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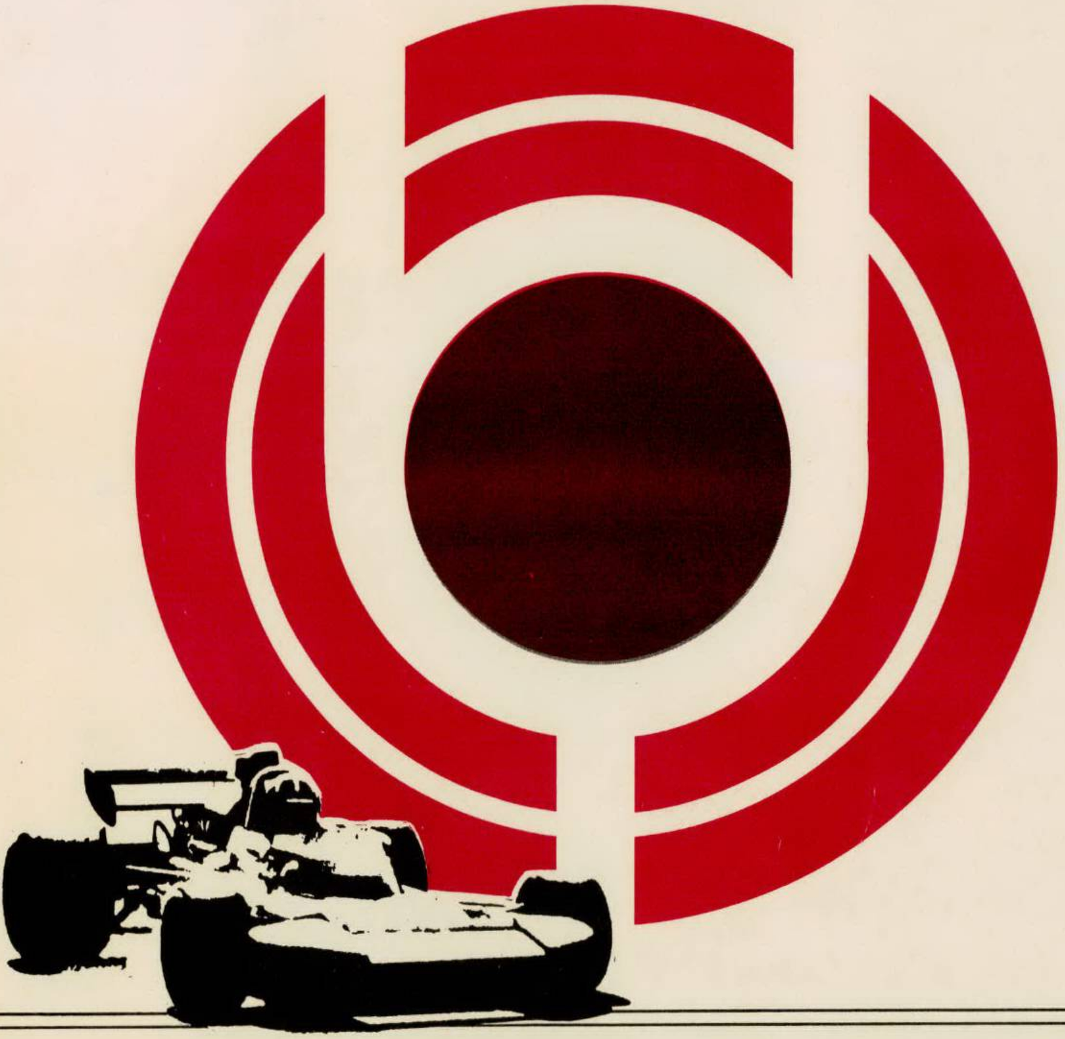

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Indianapolis, IN

SESSION I

AMERICAN ELECTROPLATERS' SOCIETY, INC.

70TH ANNUAL TECHNICAL CONFERENCE - SAN FRANCISCO, CA

GENERAL INTEREST

SESSION I

General Interest Session I

The Role of Boric Acid in Dilute Chromic Acid Plating Baths

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ON THE ROLE OF BORIC ACID IN DILUTE CHROMIC ACID PLATING BATHS

by

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ABSTRACT

It has been found that deposits of metallic chromium may be plated on Pt cathodes from chromic acid with boric acid additions. From steady-state polarization studies of Pt microelectrodes in boric acid-catalyzed chromic acid, it was concluded that boric acid in aqueous solution can imitate the behavior of HSO_4^- in sulfate-catalyzed chromic acid solution. Consequently, the $B(OH)_4^-$ ion can complex with the polychromate ions through hydrogen bonding to act both as a blocking agent and as a catalyst. Since the number of dischargeable complexes with $B(OH)_4^-$ ions is very low (pK = 9), the efficiency of boric acid-catalyzed baths are much less than sulfate-catalyzed baths.

INTRODUCTION

It has been reported (1-3) that the optimum concentration for the deposition of Cr from dilute baths ranged between 25-50 g CrO_3/L catalyzed by H_2SO_4 with a CrO_3/HSO_4^- ratio of 100/1. However, Konishi and Tadagoshi (1) reported that the brightness range became narrower as the concentration of CrO_3 was reduced from the normal concentration of 250 g/L to the dilute, 50 g/L. LaBoda found (4) for high speed Cr plating that the brightness range could be increased in the dilute plating bath by adding boric acid to the bath. In the concentrated CrO_3 solutions, boric acid additions seemed to have little or no effect.

In nickel plating baths, boric acid is added as a buffer (5); but since solutions of strong acids such as chromic acid are inherently well buffered, the role of boric acid in chromium plating must be quite different. To shed light on the role of boric acid in dilute chromium plating baths, a basic study of this system was carried out using steady-state galvanostatic and potentiostatic polarization techniques.

EXPERIMENTAL

Platinum was chosen as the basis metal not only because Pt is well behaved in chromic acid solutions, but also because its electrochemical behavior in general is understood (6). The test electrodes were in the form of small beads (~0.04 cm^2 in area) melted at the end of Pt (99.99% pure) wires in an oxygen torch. After sealing the beads to the Teflon spaghetti covering the Pt lead wires, three test electrodes were sealed in a Teflon cell filled with the solution of interest. The details of the preparation of the electrode and cell, and the assembly of the system have been presented in earlier reports (7,8).

Runs were made in 0.25 M chromic acid to which either sulfuric or boric acid were added. To minimize mass transfer effects the solutions were stirred with purified N_2-gas bubbling at a rate of about 200 cm^3/min. Once the rest potential of Pt in the N_2-saturated chromic acid became virtually steady, the polarization curves were obtained on the Pt cathode as described earlier (7), with a saturated calomel electrode (SCE) as a reference electrode. All measurements were obtained at ambient temperature (23 ± 1°C).

At the end of the run, the cell was opened and the test electrode removed, washed in distilled water, and air dried. The coating on the Pt bead was analyzed with Auger electron spectroscopy (AES), and with argon sputtering, a depth profile of the concentration of the elements of interest was made in the surface deposit.

RESULTS AND DISCUSSION

In Fig. 1, the steady-state galvanostatic polarization curve is plotted for a Pt cathode in uncatalyzed 0.25 M chromic acid (circles). After the run, examination of the bead showed a darkening of the surface and the AES indicated that large amounts of oxygen (about 40 atomic percent, a/o) were associated with the Cr to a depth of 50 Å. Such a deposit may be considered as a smut of chromic oxides.

The plot for a Pt cathode in 0.25 M chromic acid catalyzed by 0.0025 M H_2SO_4 is indicated by the squares in Fig. 1. In this case, the bead was bright and AES analysis indicated that a thin layer of metallic Cr was deposited on the Pt surface (oxygen was about 4 to 5 a/o).

Finally, the curve for 0.25 M chromic acid catalyzed by 0.08 M H_3BO_3 is denoted by the triangles in Fig. 1. Although the bead was bright, the AES analysis detected a thin metallic layer of chromium with a high oxygen content (20-30 a/o).

The open circuit potential is a local cell potential determined by the oxidation of Pt

$$Pt + H_2O \rightarrow Pt\text{-}O + 2H^+ + 2e \qquad (1)$$

at anodic sites and the reduction of Cr VI ($HCr_3O_{10}^-$) (3,4) to Cr III (Cr^{+3} ions)

$$HCr_3O_{10}^- + 12H^+ + 6e \rightarrow 2Cr^{+3} + HCrO_4^- + 6H_2O \qquad (2)$$

at cathodic sites on the equipotential Pt surface (9). The overall local cell reaction is as follows.

$$3Pt + HCr_3O_{10}^- + 6H^+ \rightarrow 3Pt\text{-}O + 2Cr^{+3} + HCrO_4^- + 3H_2O \qquad (3)$$

The cathodic polarization of this local cell (10) produces the first linear section of the curves in Fig. 1 at low current densities.

At higher current densities, the potential falls below the reversible potential of the anodic process, Eq. 1 (~0.8 V) and the local cell ceases to exist. In this region the current is consumed in the reduction of Cr VI to Cr III, Eq. 2, and generates the second linear segment of the curves in Fig. 1. With the application of still higher current densities, Eq. 2 can no longer support the demanded current, and the potential falls at a limiting current to values where some other cathodic process can take place. This process, of course, is the reduction of H^+ ions with the evolution of H_2 gas in the third linear region of Fig. 1. The slope of this curve is about 0.03 which is consistent with the reported value (11) of the Tafel slope for hydrogen overvoltage on Pt. At the highest current densities, there follows a region where metallic Cr may be deposited if the conditions are proper.

Plotted in Fig. 2 are the steady-state potentiostatic polarization curves obtained on Pt in the same solutions studied in Fig. 1. As in Fig. 1, these curves consist of three linear regions separated by limiting current areas with the same interpretation. At the high current densities, however, one observes that the catalyzed curves double back on themselves which may be described as a negative resistance region. This behavior occurs because area changes take place when a deposit is laid down on the electrode surface. Under these conditions, the true area is greater than the apparent area, and as a result, the true current density is less than the apparent.

In Fig. 2, the uncatalyzed chromic acid curve does not exhibit a negative resistance region at high current densities in agreement with the observation from AES analysis that a metallic Cr deposit did not plate out on the Pt surface. As expected the sulfate-catalyzed curve does have a negative resistance region at high current densities betraying the presence of the metallic Cr layer detected by AES. Somewhat more surprising is the presence of a metallic Cr layer found by AES on Pt cathodized in boric acid-catalyzed chromic acid and shown by the negative resistance region in Fig. 2 (triangles).

Recently, Wu (12) observed that thin deposits of bright Cr could be deposited from CrO_3 solutions catalyzed by boric acid. He used high boric acid concentrations, 30 g/L or 0.48 M. In every case, the Cr layer was covered with a brown stain or film which could be removed by treatment with dilute acids. Wallace (13) also observed a similar behavior during the conventional plating of Cr from dilute sulfate-catalyzed CrO_3 (50 g/L) solutions.

To check on the ability of boric acid to catalyze the reduction of chromic acid to metallic Cr, steel panels (6.5 x 9.5 cm) were degreased, cleaned and plated in a Hull cell filled with a boric acid-catalyzed chromic acid solution (50 g/L CrO_3; 5 g/L H_3BO_3) at 10 A for 5 min at 45°C. In each case a brown film was obtained on the panel. A 1 cm wide strip was cut from each panel at the high current density end. The brown film formed on these panels was removed with cheesecloth and pumice since acids did not seem to remove the film as reported by Wu (12). Possibly the difference may have been that we dried our panels before stripping whereas he stripped the film while it was still hydrated. Then 1 cm square samples with and without the brown stain removed were analyzed by AES and XPS (x-ray photoelectron spectroscopy).

The brown film could not be examined with AES because of the extreme electronic charge built up on the insulating film. Consequently, only the film-free samples were analyzed with AES. On the samples, a film of Cr metal was detected under the brown film. Using positive ion sputtering and sputter rate of 1000 Å/min (calibrated with an SiO_2 film), the thickness of the Cr deposit was determined as 170 nm with an oxygen content of 18 a/o.

From XPS analysis, the brown film could be investigated. It was determined from binding energy measurements that the Cr in the film is in the Cr III state. Because of the very high oxygen content of the film (63 a/o), it is reasonable to assume that the brown stain is a layer of Cr_2O_3. Boron at a concentration of about 1 a/o was detected in the film.

According to the model of Cr deposition from chromic acid set forth in the literature (7,8), the Cr in a plating solution exists predominantly as the trichromate ion, $HCr_3O_{10}^-$. The added catalyzing agent must act not only as a catalyst but also as a blocking agent by forming complexes through hydrogen bonding with the trichromate. By consecutive electron transfer steps and reaction with H^+ ions, the proper complex can be reduced to $Cr(OH)_2$ which is in equilibrium with $Cr{=}O + H_2O$. The CrO can complex with a HSO_4^-

ion to form a chromous-oxy-bisulfate complex which can be specifically adsorbed on the cathode surface. From this complex, metallic Cr can be deposited and HSO_4^- ion split off (HSO_4^- acts as a true catalyst).

