

copy 2

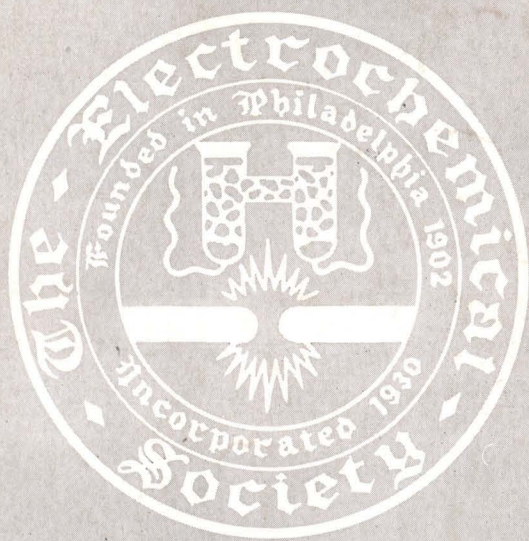
FEB 10 1955

JOURNAL OF THE

# Electrochemical Society

Vol. 102, No. 2

February 1955



แผนกห้องสมุด กรมวิทยาศาสตร์  
 กระทรวงอุตสาหกรรม

PUFON  
 EXPERIMENTAL STATION  
 LAVOISIER LIBRARY



## STURDY PERFORMANCE

The sturdy performance of GLC ANODES in electrolytic cell operations is the reason why major chlor-alkali producers rely upon them with increasing frequency.

ELECTRODE  DIVISION

**Great Lakes Carbon Corporation**

**GRAPHITE ANODES, ELECTRODES, MOLDS and SPECIALTIES**

**ADMINISTRATIVE OFFICE:** 18 East 48th Street, New York 17, N. Y.

**PLANTS:** Niagara Falls, N.Y., Morganton, N.C.

**OTHER OFFICES:** Niagara Falls, N.Y., Oak Park, Ill., Pittsburgh, Pa.

**SALES AGENTS IN OTHER COUNTRIES:** Great Northern Carbon & Chemical Co., Ltd., Montreal, Canada  
Overseas Carbon & Coke Company, Inc., Geneva, Switzerland; Great Eastern Carbon & Chemical Co., Inc., Chiyoda-Ku, Tokyo, Japan

## EDITORIAL STAFF

R. M. BURNS, *Chairman*  
NORMAN HACKERMAN, *Technical Editor*  
RUTH G. STERNS, *Managing Editor*  
CECIL V. KING, *Acting Editor*  
U. B. THOMAS, *News Editor*  
NATALIE MICHALSKI, *Assistant Editor*  
ELEANOR BLAIR, *Assistant Editor*

## DIVISIONAL EDITORS

W. C. VOSBURGH, *Battery*  
J. V. PETROCELLI, *Corrosion*  
JOHN J. CHAPMAN, *Electric Insulation*  
ABNER BRENNER, *Electrodeposition*  
H. C. FROELICH, *Electronics*  
SHERLOCK SWANN, JR., *Electro-Organic*  
IRVIN R. KRAMER, *Electrothermics and Metallurgy, I*  
A. U. SEYBOLT, *Electrothermics and Metallurgy, II*  
W. C. GARDINER, *Industrial Electrolytic*  
CARL WAGNER, *Theoretical*

## REGIONAL EDITORS

HOWARD T. FRANCIS, *Chicago*  
JOSEPH SCHULEIN, *Pacific Northwest*  
J. C. SCHUMACHER, *Los Angeles*  
G. W. HEISE, *Cleveland*  
PAUL S. BRALLIER, *Niagara Falls*  
OLIVER OSBORN, *Houston*  
EARL A. GULBRANSEN, *Pittsburgh*  
A. C. HOLM, *Canada*  
J. W. CUTHBERTSON, *Great Britain*  
T. L. RAMA CHAR, *India*



## ADVERTISING OFFICE

JACK BAIN  
*Advertising Manager*  
545 Fifth Avenue  
New York 17, N. Y.

PHONE—Murray Hill 2-3345

# Journal of the Electrochemical Society

216 West 102nd Street, New York 25, N.Y.

FEBRUARY 1955

VOL. 102 • NO. 2

## CONTENTS

### Editorial

Support of International Chemistry..... 33C

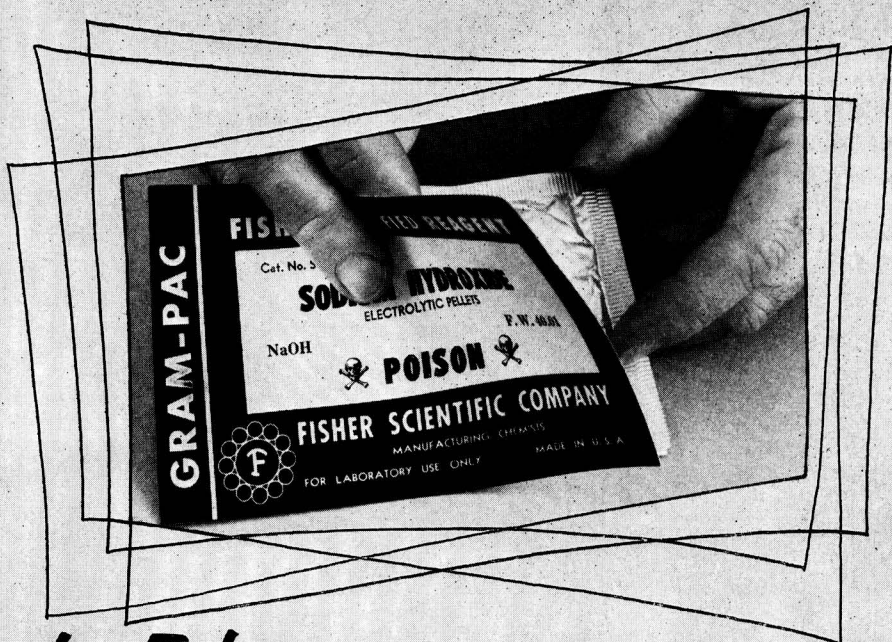
### Technical Papers

- Polarization Studies of Copper, Nickel, Titanium, and Some Copper and Nickel Alloys in Three Per Cent Sodium Chloride. *H. B. Bomberger, F. H. Beck, and M. G. Fontana*... 53
- Effect of Oxygen, Chlorides, and Calcium Ion on Corrosion Inhibition of Iron by Polyphosphates. *H. H. Uhlig, D. N. Triadis, and M. Stern*..... 59
- Solid Dielectric Breakdown Techniques. *J. J. Chapman, L. J. Frisco, and J. S. Smith*..... 67
- Nitrides of Chromium and Chromium-Titanium Alloys. New Film-Type Resistance Elements. *E. R. Olson, E. H. Layer, and A. E. Middleton*..... 73
- Electrolytic Preparation of Molybdenum from Fused Salts, IV. Preparation of Reduced Molybdenum Chlorides from Molybdenite Concentrate. *Seymour Senderoff and Roger J. Labrie*..... 77
- Deposition of Titanium Coatings from Pyrosols. *A. W. Schlechten, M. E. Straumanis, and C. B. Gill*..... 81
- The Crystallographic Dependence of the Oxidation Potential of Solid Copper. *W. E. Trager and W. D. Robertson*..... 86
- Polarographic Investigation of Organic and Inorganic Compounds in an Ammonia-Ammonium Nitrate Solvent. *Guy William Leonard, Jr., and Douglas E. Sellers*..... 95

### Current Affairs

- |   |     |                                      |     |
|---|-----|--------------------------------------|-----|
| Society Plans Spring Meeting in Cincinnati..... | 35C | Meetings of Other Organizations..... | 43C |
| Division News.....                              | 35C | Letters to the Editor.....           | 43C |
| Section News.....                               | 36C | Book Reviews.....                    | 45C |
| News Items.....                                 | 38C | Recent Patents.....                  | 45C |
| Personals.....                                  | 41C | Literature from Industry.....        | 47C |
| New Members.....                                | 41C | New Products.....                    | 48C |
| ECs Membership Statistics.....                  | 42C | Employment Situations.....           | 48C |

Published monthly by The Electrochemical Society, Inc., Mount Royal and Guilford Aves., Baltimore 2, Md., combining the JOURNAL and TRANSACTIONS OF THE ELECTROCHEMICAL SOCIETY. Editorial offices: 216 West 102nd Street, New York 25, N. Y. Statements and opinions given in articles and papers in the JOURNAL OF THE ELECTROCHEMICAL SOCIETY are those of the contributors, and The Electrochemical Society assumes no responsibility for them. Noneductible subscription to members \$5.00; subscription to nonmembers \$15.00. Single copies \$1.25 to members, \$1.50 to nonmembers. Copyright 1955 by The Electrochemical Society, Inc. Entered as second-class matter November 15, 1947, at the Post Office at Baltimore, Md., under the act of August 24, 1912.



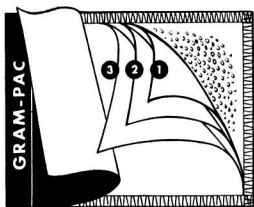
# *the Fisher* **GRAM-PAC**

*First major improvement in  
reagent packaging in years*

This completely sealed, tough, laminated package eliminates the traditional (and expensive) quarter-pound bottle. It eliminates overlapping sizes, cuts ordering costs, reduces shipping costs and there is no breakage to contend with.

GRAM-PAC permits the packaging of "individual" amounts of reagents for easier distribution and greater laboratory convenience. They are packed 10 PACS to a box and 12 boxes to a case. Eventually, all Fisher Certified Reagents will be available in the inexpensive, contaminant-free GRAM-PAC, including the nearly 200 chemicals specified by the American Chemical Society.

Another "first" from the Fisher Chemical Manufacturing Division . . . to make life easier . . . for you.



