A Functional Trivalent Chromium Process to Replace Hexavalent Chromium Plating

R.P. Renz, CEF, J.J. Fortman, Ph.D., E.J. Taylor, Ph.D., & M.E. Inman, Ph.D.
Faraday Technology, Inc.,
315 Huls Drive,
Clayton, OH 45315

This project is investigating the various parameters affecting the plating of chromium from a trivalent chromium bath using electrical mediation. Since the project is still active, this is an update on our accomplishments to date involving the bath chemistry, diffusion layer, and charge modulated reverse electric field waveforms. This paper will report on the progress toward scaling up to a pilot-scale electroplating line for both shock absorber rods and pump rotors. Project includes 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.

For more information, contact:

Phillip Miller
Faraday Technology, Inc.
315 Huls Drive
Clayton, OH. 45315

Phone: (937)-836-7749
FAX: (937)-836-9498

Introduction

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, Altmayer, 1995) 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, Altmayer, 1995) 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.

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 (Banker, 1995). 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 (Banker, 1995).

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 environmental effects, production volume, and potential for exposure (Ember, 1991). Under former USEPA administrator William K. Reilly's Industrial Toxic Program, the high-priority toxic chemicals were targeted for 50% reduction by 1995 (Hanson, 1991).

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, upon 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) (Taylor, 2001).

Cr(VI) is widely recognized as a human carcinogen. In a study recently published (Gibb, 2000), 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 above, the relative exposure levels were calculated and on the basis of their findings, the authors have 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 (EPA, 2000). 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 the EPA report cited in this paragraph.

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. Although aluminum is ubiquitous in our society today - cooking utensils are formed from aluminum, soda cans are formed from aluminum; but aluminum is, depending on the route of exposure and dose, potentially toxic (Occupational Safety and Health Guideline for Aluminum).

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 the human (Taylor, 2001).

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 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 4-20 g/liter vs. 150-300 g/liter 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 (Shahin, 1992). 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 (Snyder, 1989). 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 (Snyder, 1989).

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

(Scott, 1991; Constantin et al., 1991; Hwang, 1991) and the effect of current waveforms on chromium deposit structure, distribution, brightness, and hardness (Tu et al., 1990; Dash et al., 1991). By including proprietary organic additives, Cr(III) plating baths are commercially available (though not widely used) for decorative chromium coating applications. However, the additives are difficult to control because of their low concentration. Furthermore, the additives react and breakdown with time to form contaminants. Due to these contaminants, the used Cr(III) bath and rinse water cannot be replenished and recycled due 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 to plate 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. Due to the rapid drop in current efficiency, the practical limit for existing conventional DC Cr(III) plating is 2.5 μm (Tu et al., 1993). 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:

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

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

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 x 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 hydrogen evolution reaction), and the increase of impurities in the plating film. All 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. Faraday's 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 Figure 1. It essentially 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).

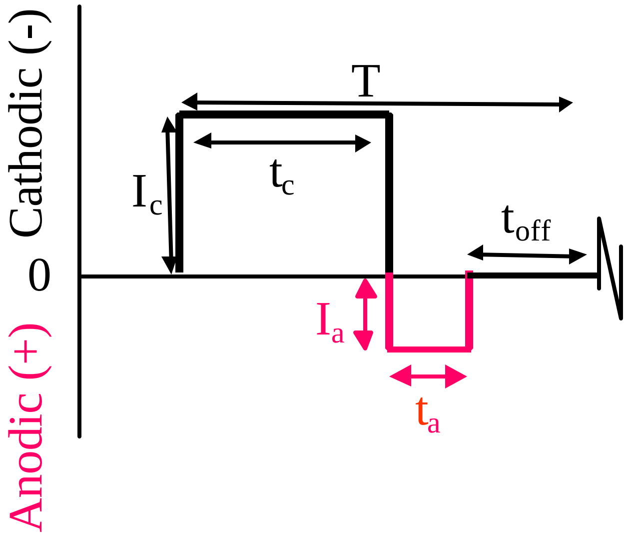

Figure 1: Schematic of an Electrically Mediated Waveform.

The current density during the cathodic on-time and anodic on-time is 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_o) and cathodic and anodic peak current density (i_c and i_a) are determined from the following equations:

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

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

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

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

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

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

Another condition is:

$$D_c + D_a \le 1 \quad (9)$$

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 compared to conventionally used DC plating. In DC plating, the cathodic current is turned on and held for the duration of the plating process.

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:

$$H_2 \rightarrow 2\ H^+ + 2e^- \qquad (10)$$

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 our 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 in 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:

$$H_2 \rightarrow 2\ H^+ + 2e^- \qquad (11)$$

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. 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 Figure 2. The corresponding thickness of the Nernst diffusion layer, δ, is also shown in Figure 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 (1983) has indicated 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 (1988) 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 A/cm^2.