If boric acid behaves as a catalytic agent for the reduction of chromic acid to metallic Cr, it must imitate the behavior of sulfuric acid (HSO_4^- ion). It is known (14) that boric acid in water can hydrolyze to a tetrahydroxide ion with a pK of 9.00.

$$H_3BO_3 + H_2O \rightleftarrows B(OH)_4^- + H^+ \qquad (4)$$

The $B(OH)_4^-$ may then hydrogen bond with the double bonded oxygens on the trichromate ion to form a complex with one end blocked so that the opposite end may be reduced as described before (7,8). In the role of a catalyst, $B(OH)_4^-$ ions may hydrogen bond with the CrO formed during the reduction process to make the chromous-oxy-borontetrahydroxide complex from which metallic Cr may be deposited. Since the concentration of the tetrahydroxide ions should be small (large pK and strong acid environment), the number of proper complexes (8) for discharge would be much less than with HSO_4^- ions. From this viewpoint, one would expect that the rate of Cr deposition from the boric acid-catalyzed solution would be much less than for the bisulfate-catalyzed case. This expectation, of course, is realized in the very thin deposits obtained with H_3BO_3 as a catalyst.

It was observed (2) that a yellow adherent film was formed on steel tube cathodes in sulfate-catalyzed, dilute, chromic acid solution at very high rates for bright Cr deposition. This observation was accounted for by the codeposition of hydrated chromium oxide species from the bisulfate complexes. Since the rate of Cr deposition from H_3BO_3-catalyzed chromic acid is so low, brown films of hydrated chromium oxide are deposited even at the lowest current densities for which metallic Cr may be plated. As long as these stains remain hydrated, they may be removed with standing in the chromic acid. Once such films are dehydrated for analysis with AES or XPS, the brown or yellow film is converted to an insulating layer of Cr_2O_3 which is resistant to attack by strong acids. Some evidence for the concept of the codeposition of the chromous-oxy-borontetrahydroxide complex along with its discharge to metallic Cr and $B(OH)_4^-$ ion (true catalytic action) is the detection of boron in the brown film with XPS.

It is concluded from these studies, that boric acid added to dilute chromic acid solutions acts as a blocking agent to form the proper complex through hydrogen bonding for reduction of Cr VI to chromous hydroxide, and as a catalyst by bonding to the chromous hydroxide to make the chromous-oxy-borontetrahydroxide complex from which metallic Cr is deposited. Since the pK for the $B(OH)_4^-$ ion reaction is large, the concentration of proper complexes with trichromate ion is expected to be small in such an acid environment. Consequently, the rate of deposition of Cr from an H_3BO_3-catalyzed chromic acid bath is low and the deposit is accompanied by a brownish stain or film of hydrated chromium oxides.

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REFERENCES

1. S. Konishi and M. Tadagoshi, Metal Fin., 71, 49 (Nov 1973).
2. M. A. LaBoda, A. H. Holden and J. P. Hoare, J. Electrochem. Soc., 127, 1709 (1980).
3. J. P. Hoare, M. A. LaBoda and A. H. Holden, Plating and Surf. Fin., 69, 101 (May 1982).
4. M. A. LaBoda, private communication.
5. W. L. Pines, et al., in Modern Electroplating, F. A. Lowenheim, ed., Wiley, New York, 1963, p. 262.
6. J. P. Hoare, Electrochimica Acta, in press (1982).
7. J. P. Hoare, J. Electrochem. Soc., 126, 190 (1979).
8. J. P. Hoare, A. H. Holden and M. A. LaBoda, Plating and Surf. Fin., 67, 42 (March 1980).
9. J. P. Hoare, The Electrochemistry of Oxygen, Wiley, New York, 1968, p. 358.
10. J. P. Hoare, J. Electrochem. Soc., 112, 602 (1965).
11. S. Schuldiner, J. Electrochem. Soc., 99, 488 (1952); 101, 426 (1954); 106, 891 (1959).
12. S. H. L. Wu, Plating and Surf. Fin., 67, 36 (July 1980).
13. A. J. Wallace, Plating and Surf. Fin., 67, 66 (Sept 1980).
14. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience-Wiley, New York, 1972, p. 231.

FIGURE CAPTIONS

Fig. 1 Steady-state galvanostatic polarization curves obtained on a Pt cathode in N_2-stirred uncatalyzed chromic acid 0.25 M CrO_3 (circles), chromic acid catalyzed by 0.0025 M H_2SO_4 (squares) and chromic acid catalyzed by 0.08 M boric acid (triangles): open symbols denote increasing cd, and filled, decreasing. A line with a slope of 0.030 V/decade is drawn to show data are consistent with H_2 overvoltage on a Pt cathode.

Fig. 2 Steady-state potentiostatic polarization curves obtained on a Pt cathode in the same solutions as those in Fig. 1 with identical notation.

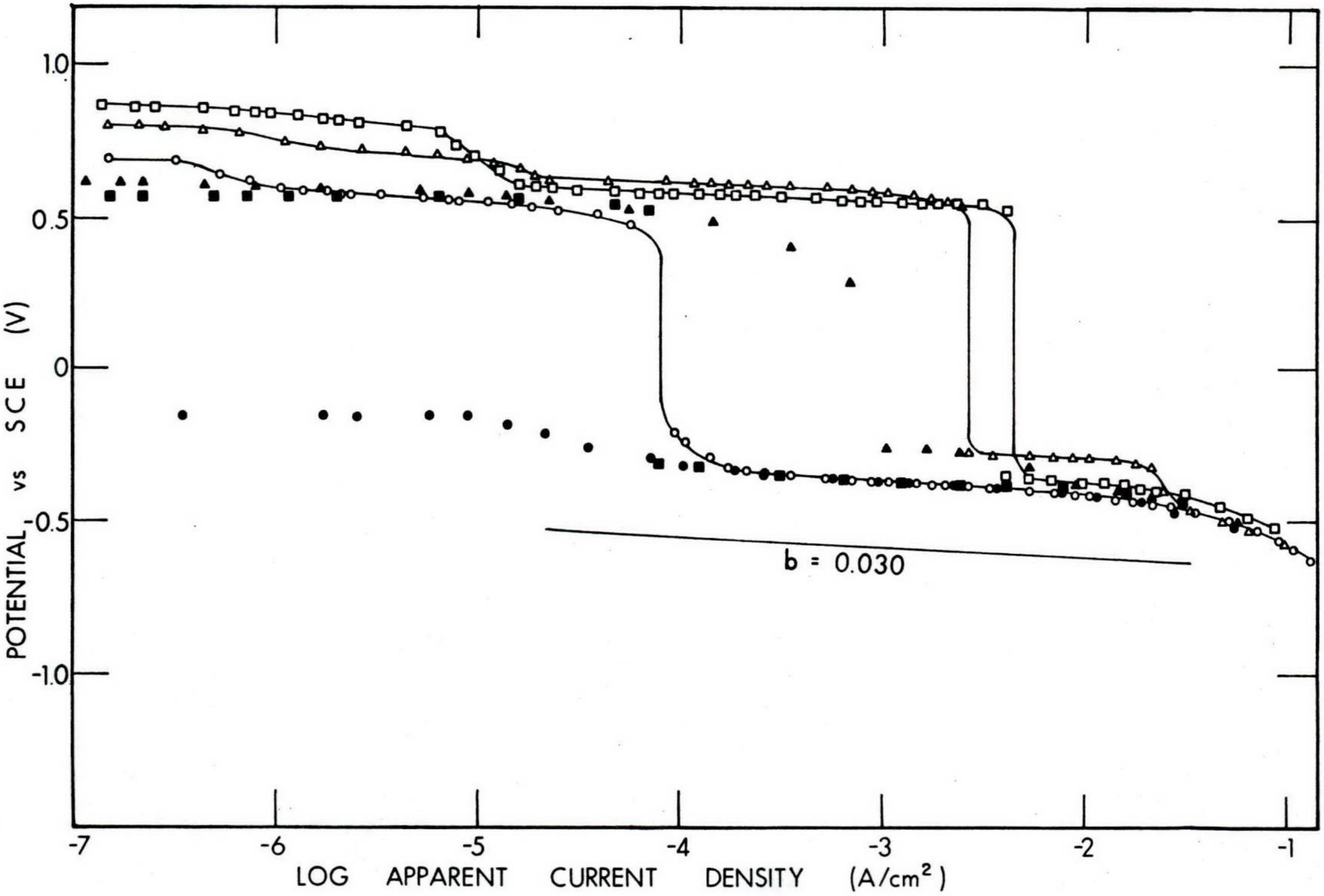
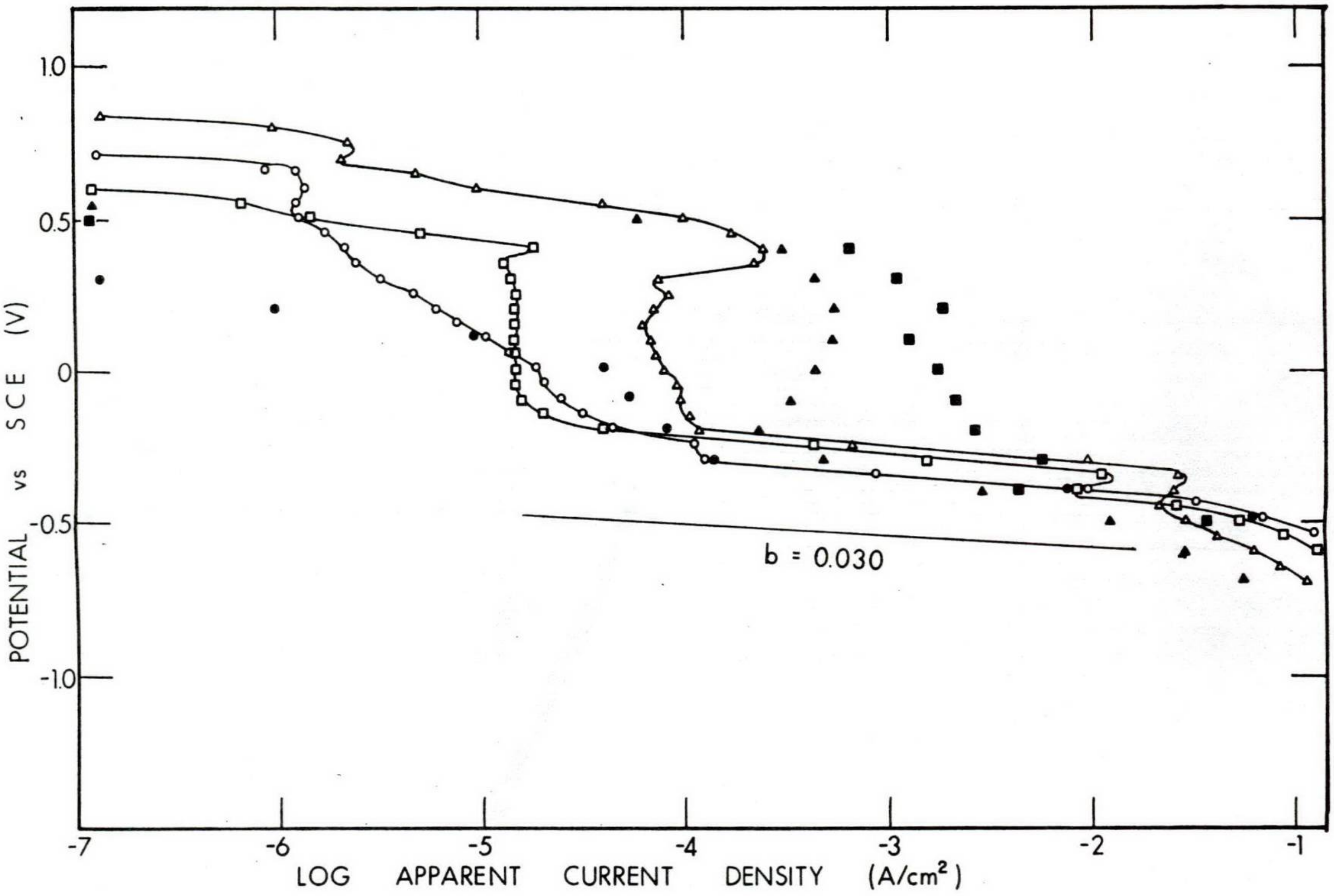

1.0
0.5
0
-0.5
-1.0
POTENTIAL vs SCE (V)
-7
-6
-5
-4
-3
-2
-1
LOG APPARENT CURRENT DENSITY (A/cm^2)
b = 0.030

FIGURE 1



1.0
0.5
0
-0.5
-1.0
POTENTIAL vs SCE (V)
-7
-6
-5
-4
-3
-2
-1
LOG APPARENT CURRENT DENSITY (A/cm^2)
b = 0.030

FIGURE 2

I-2

General Interest Session I

Cleaning, Descaling, Passivation, and Inspection of Stainless Steels

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CLEANING, DESCALING, PASSIVATION, AND INSPECTION OF STAINLESS STEELS

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Throughout the past decades, there has evolved numerous concepts and methods for achieving a passivated surface on the various stainless steel alloys. Depending on the industry served, the concepts have included: "stainless is stainless and doesn't require further processing", to "in order to achieve a uniform and corrosion resistant passivation, well-adhered-to processes and process controls are a basic requirement".

Who is right? Both concepts may be, depending on the industry served, alloy(s) assumed, and the hardware application. A sheet metal fabricator handling Condition A 300 Series alloys for kitchen exhaust hoods does have different passivation processing needs than a shop supplying finished 17-4PH castings for a Navy aircraft application. Suppliers of eating utensils and also medical supplies have yet different criteria that is not frequently addressed by industrial applications. With the diversity of needs and specifications (or lack of) to work to, just how does the plating shop effectively and consistently service the purchase orders for "passivation" and then follow up with a certification vouching for its proper completion? It is not unusual for Customer A to inspect parts for passivation uniformity, and Customer B to accept lots based solely on the certification paper.