#### WHAT IS GRAM-PAC?

1. **POLYETHYLENE**, next to reagent, for chemical inertness
  2. **ALUMINUM FOIL**, for strength and insulation
  3. **ACETATE**, for waterproofing
- FREE SAMPLE** - a GRAM-PAC of Fisher Certified Reagent Sodium Hydroxide, ACS, is waiting for you. Write today to Fisher Scientific, 717 Forbes St., Pittsburgh 19, Pa., ask for "Sample GP 20"

## FISHER SCIENTIFIC

Boston	Cleveland	Philadelphia	Washington
Buffalo	Detroit	Pittsburgh	Montreal
Chicago	New York	St. Louis	Toronto

America's Largest Manufacturer-Distributor of  
Laboratory Appliances and Reagent Chemicals

# Vacuum metalizing?

You get more shots  
per dollar with . . .

## NEW PROCESS SYLVANIA TUNGSTEN COILS and STRAND

High-efficiency Sylvania tungsten source heater coils and strand wire were developed especially to give you top performance at minimum cost in any vacuum metalizing application.

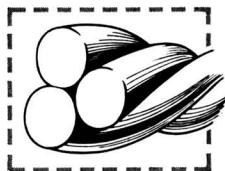
Every step in the manufacture of Sylvania vacuum-metalizing source heater materials is performed under exacting quality control in Sylvania's own plants . . . from tungsten ore, to wire, to finished coils and strand. Special tungsten wire is coiled specifically for vacuum metalizing to assure maximum service life as well as maximum evaporating capacity for your requirements.

Sylvania offers you a wide selection of ready-made tungsten coils, in single or multiple strand . . . each designed for a specific metalizing job. If you prefer to form your own coils, you have a full range of wire diameters and types to choose from.

If you have special application problems, our engineers will gladly help you work them out. Write for your copy of "Sylvania Tungsten Filaments for Vacuum Metalizing."

SYLVANIA ELECTRIC PRODUCTS INC.  
1740 Broadway, New York 19, N. Y.  
In Canada: Sylvania Electric (Canada) Ltd.,  
University Tower Bldg., St. Catherine St.,  
Montreal, P. Q.

Which is better—



**THIS?**

Sylvania research has shown that, for the same relative cross section, coils of fewer strands and larger diameter last longer in service.

**OR THIS?**



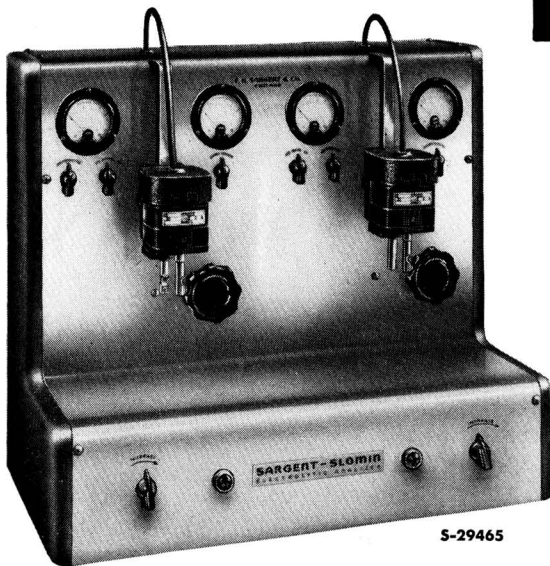
Coils made of a large number of smaller strands are subject to excessive diameter reduction . . . give shorter service life.



# SYLVANIA

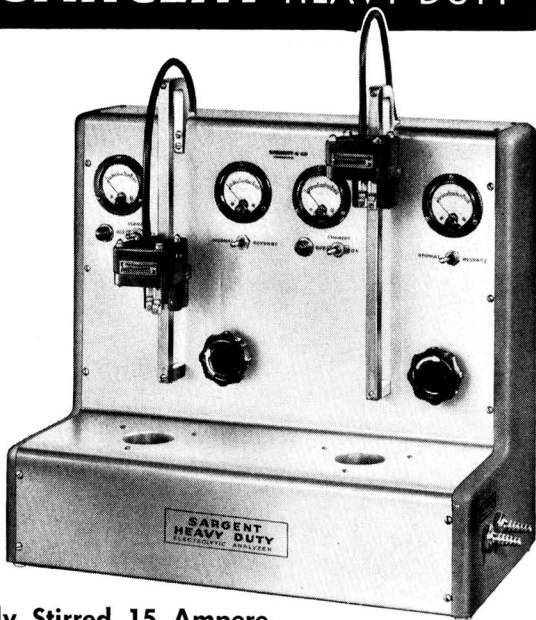
Lighting • Radio • Electronics • Television • Atomic Energy

# SARGENT SLOMIN



Motor-Stirred 5 Ampere

# SARGENT HEAVY DUTY



Magnetically Stirred 15 Ampere

Designed for continuous trouble-free performance, these electrolytic analyzers, manufactured by E. H. Sargent & Co., are durably constructed of the highest grade materials and component parts, including stainless steel front panel, cast aluminum end castings and stainless steel fittings.

Completely line operated, the Sargent analyzers employ self-contained rectifying and filter circuits. The deposition voltage between the electrodes is adjusted by means of auto-transformers, with meters indicating volts and amperes and controls on the panel. An easily replaceable fuse guards against circuit overload.

The Sargent-Slomin Analyzer stirs through a rotating chuck operated from a capacitor type induction motor, motor having a fixed speed of 550 r.p.m. with 60 cycle A.C. current or 460 r.p.m. with 50 cycle A.C. current. Motors are sealed against corrosive fumes; are mounted on cast metal brackets, sliding on 1/2" square stainless steel rods, permitting vertical adjustment of electrode position over a distance of 4". Pre-lubricated ball-bearings support the rotating shaft.

The Sargent Heavy Duty Analyzer provides efficient stirring by the interaction between the cell current and the field established by a permanent magnet, tubular in shape and coaxial with the cell holder.

The Heavy Duty has recessed wells to hold the sample beakers, wells being 6 1/4" deep, designed to contain 250 ml electrolytic beakers. The wall of each well serves as an inner wall of the water jacket, for use in either heating or cooling. Two serrated nipples for rubber tubing connections for cooling or heating water are mounted on the right end casting. In plain copper analysis, 1 gram of copper may be deposited in 15 minutes with an accuracy of approximately 0.05% without the necessity of special techniques.

All electrolytic analyzers accommodate electrodes having shaft diameters no greater than 0.059 inch. Stainless steel

spring tension chucks permit quick, easy insertion of the electrodes and maintain proper electrical contact. On the Heavy Duty Analyzer, the cathode chuck is eccentrically mounted, providing adjustability to accommodate electrodes up to 50 mm diameter. Special Sargent high efficiency electrodes are available for both analyzers.

Analyzers are complete with cord and plug for attachment to standard outlets. For operation from 115 volt, 50 or 60 cycle A.C. circuits.

	SARGENT-SLOMIN	HEAVY DUTY
Maximum D.C. current at each position	5 ampere	15 ampere
Maximum D.C. voltage at each position	10 volts	10 volts
Maximum power consumption	150* or 300 watts	400 watts
Height	18 inches	20 1/2 inches
Width	11 1/4" or 21 inches	21 inches
Depth	11 1/4 inches	11 1/4 inches
Net Weight	35* or 61 pounds	80 pounds
Shipping Weight	70* or 110 pounds	130 pounds

\*One position unit

**S-29459** ELECTROLYTIC ANALYZER — Motor Stirred, One Position, 5 Ampere, SARGENT-SLOMIN.....**\$275.00**

**S-29460** DITTO. But with adjustable sub-surface heater .....**\$300.00**

**S-29464** ELECTROLYTIC ANALYZER — Two Position, SARGENT-SLOMIN .....**\$425.00**

**S-29465** DITTO. But with two adjustable heaters, pilot lights and control knobs.....**\$475.00**

**S-29480** ELECTROLYTIC ANALYZER — Heavy Duty, Magnetically Stirred, Two Position, 15 Ampere, Sargent (illustrated top, right).....**\$575.00**

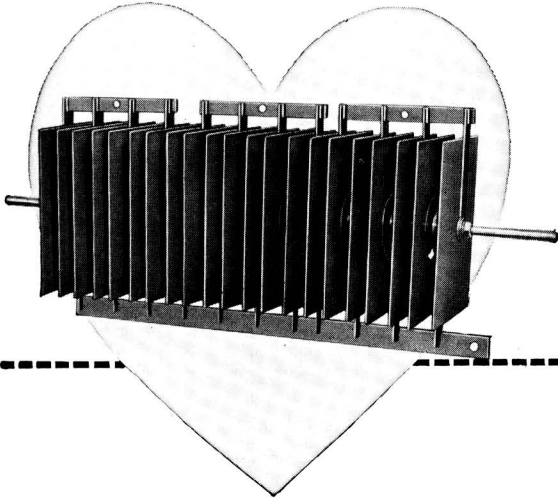
# SARGENT

SCIENTIFIC LABORATORY INSTRUMENTS • APPARATUS • SUPPLIES • CHEMICALS

*Catalog No. 100  
Now Available*

**E. H. SARGENT & COMPANY, 4647 W. FOSTER AVE., CHICAGO 30, ILLINOIS**  
 MICHIGAN DIVISION, 1959 EAST JEFFERSON STREET, DETROIT 7, MICHIGAN  
 SOUTHWESTERN DIVISION, 5915 PEELER STREET, DALLAS 19, TEXAS  
 SOUTHEASTERN DIVISION, 3125 SEVENTH AVE., N., BIRMINGHAM 4, ALA.

# Six Square Inches per Ampere\* of "Heart"!



The selenium stack is the heart of any selenium rectifier. For it is the quality of the stack and its accompanying circuitry that determines the effectiveness of a rectifier, just as the state of the heart and blood vessels of a human determine his strength and health.

