



The William Blum Lectures

#30 - James P. Hoare - 1989



The 30th William Blum Lecture
Presented at the 76th AESF Annual Convention (SUR/FIN 1989)
in Cleveland, Ohio
June 26, 1989

An Electrochemical Mystery Story: A Scientific Approach to Chromium Plating

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ABSTRACT

Any mechanism of chromium deposition must give reasonable answers to a number of puzzling questions if it is to be successful in accounting for the observations obtained in the plating room. Among those questions are the following: Why is it possible to deposit acceptable coatings from hexavalent chromium solutions, but not from simple solutions of trivalent chromium? Why must additives such as SO_4 or F ion be present in the hexavalent chromium bath for the production of bright, hard, adherent chromium films? Why is the chromium plating process so dependent on the ratio of the chromium concentration to that of the additive? What is the role of the SO ion? A mechanism for chromium deposition is proposed which accounts for these observations. The results of certain studies, and the development of the reasoning that led to the creation of a successful mechanism for chromium plating, will be presented.

In the Electrochemical Department of General Motors Research Labs, we became interested in high-rate electrochemical processes. One of the first problems studied was the high-rate removal of metal in the operation known as electrochemical machining (ECM) which is a controlled, high-rate, anodic corrosion process.¹⁻³

Since very high current densities (50 to 500 A/cm²) are employed in the ECM process, the anode (workpiece) and the cathode (tool) must be placed very close to one another (0.5 mm) to overcome the internal resistance of the solution. To prevent the solution from boiling out of the anode-cathode gap at these high current densities, the strong neutral electrolyte must be pumped through the gap at high rates (2 to 6 m/sec). Under these conditions, metal removal rates of 2 cm³/min for fully hardened steel can be obtained using 4 M NaClO₃ solution as the electrolyte. The surface finish of the machined workpiece is bright and smooth (profilometer readings range from 0.25 to 1 μm).

With the advent of front wheel drive vehicles, a need for high-speed plating of hard, engineering chromium developed, since the thickness specifications for wear- and corrosion-resistant coatings for McPherson struts is about 1 mil or 0.025 mm. With conventional chromium plating, it requires about 1 hr to deposit such coatings. Using the experience obtained from the work on ECM, our electrochemical engineer, M.A. LaBoda,⁴ developed a high-speed plating machine that deposited 1 mil of hard, bright, adherent chromium in 1 min. The question arose, how does high-speed chromium plating work?

Before one can understand the mechanism for high-speed chromium plating, one must understand the mechanism for conventional chromium plating. If the literature is consulted, one discovers that Geuter⁵ deposited metallic chromium from solutions of K₂Cr₂O₇ and H₂SO₄ as early as 1856. One also finds⁶ that chromium could not be deposited from Cr³⁺ solutions. Although it was found⁶ that an essential component of a chromium plating bath is chromic acid, Sargent⁷ reported that successful deposits of metallic chromium were obtained only with the addition of SO_4^{2-} ion to the plating bath. Both Sargent⁷ and Liebreich⁸ concluded that metallic chromium was deposited from a cathodic film. It was not until 1926 that Fink⁹ obtained a patent for a bright chromium plating bath in which the SO_4^{2-} ion was designated as a catalyst and the CrO₃/H₂SO₄ ratio must be carefully controlled at a value of 100/1. This was the first stable and predictable bright chromium plating bath.

Any number of theories have been proposed¹⁰⁻¹⁵ in which the inhibiting, amorphous oxide film on the cathode is modified or broken down by the presence of SO_4^{2-} ions so that metallic chromium may be deposited. Other suggested mechanisms¹⁶⁻²¹ consider the cathodic film to be a viscous colloidal film. Gerischer²² concluded that the growth of a semiconducting oxide film on the cathode was limited by the presence of SO_4^{2-} ion which resulted in an increase in the hydrogen overvoltage and a resultant increase in the rate of chromium deposition. The Russian workers^{19,20} consider the cathodic film in the presence of SO_4^{2-} ions to be a colloidal complex of Cr^{+6} , Cr^{+3} and SO_4^{2-} ions. This concept is also held by Saddington and Hoey.²¹ Snively²³ concluded that the chromic-chromate cathodic film was reduced by discharged atomic hydrogen, and the metallic chromium was deposited from the decomposition of chromium hydrides formed in the reduction process. From radioactive chromium studies, Ogburn and Brenner²⁴ showed that only chromium originally in the hexavalent state was deposited on the cathode. According to similar studies,^{25,26} Brenner's findings were confirmed.