With the continuing rise in operating costs and increasing needs/demands for yet higher quality hardware, the Flight Structures Division (FSD) of Western Gear Corporation, Jamestown, North Dakota, re-addressed our approach to traditional passivation processing and the subsequent inspection. Both in-house processing and outside purchased processing have since been affected. Three initial assumptions were made approximately four years ago. The first was to recognize the acknowledged replacement for Federal Specification QQ-P-35[1] and adapt the ASTM A 380[2] guidelines for cleaning, descaling, and passivation.

Secondly, a concerted effort was to be made to tailor the processing to our customers' needs in the most cost effective way to achieve consistently acceptable hardware, by inspection. The third goal was to participate with the ASTM committee work after accumulating experience in exercising the specification.

The remainder of this paper addresses common subtopics of passivation, presented in a question/answer format. They are questions frequently asked by our own people, vendors, and customer representatives. Being that in-depth discussions on given items may be appropriate to a group of readers, a list of references has been included at the end of this paper.

1. QQ-P-35 "Passivation Treatments for Corrosion Resisting Steel".
2. ASTM A 380 "Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems".

1. What is meant by passivation/passivity?

Passivity is a complex concept generally addressing oxide film theory and how it relates to given electrochemical conditions. The 10A to 50A invisible passive film allows the stainless steel alloys to assume a level of inertness to oxidizing environments. Stability of these films depends on their uniformity, metal surface pecularities, such as mechanically stressed area slip bands, carbide precipitates, and inclusions. Externally imposed variables would include exposure to a reducing condition, i.e., chlorides which increase surface activity and ultimately destroy the protective oxide film.

2. In general terms, how is the state of passivation attained?

Passivation of a metal surface requires that the entire bare metal surface be contacted by an oxidizing medium. Should part of the surface be covered with an oxide or dirt, a passive film is not generated in those spots, and corrosion activity is accelerated, due to the active/passive gradients created.

3. What is generally meant by "passivation treatment"?

This treatment consists of immersing cleaned and descaled stainless steel parts in a solution of nitric acid and dichromate salts, dissolving surface iron (contaminate and/or integral) and leaving an exposed and oxidized chromium rich surface.

Descriptive words sometimes become too numerous, and then they still do not really cover the practicality of the processing. The key words in the description are "cleaned" and "descaled".

4. What is meant by cleaning?

Cleaning frequently references two distinct stages of preparation. Precleaning includes the removal of grease, oils, paint, soil, grit, or other gross contamination that needs to be done prior to descaling or fabrication of weldments. Precleaning is accomplished by vapor degreasing, scrubbing with abrasive cleaners, solvent wipe down, high pressure stream, water jets, etc. Descaling follows the precleaning, and then comes final cleaning. Final cleaning is done immediately prior to immersing the hardware in the passivation solution to assure that all exposed metal surfaces are free of oils or other handling contaminants that inadvertently were collected after descaling. Vapor degreasing and alkaline cleaning are most frequently used for this operation. Electrolytic alkaline cleaning or acid electrocleaning (controlled electropolishing) can also be effectively used.

5. What is meant by descaling, and is it really necessary?

Removal of all thermal oxides is needed, whether it be from heat treating, forging, or casting. Manhour allowances in many facilities for "passivation processing" frequently overlooks the more labor intensive descaling procedures which may include one or more of the following:

- Mechanical Descaling - Sandblasting is the most common. Use of a 150 grit alumina produces a fairly uniform surface suitable for subsequent passivation, and it also adequately prepares surfaces that will ultimately be painted or coated with a dry film lubricant. Topography of a sandblasted surface is less desirable than a smooth surface because of its tendency to retain foreign residues and form micro bubbles that slow down the wetting action during passivation.

- Electrocleaning (alkaline) - Use of a reversible alkaline cleaner is very effective in removing heat treating scale. Unlike the sandblasting, there is no increased topography realized. Cyanide and non-cyanide containing baths are commercially available, as are the rectifiers having automatically timed reversing cycles.

- Electrocleaning (acid) - This could also be referred to as controlled electropolishing. Although not as effective for scale removal as the reversing alkaline bath, it does remove light scale (oxide discoloration), dissolves iron, and oxidizes the chromium. Almost sounds like passivation, doesn't it? It is a passivation procedure that takes approximately a 20 second cycle. There are additional controls required on the bath in order to assure that close tolerance dimensions are maintained. A metal removal rate of less than .00015" for a 20 second cycle at the Western Gear Corporation facility has proven to be acceptable for just about all of the machined hardware. Where tolerances are less than ± .0005", the electrocleaning is either not used, or the critical dimension may be masked. Also, electrocleaning should not be used on hardware requiring a coat of solid film lube.

  Electrocleaning is extended into electropolishing on many programs in order to obtain additional corrosion protection, visual effects, and/or surface finish requirements. In these cases, the metal removed may approach .001" per surface and, therefore, must be preplanned.

  Stainless steel investment castings are particularly well suited for electropolishing prior to machining. Refer to question 8.

- Acid Pickling - Acid pickling removes metal, but unlike electropolishing which liberates oxygen on the parts, the acid cleaning baths liberate hydrogen. Thus, a subsequent and timely post-bake is necessary for the pH, ferritic, and martensitic alloy grades. In the case of castings, the metallurgical variables within the castings themselves will favor non-uniform metal removed rates. Although the acid etch method is effective and has been used cautiously for many years, we recommend its usage in the aircraft hardware industry to be limited to non-structural hardware.

6. Should passivation be accomplished with a given procedure?

Yes, as long as it is documented and produces a demonstrated uniform film consistently. The procedure itself will vary from company to company, but the determination of acceptance is measureable by inspection criteria.

For all prime contractors on government programs a "Corrosion Prevention and Control Plan" is a contractually required document to be completed before hardware delivery. The submitted plan is distributed among the affected hardware users for reviews and comments which ultimately must be responded to at a design review prior to hardware delivery. With product liability being a reality for all manufacturers, pursuing a well controlled processing capability is of interest.

7. What is realistic inspection criteria for uniformity of passivation?

With the exception of the 400 series alloys, the most realistic and cost effective procedure is to 100% check using a coppersulfate solution per ASTM A 380. The 100% check is completed by processing personnel. (A subsequent QC inspection is accomplished on a sample basis.) A bath is set up for total immersion of the parts following passivation rinse. This approach has some very positive features, as listed.

- It provides the processing personnel with continual guidance as to the effectiveness of the overall cleaning, descaling, and passivation process; and when copper deposits are realized, there is a positive and timely indication of a problem whether it is traceable to the baths, procedures, or material.

- When copper sulfate reacts with iron, an exchange reaction occurs on the steel surface during which the surface iron is displaced, allowing the copper to deposit. Thus, for a failed lot, the copper sulfate bath has inadvertently become an asset to re-passivation because of the prior reaction, and chances are very good that re-running the parts will result in a favorable inspection.

Other inspection criteria has been written into various documents, as listed.

- Sample Panel - A 300 series alloy test panel is referenced to be run with loads being passivated and acceptance based on humidity test of that panel. Obvious problems using this test procedure arise since the panel simply does not represent machined hardware, particularly structural pH series alloys, forgings, castings, or machined parts.

- Humidity Test - These tests do not provide timely results, and results are generally interpretive.

- Certification - I have found that some companies accept passivation processing based solely on a certification paper stating that a given procedure was completed. This is a cost effective alternative but not too reasonable for processing structural hardware carrying unwritten liability warranties, and contract agreements such as "Corrosion Prevention and Control Plans."

8. Are there apparent degrees of passivation that are peculiar to different alloys or products?

The wrought austenitic series is by far the most readily passivated. In fact, in many cases, the oxidizing that occurs in a normal atmosphere is sufficient to provide passivity. As chromium content drops or carbon increases to tie up the available chromium, the effective passivation is reduced, and the alloy is less corrosion resistant.

As can be concluded, the 400 series alloys really are not classical stainless alloy by the same criteria as a 300 series alloy. Application of 400 alloy series hardware is best made when all surfaces are highly polished and in a lubricated environment, such as bearings. In some applications other than household cutlery, the items may be cadmium plated.

Investment castings deserve special recognition, particularly the structural pH alloy type. Some processed lots will resist acceptance of passivation much more than others. This can be traceable to a carbon pickup which results from reactions between the molten metal and mold, or it can be due to cooling rates and formation of a delta iron. Much of the segregation can be eliminated or reduced if the casting has been through a homogenization high temperature heat treatment. At Western Gear Corporation, troublesome lots are experienced periodically and do require repetitive cleaning and a descaling cycle in order to attain a good surface.

9. What process controls are desirable?

Depending on the company QC organization and the customers served, a greater (or lesser) amount of paper controls exist. I will assume that adequate controls/inspection are available for the cleaning and descaling processes, and start with passivation.

- Passivation Bath - A relatively simple way to control the bath and assure its activity is by drawing a one gallon sample (for the Lab) each time the bath is renewed. Then, during the duration of bath use, the Lab sample bath becomes a reference referee should a problem arise. Problem parts are then run in the Lab sample. If they accept passivation, then the processor's bath is likely the cause. Should they fail, then there is a material or procedural problem. No bath titration analysis is done at Western Gear, since the bath is frequently renewed and made up to the concentration called for in the in-house specification.

At one time, monitoring of the bath using the hydrometer methods was done. After some frustrating results with the "certified hydrometers", and an evaluation of these hydrometers for accuracy and spread, we learned that the reliability of reading was not satisfactory and generally misleading. At that time, the one gallon Lab sample approach was adopted.

As mentioned in item 7, the primary process control of the invisible film is the use of a 100% immersion of parts in the copper sulfate solution. This does not apply to the 400 series alloys and is used cautiously with the 303 free machining grades. Free machining grades contain non-metallic stringers which act as chip breakers. They also selectively protect surface iron from being removed during passivation.

10. Does the coppersulfate test work 100% of the time?

Not 100%, but just about. There is a nasty phenomenon that does occur on occasion, called pseudo passivation. In plain words, it means that the processor can indeed very conscientiously complete the entire passivation cycle, pass a coppersulfate test, ship your parts, and then the parts will fail miserably in your facility. No one has, to my understanding, really been able to document the explanation of why parts can be passivated, then after handling revert back to an active state. However, re-running of the parts does correct the situation, particularly if the parts are processed through an acid electroclean process.

Other observations and practices that reduce rework time of pseudo-passivated hardware include:

- Rinse water - use of warm D.I. is more favorable than cold tap water (in North Dakota). In some geographical areas, there may be chlorides in the tap water that cause deterioration of the passivation oxide layer during all passivation processes, including the final rinse.

- Follow the water rinse with an alcohol dip plus fan dry before immersing in the copper sulfate bath. A wet part having unstable passivation may not respond to the test.

11. Is the passivation processing costly?

Costs and delivery are important criteria for staying in business. As with any process, costs vary depending on labor rates, quantity, degree of automation, geometry, and requirements. ROM estimates of manhours can be offered and accepted as relative figures only (assume 100 piece lot).

	Manhours/Part
Cleaning	.002
Descaling	
Sandblasting	.010
Electroclean (alkaline)	.002
Electroclean (acid)	.002
Passivate/Inspect	.004

Standard total run times for many jobs is in the order of .01 manhours.

12. Is there an industry wide specification available that addresses cleaning, descaling, passivation, and inspection processes for stainless steel alloys?

    Yes. ASTM A 380 is now one of the available documents, starting with the '78 revision. Federal Decument QQ-P-35 had been and still is widely recognized. However, the Army (custodian) withdrew interest and formally accepted ASTM A 380 as its replacement document in 1980 (refer to addendum). The '78 revision of the ASTM document incorporated much of the QQ-P-35 information.

    ASTM A 380 addresses recommendations and precautions for cleaning and descaling the stainless steel alloys. From it, a suitable in-house document can be formatted. However, that still leaves the industries processors with innumerable individualized documents that might more suitably be addressed in a new revision of the ASTM document.

13. What can be done to facilitate changes, if desired, to the ASTM document?

    First, please review the referenced document. It addresses a wide range of industries and will likely generate a wide range of responses/impressions.

    Second, please document your impressions, ideas, and desires relative to use (or potential use) of the document in your facility.

    Third, please send your notes to the author of this paper. You are also welcome to make a telephone call.

14. Can the use of ASTM A 380 or a revision of it be a benefit to processors and their customers?

    The practices of passivation processing vary considerably as do the needs from industry to industry. As the requirements vary, so do costs, whether they be short term or related to product liability. Should a purchase order reference ASTM A 380 or other document that provides guidance and an initial understanding for processing, then it has assisted in vendor-customer communications and definition of cost.

REFERENCES

1) Peckner and Bernstein, Handbook of Stainless Steels, McGraw-Hill, 1977, (Chapters 16, 24, and 38). Discusses in-depth processing and theory.

2) Hall (ed.), Metal Finishing and Guide Book Directory, Metals and Plastics Publications, Inc., Hackensack, N.J. Published annually and received with subscription to Metal Finishing. Good for description of individual chemical.

3) Ugiansky, Payer (ed.), Stress Corrosion Cracking, The Slow Strain Rate Technique, ASTM, 1979 (pp. 312-313). Discusses SCC susceptibility of various stainless alloys.

4) NACE Task Group, Corrosion Problems Due to Carbon Pickup in Stainless Alloy Castings, NACE Headquarter, Houston, Texas, Publication No. 5A179. Discusses causes and cites examples.