## IT'S A PROVEN FACT, RAPID RECTIFIER STACKS STAND UP LONGER IN HARD SERVICE. HERE'S WHY:

- 1) Rapid allows 6 square inches per ampere of plate surface in full wave bridge circuits. For years we have maintained this standard (somewhat higher than other makes), since we feel allowing this much area results in maximum life expectancy.
- 2) The plates in Rapid stacks use triple purified Selenium.
- 3) They are carefully tested and balanced for even current distribution.
- 4) They are coated with an exclusive material rendering them absolutely impervious to the corrosive conditions existing in plating rooms.
- 5) The plates are spaced an average of 1/2 inch, diminishing the possibility of dust, dirt and corrosive material becoming lodged between plates, thus allowing heat to dissipate readily.

Rapid designs its stacks to much higher standards than most other manufacturers.\*\*

For example:

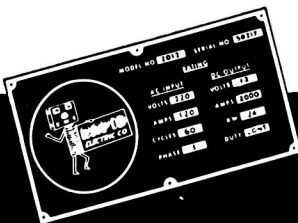
In tests performed at ambient temperatures of over 30°C, a recognized electrical manufacturers' group standard allows a temperature rise in the stack of 60°C; and, a rise of 40°C at the same ambient temperature for 1000 hours is permitted without derating.

Rapid standards permit a maximum stack temperature rise of only 22°C above the ambient. This low rise is made possible only because of the large area used per ampere, the plate spacing, high purity of Selenium used, the advanced circuitry and the engineering skill which designs the complete rectifier unit for the specific job.

So, when you buy a rectifier, check its heart. Make sure the one you buy offers the most advanced design for longest life . . . In other words, make sure you get a Rapid Rectifier.

\*In forced air cooled, three phase, full wave bridge circuit units.

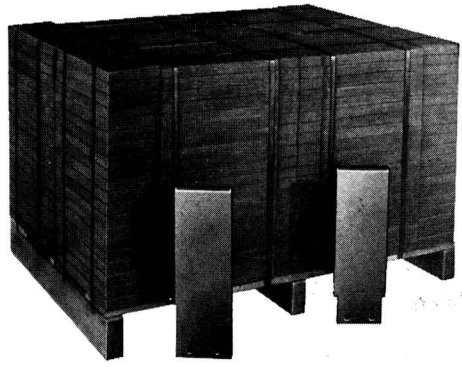
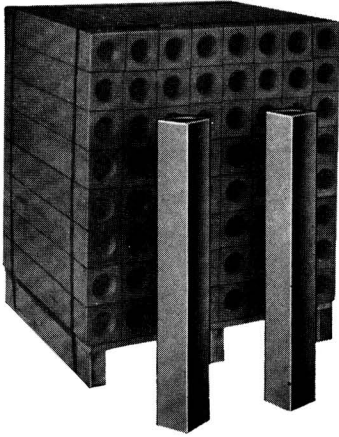
\*\*All three phase rectifiers are designed with a full wave circuit.



THE NAMEPLATE THAT MEANS *"More Power to You!"*

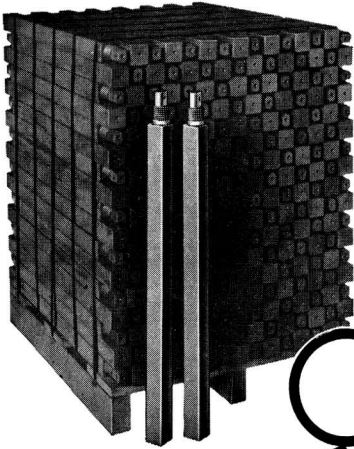
# RAPID ELECTRIC COMPANY

2881 Middletown Road • New York 61, N. Y. • Phone: Talmadge 8-2200



**SAVE!**  
with

# **STACKPOLE** *Anodes*



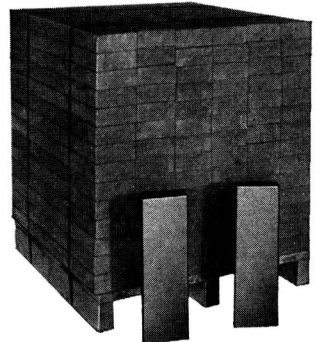
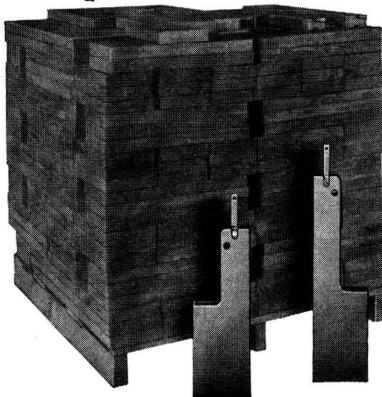
In almost every case and in practically any type of chlorine cell, Stackpole *treated* graphite anodes result in worthwhile cost savings . . . because they deliver long-life, low-voltage operation in fullest measure.

From square rods to special shapes for mercury cells, these anodes are a sound investment in long-run economy.

A test by comparison with conventional anode types offers convincing evidence of their greater efficiency.

• **STACKPOLE CARBON COMPANY, St. Marys, Pa.**

**EVERYTHING IN CARBON BUT DIAMONDS**





*It's my job to prevent trouble! That's why I consider "KARBATE" products wherever corrosion is a factor.*



**Do You Know . . .**

- . . . that "Karbate" impervious graphite is inert to a greater range of corrosive conditions than any other widely used material of construction?
- . . . that the price of "Karbate" equipment compares favorably with those of less corrosion-resistant materials?
- . . . that standard designs of "Karbate" equipment take full advantage of this material's high compressive strength to assure ruggedness beyond the toughest service requirements?
- . . . that "Karbate" brand impervious graphite — the original and most widely used brand—is manufactured exclusively by National Carbon Company?

**Don't wait** until other materials fail — consider "Karbate" impervious graphite equipment *right from the start* when building a new plant or expanding present facilities. Our technical and engineering staffs are at your service.

**TEST YOUR  
KNOWLEDGE OF  
KARBATE  
BRAND  
IMPERVIOUS  
GRAPHITE  
EQUIPMENT**

*The term "Karbate" is a registered trade-mark of Union Carbide and Carbon Corporation*

**NATIONAL CARBON COMPANY**

**A Division of Union Carbide and Carbon Corporation  
30 East 42nd Street, New York 17, N. Y.**

*Sales Offices: Atlanta, Chicago, Dallas, Kansas City, Los Angeles, New York, Pittsburgh, San Francisco*

**IN CANADA: Union Carbide Canada Limited, Toronto**



**Pumps—  
Catalog Section  
S-7250**



**Pipe and Fittings—  
Catalog Section  
S-7000**



**Heat Exchangers—  
Catalog Sections  
S-8740 and S-8840**

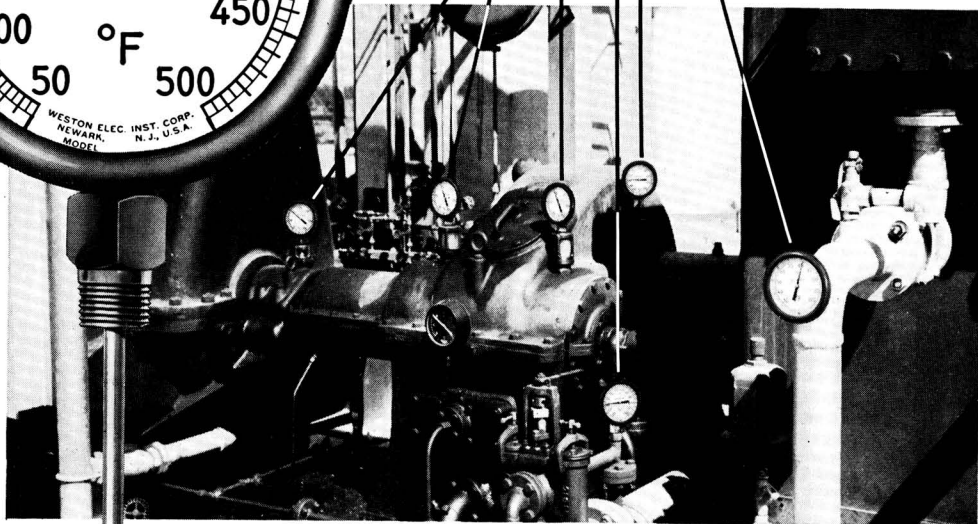
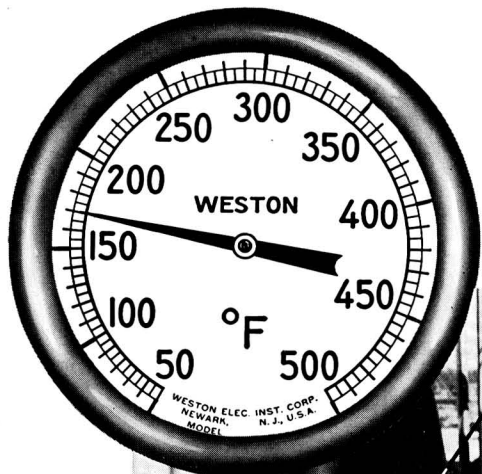


**Cascade Coolers—  
Catalog Section  
S-8820**



**HCl Absorbers—  
Catalog Section  
S-7460**

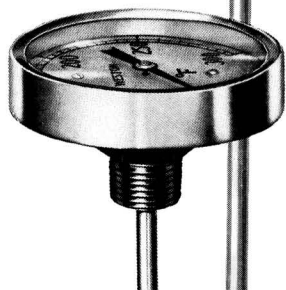
# AT EVERY CHECKPOINT



## **WESTON** *all-metal* THERMOMETERS (with Multiple Helix\*)

Here's another typical example of how large processing plants have solved temperature checking problems, and cut thermometer costs besides. With a WESTON dial-type thermometer at every checkpoint, temperatures are read at a glance . . . in far less time, and with far greater accuracy. Their sturdy all-metal construction resists breakage, gives them far longer life on operating equipment. And the exclusive WESTON multiple helix employed assures dependable accuracy during all this long life.