In spite of all of the work done on bright chromium plating, it is generally agreed²⁷⁻²⁹ that a satisfactory theory for the electrodeposition of bright, metallic chromium coatings had not been proposed up to that time.

At GMRL, we considered the fact that chromium could be deposited from Cr^{+6} , but not from simple aqueous solutions of Cr^{+3} ions, to be the first roadblock to the understanding of bright chromium plating. It is known^{30,31} that Cr^{+3} ions in the presence of water will form a hexa-aqua complex which is so stable that metallic chromium cannot be separated from it. With this in mind, what is so magical about chromium in the hexavalent state that it can be reduced through the trivalent state to the metallic state without the formation of the hexa-aqua complex, $\text{Cr}(\text{H}_2\text{O})_6^{+3}$?

It is known³²⁻³⁴ that the metal-oxygen bonds of the chromate ion are directed toward the corners of a regular tetrahedron (Fig. 1), and that the chromate ions can polymerize dependent on the pH of the environment. It has also been observed³⁵ that the degree of polymerization of chromate is indicated by the color of the solution. Solutions of chromate ion are yellow; of dichromate, orange; of trichromate, red; and of tetrachromate, brown. The more acidic the solution, the deeper its color and the higher the degree of polymerization.

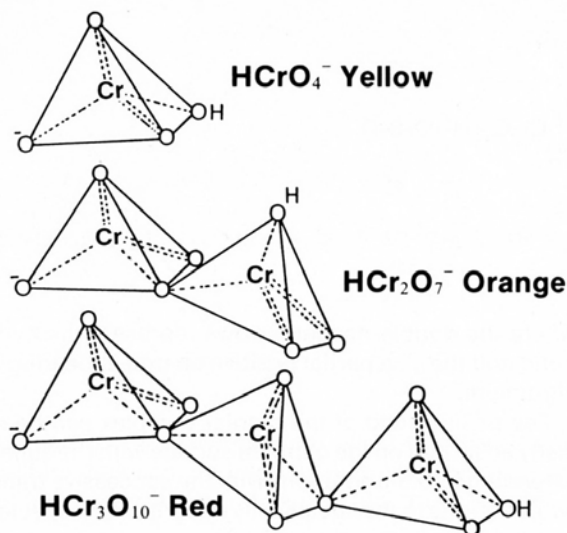


Figure 1 - Chromate structures.

Since chromic acid solutions above 1 M which are used in chromium plating baths are red,³⁶ we concluded³⁷ that the active species in such solutions is the trichromate ion, $\text{HCr}_3\text{O}_{10}^-$. The closest approach of the negatively charged trichromate ion to the cathode surface is the outer Helmholtz layer^{38,39} (Fig. 2). During the process of chromium reduction under these conditions, electrons are transferred to one end of the trichromate ion by quantum mechanical tunnelling through the potential energy barrier of the double layer⁴⁰⁻⁴² at the cathode surface. In this way, the chromium atom at one end of the trichromate ion will be reduced to Cr^{+3} producing a chromic dichromate species.

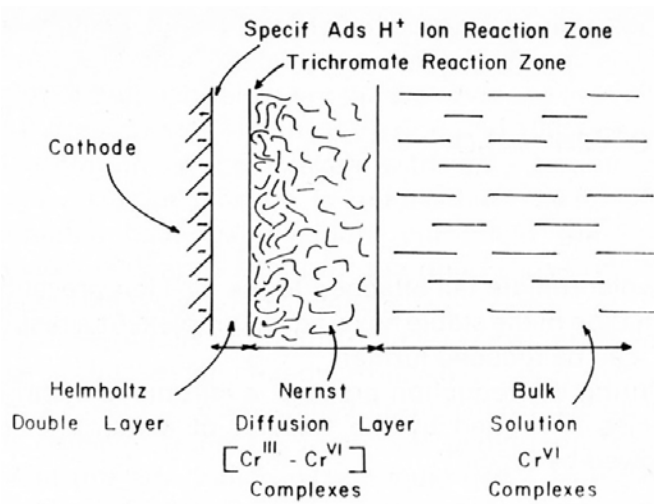
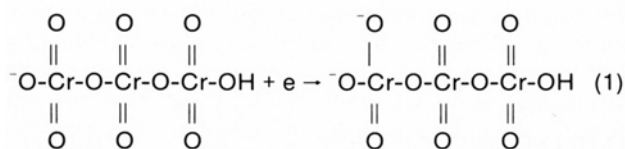
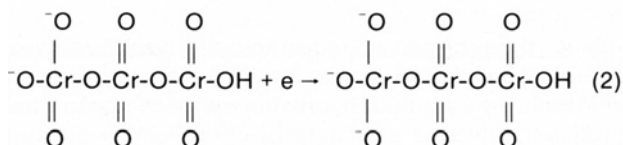


Figure 2 - Simplified sketch of the cathode-solution interface.