5) Fontana and Greene, Corrosion Engineering, McGraw-Hill, New York, 1967 (predominently Chapter 5). However, numerous references throughout the book either directly or indirectly address passivity.

6) Faust, Electropolishing, Metal Finishing issues July 82, (pp. 21-25), August 1982 (pp. 59-63), September 1982 (pp. 89-93), Metals and Plastics Publications, Inc., Hackensack, N.J.

7) Federal Specification QQ-P-35 (1973) entitled, "Passivation Treatments for Corrosion Resisting Steel".

8) ASTM A 380 1978, entitled "Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems".

In addition to the eight listed references, there are major company specifications and intercompany papers addressing passivity that are generally available to their vendors on request.

Addendum

ANSI/ASTM A 380-78
31 January 1980
USED INSTEAD OF
QQ-P-35B
5 April 1973

ACCEPTANCE NOTICE

The above non-Government Document was adopted on 31 January 1980 and is approved for use by the DoD. The indicated industry group has furnished the clearances required by existing regulations. Copies of the document are stocked by DoD Single Stock Point, Naval Publications and Forms Center, Philadelphia, PA 19120 for issue to DoD activities only. Contractors and industry groups must obtain copies from ASTM, 1916 Race Street, Philadelphia, PA 19103.

Title of Document: Cleaning and Descaling Stainless Steel Parts, Equipment, and Systems

Date of Specific Issue Adopted: 28 July 1978

Releasing Industry Group: American Society for Testing and Materials

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I-3

General Interest Session I

Trivalent Chromium: A Commercially Viable Alternative

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TRIVALENT CHROMIUM: A COMMERCIALLY VIABLE ALTERNATIVE

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Abstract

A high performance, decorative trivalent chromium plating process with superior properties has been developed. The new process has been found to be dependable and more tolerant to metallic contamination than previous systems, based on development of a unique addition agent system. Production experience has proven that the new system can be readily adapted to existing equipment and plating cycles and that it provides improved productivity, quality, bath reliability and reproducibility of deposit appearance and properties. Deposits have an inherent microdiscontinuous surface, outstanding covering power, good color and hardness comparable to that of hexavalent chromium. In exterior applications, corrosion performance compares favorably with hexavalent systems. Numerous operational advantages demonstrate the utility of this new technology.

Introduction

Chromium deposition from electrolytes containing trivalent chromium salts has been in commercial use since the late 1970's. The benefits of trivalent chemistry are improved covering power, absence of high current density burning, low metal concentration, elimination of hexavalent chromium and improved performance; all of which lead to increased productivity and reduced cost of operation.

The commercialization of a trivalent chromium plating process was a long time in coming. Initial deposition of chromium from such electrolytes took place in the late 1800's.[1-3] Over the years, considerable research has gone into attempts to develop a practical trivalent chromium plating process.[4-21] Unfortunately, most of these processes exhibit inherent disadvantages, and fail to match the dependability of hexavalent chromium baths.

Problems encountered in attempting to develop a viable trivalent chromium plating process were largely due to the complex nature of the chemistry of chromium (III) in aqueous solutions. It was suggested that cations such as chromium (III) are strongly solvated.[22] They form aquo-complexes,[23] whose inner coordination sphere is so tightly bound that chromium cannot readily be released from the complex. In order to deposit chromium metal from trivalent chromium electrolytes, one must prevent the trivalent chromium ion from forming these very stable aquo-complexes.[24] The most feasible solution to this problem is to replace the water molecules surrounding the chromium ion by other complexing ligands. The new metal complex that is formed should be sufficiently stable to retain the chromium as part of the complex yet permit the chromium to be released during electrolysis and subsequently deposited on the cathode.

In the early 1970's various government agencies encouraged the metal finishing industry to curb the use of hexavalent chromium. Chromic acid has undesirable characteristics. It is toxic and corrosive to the skin causing ulcers; inhalation causes damage to the respiratory system, and it is a suspected carcinogen. In anticipation of further government regulations, a research program was initiated which results in development of the novel trivalent chromium process described in this paper.

Solution Composition

The plating solution composition is summarized in Table I. The bath contains conductivity salts, a buffer, catalyst, complexing ligand, trivalent chromium salts and a reducing agent.

The conductivity salt is a dry mix containing alkali metal and ammonium salts, (e.g., chlorides, fluoborates and sulfates) which improve the conductivity of the bath. These chemicals are lost by drag-out. The conducting salts also contain other chemicals which are essential to the proper function of the bath. These include boric acid and a reducer which controls the reaction at the anode.

The reducing agent limits the formation of hexavalent chromium during electrolysis where the use of insoluble anodes results in trivalent chromium being oxidized to hexavalent. The reducer is lost by drag-out.

The catalyst's main function is to improve chromium distribution on areas where air agitation is not very effective; it also reduces surface tension to minimize drag-out losses.

The role of the complexing ligand is to form the proper water soluble complex with the chromium ion allowing the metal to be readily deposited at the cathode. The complexing ligands, generally simple aliphatic carboxylic acids, together with the trivalent chromium, chlorides, sulfates and ammonia form the coordination complex from which chromium is deposited. The complexant is lost both by drag-out and through electrolysis.

Chromium is supplied to the bath in the form of trivalent salts such as, chromium sulfate ($Cr_2(SO_4)_3.XH_2O$) and/or chromic chloride ($CrCl_3.6H_2O$). The sulfate salt is generally preferred because of the cost factor.

The process solution is maintained by replenishment based on drag-out and/or electrolytic consumption. Electrolytic consumption exceeds drag-out loss for the complexant, chromium and catalyst and these are maintained by making additions on an ampere hour basis. Analysis for these materials provides the final control.

Operating Conditions

Operating parameters are summarized in Table II. The pH range of this bath is 2.8-3.5. An optimum pH range of 3.0-3.2 provides the most effective compromise between deposition rate and covering power. Below a pH of 2.8 the covering power of the bath is reduced though plating speed is increased. At pH values about 3.5 one obtains improved coverage at the expense of plating speed. The pH has to be monitored instrumentally and maintained within the specified range by addition of ammonium hydroxide.

The optimum operating temperature range is 18°-30°C (64°-85°F). Covering power increases at the lower end of the temperature range, while higher temperatures will decrease the coverage and tend to produce nonuniform, dark chromium deposits. Operating the process continuously on a production basis, above 0.5 ampere per liter, may increase the temperature above the specified range and require cooling of the solution.

Cathode current densities of 10-21 A/dm^2 (100-200 A/ft^2) are generally employed. It was noted that plating at high current densities, i.e., up to 40 A/dm^2, does not produce burning. This lack of burning at high current densities is associated with a decrease in cathode efficiency with increasing current density.

Efficiencies of 11-14 percent have been obtained for this plating process, which is nearly identical to the values of 12-15 percent for hexavalent systems. The reason that efficiencies of both processes are so close is the fact that chromium metal is deposited from the trivalent state in both processes.[25] The deposition of chromium metal from trivalent chromium solutions was discussed earlier. The mechanism for the electrodeposition of metallic chromium from conventional chromic acid - sulfate plating systems takes the form of reduction of chromium (VI) by electron transfer to chromium (III). In the conventional hexavalent chromium plating process it is from this chromium (III) state that the deposition of chromium takes place. To protect the chromium (III) formed from reacting with water to form the very stable aquo-complex, $Cr(H_2O)_6^{+3}$, a chromic-dichromate complex is formed.[26]

Air agitation is utilized to insure uniform metal distribution. Agitation must cover the entire area under the cathode surface. Too little agitation may produce uneven metal distribution while too much may reduce coverage.

Equipment

Equipment for commercial operation of this process is summarized in Table III. Plating tanks must be of plastic or rubber lined. Lead-lined tanks cannot be used. Existing hexavalent chromium tanks having acceptable liners can be used only if they are thoroughly cleaned and leached to remove all traces of hexavalent chromium and lead.

High purity carbon (graphite) anodes equipped with a copper core are used, and connections should be made which are both mechanically and electrically sound. Bus bars must be protected from the plating solution to avoid contamination of the plating bath.

Plastic air lines, such as those designed for nickel processes, can be utilized to supply air agitation to the bath. A sufficient number of lines should be installed to cover the anticipated cathode area.

Since the optimum temperature range is 18°-30°C (64°-86°F), some means of cooling is necessary for high volume, continuous production. Teflon coils or plate heat exchangers using cold water or refrigeration may be used. Cooling the solution below 15°C (60°F) should be avoided as crystallization of salts can occur restricting solution flow. In cold weather heating may be required to prevent precipitation of salts during idle periods.

To accommodate wide variations of anode and cathode areas, anode to cathode spacing, and other sources of voltage drops, rectifiers that provide 6-24 volt output have been found to be satisfactory. Trivalent solutions are less conductive than hexavalent chromium, and generally require higher voltages. Where possible, the anode to cathode distance may be decreased to offset the additional voltage required. Reducing the voltage will decrease the energy input and reduce the amount of cooling required.

Filtration of the trivalent chromium bath is recommended, especially to remove any precipitate formed from treatment of the bath for metallic contamination. Filters suitable for use with high chloride nickel solutions have been found to be satisfactory.

Ventilation is recommended as a standard operating procedure to remove any gases evolved.

Additional equipment, which may prove beneficial for process control includes; a pH meter, ampere-hour meter, hydrometer and stalagmometer.

Contamination and Purification

Trivalent chromium solutions are more sensitive to heavy metal contamination, such as, copper, iron, lead, nickel and zinc than hexavalent chromium, as shown in Table IV. These tolerance levels for heavy metal contamination are at optimum conditions, and in practice will generally be lower, since more than one contaminant normally will be present in the bath. However, production experience has indicated the process is more tolerant to nickel and iron contamination by a factor of 2 and 4 respectively compared to other commercial processes. The effect of these impurities in trivalent chromium deposits is to produce hazy-white to very dark, streaked thin deposits having poor coverage. Nickel contamination is due to improper rinsing between the nickel and chromium. This problem can generally be corrected by an efficient rinse cycle.

Lead contamination is the result of leaching of lead salts from liners previously used for hexavalent chromium baths. In spite of thorough cleaning, some lead and chromium salts can remain in the lining. Lead contamination can be removed by low current density electrolysis as well as by precipitation.

Copper, iron and zinc contamination results from dropped parts or attack on unplated areas, as for example, blind holes and open tubing. Fortunately, these impurities can be removed either by precipitation and filtration or by low current density electrolysis. Good results can be obtained by electrolyzing at 1 to 3.2 A/dm^2 (10-30 A/ft^2) using nickel plated cathodes with high surface areas.

Frequency of bath purification will depend on the efficiency of the rinsing between nickel and chromium, type of work being plated, number of parts falling into the tank and plating time. Where nickel drag-in is an ongoing problem, and cannot be corrected because rinsing procedures cannot be improved, treatment of the bath on a routine basis may be necessary.

Use of a Controller material, which allows plating of acceptable chromium deposits from contaminated baths, and a cyanide free Precipitant for this process will be discussed under "Production Experience".

Physical Properties

The color of the chromium deposit plated from the process described in this paper, is close to that of hexavalent chromium. Figure I, compares two identical parts, one plated in a hexavalent bath and one plated in a trivalent chromium bath. Results show very little difference in color between the two. Figure II shows a variety of parts that have been plated in this trivalent chromium process and the excellent results that have been obtained.

Hardness measurements were made, using a Diamond Pyramid Indenter under a 100 gram load, on chromium deposits ranging in thickness from 58 µm to 74 µm (0.0023 to 0.0029 inches). The results summarized in Table V indicate that the new trivalent chromium system produces deposits which compare favorably with the hardness of hexavalent chromium deposits.

Deposits from this process, like those from other trivalent processes, are microporous up to 0.2-0.3 µm and microcracked above 0.6 µm. A cross-section view of a typical deposit is shown in Figure III. The photomicrograph shows the pores and cracks traversing the thickness of the chromium plate. The photomicrograph of a cross-section of a chromium plate from a chromic acid bath is compared in Figure IV. The chromic acid deposit shows many short, random pores which never come close to traversing the thickness of the chromium deposit.

Deposit Composition

A significant difference was found in the chromium deposit composition between trivalent and hexavalent chromium deposits as shown in Table VI. Differences in composition could certainly account for the variation, in such properties as color, stress and inherent microporosity/microcracking.

Corrosion Performance

Corrosion performance of these trivalent chromium deposits, which have a natural microporosity, was compared with both microporous and nonmicroporous hexavalent chromium systems. Comparison was made using duplex nickel-chromium as well as thin nickel (5-8 μm) chromium systems.

All deposits were plated on 10 x 17 cm (4 x 6 inch) steel panels. Identical bright nickel deposits were utilized on all test panels. Microporosity in the hexavalent chromium was induced by interposing a 1 to 2 μm nickel deposit containing fine, insoluble particles between the final bright nickel and hexavalent chromium deposits.

Duplex nickel-chromium panels were exposed to marine and industrial environments. The marine exposure was at Kure Beach, North Carolina at a site 240 m (800 ft.) from the ocean. The industrial site was a roof in Warren, Michigan, which has a moderately severe industrial environment. The thin nickel-chromium deposits were subjected to a neutral salt-spray test.[27] Test panels were rated according to a standard ASTM rating system.[28]

Table VII summarizes the corrosion performance data for duplex-nickel-chromium on steel. The corrosion performance of trivalent chromium deposits is equivalent to those of hexavalent chromium in the industrial environment, and significantly better than hexavalent chromium in the marine environment. Corrosion performance of microporous hexavalent chromium is only slightly better than trivalent chromium in both industrial and marine exposure.