Available in a broad selection of types, sizes, ranges and stem lengths, WESTON thermometers are today standard on all types of mobile and stationary equipment and machines, large and small; as well as on piping, conduit, ducts, etc. Ask your distributor, or local WESTON representative for complete information, or write for descriptive bulletin . . . WESTON Electrical Instrument Corporation, 614 Frelinghuysen Avenue, Newark 5, New Jersey.



\*This WESTON-made sensing element is the more costly, non-sagging, multiple-helix. Carefully aged over a broad temperature range for long periods, it assures better accuracy, over a longer life.

## **WESTON**

5537

# *Thermometers*

Stocked  
by leading  
Distributors



## Support of International Chemistry

**I***NTERNATIONAL* agreement in matters pertaining to nomenclature, atomic weights, constants, symbols, and terminology was facilitated by the establishment in 1918 of the International Union of Pure and Applied Chemistry. The governing body of this organization, the Council, is composed of delegates appointed by national agencies in each of the member countries. In the United States, the national agency is the Division of Chemistry and Chemical Technology of the National Research Council. The Electrochemical Society is one of the five technical societies represented on this Division of N.R.C., and accordingly is a participant in the affairs of the International Union. Thus, members of the Society, an organization already international in character, may regard themselves as members of the world body.

The extensive interests and activities of IUPAC are probably not as widely known as they should be. It will be recalled that the XVIth Biennial Conference of the organization was held in New York in September 1951, that the last meeting was in Stockholm in 1953, and that the next one will be in Zurich next July. The Union has five sections devoted to the practices of fundamental chemistry and one to applied chemistry. The work of these sections is carried out by 46 commissions and subcommissions. The late Professor Marston T. Bogert was president of IUPAC from 1938 to 1947. Many other American chemists have served in official capacities.

IUPAC is a purely voluntary organization that has in recent years derived its financial support from national contributions and grants-in-aid from UNESCO. With the growing role of world-wide chemistry and the complexity of its ramifications, it is essential that a full paid secretariat be established at an estimated cost of \$30,000 a year. The share of the United States in this expense is \$5,000 and it is proposed to raise this from American chemists by voluntary subscription. Contributions of \$1.00 or more may be made to the IUPAC Fund, U. S. National Committee of IUPAC, Division of Chemistry and Chemical Technology, National Research Council, Washington 25, D. C. Subscribers to the fund will receive newsletters from time to time describing the work and current affairs of IUPAC. It is deserving of the support of American chemists, and provides an excellent opportunity for international collaboration in the advancement of chemistry.

—RMB

# ELECTROMETRIC pH DETERMINATIONS

By ROGER G. BATES, National Bureau of Standards

This book brings a long-needed measure of order to a frequently misunderstood field by means of a two-pronged attack on its problems. It first presents a theoretical and experimental basis for a practical electrometric scale of acidity and compares the various possible scales with respect to their validity and usefulness. It also provides—in practical handbook form for the assistance of all who measure pH—a discussion of the techniques of pH determination and modern commercial pH equipment. Bates explains clearly the reasons why the pH value is not an exact physical quantity and shows how far theory can go in pH measurement. He also presents a full discussion of the standard pH scale (conventional activity scale) and the National Bureau of Standards pH standards, which are gradually being adopted throughout the world.

1954 331 pages Illustrated \$7.50

## A SHORT TEXTBOOK OF COLLOID CHEMISTRY

By BRUNO JIRGENSONS, University of Texas, and  
MARTIN E. STRAUMANIS, University of Missouri

A completely revised version of a text originally published in Germany in 1949; now translated and brought up to date by the authors. It stresses the basic facts and relationships of both inorganic and organic colloids, and explains the experimental methods briefly.

1954 420 pages Illustrated \$8.00

## THE INSULATION OF ELECTRICAL EQUIPMENT

Edited by WILLIS JACKSON, Metropolitan Vickers Electrical Company, London

A compilation of 11 lectures delivered at a special session at the Imperial College by leading British authorities in research and industry. Gives clear, precise descriptions of the principles, research, and present status of almost every aspect of the insulation of electrical apparatus.

1954 340 pages 152 Illustrations \$7.75

New 4th Edition of

# STORAGE BATTERIES

A General Treatise on the Physics and Chemistry  
of Secondary Batteries and Their Engineering  
Applications.

By GEORGE WOOD VINAL, formerly of the National  
Bureau of Standards

Reflecting the many technological advances in battery design and construction that have taken place in the past fourteen years, this new Fourth Edition has been almost entirely rewritten to bring you completely up to date. The book continues to be the unparalleled reference in its field—an authoritative source of battery data, as well as a stimulus to fresh thinking for the electrical engineer. Physical and chemical properties of the materials used in making batteries are discussed, and the reader is given a general description of the various manufacturing processes. All phases of storage battery operation are covered and all important industrial applications are thoroughly described.

1955 446 pages Illustrated \$10.00

## FERROUS PROCESS METALLURGY

By the late JOHN L. BRAY, formerly of Purdue University

1954 414 pages Illustrated \$6.50

## MINERALS for the CHEMICAL and ALLIED INDUSTRIES

By SYDNEY J. JOHNSTONE, formerly of the Imperial Institute, London

1954 692 pages \$11.50

Mail Coupon for your ON-APPROVAL copies today

JOHN WILEY & SONS, Inc.

JBCS-25

440 Fourth Avenue, New York 16, N.Y.

Please send book(s) checked below for me to examine ON APPROVAL. Within ten days I will either return same and owe you nothing or will remit the price(s) indicated, plus postage.

- Electrometric pH Determinations, \$7.50
- Storage Batteries, new 4th Edition, \$10.00
- A Short Textbook of Colloid Chemistry, \$8.00
- The Insulation of Electrical Equipment, \$7.55
- Ferrous Process Metallurgy, \$6.50
- Minerals for the Chemical and Allied Industries, \$11.50

NAME \_\_\_\_\_

ADDRESS \_\_\_\_\_

CITY \_\_\_\_\_ ZONE \_\_\_\_\_ STATE \_\_\_\_\_

SAVE POSTAGE! Check here if you ENCLOSE payment, in which case we pay postage. Same return privilege.

# Polarization Studies of Copper, Nickel, Titanium, and Some Copper and Nickel Alloys in Three Per Cent Sodium Chloride<sup>1</sup>

H. B. BOMBERGER

*Rem-Cru Titanium, Inc., Midland, Pennsylvania*

AND

F. H. BECK AND M. G. FONTANA

*The Ohio State University, Columbus, Ohio*

## ABSTRACT

Polarization characteristics were determined for some metals and alloys in flowing salt solutions. Relationships between potential and time, potential and applied current, applied current and corrosion rate, and solution velocity and corrosion rate were considered. Copper and brass anodes dissolved readily. Nickel and copper-nickel alloys exhibited anodic polarization. Titanium anodes resisted dissolution by film growth and extensive polarization.

## INTRODUCTION

A study of the polarization properties of an electrode provides information about the type, nature, and rate of the reaction or reactions taking place and is therefore helpful in explaining corrosion phenomena (1-4). In this investigation an attempt was made to explain the behavior of some commercial materials by studying them as individual electrodes and observing their tendency to polarize and corrode.

## EXPERIMENTAL PROCEDURE

The test solution was prepared by dissolving 3% by weight of reagent grade sodium chloride in double distilled water. This was held at  $30^{\circ} \pm 1^{\circ}\text{C}$  in a 20-l flask and circulated through the test system by means of a Hastelloy C pump. Flow rate was determined with flowmeters, and controlled by stop cocks in the system and an autotransformer in the motor circuit.

Test units, as indicated in Fig. 1, were constructed so that flat test specimens formed part of one side of a rectangular shaped cell through which the solution passed with a minimum of turbulence. Test specimens were 6 in. long and had an effective width of 1 in. They were held  $\frac{1}{4}$  in. away from, but parallel to, a platinum electrode of the same size on the opposite side of the tube.

Polarization was accomplished by passing a controlled direct current between the platinum and test electrodes. Potentials of the test electrodes were determined periodically by means of an L & N potentiometer and a saturated calomel reference electrode. Tests were continued until the electrode potentials were essentially constant for a few hours, i.e., less than 5 mv/hr variation. In some cases as long as 48 hr were required. For potential measurements the small tip of the calomel electrode was inserted through an opening in the center of the platinum electrode and placed close to the surface of the test electrode to minimize the  $IR$  drop. The  $IR$  drop across the film was estimated by a method suggested by Pearson (5) and found to be negligibly small for all materials except the titanium anodes.

New specimens and solutions were prepared for each test. For  $1-1\frac{1}{2}$  hr before the beginning of each test, solutions were vigorously aerated with air or purified argon. This resulted in 5.15 and 0.05 ml of dissolved oxygen per liter of solution for the air and argon flushed solutions, respectively. Periodic sampling indicated that these values and the  $p\text{H}$ , between 6 and 7, remained nearly constant during all tests.

Test specimens (Table I) were abraded with No. 240 grit emery cloth and all but the titanium were annealed for 1 hr at  $1200^{\circ}\text{F}$  in purified argon followed by furnace cooling. Before testing, the copper and brasses were swabbed with a 10% solution of potassium cyanide; the other samples were abraded lightly with emery cloth. All were washed in distilled water and acetone and dried in a desiccator until installed in the test cells. Corrosion rates were

<sup>1</sup> Manuscript received November 4, 1953. This paper was prepared for delivery before the Wrightsville Beach Meeting, September 13 to 16, 1953, and is based on a dissertation presented in partial fulfillment of the requirements for the Ph.D. degree of one of the authors (H.B.B.) at Ohio State University.