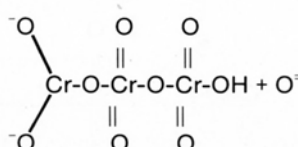
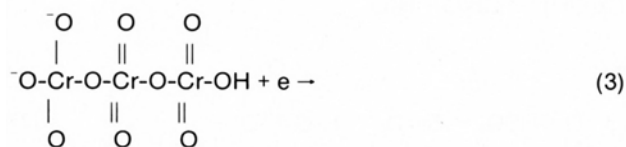
The tetrahedra are symbolized for the sake of simplicity by the following structures. Cr^{+6} is reduced to Cr^{+5} by the first electron transfer.



With the second electron transfer, Cr^{+5} is reduced to Cr^{+4} :



and finally to Cr^{+3} with the transfer of the third electron and the loss of oxygen:

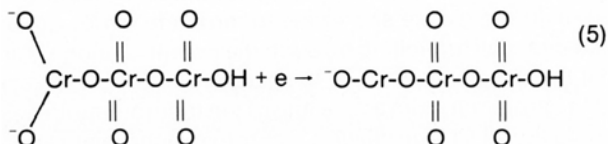


which reacts immediately with H^+ ions to form water:

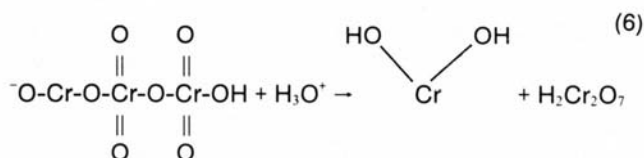


The dichromate tail attached to the Cr^{+3} ion prevents the formation of the stable hexa-aqua complex. As a result, the Cr^{+3} can be reduced further.

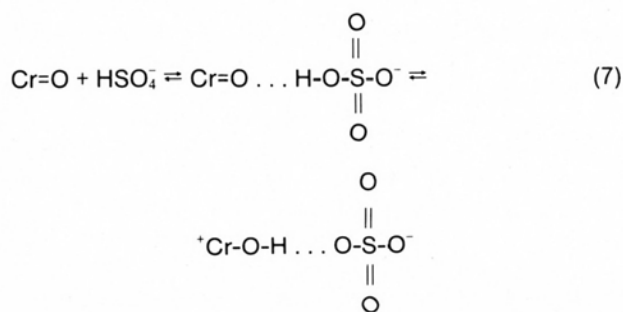
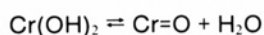
During the reduction process, a chromous dichromate species is formed by the transfer of a fourth electron followed by Eq. 5.



In strong acid solutions, the chromous dichromate may decompose to chromous hydroxide and a dichromate which can polymerize back to a trichromate by condensation with other chromates:



Equation 6 may be considered an acid-catalyzed hydrolysis reaction. If an additive such as the HSO_4^- ion is not present in the bath, the chromous hydroxide will discharge to black chromium, which is a mixture of chromium oxides and metallic chromium.⁴³⁻
⁴⁵ At this point in the mechanism, the HSO_4^- ion can exert its catalytic activity by forming a chromousoxybisulfate complex through hydrogen bonding.

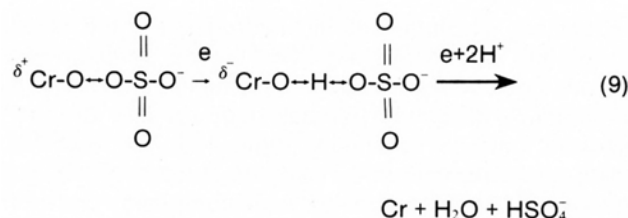


This complex exists as a dipole with a fractional positive charge on the chromium atom because of electronic resonance, which can be expressed as:



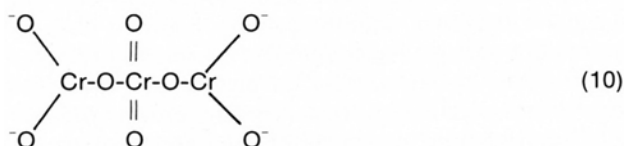
where the double-headed arrows represent the hydrogen bond and the δ^+ a partial positive charge appearing on the chromium.