Thin nickel - chromium (III) deposits appear to be more susceptible to corrosion than those obtained from hexavalent chromium, under the same conditions after six hours in neutral salt spray. As a result, it is necessary to use a suitable post-dip in order to enhance the corrosion resistance of these deposits.

Production Experience

The two key factors to consider when taking a new process from the research laboratory to a production situation are:

1. Will the process produce consistent results on a day to day basis under production conditions? Specifically, can the process stand up to around-the-clock operation with minimal technical control and no loss of production?
2. Will the process operation be cost effective? How is the cost of the finished product affected by the process?

The new trivalent chromium process has now operated in the field for over two years in a wide range of applications including steel stampings, wire goods, and tubular steel.

What lessons have been learned from field experience on the ability of the process to produce consistent results? Historically, trivalent chromium was considered a greater control problem than hexavalent chromium due to the number of additions required to maintain the process. Trivalent systems also have exhibited relatively low tolerance to metallic impurities when compared to hexavalent systems.

Production experience has shown that maintenance of bath constituents has not been a major problem. Laboratory facilities used to maintain the process have ranged from as little as a pH meter to fully equipped laboratories. A typical control program consists of the following:

1. Daily pH check
2. Weekly chromium analysis
3. Weekly conductive salt analysis
4. Weekly Hull Cell tests
5. Monthly metallic impurity check

Process control other than the impurity check, does not require special laboratory equipment or procedures. Laboratories presently equipped to maintain nickel and hexavalent chromium process solutions are adequate. Moreover, "in-tank" conditions are duplicated very closely by Hull Cell panel testing which can be used to predict the effect of additions to the trivalent process.

Field experience has also shown that the new trivalent process has an improved tolerance for the two major metallic impurities encountered in production, specifically nickel and iron. The major effect of these two impurities is black deposits in the high current density areas. Production experience has shown that 400 mg/L nickel and 1000 mg/L iron is trouble free and values even as high as 550 mg/L nickel and 2000 mg/L iron have been tolerated. Even with a highly tolerant process, impurity control is still important in order to maintain consistent production.

Two unique service tools were developed for use in the trivalent process to insure consistent production. The first material is the Controller - whose function is to surpress the formation of black deposits resulting from high nickel and iron levels. The Controller is added at the first sign of trouble and allows production to continue until the impurities can be removed as part of planned maintenance. The second service tool is designated as a Precipitator and its function, as the name implies, is to remove harmful nickel and iron impurities by precipitation and subsequently removing them by filtration. The unique features of the Precipitator are:

1. Use of the Precipitator in excess will not permanently damage the process due to breakdown of the chromium complex.

2. The Precipitator can be added directly to the process while in operation.

3. The metallic precipitate formed is very coarse, facilitating its easy removal thru a filter without excessive plugging and eliminating redeposition of powdery deposits on the plated work.

4. The precipitate requires no special waste treatment.

5. Unlike other precipitators, it is free of cyanide and its derivatives.

Consistent operation is but one factor in a successful process. For a new process to be practicable, it must be economical. The cost of installation and chemical maintenance must be offset by its operating characteristics.

When considering installation of a trivalent system, the present operating cycle must be considered in determining the number of stations available for use in the new process. A typical trivalent cycle is shown in Table VIII. Good rinsing between nickel and chromium is essential in order to prevent the carryover of nickel salts into the trivalent solution. A "dry-tank" is preferred ahead of the trivalent process to limit volume build-up in the trivalent chromium tank. Dilute chromium activating solutions used in many hexavalent chromium cycles are not necessary. For cycles using thin nickel or ferro-nickel deposits, or in operations processing tubular steel, a proprietary post-dip is required to remove any entrapped chloride ion and to passivate unplated or low current density areas where a thin underlying deposit may be porous.

The trivalent system has been introduced into existing hexavalent chromium plating cycles with little or no changes. Installation of the trivalent process requires that all hexavalent chromium salts be removed from existing tanks. In older installations, the use of drop-in tank liners may be more cost efficient than cleaning existing tanks. Cooling requirements will vary for individual installations. A trivalent process running in Michigan and applying less than 2 amperes per gallon current to the process tank has been operated satisfactorily using tap or well water for cooling, whereas a bath operated in the South with currents over 2 amperes per gallon definitely requires refrigeration. The key factor influencing the selection of a rectifier is to insure that the amperage available is high enough to take full advantage of its potential for increased productivity.

In analyzing the comparative cost of conventional and trivalent chromium processes, several factors must be considered. In terms of the cost of chemicals consumed, the hexavalent system is more economical to operate. Typical trivalent chromium chemical cost is 2-3 times the cost of hexavalent chromium. The cost differences are from drag-out based on the higher make-up cost per gallon of trivalent chromium. One important aspect of running trivalent chromium is to eliminate drag-out through the use of delay times over the trivalent tank and drag-out rinses.

Despite the increased chemical cost, the trivalent process is still more cost effective to operate due to its improved productivity. The following features have been demonstrated under full production conditions:

1. The trivalent process has the unique ability to eliminate high current density burning and provide excellent low current density coverage, allowing more parts to be plated per rack. Increases in rack area up to 50% have been achieved in trivalent installations. In addition, current robbers, shields and, in many cases, auxiliary anodes have all been eliminated from racks.

2. Further economies in operation are achieved by drops in reject rates up to 50%. The trivalent process not only eliminates high current density burns and many chrome stains; it also does not produce the whitewash stains caused by electrical current interruption which plague many operations.

3. Labor cost savings are achieved by elimination of color buffing operations for chromium burns and whitewash. Use of trivalent chromium has allowed, in several operations, one and sometimes more employees per shift to be relieved from chrome buffing duty to pursue more productive work.

The cost of waste treatment for both trivalent and hexavalent chromium can vary widely, depending on existing equipment and local regulations. In many cases, it is possible to simply neutralize and precipitate the trivalent effluent in the existing facilities. The high cost of chemically reducing the hexavalent chromium, which can run as high as $1.25/pound of chromium, is completely eliminated.

Further cost savings are available through reduction of metallic sludges. Trivalent chromium contains 25 grams/Liter total chromium compared to 120-140 grams/Liter chromium in a standard hexavalent process. Given equal drag-out conditions, the weight of sludge to be disposed of from a trivalent chromium process is reduced by a factor of 5 or 6.

Elimination of hexavalent chromium itself is a major benefit of the trivalent process. Removal of dangerous chromic acid spray, elimination of storing and handling problems, as well as the elimination of hexavalent chrome bleed-out in racking areas are also important considerations.

Finally, the trivalent process, because of its excellent covering power, produces a quality chromium finish on parts which were previously run through nickel-only cycles because of chromium coverage problems. The process is particularly well adapted to completely cover holes and slots which, in the past, have been marginally acceptable. Complex wire displays, which were sent out for zinc plate to obtain a uniform appearance, are now nickel-chromium plated with complete coverage. In addition, the trivalent system is not sensitive to high nickel brightener levels.

Conclusion

A practical trivalent chromium process has been developed and subjected to over two years of field experience. The benefits of this process are significantly improved chromium coverage which allows more parts per rack, reduced reject rate, improved quality, reduced waste treatment cost and elimination of toxic chromic acid. These advantages result in a significant increase in productivity which, in turn, leads to reduced unit cost.

Corrosion performance, for exterior application, compares favorably with hexavalent systems, both in marine and industrial environments. For interior specifications using thin nickel deposits, a post-dip treatment is required for equivalent protection.

The future of trivalent chromium plating, as an alternative to the hexavalent process appears bright since a highly reliable process is now available which offers significant improvement in productivity in addition to a substantial reduction in environmental risk.

BIBLIOGRAPHY

1. Junot de Bussy, French Patent 3,564 (Nov. 17, 1948)
2. R. Bunsen, Ann., 91, 619-25 (1854)
3. U.S. Patent 526,114
4. Tegelsberger, Z. Angew. Chem., pp. 1123-8 (1899)
5. S.O. Cowper-Coles, Chem. News, 81, 16-18 (1900)
6. J. Feree, Bull. Soc. Chem., 25, 617-18 (1900)
7. B. Neumann, Z. El. Chem., 7, 656-61 (1901)
8. H. R. Carveth and W. R. Mott, J. Phys. Chem., 9, 231-56 (1954)
9. J. Voisin, Revue de Metallurgi, 7, 1132-48 (1910)
10. W. Traube and A. Goodson, Ber., 49, 1679-91 (1916)
11. W. Traube, E. Burmeister and R. Stahn, Z. f. anor. allgem. Chem., 147, 50-67 (1925)
12. W. Pfanhauser, Galvanotechnik, 7th Ed., p. 586 (1928)
13. C. H. Proctor, Metal Ind., 26, 170 (1928)
14. U.S. Patent 1,781,789
15. U.S. Patent 2,088,615
16. U.S. Patent 2,377,229
17. U.S. Patent 2,704,273
18. U.S. Patent 2,801,214
19. U.S. Patent 3,006,823 and 3,069,333
20. U.S. Patent 3,706,363; 3,706,537; 3,706,638; 3,706,639; 3,725,214
21. U.S. Patent 4,054,494
22. R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Academic Press, New York, 2nd Ed., 1959, p. 70

23. J. P. Hunt and H. Traube, J. Chem. Phys., 19, 602 (1951); 18, 757 (1950)

24. J. P. Hoare, On the Mechanism of Chromium Electrodeposition, I. Uncatalyzed Chromate Solution, Journal of the Electrochemical Soc., 126, No. 2, pp. 190-99, Feb., 1979

25. G. J. Sargent, Trans. Amer. Electrochem. Soc., 37, 479-497 (1920)

26. J. P. Hoare, A. H. Holden and M. A. LaBoda, On the Kinetics of High Speed Plating of Chromium, Plating and Surface Finishing, pp. 42-46 March, 1960

27. ASTM B 117, Standard Method of Salt Spray Testing

28. ASTM B 537, Standard Recommended Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure

TABLE I

SOLUTION COMPOSITION

MATERIAL	CONCENTRATION
Conductivity Salt	225 g/L (30 oz/gal)
Catalyst	1 mL/L (0.1% by volume)
Complexant	80 mL/L (8.0% by volume)
Chromium Metal	22 g/L (2.9 oz/gal)
Reducer	2 g/L (0.26 oz/gal)

TABLE II

OPERATING PARAMETERS

OPERATING CONDITIONS	RANGE
pH (Electrometric)	2.8-3.5
Temperature	18°-30°C (64°-86°F)
Cathode Current Density	10-21 A/dm^2 (100-200 A/ft^2)
Anode Current Density	5-10 A/dm^2 (50-100 A/ft^2)
Specific Gravity	1.2-1.3
Surface Tension	30-50 Dynes/Cm
Agitation	mild, uniform air

TABLE III

EQUIPMENT

Tanks	Plastic or Rubber lined
Anodes	Carbon (Graphite) Copper Core
Agitation	Air
Cooling/Heating	Required
Filter	Necessary to remove purification products
Rectifiers	6 - 24 Volts
Ventilation	For gas evolution

TABLE IV

METALLIC CONTAMINANTS

METAL	TOLERANCE UNDER OPTIMUM CONDITIONS
Copper	20 ppm
Iron	500 ppm
Lead	20 ppm
Nickel	200 ppm
Zinc	50 ppm

TABLE V

HARDNESS TRIVALENT VS. HEXAVALENT CHROMIUM

CHROMIUM DEPOSIT	HARDNESS DPH*
Trivalent	803-974
Hexavalent	800-1100

*Measurements were made using the diamond pyramid indenter under a 100 gram load

TABLE VI

DEPOSIT COMPOSITION

TRIVALENT VS. HEXAVALENT CHROMIUM

CHROMIUM DEPOSIT	CARBON WT %	OXYGEN WT %	CHROMIUM WT %
Hexavalent	0.0	0.4	99+
Trivalent	2.9	1.6	95+

TABLE VII

CORROSION RESULTS

DUPLEX NICKEL - CHROMIUM ON STEEL

SET	SEMI-BRIGHT NICKEL um	BRIGHT NICKEL um	CHROMIUM um	ASTM RATINGS	
				INDUSTRIAL 5 MONTHS	MARINE - KURE BEACH 6 MONTHS
1	18	7.5	0.25 - 1	9/8	7/6
2	18	7.5	0.25 - 1,2	10/8	10/10
3	18	7.5	0.25 - 3	9/9	9/7