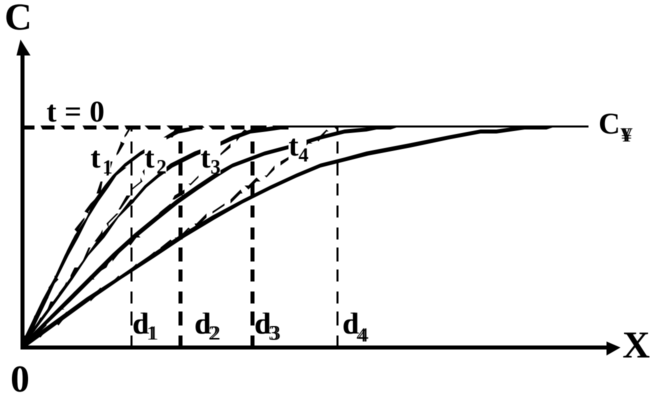

Figure 2: Mass Transfer in Charge Modulation by Diffusion.

Prior Work

In previously reported work we accomplished the following milestones:

- Plated from a trivalent chromium sulfate bath where the consumable was in the price range of chromic acid, (Renz, 2001).
- Simplified bath chemistry using an electrically mediated waveform, (Renz, 2001).
- Increased chromium plating thickness to 250 µm, (Renz, 2001).
- Maintained plating rate similar to hexavalent chromium, (Renz, 2001).
- Determined maximum diffusion layer thickness for plating from trivalent chromium sulfate bath, (Renz, 2002).
- Determined acceptable range for achieving bright plating, (Renz, 2002).
- Replated chromium on chromium, (Renz, 2002).

Experimental

University of Dayton Research Institute Test Results

Coupons plated with chromium (~300-375 µm) from our trivalent chromium process were submitted to UDRI for corrosion resistance tests comparing them to coupons coated with materials applied using a laser coating process. The substrate materials were 4150 alloy steel and stainless steel. The laser-generated coatings were Laser Clad Versalloy 50 (“C”), Laser Glazed Flame Sprayed Chrome Carbide (“CRC”), Laser Glazed Flame Sprayed Versalloy 50 (“V”), and Laser Glazed Flame Sprayed Tungsten Carbide/Cobalt, and Versalloy 50 (“WV”) in a (50/50) weight percent mix. Corrosion testing was performed in accordance with ASTM B-117. An exposure time of 240 hours (10 days) was selected because it is a typical standard pass/fail exposure time used to qualify chromium plating. No intermediate inspections were required, so the samples were run for the full 240-hour cycle without interruption. The samples were examined upon removal and compared to the chromium plated samples to evaluate their relative corrosion resistance. The stainless steel chromium plated samples showed no attack. The 4150 alloy steel chromium plated samples corroded only in the exposed areas of the substrate. The chromium plated areas showed no signs of attack. The stainless steel samples with “C” coatings showed no corrosion of the substrate. However, pits in the coating were attacked. The 4150 alloy steel “C” coating sample showed corrosion only in pitted areas of the coating. The stainless steel samples with “CRC” coatings showed corrosion in the coating in pitted areas and at the interface between the treated and non-treated areas with no substrate corrosion. The 4150 alloy steel sample with the “CRC” coating showed corrosion in the treated areas of the coating containing pits. The stainless steel samples with “V” coatings showed corrosion in the coating in cracked areas with no substrate corrosion. The 4150 alloy steel sample with the “V” coating showed substrate corrosion at coating cracks. The stainless steel samples with “WV” coatings showed mild corrosion in the coating with no substrate corrosion. The 4150 alloy steel sample with the “WV” coating showed some discoloration in the non-treated areas on the coating.

In summary, the chromium plating and the underlying substrate did not appear to be affected by exposure to the salt spray. The “C” coatings generally held up well except for some corrosion observed in pitted areas of the treated coating. The “CRC” coatings showed no corrosion problems except for pitted areas in the laser treated coating area of the 4150 substrate sample and corrosion of the non-treated area on the 416 substrate sample. The “V” coating samples all showed corrosion in cracked and pitted areas of the laser treated coated areas and discoloration in the non-treated areas. The 416 substrate sample showed a severe attack in both the treated and non-treated areas pf the coating. The "WV" coatings showed some corrosion in cracked areas in the laser treated coating and/or the interface between the treated and non-treated coating areas.

In addition to the corrosion resistance of the laser processes not being so good as the chromium plated samples, the laser process affected the substrate material due to the high temperatures encountered during processing. Process temperatures during the chromium plating process were limited to the cleaner temperature (~70°C, the highest temperature), which is too low to affect the substrate.

Commercialization Scale-Up

In order to plate actual production parts using our trivalent chromium process we have constructed a plating set-up to accommodate shock absorber rods and a pump auger. With this set-up we are able to demonstrate trivalent chromium bath plating that will be evaluated by vendors using their standard qualification tests used to verify their production capabilities. Figure 3 shows the complete set-up. Starting at the left on the sawhorses is a spray rinse tank, an alkaline electrocleaner tank, and a stagnant tank that will be connected to an A CELL cell to reclaim chromium plating solution. Within the enclosure are the nickel strike plating tank and the trivalent chromium plating tank. Next is the temperature control system for maintaining the temperature in the chromium plating tank. An immersion heater is used to heat the bath and a chiller is used to provide cold water for cooling the bath. At the right is a reversing pulse rectifier (on a cart) used for chromium plating. An oscilloscope on top of the rectifier is used to monitor the waveform.