The positive end of the dipolar complex can be specifically adsorbed on the cathode surface with the sulfate end extending into the solution. With the successive transfer of two electrons to the specifically adsorbed Cr^{+2} species, Cr^{+1} and finally metallic chromium along with the regenerated HSO_4^- ion are obtained.

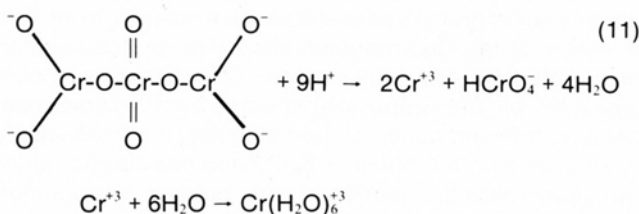


With the discharge of two electrons, metallic chromium is deposited on the cathode and bisulfate ion is released into solution. In this case, the HSO_4^- ion satisfies the conditions for a catalyst.

An objection to this mechanism is the possibility that electrons may be transferred to both ends of the trichromate ion. Should this event occur, a dichromic chromate complex would form instead of the chromic dichromate complex:

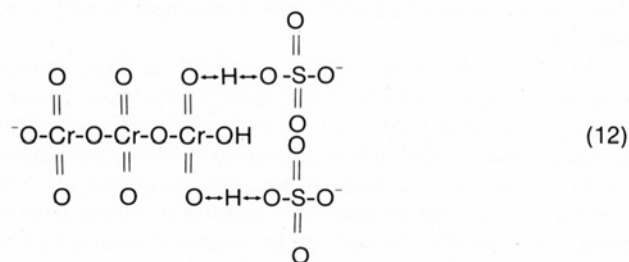


In strong acid solutions, it is proposed that the dichromic chromate complex will decompose to chromic ions which react immediately with H_2O to form the stable hexa-aqua complex:



Consequently, metallic chromium will not be deposited.

Bisulfate ions can complex by hydrogen bonding with any of the oxygen atoms double-bonded to chromium:



It is assumed that the transfer of electrons to a chromium atom on which both double-bonded oxygens are complexed with HSO_4^- ions is strongly inhibited. In this way, one of the terminal chromium atoms of the trichromate ion can be shielded from electron transfer so that only the other terminal chromium atom can be discharged. As a result, the HSO_4^- ion not only plays the role of a catalyst, but also that of a blocking agent.

Again, an objection to this mechanism may be raised since bisulfate ions can complex with any of the six double-bonded oxygen atoms of the three chromium atoms of the trichromate ion. One may consider a distribution of all possible permutations of trichromateoxybisulfate complexes in equilibrium with one another:



where n may have any integral value from one to six. Since these complexes may rotate in solution, 24 distinguishable complexes may be determined (Fig. 3). The equilibrium distribution of these complexes depends on the ratio of bisulfate to chromic acid concentrations.

When the $\text{CrO}_3/\text{H}_2\text{SO}_4$ ratio has a value of 100/1, the distribution of complexes (Fig. 4) is such that a maximum number of complexes exists with only one terminal chromium atom blocked with hydrogen-bonded bisulfate ions. Such complexes discharge to metallic chromium. For low H_2SO_4 concentrations, the distribution shifts to a point where most of the complexes have both terminal chromium atoms unblocked. In this case, reduction of trichromate ions only results in the reduction of Cr^{+6} to Cr^{+3} and the evolution of hydrogen. One refers to this situation as an under-catalyzed bath. For high H_2SO_4 concentrations, the distribution shifts to a point where most complexes have both terminal chromium atoms blocked. Here, only H_2 is evolved and this condition is referred to as an over-catalyzed bath. The shape of the distribution curve is such that if one deviates significantly from the 100/1 ratio, the concentration of complexes with only one terminal chromium atom blocked is reduced to the point that acceptable coatings of bright chromium will not be obtained, thus accounting for the great sensitivity of the process to the $\text{CrO}_3/\text{H}_2\text{SO}_4$ ratio.