1 - Hexavalent Chromium
2 - Microporous
3 - Trivalent Chromium

TABLE VIII

TYPICAL TRIVALENT CHROMIUM OPERATING CYCLE

NICKEL OR FERRO-NICKEL PLATE

NICKEL DRAG-OUT

COLD WATER RINSE

COLD WATER RINSE

DRY TANK

TRIVALENT CHROMIUM

DRAG-OUT TANK

COLD WATER RINSE

COLD WATER RINSE

POST-DIP

COLD WATER RINSE

HOT WATER RINSE

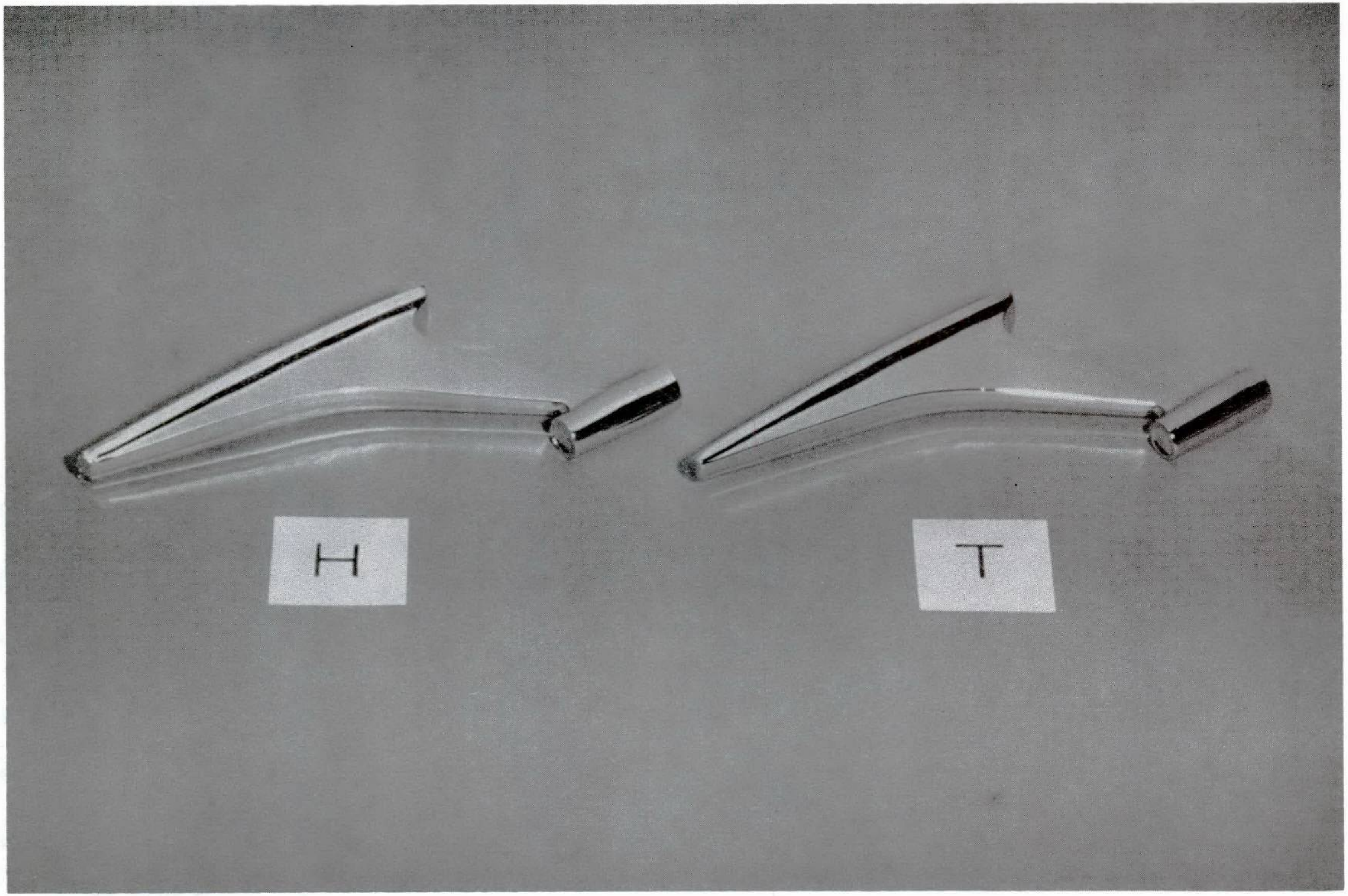

Fig. 1 Comparison of chromium deposits plated from hexavalent and trivalent solutions.

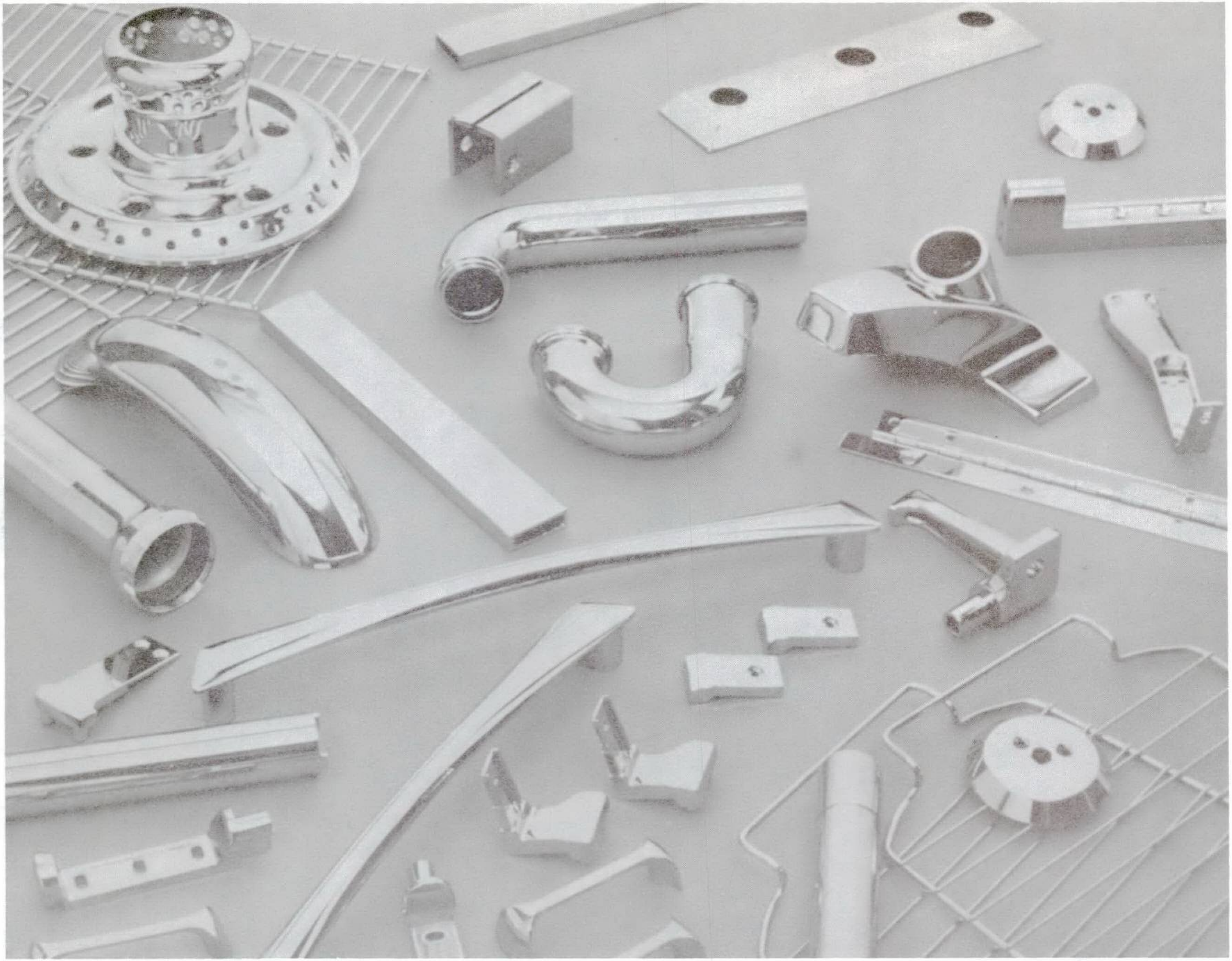

Fig. 2 Various parts which have been plated from trivalent chromium baths.

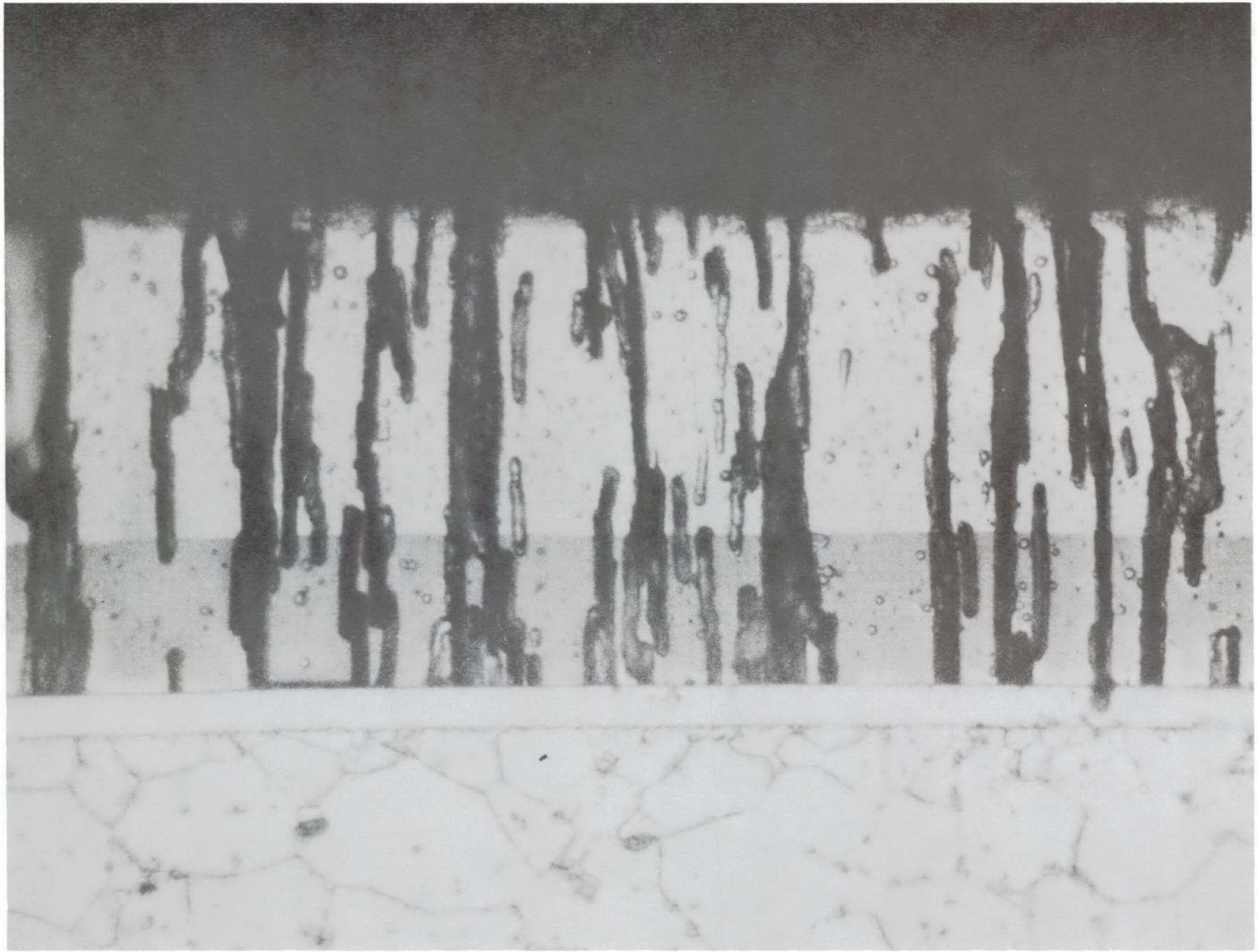

Fig. 3 Photomicrograph of 90 μm thick chromium deposited from a trivalent bath.

Fig. 4 Photomicrograph of 90 µm thick chromium deposited from a hexavalent bath.

I-4

General Interest Session I

Zinc/Graphite—A Potential Substitute for Anti-Galling Cadmium

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ZINC/GRAPHITE - A POTENTIAL SUBSTITUTE FOR ANTI-GALLING CADMIUM

By

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Introduction

A chronic problem which has plagued the automotive industry for years is a phenomenon known as "stick-slip" friction. It happens when coated fasteners such as phosphated and oiled or zinc plated nuts and bolts are tightened with power tools. As the name "stick-slip" implies, there may be a momentary tendency during tightening, for the coated fasteners to stick and then break loose or slip. The coefficient of friction and the integrity of the coating play a significant role in this "stick-slip" phenomenon.

As an example, let us consider a poorly phosphated batch of bolts used during mechanical assembly. If the power tool used to drive down the bolts is torque controlled it may shut down prematurely due to stick-slip. If this occurs, the mechanical assembly will be improperly secured and will require rework upon identification by an inspection system. This results in less assembly line productivity and higher costs. Even where the coating is electroplated zinc, the galling nature of the deposit can produce similar stick-slip problems.

For years cadmium electroplating has been used in applications where good lubricity, sacrificial corrosion protection and anti-galling properties were required. Recently the increasing cost of cadmium together with mounting toxicological implications[1] has spurred much activity to find reliable substitute coatings. This paper describes a plating process for producing zinc/graphite coatings which have frictional and corrosion performance properties comparable to those of electroplated cadmium coatings.

Experimental

Numerous plated deposits and composites have been reported to have low friction and/or anti-galling properties.[2-5] Using this information as a guide, steel fasteners were plated in the laboratory by conventional plating techniques. These systems included electroless nickel with and without molybdenum disulfide, electroplated zinc and electroplated cadmium with and without a chromate conversion coating. Plain steel, Teflon-coated, and commercial phosphated and oiled fasteners also were used in the studies. In addition, fasteners were plated with a co-deposit of graphite in a zinc matrix by using a laboratory developed plating bath. This bath consisted of a conventional acid zinc formulation containing commercial proprietary addition agents and a refined grade of collodial graphite having a 2μm average particle size. The graphite content was varied from 5 to 75 g/l. Two of the bath formulations investigated are shown in Table 1.