Figure 3: Pilot Line Set-Up

The plating tank contains a pump and eductor to provide uniform flow past the work surfaces. Figure 4 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 is be placed in the middle.

Shock absorber rods and pump augers, shown in Figure 9, will be chromium plated and then evaluated by standard tests performed on production parts at their respective vendors. In addition the Naval Depot at Cherry Point will be evaluating our chromium plating on cylindrical samples.

We are participating in Phase II of the Functional Trivalent Chromium Plating task being conducted by Concurrent Technologies Corporation. They will be testing chromium plated coupons for corrosion resistance, taber abrasion, pin-on-disk wear, and adhesion, microcrack analysis

Figure 4: Top View of Plating Tank

Figure 5: Parts to be Chromium Plated

Conclusions

In summary, while we have completed the EPA Phase II project we are continuing research to commercialize our trivalent chromium plating process. We have established the following:

- Plated from a trivalent chromium sulfate bath where the consumable was in the price range of chromic acid, (Renz, 2001).
- Simplified bath chemistry using an electrically mediated waveform, (Renz, 2001).
- Increased chromium plating thickness to 250 µm, (Renz, 2001).
- Maintained plating rate similar to hexavalent chromium, (Renz, 2001).
- Determined maximum diffusion layer thickness for plating from trivalent chromium sulfate bath, (Renz, 2002).
- Determined acceptable range for achieving bright plating, (Renz, 2002).
- Replated chromium on chromium, (Renz, 2002).
- Shown that the corrosion resistance of trivalent chromium deposits are superior to laser treated coatings.
- Constructed a pilot-line plating set-up to plate parts currently used in production to allow commercial evaluation.

Acknowledgement

This study was 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. Altmayer, F., *Plating and Surface Finishing*, 82(2), 26 (1995).

2. Banker, L., "Chromium Air Emissions Standards for Hard, Decorative Chromium and Chromium Anodizing," *16th AESF/EPA Conference*, Orlando, FL, February, 1995.

3. Chin, D.T., *J. Electrochem. Soc.*, 130(8), 1657 (1983).

4. Constantin, M., Grunwald, E., Varhely, C., and Juhos, C., *Galvanotechnik*, 82(11), 3819 (1991).

5. Dash, J., Jin, J., and Hotchkiss, L., *Proc. AESF Annu. Tech. Conf.*, Vol. 78, pp 947-952, 1991.

6. Ember, L.R., *Chemical and Engineering News*, February 18, 1991.

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. Gibb, H.J., Jones, P.S.J.,Pinsky, P.F., Rooney, B.C., American Journal of Industrial Medicine, 38 115-126 (2000).

9. Hanson, D.J., *Chemical and Engineering News*, June 3, 1991.

10. Hwang, J.-Y., *Plating and Surface Finishing*, 78(5), 118, (1991).

11. "Occupational Safety and Health Guideline for Aluminum," Occupational Safety and Health Administration, U.S. Department of Labor.

12. Renz, R.P., Fortman, J.J, Taylor, E.J., and Inman, M.E., *"Effects of Bath Chemistry, Solution Hydrodynamics, and Electrical Mediation on Trivalent Chromium Plating,"* AESF SUR/FIN 2001.

13. Renz, R.P., Fortman, J.J, Taylor, E.J., and Inman, M.E., *"Functional Trivalent Chromium Plating Using Electrical Mediation: An Alternative to Conventional Hexavalent Chromium Plating,"* AESF Week 2002.

14. Renz, R.P., Fortman, J.J., Taylor, E.J., and. Inman, M.E, *"Electrically Mediated Process for Functional Trivalent Chromium to Replace Hexavalent Chromium: Scale-up for Manufacturing Insertion,"* AESF SUR/FIN 2002.

15. Scott, G., US Patent 5196109, August, 1991.

16. Shahin, G.E., *Plating and Surface Finishing*, 79(8), 19, 1992.

17. Snyder, D.L., *Products Finishing*, 61, August (1989).

18. Taylor, M.L., "Comments Regarding the Chemistry and Health Effects of Chromium (VI) vs. Chromium (III)", Private Research Report, June (2001).

19. Tu, Z.-M., Yang, Z.-L., and Zhang J.-S., *Plating and Surface Finishing*, 77(10), 55 (1990).

20. Tu, Z.-M., Yang, Z.-L., Zhang, J.-S., An, M.-Z., and Li, W.-L., *Plating and Surface Finishing*, 80(11), 79 (1993).

21. Vilambi, N.R.K., and Chin, D.-T., "Selective Pulse Plating of Copper from an acid Copper Sulfate Bath," *Plating and Surface Finishing*, 75, 67 (1988).