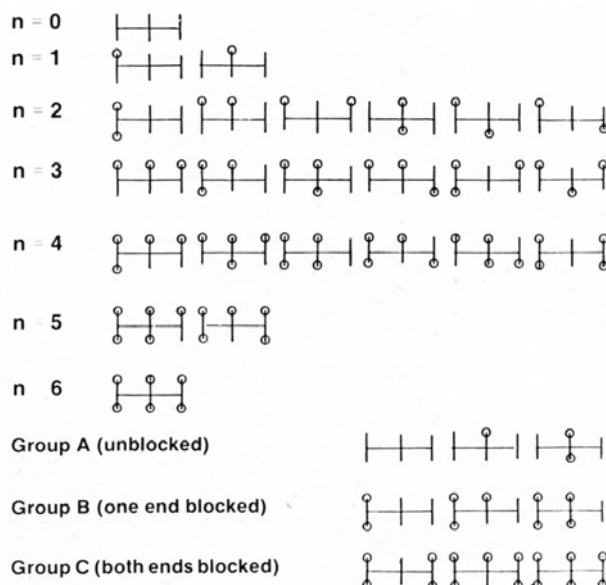


Figure 3 - Distinguishable trichromate-bisulfate complexes

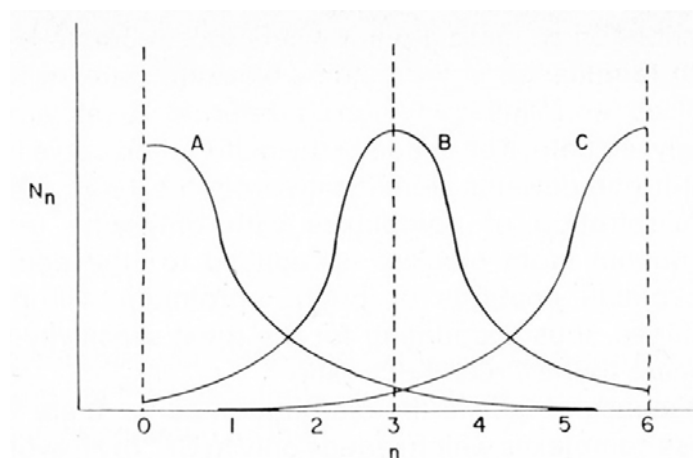


Figure 4 - Ideal distribution curves for the number of trichromate-bisulfate complexes (N_n) as a function of the number, n , of $\text{Cr}=\text{O}$ bondhydrogen bonded to HSO_4^- ions for $\text{CrO}_3/\text{H}_2\text{SO}_4$ ratios (A) 10/1, (B) 100/1 and (C) 1/1.

Because of tails in the distribution curve, there will be those complexes which reduce only to Cr^{+3} or H_2 evolution, and, as a result, the Cr^{+3} concentration may build up in the bath causing deterioration of the plating process. To prevent this Cr^{+3} build-up, one must use a high oxygen overvoltage PbO_2 anode at which Cr^{+3} is oxidized to Cr^{+6} with the attainment of a stable bath operation.

According to this model, the chromic acid plating bath is viewed as an equilibrium distribution of H_3O^+ ions, H_2O molecules, HSO_4^- ions, HCrO_4^- ions, HCr_2O_7^- ions, $\text{HCr}_3\text{O}_{10}^-$ ions and all possible complexes of the chromates and polychromates with hydrogen-bonded sulfate. Most of the chromium exists as the trichromate ion since the color of the bath is red. It is proposed that the cathodic film is a mixture of partially reduced trichromate complexes (chromic dichromate and dichromic chromate ions complexed with HSO_4^- ions to various degrees). Accordingly, these Cr^{+6} - Cr^{+3} complexes are less soluble than the un-reduced Cr^{+6} complexes. Here, these partially reduced complexes precipitate out in the Nernst diffusion layer next to the cathode surface to form the dark film which is seen streaming off the cathode when the plating current is interrupted. As the trichromate complexes with only one end blocked are removed from the cathode film by reduction to metallic chromium during the plating process, they are replaced by shifts in the equilibrium established between the complexes to maintain a steady plating rate. Evidence for the existence of such complexes in the plating bath was obtained from conductance⁴¹ and cyclic voltammetric⁴² studies.

During the plating process, fresh trichromate complexes must diffuse from the bulk of solution through the diffusion layer to be discharged to metallic chromium from the viscous film at the cathode surface. Consequently, any process that will reduce the diffusion path will increase the rate of the diffusion-controlled chromium deposition. It is known that stirring the plating bath, which diminishes the thickness of the diffusion layer, will increase the chromium plating rate. But even with the most efficient stirring, the plating current is limited by the resistance of the plating cell.

