the following:

- Chromium deposited from a trivalent process can be interrupted and continued successfully.
- A pilot-line plating set-up is being constructed to plate parts currently used in production to allow commercial evaluation.

Acknowledgement

This study is being supported by the U.S. Environmental Protection Agency Contract 68-D-00-274 and private sources. Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through Contract Number Contract 68-D-00-274 to Faraday Technology, Inc., it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

The authors acknowledge the efforts of P. Miller for technical editing of the manuscript. The financial support of Faraday Technology, Inc. corporate R&D is also gratefully acknowledged.

References

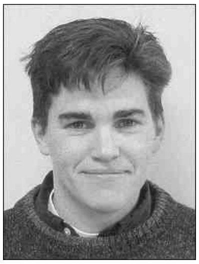
1. F. Altmayer, *Plating and Surface Finishing*, **82**, 26 (February 1995).
2. L. Banker, *Proc. 16th AESF/EPA Conference*, AESF, Orlando, FL, 1995.
3. L.R. Ember, *Chemical and Engineering News*, February 18, 1991.
4. D.J. Hanson, *Chemical and Engineering News*, June 3, 1991.
5. M.L. Taylor, "Comments Regarding the Chemistry and Health Effects of Chromium (VI) vs. Chromium (III)", Private Research Report, June (2001).
6. H.J. Gibb, P.S.J. Jones, P.F. Pinsky & B.C. Rooney, *American Journal of Industrial Medicine*, **38**, 115 (2000).
7. EPA-453/R-99-007, "National Air Toxics Program: the Integrated Urban Strategy, Report to Congress," Office of Air Quality Planning and Standards, Research Triangle Park, NC, July 2000.
8. "Occupational Safety and Health Guideline for Aluminum," Occupational Safety and Health Administration, U.S. Department of Labor.
9. G.E. Shahin, *Plating and Surface Finishing*, **79**, 19, (August 1992).
10. D.L. Snyder, *Products Finishing*, 61 (August 1989).
11. G. Scott, US Patent 5,196,109, (1991).
12. M. Constantin, E. Grunwald, C. Varhely, & C. Juhos, *Galvanotechnik*, **82**(11), 3819 (1991).
13. J.-Y. Hwang, *Plating and Surface Finishing*, **78**, 118 (May 1991).
14. Z.-M. Tu, Z.-L. Yang, & J.-S. Zhang, *Plating and Surface Finishing*, **77**, 55 (October 1990).
15. J. Dash, J. Jin, & L. Hotchkiss, *Proc. AESF Annual Tech. Conf.*, **78**, 947 (1991).
16. Z.-M. Tu, Z.-L. Yang, J.-S. Zhang, M.-Z. An, & W.-L. Li, *Plating and Surface Finishing*, **80**, 79 (November 1993).
17. D.-T. Chin, *J. Electrochem. Soc.*, **130**, 1657 (1983).
18. N.R.K. Vilambi & D.-T. Chin, *Plating and Surface Finishing*, **75**, 67 (1988).
19. R.P. Renz, J.J. Fortman, E.J. Taylor, & M.E. Inman, *Proc. AESF SUR/FIN 2001*, AESF, Orlando, FL, 2001.
20. R.P. Renz, J.J. Fortman, E.J. Taylor, & M.E. Inman, *Proc. AESF Week 2002*, AESF, Orlando, FL, 2002.

About the Authors

Robert Renz, P.E., CEF is the engineering manager at Faraday Technology, Inc. He has published numerous papers and holds several U.S. patents, with several more pending. Renz received his BS degree in metallurgical engineering from the University of Cincinnati. He has nearly 30 years of industrial metal finishing and waste treatment experience prior to joining Faraday. Renz's experience at General Motors Corp., Delphi Chassis Division includes chromium plating, tin plating, and zinc phosphating. He serves as a member of AESF's Hard Chromium Plating Committee.

Dr. John Fortman is employed at Faraday in a capacity as a senior chemistry advisor. He is a retired professor and Associate Chair of Chemistry from Wright State University in Dayton, OH, where he taught all levels of freshman chemistry as well as senior inorganic chemistry for 30 years. He has more than 80 publications and more than 100 technical presentations. He received his BS from the University of Dayton, and his PhD in physical inorganic chemistry from the University of Notre Dame. He had a part-time appointment at the Aerospace Research Labs at Wright Patterson Air Force Base from 1966 to 1970, and was a visiting associate professor at Purdue in 1973-74. He has worked on a variety of topics, including ion exchange separations, spray deposition of cathodoluminescent materials for clear thin coatings on glass, and electronics structures of metal complexes.

Dr. E. Jennings Taylor is the chief technical officer at Faraday. He founded the company to develop and commercialize innovative electrochemical technology using sophisticated charge-modulated electric fields. The company's intellectual property has been successfully transferred both to government agencies and large manufacturers in the form of process engineering technology and products. He holds a BA in chemistry from Wittenberg University, an MA in technology strategy and policy from Boston University, and MS and PhD degrees in materials science from the University of Virginia. He has published more than 70 technical papers and articles and holds 11 patents. He serves on the AESF Pulsed Electrodeposition Processes Committee and is chairman of the Research Board.



Dr. Maria E. Inman is the research manager at Faraday Technology, Inc., where she supervises all R&D activities. She holds a BE (Hons.) in metallurgical and materials engineering and a PhD in materials engineering from the University of Auckland, New Zealand. Prior to joining Faraday Technology, she completed a two-year term as a post-doctoral research associate at the Center for Electrochemical Science and Engineering at the University of Virginia. She is a member of NACE, AESF and the Electrochemical Society. She is co-inventor on several patent applications and is the author of numerous technical publications.