BATH FORMULATIONS (g / l)

	POTASSIUM	SODIUM
$ZnCl_2$	78	78
KCl	210	—
NaCl	—	165
H_3BO_3	30	30
pH	5.0 - 5.7	5.0 - 5.7

Table 1

Unbagged anodes were used for both formulations. Steel nuts and bolts were processed through the baths either on racks or in barrels. The bath agitation cycle was found to be very critical to obtain deposits containing high graphite contents in the electrodeposit. Prior to plating, the bath was vigorously agitated to insure homogeneous graphite suspension. During the plating, the solution agitation -- and in the case of barrel plating the barrel rotation -- was interrupted for 30 seconds for every minute of plating time. About half of the plated fasteners were post treated with a chromate conversion film.

Of the two formulations, the bath made up with potassium chloride produced the brightest deposits. However, since specularity is not a requirement for fastener applications, and sodium chloride is plentiful and inexpensive, the sodium chloride formulation was used for most of the studies.

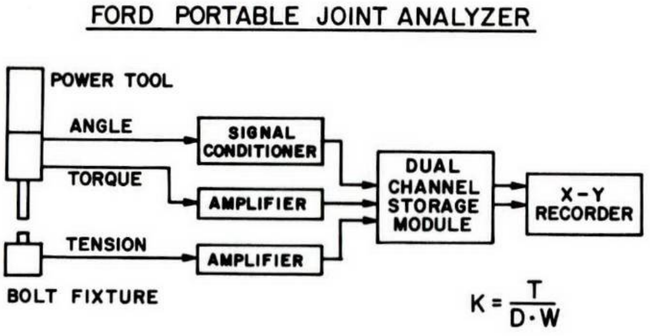


Fig. 1

The relative coefficient-of-friction-values for the various coated steel nuts were determined by using the Ford Portable Joint Analyzer. This equipment is shown schematically in Figure 1 and measures the relationship between angle of fastener rotation, applied torque and tension. For each measurement a nut was started on a bolt by hand in the fixture and then further tightened with a pneumatic power tool. The angle of rotation, which was measured by a torque-degree transducer, was electronically fed into the Encoder signal conditioner and stored in the Physical Data Channel Transfer module. Simultaneously, the tension and torque data were amplified and likewise stored in the memory module. The resulting data were then plotted out on an x-y recorder. From these plots the relative coefficient of friction value, K, was calculated at 40 ft.-lb. torque by the relationship K=T/DW where T is torque, D is the bolt diameter and W is the bolt tension.

Corrosion performance of cadmium plated and selected zinc/graphite composites was evaluated both by means of the ASTM B117 5% salt spray test and in one-winter mobile/road tests conducted in Buffalo and Detroit.

Results and Discussion

Figure 2 shows an x-y recorder plot of phosphated and-oiled fasteners displaying good and poor friction performance. In the case of poor performance, which is an illustration of stick-slip friction, excessive oscillation of the torque load results as the fastener is spun on the bolt. This oscillation is accompanied by a loud screeching noise. Furthermore the final tension achieved is insufficient. In the case of good performance of satisfactorily coated fasteners, the torque load is uniformly increased as the angle of fastener rotation is advanced, resulting in a firmly secured assembly with the required tension level.

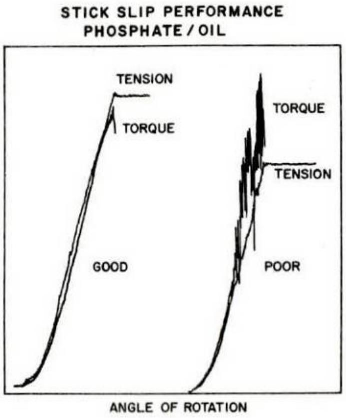


Fig. 2

Relative coefficient of friction values for steel nuts coated with various systems are given in Table 2.

RELATIVE COEFFICIENT OF FRICTION VALUES/ENGINE FASTENERS	
TEFLON	0.23
PHOSPHATE/OIL	0.20
ELECTROLESS NICKEL	0.17
ZINC ELECTROPLATE	0.16
ELECTROLESS NICKEL/MoS_2	0.16
BARE STEEL/OIL	0.15
ZINC/GRAPHITE	0.13
CADMIUM ELECTROPLATE	0.12

Table 2

From this table it is evident that both oiled phosphate coatings and zinc electroplate, which are commonly used in automotive fastener applications, are poor finishes in terms of uniform coating lubricity. Surprisingly, a Teflon finish was not even as good as phosphated-and-oiled fasteners. It was also found that uncoated steel was better than electroless nickel systems. As indicated in Table 2, the system with the greatest potential of matching the frictional properties of cadmium was a zinc/graphite composite which gave a value of 0.13 compared to 0.12 for cadmium. These zinc/graphite composite coatings were originally plated from a bath which contained 120 g/l of an unrefined grade of graphite. Additional improvements in friction levels were found by using a refined grade of graphite.

Coefficient of friction values for zinc graphite composite coatings as a function of the refined-grade graphite content, with and without a chromate conversion film, are shown in Figure 3.

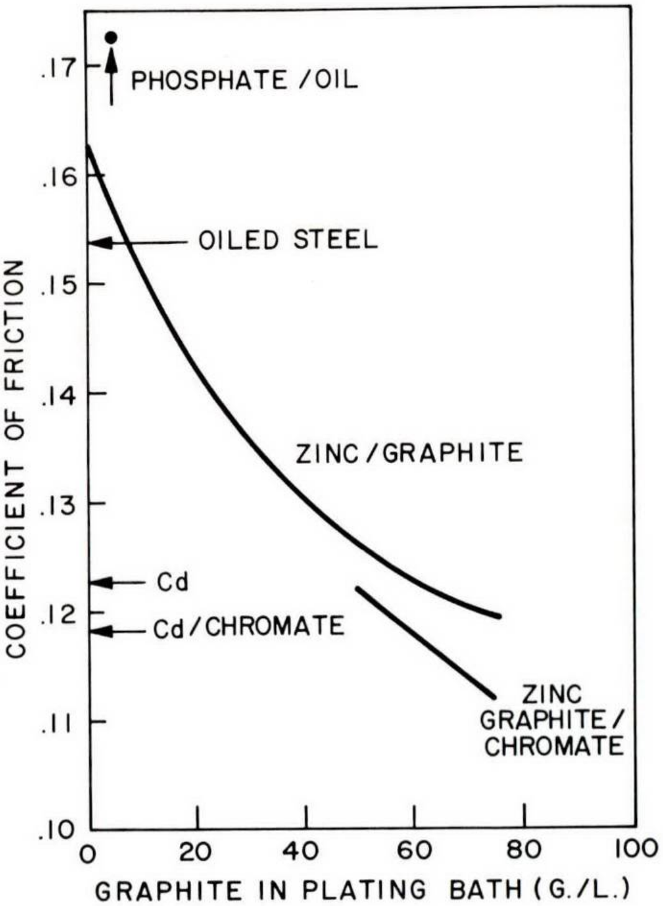
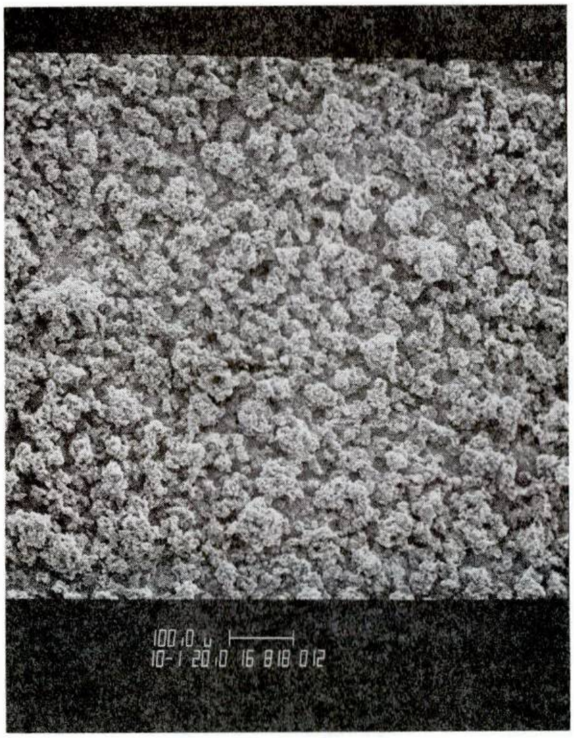


Fig. 3

Also shown in this figure, as points of references, are the coefficient of friction values for coatings of phosphate/oil and zinc which display inconsistent stick-slip performance. For phosphate and oil the average measured coefficient of friction was 0.20, while for zinc it was 0.16. Oiled steel, which is satisfactory for certain applications where minimal corrosion protection is required, had a coefficient of friction of 0.15.

With respect to the zinc/graphite composite the coefficient of friction decreased as the graphite content was increased from 5 to 75 g/1. At 20, 50 and 75 g/1 the coefficient of friction values were 0.14, 0.13 and 0.12, respectively. The 0.12 value corresponded to the same value measured for cadmium. For the composite plated in the 75 g/1 graphite bath, the coefficient of friction was reduced to 0.11 when the deposit was passivated with a chromate conversion film.



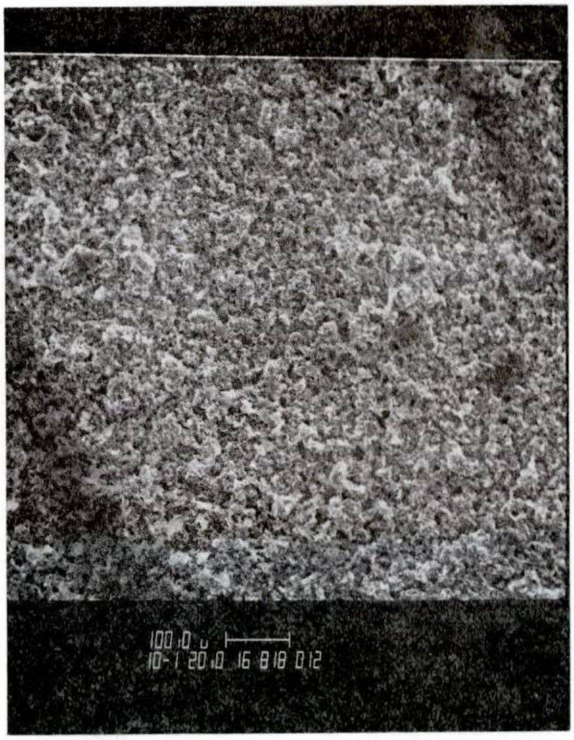


Fig. 4 - 20 g/l graphite bath Fig. 5 - 50 g/l graphite bath
Surface morphology of panels plated in vertical position

Figures 4 and 5 are SEM photographs showing the surface morphology @ 100X magnification of steel panels plated with zinc/graphite in a vertical position. Figure 4 shows a coated panel plated in a 20 g/l graphite bath, and Figure 5 shows a sample plated in a 50 g/l bath. Figure 6 and 7 show the surface morphology of steel nuts barrel plated in a bath containing 50 and 70 g/l respectively. These last two figures show a much smoother appearance than figures 4 and 5. Apparently, the tumbling action of the barrel plated nuts produced a burnished effect on the plated composite.

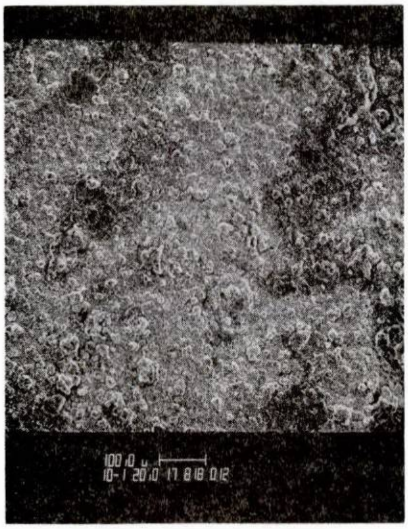


Fig. 6 - 50 g/l graphite bath

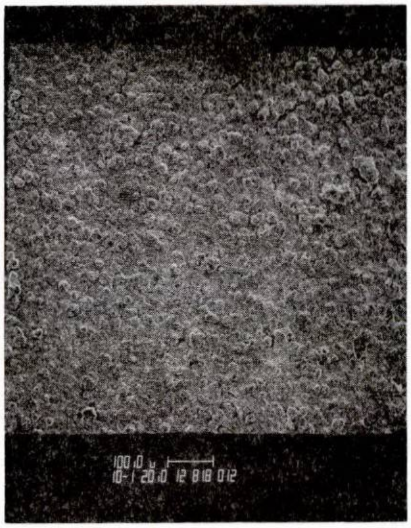


Fig 7. - 75 g/l graphite bath

Surface Morphology of Barrel Plated Nuts

SALT SPRAY PERFORMANCE

COATING SYSTEM	g / l GRAPHITE	MILS	LIFE (HRS)
PO_4 / OIL	—	0.35	48
Zn / Gr	50	0.5	72
Zn / Gr / CrO_4	50	0.5	120
Zn / Gr	75	0.5	48
Zn / Gr / CrO_4	75	0.5	120
Zn / Gr	120	0.5	48
Zn / Gr / CrO_4	120	0.5	120
Cd / CrO_4	—	0.5	288

Table 3

Table 3 shows the salt spray performance of nuts coated with phosphate/oil; zinc/graphite; zinc/graphite (chromate film); and cadmium with a chromate film. Coatings of zinc/graphite and phosphate/oil provided minimal corrosion protection of the steel substrate (48-72 hr). The salt spray performance of the zinc/graphite composite was improved to 120 hours by passivating the composite with a chromate film. Cadmium plate with a chromate conversion film showed the best performance (280 hours).

