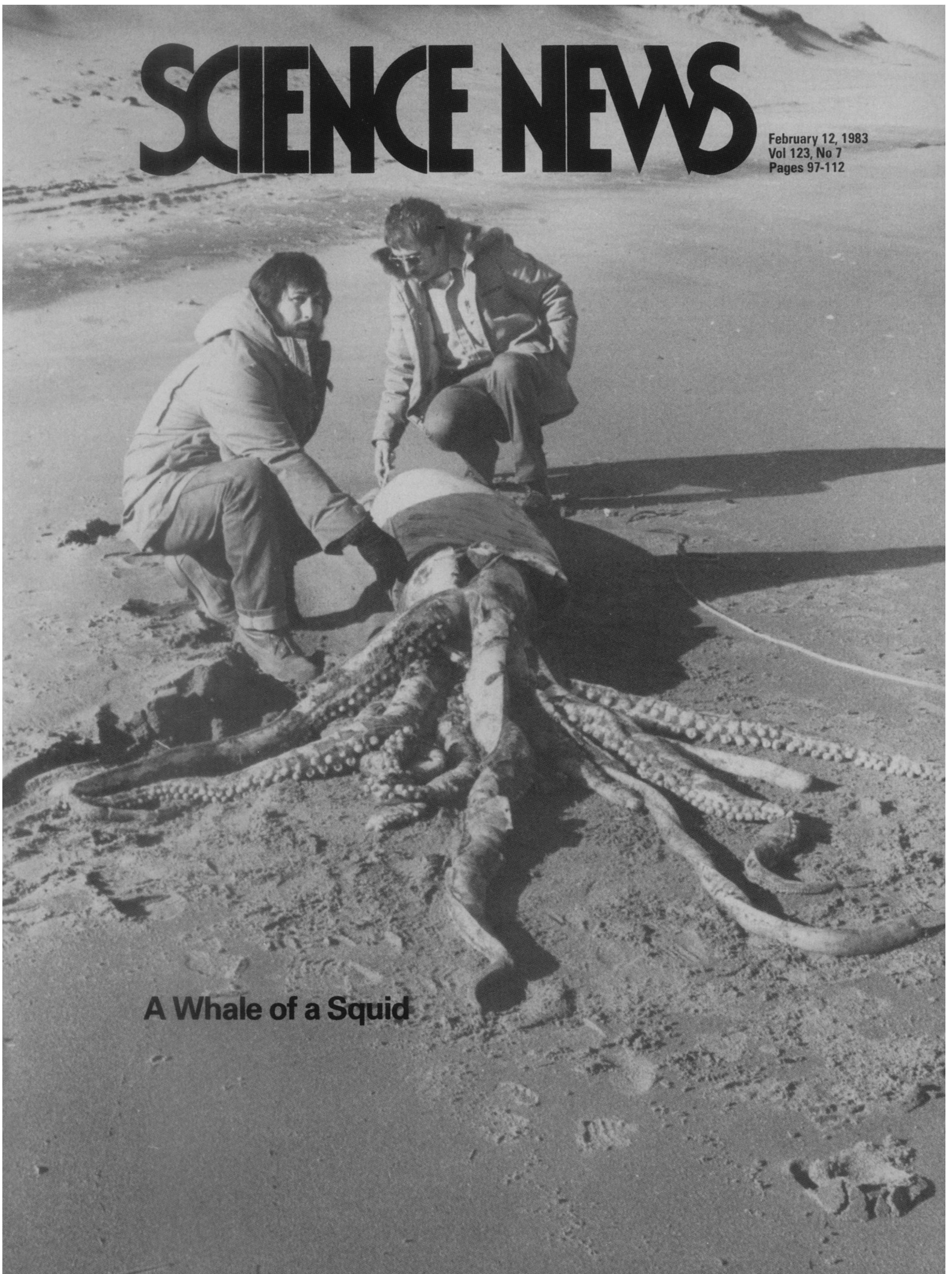


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A Whale of a Squid

The Chromium Mechanism

The first comprehensive explanation of electrochemical activity during the plating of chromium has recently been formulated at the General Motors Research Laboratories. This understanding has aided in transforming chromium plating into a highly efficient, high-speed operation.

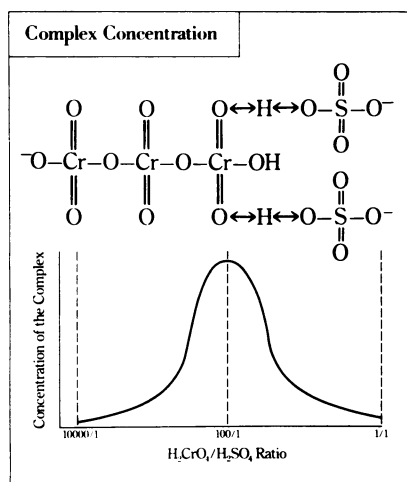


Figure 1: The electroactive complex and a theoretical plot of its concentration as a function of chromic acid to sulfuric acid ratio.

Figure 2: The electroactive complex diffuses from the bulk electrolyte solution (A) through the diffusion layer (B) to the Helmholtz double layer (C) to be discharged as metallic chromium (D) on the cathode (E) surface.

FOR MANY industrial applications, chromium coatings of more than 0.2 mil thickness are required for wear and corrosion resistance. But the conventional method of plating chromium is neither fast nor efficient. Nor, until the recent work of a GM researcher, had the steps involved in the century-old plating process been explained in detail. Through a combination of theory and experiment, Dr. James Hoare has devised the first comprehensive mechanism for chromium plating. This increased understanding has helped electrochemists at the General Motors Research Laboratories develop a system that plates chromium sixty times faster than the conventional method, while improving energy-efficiency by a factor of three.