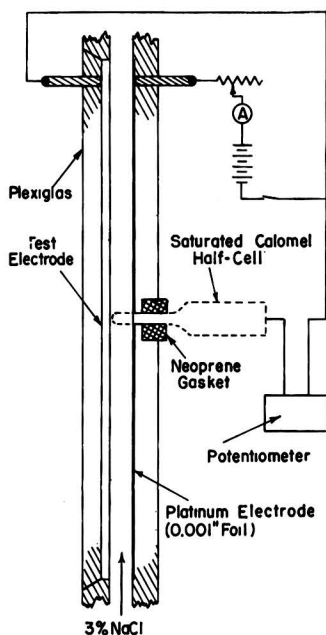


FIG. 1. Schematic diagram of test unit and electrical system.

calculated from the exposed surface area and the loss of weight for the given test periods.

#### DISCUSSION AND RESULTS

No weight loss or tarnishing was observed on any of these materials when exposed to the argon flushed solutions, indicating little if any local cell action. In view of the energy requirements, corrosion of copper should not occur under these conditions, but nickel, zinc, and titanium should replace hydrogen ions in solution (6). This, however, does not occur readily because of polarization or passivation effects peculiar to these materials. Corrosion rates for these materials exposed to air-saturated solutions for given times are listed in Table II along with corrosion and polarization potentials. Under these conditions, reduction of oxygen, requiring less energy than reduction of hydrogen ions, occurred as the main cathodic reaction, and some corrosion was observed on all materials except nickel and titanium.

In general, cathodic polarization of these materials in the argon flushed solutions was manifested by a change of potential to a greater anodic value (more negative) than observed in the air-saturated solu-

TABLE I. Nominal composition, grain size, and hardness of materials

Material	% Cu	% Zn	% Ni	% Fe	% Mn	% Other elements	A.S.T.M. grain size	Vickers hardness
Deoxidized copper..	99.90	—	—	—	—	0.025P	4	38
Cartridge brass.....	70	30	—	—	—	—	4	50
Red brass.....	85	15	—	—	—	—	5	50
Cupro-nickel.....	70	—	30.0	0.57*	—	—	5	97
Monel.....	30	—	67	1.4	1.0	0.15C 0.1Si	5	97
"A" Nickel.....	0.1	—	99.4	0.15	0.25	0.06C 0.05Si	5	93
Rem-Cru Titanium..	99 + Ti, 0.2C, 0.15N							278

\* Determined by analysis.

TABLE II. Steady-state potentials in volts vs. saturated calomel, and corrosion rates in mpy for materials in 3% NaCl flowing at 50 ft/min and 30°C

Materials	Test time, hr	Air-saturated solutions			Argon-flushed solutions*	
		Corrosion rate	Corrosion potential	Max. cathodic polarization	Corrosion potential	Max. cathodic polarization
Copper.....	8	9.0	-0.250	-1.25	-0.260	-1.32
70-30 Brass.....	24	8.8	-0.225	-1.29	-0.320	-1.30
Red brass.....	24	15	-0.193	-1.07	—	—
Nickel.....	24†	0.0	-0.120	-1.29	-0.200	-1.26
70-30 Cu-Ni.....	24†	6.0	-0.191	-1.27	—	—
Monel.....	24†	0.8	-0.10	-1.31	—	—
Titanium.....	7	0.0	-0.10	-1.26	-0.10	-1.40

\* No observable corrosion.

† Cathodes tested for 48 hr.

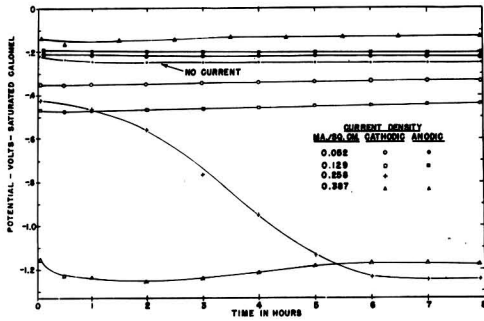


Fig. 2. Polarization of copper in air-saturated 3% NaCl solution (50 ft/min, 30°C).

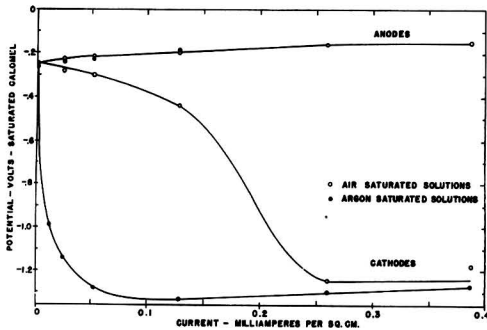


Fig. 3. Polarization of copper in 3% NaCl solutions (50 ft/min, 30°C).

tions, since the main cathodic reaction in this case is the reduction of hydrogen ions. This may be the reason the corrosion potentials are generally more anodic in the air-free solutions (see Table II) since the local cell cathodes are apparently polarized to a greater anodic value and thus displace the corrosion potential to a more anodic value.

**Copper.**—Typical time-potential curves for copper, given in Fig. 2, show that nearly constant potentials were obtained within 8 hr in 3% NaCl flowing at 50 ft/min. Steady-state potentials are plotted against applied current density in Fig. 3. Copper anodes polarized little with increased current density, suggesting that copper passes readily into solution and that the potential change is due to concentration polarization. Cathodic polarization is a function of current density and oxygen concentration. At low current densities the cathodic reaction is the reduction of oxygen, but at high current densities the rate of oxygen consumption exceeds the rate of supply by diffusion. Thus, the potential changes until the reduction of hydrogen ions also takes place. The apparent decrease in cathodic polarization at the high current densities may have resulted from partial depolarization by chlorine.

Fig. 4 shows that the corrosion rate of copper

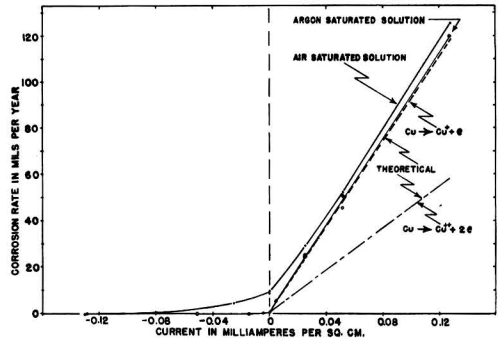


Fig. 4. Corrosion of copper in 3% NaCl solution flowing at 50 ft/min, 30°C.

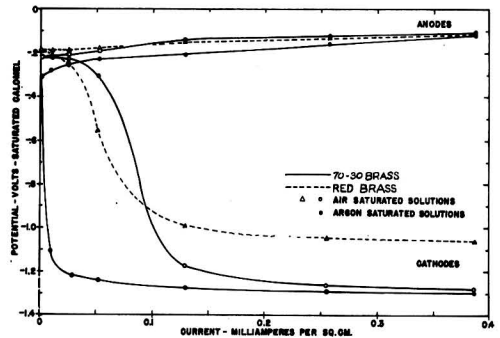


Fig. 5. Polarization of brasses in 3% NaCl solutions (50 ft/min, 30°C).

anodes (based on 8-hr tests) is proportional to the current density and indicates that copper goes into solution as monovalent ions. The corrosion rate in air-saturated solutions is decreased with increased cathodic current until corrosion is almost averted at a current density of  $-0.08 \text{ ma/cm}^2$ .

The effect of flow rate on the corrosion of copper was studied. Copper corroded almost linearly with solution velocity, from 6 to 78 mils per year, on exposure in air-saturated solutions moving between 10 and 440 ft/min. Cathodes at  $-0.026 \text{ ma/cm}^2$  corroded at less than 4 mpy until the flow rate increased beyond 150 ft/min where the behavior was almost linear to 48 mpy at 440 ft/min. Anodes at  $0.026 \text{ ma/cm}^2$  indicated that corrosion is almost linear with velocity, from 30 to 86 mpy, over the range 50 to 440 ft/min. At 600 ft/min attack was nonuniform and results were inconsistent, presumably because of film erosion by excessive turbulence.

Good correlations between flow rate and electrode potential could not be obtained. In general, however, the potentials appeared to become less anodic with increased flow rate, possibly because of decreased polarization of the local cathodes.

**Brasses.**—The behavior of 70-30 brass was similar

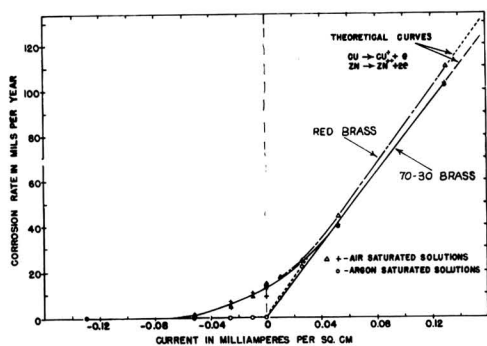


Fig. 6. Corrosion of brasses in 3% NaCl solutions (50 ft/min, 30°C).

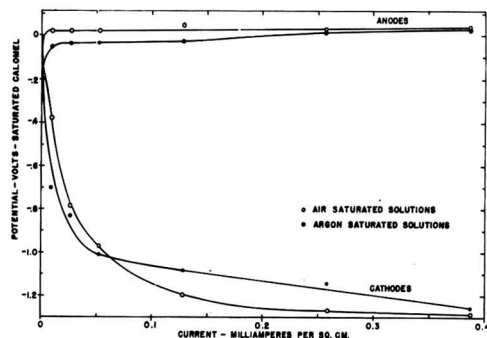


Fig. 7. Polarization of nickel in 3% NaCl solutions (50 ft/min, 30°C).

to that of copper. The potential became quite steady within 8 hr, but the potential of the red brass, in air-saturated solutions flowing at 50 ft/min, varied considerably for almost 24 hr. Fig. 5 indicates that the cathodic polarizations of brasses in air-saturated solutions is more pronounced than that of copper. The curved portions of the anode curves suggest a slight anodic overvoltage, whereas the linear portion is indicative of concentration polarization.