From our experience with electrochemical machining studies, the anode and cathode must be placed very close together (about 0.25 cm) to obtain the high-speed plating of chromium. To prevent the evaporation of the electrolyte in the narrow anode-cathode gap at high current densities (on the order of 16 A/cm^2), the plating solution must be pumped through the gap at high flow rates (up to 6 m/sec). This high flow rate of solution accomplishes several essential steps in the high-speed plating process. It brings fresh solution into the inter-electrode gap; sweeps the spent, highly resistant solution out of the gap; reduces the thickness of the cathode film, and hence, the diffusion path; and controls the temperature of the solution in the gap.

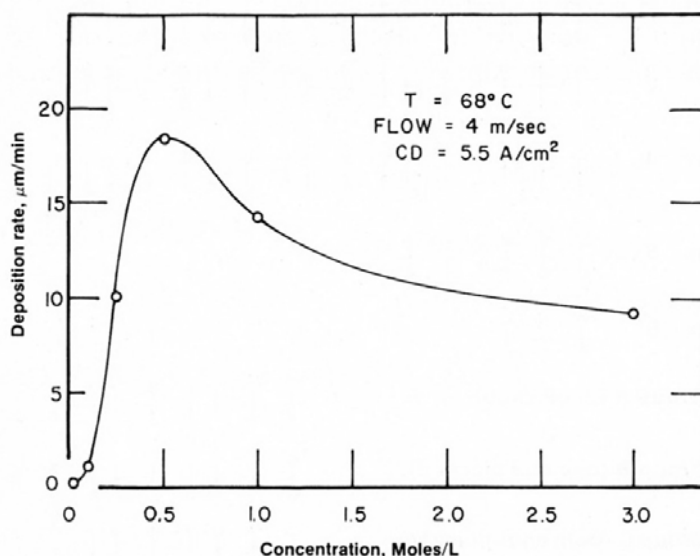


Figure 5 - Plot of coulombic efficiency (circles) and deposit thickness (triangles) for high-speed deposition of chromium on mild steel at 68°C.

As the applied current is increased, the rate of the diffusion-controlled plating process is increased. When the current becomes high enough, a point is reached at which the trichromate complexes are discharged as fast as they reach the cathode-solution interface. In this case, the rate is no longer diffusion-controlled and the process comes under kinetic control. The plating rate no longer depends on the solution flow rate (Fig. 5), but on kinetic parameters such as temperature and concentration. For a given applied current density, it was found⁴¹ that the high-speed chromium plating process passes through a maximum rate as a function of the CrO_3 concentration (Fig. 6), the solution flow rate and the temperature. This behavior occurs because of two opposing effects. As the flow rate, temperature and concentration increase, the conductivity increases and the diffusion path becomes shorter, all of which increase the deposition rate; but also, the solution viscosity increases and the rate of the codeposition of H_2 increases, resulting in a decreased plating rate. Experimentally, it was found⁴¹ that maximum operating conditions were achieved at a solution composition of 50 g/L CrO_3 + 0.5 g/L H_2SO_4 flowing at a rate of 4 m/sec at 68°C. At 7 A/cm², a coating of bright, adherent hard chromium was deposited at a rate of 26 $\mu\text{m}/\text{min}$ and a current density of 52 percent.

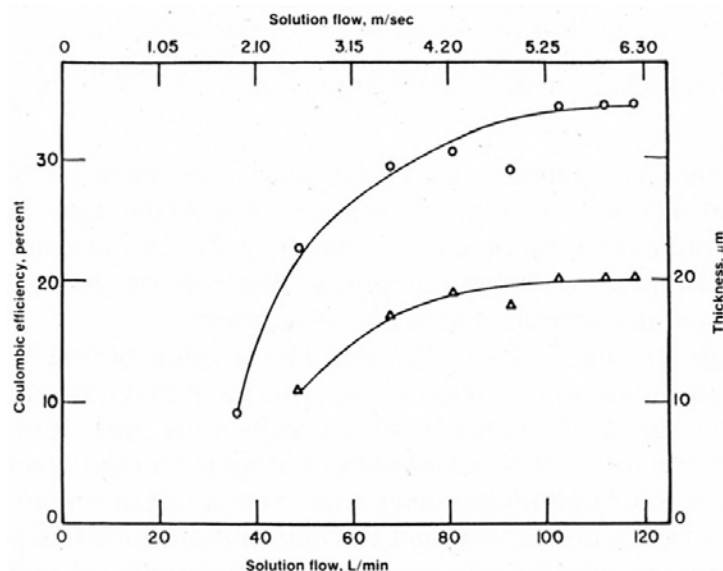


Figure 6 - A plot of chromium deposition rate ($\mu\text{m}/\text{min}$) as a function of the chromic acid concentration for the conditions noted.