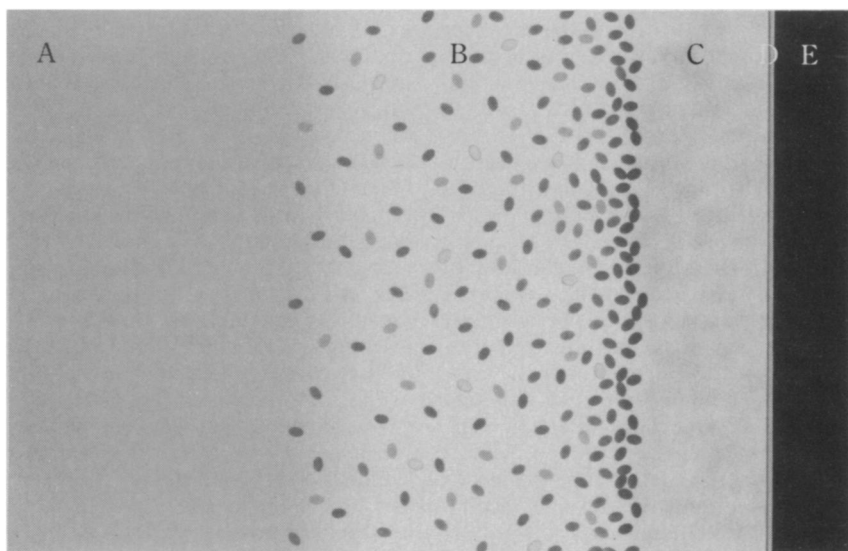
The electrolyte for plating is

a chromic acid solution which contains various chromate ions: chromate, dichromate and trichromate. From a series of steady-state polarization experiments, Dr. Hoare concluded that trichromate is the ion important in chromium deposition.

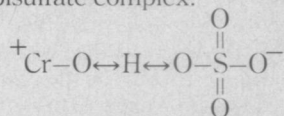
Sulfuric acid has been recognized as essential to chromium plating and has been assumed by some to be a catalyst for the process. In this strongly acidic solution, sulfate should be mostly present as the bisulfate ion (HSO₄⁻). Dr. Hoare found, contrary to expectations, that the addition of sulfuric acid to the plating bath decreased the conductivity of the solution.

Combining these findings with the results of previous investigations, Dr. Hoare concluded that the electroactive species was a trichromate-bisulfate complex (see Figure 1). From equilibrium considerations, he theorized that the maximum concentration of this species occurred at a 100-to-1 chromic acid/sulfuric acid ratio. The observation that the maximum rate of chromium deposition also occurred at this ratio supports the conclusion that this trichromate-bisulfate complex is the electroactive species.

During the plating process, the complex diffuses from the bulk solution toward the cathode (see Figure 2). Electron transport takes place by quantum mechanical tunneling through the potential energy barrier of the Helmholtz double layer and the unprotected chromium in the complex (Cr atom



on the left in Figure 1) loses electrons by successive steps, going from Cr^{+6} to Cr^{+2} . Decomposition of the resulting chromous dichromate complex takes place by acid hydrolysis to form a chromous-oxybisulfate complex:



The positive end of this complex is adsorbed onto the cathode surface. Electrons are transferred from the cathode to the adsorbed chromium ion, forming metallic chromium and regenerating the $(\text{HSO}_4)^-$ ion. Thus, Dr. Hoare's mechanism explains how sulfuric acid, in the form of the bisulfate ion, participates in the plating process.

IT HAS long been known that chromium cannot be plated from a solution when initially present as Cr^{+3} because of the formation of the stable aquo complex, $[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$. Yet chromium can be plated when initially present as Cr^{+6} even though it must pass through the Cr^{+3} state before being deposited. Dr. Hoare's mechanism handles this paradox by explaining that the chromium ion being deposited (on the left in Figure 1) is protected by the rest of the complex as it passes through the Cr^{+3} state, so that the stable aquo complex cannot form.

The diffusion of the electroactive complex apparently controls the rate of the process, so that

shortening the diffusion path increases the speed of chromium deposition. A high rate of relative motion between the electrolyte and the cathode will shorten the path. This can be accomplished by rapid flow or by agitation of the electrolyte.

Dr. Hoare found that the rate of chromium deposition increased with electrolyte flow until the process was no longer diffusion-controlled. He also found that the use of dilute electrolyte significantly increased plating efficiency.

"This project is an excellent example," says Dr. Hoare, "of how basic research and engineering principles can be combined to develop a new, successful process. Now, we'd like to take on the challenge of plating successfully from Cr^{+3} , which would be an even more efficient way to provide corrosion and wear resistance."

General Motors



THE MAN BEHIND THE WORK

Dr. James Hoare is a Research Fellow at the General Motors Research Laboratories. He is a member of the Electrochemistry Department.

Dr. Hoare served as an electronics technician in the U.S. Navy during the Second World War. In 1949, he received his Ph.D. in physical chemistry from the Catholic University of America. After an assistant professorship at Trinity College in Washington, D.C., he joined the US Naval Research Laboratory as a physical chemist. He became a staff member at General Motors in 1960.

Dr. Hoare's sustaining interest has been in electrochemical kinetics and the mechanisms of electrode processes. He is best known to the scientific community for his basic studies of hydrogen and oxygen electrode mechanisms. His book, *The Electrochemistry of Oxygen*, published in 1968, is considered a work of primary importance to the field. In addition to his work on chromium plating, he is responsible for the fundamental research that helped make electrochemical machining a precision process.