Corrosion rates are plotted against current in Fig. 6 for 70-30 brass and red brass based on 24-hr tests. Cathodic current densities above  $-0.07$  ma/cm<sup>2</sup> appeared to polarize local cathodes sufficiently to prevent corrosion in air-saturated solutions. Since much of the corrosion occurs before appreciable polarization takes place, longer test periods would have resulted in lower average corrosion rates for the cathodes. At an anodic current of about  $0.05$  ma/cm<sup>2</sup> local anodes polarized to the extent that local action ceased and dissolution was then proportional to the applied current as indicated. Theoretical corrosion rates were calculated from the applied current using the following equation and assuming that the copper went into solution only as monovalent ions; zinc forms only divalent ions:

$$C.R. = KIt/F [(XM/V)_{Cu} + (XM/V)_{Zn}] \quad (I)$$

where  $X$  represents mole fractions of the elements in the brass with molecular weights  $M$  and valence  $V$ ,  $K$  is a proportionality constant,  $F$  is Faraday's constant, and  $I$  is the applied current for time  $t$ .

**Nickel.**—Nickel acquired a steady potential in flowing argon-flushed solutions within 24 hr, but cathodes in air-saturated solutions required about 48 hr. Fig. 7 shows an anodic polarization of about  $0.15$  v in both air- and argon-saturated solutions, by extrapolating the straight portions of the curves to zero current. Because of this anodic polarization, nickel should not be expected to replace hydrogen ions in significant amounts in neutral salt solutions. It is also noteworthy that the cathodic polarization of nickel in air-saturated NaCl appears to be greater at low current densities than that of the other materials under these conditions. According to work by LaQue (7) the metal does not seem to polarize nearly as readily in flowing sea water.

Fig. 8 shows that little or no corrosion was observed in the air- and argon-flushed solutions and that dissolution followed Faraday's law. Corrosion was nonuniform, being of the pitting type.

Although corrosion of the nickel was not observed

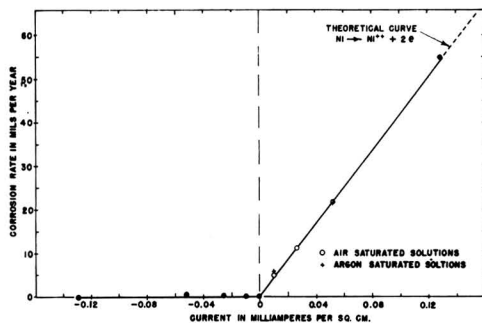


Fig. 8. Corrosion of nickel in 3% NaCl solutions (50 ft/min, 30°C).

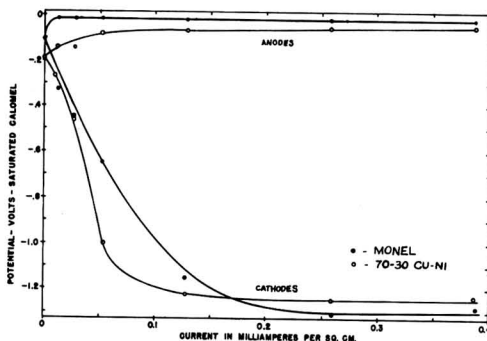


Fig. 9. Polarization of Cu-Ni alloys in air-saturated 3% NaCl solution (50 ft/min, 30°C).



without applied current, the metal dissolved slowly at all low cathodic current densities in flowing 3% NaCl, and the test system repeatedly acquired a black insoluble film. This deposit dissolved readily in potassium cyanide solutions but not in ammonium chloride, thus suggesting that it was  $Ni_2O_3$  and not  $Ni(OH)_3$ . The maximum cathodic corrosion rate observed was 0.9 mpy at a current density of  $-0.052$  ma/cm<sup>2</sup>. At and above  $-0.258$  ma/cm<sup>2</sup> protection seemed to be complete and no attack was observed. This corrosion is believed to have resulted from the small accumulation of dissolved chlorine.

**Copper-nickel alloys.**—Monel and 70-30 cupro-nickel and anodes of these materials acquired a steady state in about 24 hr, but the cathodes required about 48 hr in air-saturated solutions. The polarization curves, given in Fig. 9, indicate that anodes of these alloys, like nickel, are characterized by substantial polarization, being about 0.08 and 0.10 v, respectively, at low current densities. Nickel and copper-nickel alloy cathodes appear to polarize more readily and to a greater extent than any of the other materials tested under the given conditions (as indicated in Fig. 12).

Fig. 10 shows that some local cell action does take place on the alloys but that it can be polarized by a small applied current. Unlike nickel, no evidence of induced corrosion was observed with cathodic currents. Anodes dissolved at a slower rate than equation (I) indicated. Apparently in this case, anode reactions are not only the formation of divalent nickel and monovalent copper ions, but may include the formation of divalent copper ions and the discharging of hydroxyl and chloride ions as well.

**Titanium.**—Titanium and titanium cathodes acquired a steady state in less than 2 hr, but the anodes with more than 0.026 ma/cm<sup>2</sup> changed considerably in potential for almost 7 hr. This was true for both the air- and argon-flushed 3% NaCl flowing at 50 ft/min. The metal without impressed current

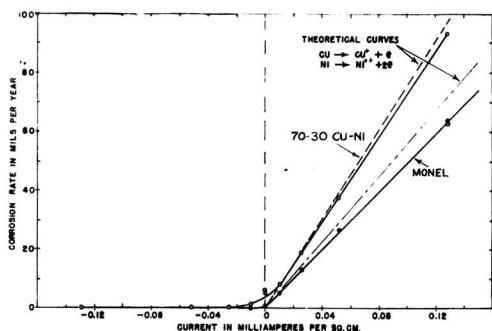


FIG. 10. Corrosion of Cu-Ni alloys in air-saturated 3% NaCl solution (50 ft/min, 30°C).

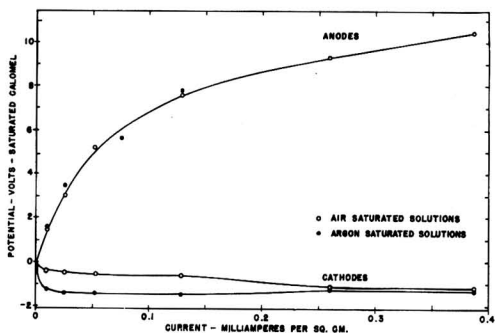


FIG. 11. Polarization of titanium in 3% NaCl solution (50 ft/min, 30°C).

TABLE III. Corrosion of titanium anodes in air-saturated 3% NaCl flowing at 50 ft/min and 30°C for 7 hr

Applied current density in ma/cm <sup>2</sup>	Corrosion rate in mpy	Approximate resistance in ohms/cm <sup>2</sup>	IR drop, v	Max. anode polarization potential v (including IR)
0.010	0.0	—	—	1.50
0.026	0.0	2000	0.05	3.00
0.052	0.0	2300	0.10	4.80
0.129	2.2	2000	0.26	7.45
0.258	4.1	2500	0.65	9.35
0.387	94	2700	1.05	10.50

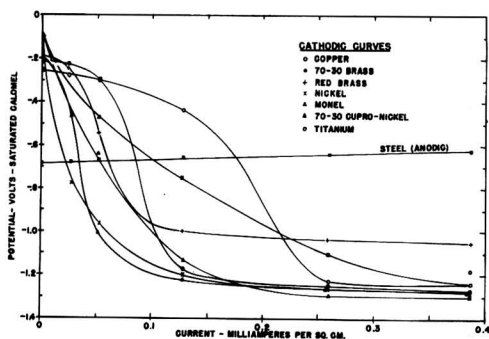


FIG. 12. Anodic polarization of steel and cathodic polarization of other materials in air-saturated 3% NaCl solutions flowing at 50 ft/min, 30°C.

had a potential of  $-0.10$  v. Schlain (8) reported appreciable change in potential with time in air-saturated static 3% NaCl until a potential of 0.44 v was attained after 100 hr. Hackerman and Hall (9) noted slow drifting of the potential in air-saturated 0.5M NaCl for several days until a final potential of 0.17 v was observed. LaQue (7) reported a corrosion potential of  $-0.10$  v for high purity titanium in flowing sea water. Environmental or test variables may account for these differences in results.

The extensive anodic polarization observed in Fig. 11 is believed to be due in part to an adherent in-

soluble film of high ohmic resistance as noted in Table III. Corrosion data are given there also.

At small anodic currents there was no evidence of corrosion until 0.129 ma/cm<sup>2</sup> was employed which resulted in a slight but nonuniform metal loss and film growth. Identification by electron diffraction of a light golden film, developed at low currents, was not successful. However, data did indicate that the film was crystalline and that it was not TiO, Ti<sub>2</sub>O<sub>3</sub>, TiCl<sub>2</sub>, nor a form of TiO<sub>2</sub>. TiH<sub>2</sub> was observed as a reaction product on the cathodes.

The cathodic polarization of titanium is also given in Fig. 12 along with cathode curves for the other materials. LaQue (7) observed similar degrees of polarization of titanium in sea water at current densities of 0.1 and 0.2 ma/cm<sup>2</sup>, but at lower current densities polarization occurred much more readily in sea water than noted in this work.

#### SUMMARY

Corrosion and polarization studies were made on a number of materials in flowing 3% NaCl. None of the materials showed evidence of corrosion in argon-flushed solutions. Cathodic curves, given in Fig. 12, indicate that nickel and the nickel alloy cathodes polarized more readily than the others tested. LaQue (7) noted that nickel is less readily, and titanium more readily, polarized in sea water than was observed in this work. These differences may be due to environmental factors. Nickel and nickel anodes polarized approximately 0.1 v at low current densities, but the titanium anodes polarized more than 10 v at 0.387 ma/cm<sup>2</sup>.

Mears and Brown (1) and, later, May and LaQue (10) demonstrated that data of this type can also be used for estimating local cell polarization curves by plotting the observed potentials against calculated currents based on a number of assumptions.