Since salt spray data cannot be directly translated to snow belt road corrosion performance, one means of evaluating the corrosion resistance of new plating systems is to expose the test samples on truck trailers driven in the Detroit and Buffalo area. Figure 8 shows the manner in which the exposure test was carried out.

Fig. 8. Truck trailer used for field corrosion studies

1 WINTER TRAILER EXPOSURE
(BUFFALO & DETROIT)

COATING	THICKNESS (MILS)	PERFORMANCE
ZINC / GRAPHITE	0.2-0.7	NO RUST
ZINC / GRAPHITE CHROMATE	0.2-0.7	NO WHITE OR RED RUST
CADMIUM / CHROMATE	0.5	NO WHITE OR RED RUST
PHOSPHATE / OIL	0.35	RED RUST

Table 4

Table 4 shows the corrosion performance of various coated steel nuts after one winter trailer exposure in the Detroit and Buffalo areas. As shown, the zinc/graphite composite and the cadmium deposit both protected the steel surface from corrosion. In contrast the nuts coated with phosphate and oil failed by red rusting. This test is continuing and it will be interesting to observe the results after two or more winters.

SUMMARY OF PROPERTIES

	PHOSPHATE/OIL	ZINC/GRAPHITE	CADMIUM
"Stick-Slip" Friction	Inconsistent	Low	Low
Salt Spray Performance	Inconsistent	Fair	Excellent
Field Performance	Poor	*	Good
Assembly Productivity	Inconsistent	Excellent	Excellent
Shelf Life	Poor	Excellent	Excellent
Bath Toxicity	Low	Low	High

*Tests in Progress

Table 5

Table 5 is a summary of coating properties, wherein the zinc/graphite composite is compared to commonly used automotive fastener finishes: phosphate/oil and cadmium electrodeposit. Both cadmium and the zinc/graphite composite show a marked superiority over phosphate/oil in "stick-slip friction," corrosion performance, and assembly productivity. With regard to plating bath toxicity, the zinc/graphite composite holds a decisive advantage over cadmium.

Summary and Conclusions

A laboratory plating process has been developed that produces zinc/graphite composites which have anti-friction and outdoor mobile corrosion properties comparable to cadmium. These results indicate that the zinc/graphite composite has the potential of replacing cadmium deposits currently used for automotive fasteners application. However costs, commercial reproducibility, and other possible limitations have not been evaluated for production usage of fasteners plated with the zinc/graphite composite.

Acknowledgements

We are grateful to J. R. Baughman for the assistance he provided in evaluating the coating lubricity properties of test samples used in this program.

References

1. Alternatives to Cadmium, Plating and Surface Finishing 69, 35 (1982).
2. T. Tomaszewski, L. Tomaszewski, H. Brown, J. Plating 56, 1234 (1969).
3. K. Parker, J. Plating 61, 834 (1974).
4. M. Ghouse, M. Viswanathan, E. Ramachandran, J. Metal Finishing 78, 57 (1980).
5. Cadmium Council, "Cadmium Looks to the Future," New York, New York.

I-5

General Interest
Session I

Analysis of Plating Baths by Differential Pulse Polarography

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ANALYSIS OF PLATING BATHS BY DIFFERENTIAL PULSE POLAROGRAPHY

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Polarographic techniques offer two important advantages in plating analysis: a large dynamic working range and the ability to determine both metals and nonmetals in a bath. The wide dynamic range allows these techniques to be used not only to determine major bath components, but trace contaminants and additives as well. Thus, the same technique used to monitor bath composition can also be used for troubleshooting and analysis of waste-water effluents. Detection limits of 10^{-8} M in differential pulse polarography (DPP) have been reported.[1] For Pb^{2+} in solution, this would correspond to 2 μg/L.

The range of applications of polarography is shown in Table 1. This list is far from comprehensive, but it serves to point out a few facts. First, it is often possible to determine the oxidation state of the metal being analyzed. For example, it is possible to determine the concentration of stannous and stannic tin in a bath, as well as the total tin. This ability to speciate metals is important in cases where only one of the species contributes to efficient plating.

Secondly, a variety of commmonly used organic additives with electroactive functional groups can be determined by DPP.[2] A few key classes of electroactive organics which are used as brighteners or levelers in the plating industry are aldehydes, aromatic nitro compounds and azo or diazo compounds.

Finally, it should be noted that anions such as cyanide can be measured by DPP. Although these anions are not themselves electroactive, their presence facilitates the oxidation of mercury, so they can be measured indirectly.

In addition DPP is easy to use and often requires little or no sample preparation. It is a low-cost alternative to other trace analytical methods. In this paper a brief description of the DPP technique and its applications to the analysis of plating baths are discussed. Also, the effect of key experimental parameters and the use of these parameters to solve analytical problems are explained.

Polarographic Apparatus

A basic system for polarographic analysis consists of a potentiostat, a sample cell with electrodes and a recorder. The potentiostat is used to apply a voltage ramp to the electrodes in the sample cell. The current passing through the cell as a function of voltage is then measured, and sent to the recorder. The amount of current which passes is used to determine the concentration of the analyte in the cell. The voltage at which the current appears is characteristic of the type of analyte present.

The sample cell is in some ways analogous to a small plating bath. The sample is mixed with a supporting electrolyte in the cell, and the electrodes are placed into the solution. A typical three electrode system is made up of a platinum wire counter electrode, a dropping mercury working electrode (DME) and a reference electrode. The platinum counter electrode is used simply as an inert anode in most polarographic work. It can also serve as a cathode, depending on the voltage applied to the cell, but the reactions at the counter electrode are not really of interest. It is there simply to complete the circuit.

The reference electrode is used to provide an accurate and reproducible measurement point for the applied voltage. The reference electrode contains an electrochemical half-cell, for example Ag/AgCl, which is separated from the sample solution by a salt bridge.

The working electrode is the one at which the analyte is oxidized or reduced. Mercury is used as a working electrode material because it acts as an excellent cathode for a variety of analytes. There are two key advantages to using a DME. First, the reduction of hydrogen ion to hydrogen occurs at a more negative potential at mercury than at most other electrode materials. This means that a wider voltage region can be scanned, allowing the investigation of a large variety of compounds. Secondly, each mercury drop presents a clean electrode surface to the sample solution. This means that the current measured will not depend on the previous history of the electrode.

The voltage waveform applied to the electrodes depends on the technique selected. The most commonly used technique for routine analysis is DPP, since it provides high sensitivity and easily measured peaks, when current is recorded as a function of applied potential. In the work reported here differential pulse polarography was done using commercially available equipment. *

Determination of Cu^{2+} in an Acid Sulfate Bath

In this first example, DPP is used to quantify a major bath component, Cu^{2+}, in an acid sulfate bath.[3] A typical set of polarograms is shown in Fig. 1. Five polarograms are shown, corresponding to a blank, sample and three additions of a copper standard. The analysis was performed by first placing 10 mL of supporting electrolyte in the polarographic cell, deaerating the solution by bubbling pure nitrogen through it for 5 minutes, and recording the blank scan. The supporting electrolyte is one of the main experimental parameters which the analyst can control. In addition to its basic function of providing solution conductivity, the electrolyte greatly affects the position of the polarographic peaks. Proper choice of electrolyte can often eliminate interferences and insure that the analyte peak is well

* IBM Instruments EC/225 Polarographic/Voltammetric Analyzer, with a 7424 X-Y Recorder.

defined. After the blank run, a small aliquot, 10 μL, of a bath sample was added to the cell, and a second scan was recorded. The peak due to Cu^{2+} occurred at about -0.5 V vs. the saturated calomel reference electrode (SCE). Three successive additions of Cu^{2+} standard were then made to the cell, and a polarogram was recorded after each addition. A plot of peak height vs. concentration of Cu^{2+} added was used to determine the sample concentration, as shown in Fig. 2. The result was reported as g/L $CuSO_4 \bullet 5H_2O$, since this was the salt used to replenish the bath. The instrumental parameters used for the analysis are shown in Table 2.

This entire analysis took less than 15 minutes. Each polarogram was recorded in 70 seconds. Even shorter analysis times could be achieved by using fewer standard additions, or by using a calibration curve method. The analysis time can also be cut down by deaerating enough supporting electrolyte for several runs at the same time.

Simultaneous Determination of Pb^{2+} and Sn^{2+} in a Plating Bath

In this analysis, a voltage window was chosen which allowed two peaks to be observed in each polarogram as shown in Fig. 3. The two peaks, at -0.48 V and -0.62 V vs SCE are due to the reduction of Pb^{2+} and Sn^{2+} respectively.[3,4] The instrumental parameters used in the analysis are listed in Table 3. A brief description of these parameters and their effect on the shape of the polarogram follows.

E initial and E final are simply the voltages at which the scan begins and ends. The scan rate determines the time required for each 'run'. The scan rate, together with the drop time, also determines the number of data points collected per polarogram. In DPP two current measurements are made near the end of each drop and the difference current is plotted. The previously measured current is held until the new value is measured. This accounts for the small steps observed in the polarogram. Generally, scan rates from 1-20 mV/sec are used in DPP, to minimize the width of these steps.

Drop time can also affect the sensitivity of the polarogram. Longer drop times result in larger electrode area, and thus higher current. Of course, since the drop is an expanding sphere, the increase in area is not linear with time. Drop times from 0.5 to 2.0 seconds are commonly used.

The last parameter is the pulse amplitude. To fully understand the effect of this parameter, it would be necessary to examine the DPP waveform in detail, which is outside the scope of this paper. An extensive literature on polarographic techniques exists for anyone interested in further study.[5-7] From a practical standpoint, however, the following rules hold: A large pulse amplitude results in peaks which are higher and broader. A small pulse amplitude results in shorter and narrower peaks. Pulse amplitudes typically range from 5 mV to 115 mV, with 50 mV giving a nearly optimum trade-off between sensitivity and resolution.

In the determination of Pb^{2+} and Sn^{2+}, resolution is a primary concern, and the choice of pulse amplitude can be used to good advantage. Since the two peaks are only about 150 mV apart, they can begin to overlap, particularly at high concentrations. By using a small pulse amplitude, 5-30 mV, and by diluting the bath sample sufficiently, good resolution between the peaks is obtained.

Determination of Formaldehyde in an Electroless Copper Bath

Figure 4 demonstrates the use of DPP to determine an organic constituent, formaldehyde, in an electroless copper bath.[3] Again, a standard addition experiment was done to quantify the formaldehyde. It should be pointed out that formaldehyde is unstable in highly alkaline supporting electrolyte, so the analysis should be completed quickly once the bath sample is added to the cell. Despite this minor disadvantage, the alkaline supporting electrolyte was the best choice for this particular bath. It provided a well defined peak, the height of which increased linearly with concentration in the range studied. In addition, the alkaline conditions insured that the cyanide, which was also present in the bath, did not evolve. The instrumental parameters used are listed in Table 4.

Determination of Cyanide in a Plating Bath

Certain anions can also be determined by DPP. Figure 5 shows the determination of cyanide in a plating bath.[8-10] The instrumental parameters used are listed in Table 5. This analysis is based on an indirect reaction, as shown below:

$$Hg + 2CN^- \longrightarrow Hg(CN)_2 + 2e^- \qquad (1)$$

The formation of the salt, HgCN, causes the mercury oxidation to occur at a less positive potential than usual. The height of the oxidation peak varies linearly with the cyanide concentration. Other anions which have this effect include chloride, bromide and iodide.[11] Certain sulfur containing organics, such as thiourea, can form insoluble complexes with mercury which have the same effect.[12]

Summary

DPP is a versatile, sensitive and rapid technique that offers several advantages for the analysis of plating baths. These few examples represent only a fraction of the plating analyses which can be handled by DPP. When other electroanalytical techniques, such as stripping voltammetry and voltammetry at various solid electrodes, are also considered, the potential applications are even greater. The ability of these methods to determine both metals and non-metals and the low cost of modern electroanalytical instrumentation make a powerful case for adding these capabilities to any laboratory where plating bath analysis is done.

REFERENCES:

1) A.M. Bond, Modern Polarographic Methods in Analytical Chemistry, Marcel Dekker, Inc., New York, NY, 1980.

2) M.B. Baizer, Organic Electrochemistry, Marcel Dekker, Inc., New York, NY, 1973.

3) M.L. Rothstein, W.M. Peterson and H. Siegarman, Plating and Surf. Finish., 68, 78 (June 1981).

4) A.J. Bard, ed., Encyclopedia of Electrochemistry of the Elements, Vol. 4, Marcel Dekker, Inc., New York, NY, 1975; p. 235.

5) L. Meites, Polarographic Techniques , Interscience Publishers, New York, NY, 1955.

6) D.T. Sawyer and J.L. Roberts, Jr., Experimental Electrochemistry for Chemists , Wiley-Interscience, New York, NY, 1979.

7) A.J. Bard and L.R. Faulkner, Electrochemical Methods , John Wiley and Sons, New York, NY, 1980.

8) E. Kirowa-Eisner, D. Talmor and J. Osteryoung, Anal. Chem., 53, 581 (1981).

9) K. Wisser, Z. Anal. Chem., 286, 351 (1977)

10) Y. Okinaka and C. Wolowodiuk, Plating and Surf. Finish., 66, 50 (Sept. 1979).

11) G. Colovos, G.S. Wilson and J.L. Moyers, Anal. Chem., 46, 1051 (1974)

12) M.R. Smyth and J.G. Osteryoung, Anal. Chem., 49, 2310 (1977).