Since chromic acid plating solutions severely attack chemical process pumps, it was realized that such pumps would not survive a commercially useful life. To solve this problem, an air pressure flow system (APFS) was developed by M.A. LaBoda.⁴ In this plating machine (Fig. 7), the plating solution was passed back and forth from one Teflon-lined, 100-L steel holding tank, through the plating fixture (Fig. 8), to a second similar tank. The alternating flow of solution was controlled by a network of solenoids in the flow lines and an electronic programmable timer. Since the high-speed plating machine is a closed system, acid, toxic fumes of the chromic acid bath are avoided.

To plate from a trivalent chromium bath, one must destabilize the strong hexa-aqua- Cr^{+3} inner coordination complex. This has been accomplished successfully by a number of commercially available baths through the use of additives. Most successful baths contain a sulfur compound such as thiourea or sodium thiosulfate and a hydroxy carboxylic acid such as glycolic acid.⁴⁶ Besides these destabilizers, NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ is present as a supporting electrolyte and as a complexing agent; boric acid as a buffer; a reducing agent such as sodium hypophosphate^{47,48} to convert Cr^{+3} to Cr^{+2} since the divalent complex may be more readily discharged; and possibly a wetting agent. It should be noted,⁴⁹ though, that chromium deposition from trivalent baths is slow and the properties of thick deposits are poor. It has come to this worker's attention that it has been reported⁵⁰ that thick, hard coatings of metallic chromium have been deposited at a rate of 1 $\mu\text{m}/\text{min}$ from a Cr^{+3} bath derived from the reduction of a Cr^{+6} solution.

For wear- and corrosion-resistant coating applications, it is this researcher's opinion that there is no substitute on the horizon for the wet electrodeposition of hard chromium deposits.

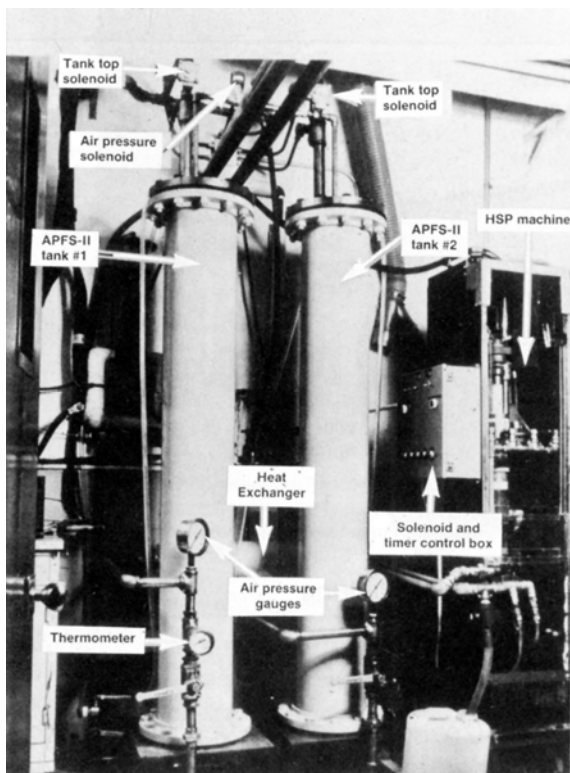


Figure 7 - High-speed plating machine.

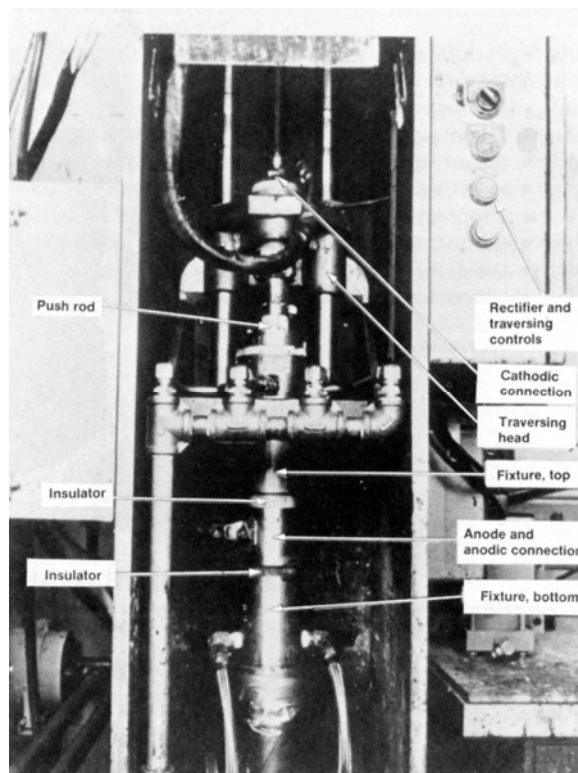


Figure 8 - Plating fixture.