According to Wesley (11), curves of this type, plotted with an anodic polarization curve, should be useful in estimating corrosion rates of galvanic couples. For example, the point of intersection of the

steel curve (Fig. 12) with the copper curve should represent the maximum current and, thus, the maximum corrosion rate of such a couple of equal areas, at zero *IR* drop and under the given conditions. An attempt to confirm this was unsuccessful with the closed system employed. Contamination by iron products drastically altered test conditions, preventing detectable polarization of the copper cathode, so that corrosion proceeded at a very rapid rate.

#### ACKNOWLEDGMENTS

This investigation was conducted under a Fellowship granted by the International Nickel Company, Inc., New York, New York, and under contract N6ori-17, Task Order II, between the Office of Naval Research and the Ohio State University Research Foundation. The interest and support of The International Nickel Company, Inc., and the Office of Naval Research are appreciated.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

#### REFERENCES

1. R. B. MEARS AND R. H. BROWN, *This Journal*, **97**, 75 (1950).
2. C. WAGNER AND W. TRAUD, *Z. Elektrochem.*, **44**, 392 (1938).
3. M. POURBAIX, *Corrosion*, **6**, 395 (1950).
4. R. H. BROWN, G. E. ENGLISH, AND R. D. WILLIAMS, *ibid.*, **6**, 186 (1950).
5. J. M. PEARSON, *Trans. Electrochem. Soc.*, **81**, 485 (1942).
6. W. M. LATIMER, "The Oxidation States of the Elements and Their Potentials In Aqueous Solutions," p. 293, Prentice Hall, Inc., New York (1938).
7. F. L. LAQUE, *Proc. Am. Soc. Testing Materials*, **51**, 495 (1951).
8. D. SCHLAIN, *U. S. Bur. Mines Rept. Invest.* 4965, April 1953.
9. N. HACKERMAN AND C. D. HALL, JR., *This Journal*, **101**, 321 (1954).
10. T. P. MAY AND F. L. LAQUE, *Corrosion*, **10**, 91 (1954).
11. W. A. WESLEY, *Proc. Am. Soc. Testing Materials*, **40**, 690 (1940).

# Effect of Oxygen, Chlorides, and Calcium Ion on Corrosion Inhibition of Iron by Polyphosphates<sup>1</sup>

H. H. UHLIG, D. N. TRIADIS, AND M. STERN

*Corrosion Laboratory, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts*

## ABSTRACT

Data are presented showing that sodium polyphosphates are effective corrosion inhibitors for steel, provided the dissolved oxygen concentration is above a critical minimum. Presence of calcium ion appreciably improves inhibition under all conditions. In solutions containing less than the critical amount of oxygen (1 ml/l), 60 ppm sodium polyphosphate accelerates corrosion. This is also true when 60 ppm Ca<sup>++</sup> is added to the polyphosphate solution, although the critical oxygen concentration is now about 0.15 ml/l.

Sixty ppm sodium polyphosphate effectively inhibits against corrosion in solutions containing up to 0.01% NaCl; above this concentration, passivity by dissolved oxygen is lost, and the inhibitor is no longer effective. However, the calcium complex continues to function to some extent even at high chloride ion concentrations.

The foregoing corrosion data combined with polarization and potential studies indicate that sodium polyphosphates inhibit by favoring the passivation of steel by adsorbed oxygen. The hydrous FeO film normally present on iron presumably reacts with polyphosphate to form a soluble complex, permitting higher surface concentrations of oxygen for a given concentration in solution. Corrosion control under these circumstances is mixed, and pitting occurs in presence of chlorides. Calcium salt additions lead to formation on cathode areas of a diffusion barrier film of unknown structure containing both calcium and phosphorus. This film appreciably reduces the corrosion rate, with control of corrosion, however, remaining mixed. Reasons for the need of continuous flow and aeration in practical systems are discussed.

## INTRODUCTION

Inhibiting corrosion of iron and steel in water solutions by small additions of sodium polyphosphates, of which sodium metaphosphate is an example, has been described in the literature since 1940 (1-4). Engineering applications have sometimes led to doubtful results (5-7). Laboratory tests show that high concentrations of metaphosphates increase corrosion (3), but smaller additions reduce attack, optimum effects being obtained in the presence of calcium ion (3), together with agitation or continuous flow of inhibited solution, and in presence of dissolved oxygen (4). The mechanism of inhibition has been variously described as being due to adsorption of the metaphosphate or of a complex (1), or to laying down of a calcium carbonate film (8), or to a film of adsorbed oxygen favored by the presence of polyphosphate (9), or to a cathode film or perhaps positively charged colloidal particles laid down by an electrodeposition process (10). Knowledge of the basic factors and mechanism of inhibition, of course, is helpful to the proper application of polyphosphates in practical systems. It appeared worthwhile, therefore, to examine these

proposals in light of additional precise data relating corrosion rates: first, to dissolved oxygen, chloride and calcium concentrations and, second, to anodic and cathodic polarization behavior.

## EXPERIMENTAL PROCEDURE

### *Corrosion Tests*

Mild steel (0.06% C, 0.33% Mn, 0.01% P, 0.029% S) samples measuring 5 x 1 x 0.13 in. (12.7 x 2.5 x 0.33 cm) were used for weight loss tests. They were abraded to 00 emery paper, degreased in distilled benzene, and pickled 1 min in 5% HCl-5% H<sub>2</sub>SO<sub>4</sub>, rinsed in water, followed by acetone and distilled benzene. The specimens, as soon after surface preparation as possible, were suspended in a Pyrex jar containing 4 l of solution, in the center of which was located a glass chimney 1 3/4 in. (4.5 cm) in diameter and 7 in. (17.8 cm) high mounted on glass legs. A sintered glass aerator located within the chimney maintained saturation of the solution with gas (flow = 150 ml/min), and also stirred the solution mildly at an estimated rate of 1 in. (2.5 cm)/sec past the specimen surface. Each specimen was suspended from a hole drilled at one end, through which a glass hook was inserted; the latter, in turn, was mounted in a tightly fitting Lucite cover over the jar. A rubber gasket, aided

<sup>1</sup> Manuscript received June 1, 1954. This paper was prepared for delivery before the Boston Meeting, October 3 to 7, 1954.

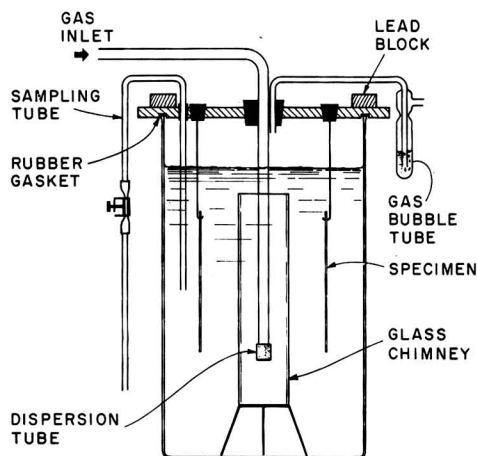


FIG. 1. Sketch of equipment for corrosion tests

by lead weights bearing down on the cover, sealed the jar against leakage of gas into or out of the gas space above the solution (Fig. 1).

The gases used for saturating the solution were bubbled through 10% NaOH to remove carbon dioxide, then through water and a glass-wool filter. Various partial pressures of oxygen were obtained by mixing nitrogen and oxygen in known amounts by use of calibrated flowmeters. Solutions were saturated for several hours or overnight before inserting the specimens. Gas concentrations in solution were calculated from known solubilities using Henry's Law, with several Winkler analyses for dissolved oxygen confirming that this procedure was satisfactory. Solutions free of dissolved oxygen were obtained by bubbling through nitrogen which had first passed over a 4-ft length of copper turnings maintained at 400°C. A sample of the deaerated solution was analyzed before tests to check for complete removal of oxygen. The pH values of the solutions were also measured before and after tests.

Following exposure, specimens were brushed under tap water, immersed in boiling 10% sodium hydroxide containing 10–20 grams of zinc powder/liter, brushed again, immersed in acetone and distilled benzene, and weighed. The polyphosphate inhibitor (Calgon<sup>2</sup>) was obtained in the form of a glass supplied through the courtesy of Hall Laboratories. This was ground in a mortar and the correct amount added to distilled water just before the tests in order to minimize reversion to the orthophosphate. According to Morgan and Swoope (11), commercial polyphosphate contains about 76% NaPO<sub>3</sub> and 24% Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.

<sup>2</sup> Produced by Calgon, Inc., Pittsburgh, Pennsylvania.

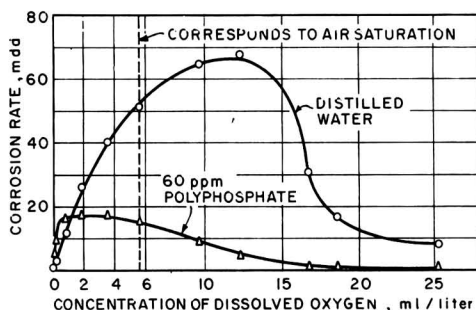


FIG. 2. Effect of partial pressure of oxygen on corrosion of mild steel in slowly moving water and in sodium polyphosphate solutions, 48-hr tests, 25°C.

Some tests were carried out with renewal of the 4l of solution each day, but results were not greatly different from those carried out with the same solution for a period of 7 days. Perhaps this is not unexpected in view of the slow reversion of polyphosphates to orthophosphates in the neutral range of pH at room temperature. Morgan and Swoope (11) found that in distilled water at room temperature, metaphosphate solutions decomposed to the extent of 10% within 30 days, and pyrophosphates were not measurably changed within this time. The majority of corrosion rates herewith reported are for the same solution retained for as long as 7 days.

All corrosion tests and potential measurements were conducted in an air thermostat maintained at  $25^{\circ} \pm 0.5^{\circ}\text{C}$ .