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About the author:

This piece was written at the time Dr. Hoare was announced as the recipient of the 1988 Scientific Achievement Award.



Dr. James Patrick Hoare, renowned for his discovery of the mechanism of chromium electrodeposition, has been selected as the 1988 recipient of the AESF Scientific Achievement Award. The award, which is the highest honor conferred by the Society, recognizes an individual who has made outstanding scientific contributions advancing the theory and practice of electroplating and allied sciences, raised the quality of products or processes, or enhanced the dignity of the profession.

Dr. Hoare was born in Denver, CO, and received his B.S. degree from Regis College. He earned his Ph.D. in physical chemistry at Catholic University of America, Washington, DC, in 1949. After several years of academic life, teaching physics and chemistry at Trinity College (Washington, DC), he began to concentrate on research, joining the Naval Research Laboratory in 1954 as a physical chemist. By 1957 he completed the transition to industrial research by joining the staff of Ford Motor Company's Scientific Laboratories in Dearborn, MI. In 1960 he began a long and fruitful association with the General Motors Research Laboratories in Warren, MI, joining the staff as a senior research chemist. By the time of his retirement in 1987, he had reached the position of Research Fellow, a status attained by only four people in the history of the laboratories.

Throughout his 40-year-long career, Dr. Hoare has been a major contributor to the science of electrochemistry and electrodeposition. He has explored several fundamental areas of electrochemistry, including hydrogen overvoltage on noble



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metal cathodes, the mechanism of electrochemical reduction of oxygen, and electrocatalysis. This work has led to a deeper understanding of electrochemical processes, such as battery science, that is not limited to electroplating. In particular, he is considered to be a world authority on the electrochemistry of oxygen.

While much of his early work concentrated on fundamental electrochemistry, his later contributions were more germane to electroplating, surface finishing, and the allied arts. He first directed his research efforts toward electrochemical metal removal processes, particularly electrochemical machining. With the perspective gained from his years of experience in fundamental electrochemistry, he exhibited a talent for explaining phenomena associated with very practical surface processes. In collaboration with M.A. LaBoda, he developed much of the definitive technical information relating to electrochemical machining.

From the perspective of many finishers, however, his greatest contribution was the uncovering of the chromium electrodeposition mechanism. For years, many theories had been propounded as scientists struggled to nail down the details of the elusive phenomena. Dr. Hoare succeeded in proposing a definitive explanation of not only conventional chromium plating, but also of the phenomena associated with high-rate high-flow chromium, and chromium plating catalysts such as sulfate, fluoride, boric acid and mixed self-regulating types.

More recently, he made important contributions to the understanding of nickel electrodeposition, shedding light on the role of boric acid in a Watts electrolyte, finding its action to be catalytic. He has also investigated high-rate deposition of nickel.

Dr. Hoare has published more than 125 technical papers, including several book chapters. He is also the author of a book, *The Electrochemistry of Oxygen*.

Although the majority of his career has been involved in research, his interests in teaching and education have never waned. He has served as a judge at science fairs in the Detroit area for over 10 years. The nurturing and growth of scientific talent has been a constant concern.

Among his many honors and awards for his work in electrodeposition and electrochemistry is an AESF Gold Medal for his paper "On Boric Acid-Catalyzed Chromic Acid Plating Baths," published in *Plating and Surface Finishing* in 1984. He also won silver medals, along with co-authors M.A. LaBoda and A.H. Holden, in 1981 and 1983. Dr. Hoare is also a two-time recipient of the General Motors' Campbell Award, the only person to receive that honor twice. He was recognized in 1981 for his contributions to the understanding of the electrochemistry of oxygen electrodes, and in 1985 for his work in defining the mechanism of chromium electrodeposition. In 1987, he received the Research Award of the Electrodeposition Division of the Electrochemical Society in recognition of his outstanding contributions to the science and technology of chromium and nickel electroplating.

In addition to his membership in the AESF, Dr. Hoare is a member of the American Chemical Society, the Electrochemical Society, the International Society of Electrochemistry, the New York Academy of Sciences, and the Catalyst Society.