#### *Effect of Dissolved Oxygen and Calcium*

Data for mild steel exposed two days to distilled water containing 60 ppm polyphosphate as a function of dissolved oxygen are shown in Fig. 2. Each point represents the average of at least two specimens. Obviously, the polyphosphate is an effective inhibitor in solutions containing more than 2 ml O<sub>2</sub>/l, but actually accelerates corrosion when the oxygen concentration is below about 1 ml/l. Similarly shaped curves and comparable corrosion rates, hence identical conclusions, are reached from 7-day exposure tests, data for which were obtained in solutions containing essentially zero up to 5.75 ml O<sub>2</sub>/l (12).

Exposures for various times up to 7 days indicate, by and large, a steady rate of attack, with evidence of temporary passivity and corresponding lack of attack in some specimens for perhaps the first few hours, or sometimes the first day or two. Specimens exhibiting irreproducible passivity of this kind either were not included in the final summary of data, or the accepted corrosion rate was obtained

from the slope of weight loss vs. time after such period as the specimens began to corrode.

In absence of dissolved oxygen, mild steel exposed to distilled water suffers an uncertain very small weight loss, the rate being a maximum of 0.2 mdd. This can be compared with about 0.3 mdd obtained by Pryor and Cohen in deaerated water (13). But in presence of 60 ppm polyphosphate, attack becomes considerably greater, the average rate being 5 mdd. Presumably, complexing action of the polyphosphate is sufficient to increase the driving force of the corrosion reaction with consequent liberation of hydrogen. Specimens immersed in deaerated polyphosphate solutions accordingly become covered with an adherent black corrosion product not observed when polyphosphates are absent. The increased corrosion rate in presence of inhibitor at zero oxygen concentration is discernible in Fig. 2, and is presented in greater detail in Fig. 3, together with data on effect of calcium chloride. From data of Fig. 4, and similar data by Hatch and Rice (3), it is obvious that higher concentrations of sodium polyphosphate produce increased attack in both aerated and deaerated solutions.

Rates of attack in deaerated sodium polyphos-

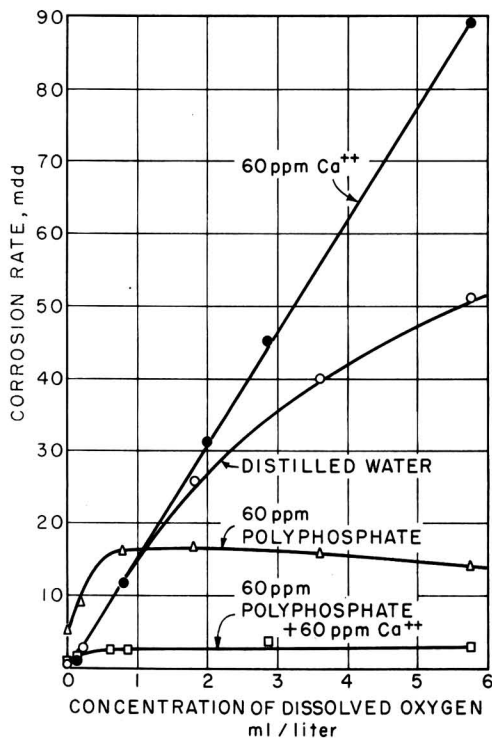


Fig. 3. Effect of  $\text{CaCl}_2$  and  $\text{O}_2$  on corrosion of mild steel in slowly moving water and in polyphosphate solutions. 48-hr tests, 25°C.

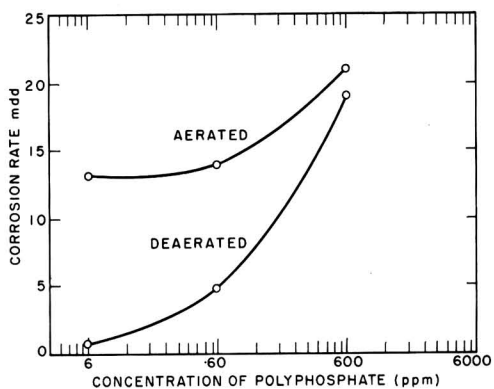


Fig. 4. Effect of sodium polyphosphate concentration on corrosion of mild steel in aerated and deaerated solutions, 48-hr tests, 25°C.

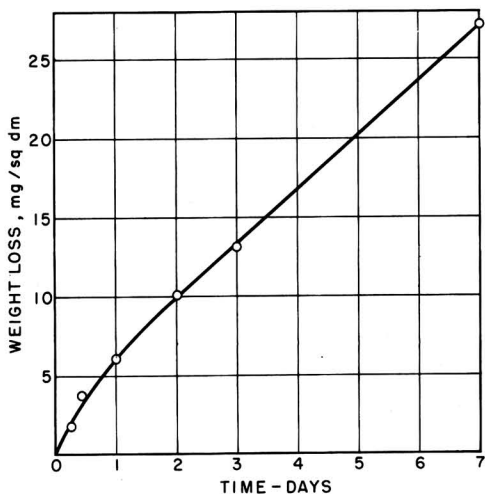


Fig. 5. Weight loss of mild steel vs. time in deaerated 60 ppm sodium polyphosphate solution, 25°C.

phate are initially higher than for final steady state (Fig. 5), probably because the iron polyphosphate complex is less corrosive than the sodium complex.

All solutions were essentially at  $\text{pH}$  7 when tests began, and changed no more than a few tenths  $\text{pH}$  unit in the alkaline direction after exposure for several days in aerated or oxygenated solutions. In deaerated sodium polyphosphate, the  $\text{pH}$  reached 9.0, suggesting that the corrosion rate would have been still higher had the  $\text{pH}$  been maintained at 7.

Fig. 2 indicates that oxygen itself is a fair passivator for mild steel when present in high concentrations, but with polyphosphate additions improving matters still further. The inhibiting effect of oxygen alone has been pointed out previously by other investigators (14, 15). A partially passivating effect of oxygen is manifest in Fig. 2, even at low

TABLE I. Corrosion rates of mild steel in deaerated solutions (48-hr exposure; average of 2 or more spec.)

Polyphosphate conc.	Corrosion rate, mdd
0.0	0.2
60 ppm	5.0
60 ppm + 60 ppm Ca <sup>++</sup> as CaCl <sub>2</sub>	0.6

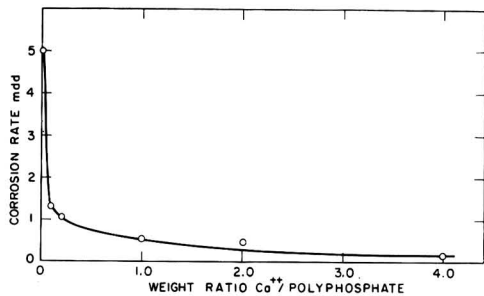


FIG. 6. Effect of weight ratio of calcium (as chloride) to 60 ppm sodium polyphosphate on corrosion rate of mild steel in deaerated solutions, 48-hr tests, 25°C.

oxygen partial pressures, by the curvature of corrosion rate plotted with oxygen concentration. Normally, in natural waters containing dissolved salts, a linear relation is maintained up to oxygen concentrations corresponding to air saturation (approximately 6 ml/l) or above. Accordingly, addition of 165 ppm CaCl<sub>2</sub> to distilled water in the authors' experiments confirmed that the corrosion rate is linear with oxygen concentration (Fig. 3), presumably because chloride ions prevent initiation of passivity within this range of oxygen concentration.

Although CaCl<sub>2</sub> accelerates corrosion of mild steel in distilled water, its presence added arbitrarily in the amount of 60 ppm Ca<sup>++</sup> (165 ppm CaCl<sub>2</sub>), improves inhibition by polyphosphates as Fig. 3 shows, confirming conclusions by Hatch and Rice (3). The corrosion rate in presence of Ca<sup>++</sup> and above 1 ml O<sub>2</sub>/l is on the average only 1/6th that in absence of Ca<sup>++</sup>. However, in complete absence of oxygen, 60 ppm polyphosphate plus 60 ppm Ca<sup>++</sup> is slightly corrosive to mild steel, although the rate of attack is less for the calcium polyphosphate complex than for the corresponding sodium salt. Data are summarized in Table I. Fig. 6 shows that further addition of CaCl<sub>2</sub> reduces the corrosion rate to a value below 0.6 mdd.

#### Effect of NaCl

In view of the fact that chloride ions are present in many natural waters and can break down passivity, the behavior of polyphosphates in presence of NaCl has practical interest. Data are summarized

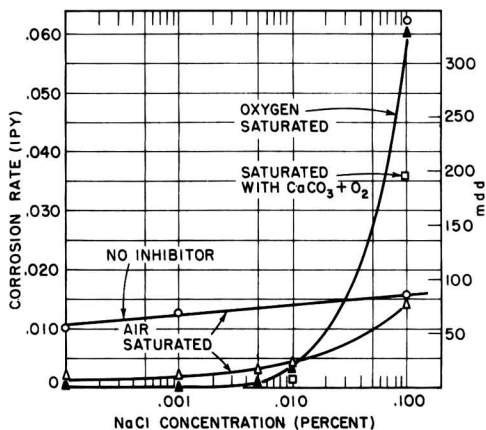


FIG. 7. Effect of sodium chloride concentration on corrosion of mild steel in water and in 60 ppm polyphosphate solutions, 7-day tests, 25°C.

in Fig. 7 for both air- and oxygen-saturated solutions. Polyphosphate present to the extent of 60 ppm is an effective inhibitor up to 0.01% NaCl (100 ppm), and oxygen-saturated solutions corrode mild steel less than do aerated solutions. At higher NaCl concentrations, however, the inhibitor is no longer effective, and high oxygen concentrations corrode steel at a much higher rate than do aerated solutions.

Calcium ion added to sodium polyphosphate appreciably reduces rate of attack, even though the concentration (approximately 3 ppm Ca<sup>++</sup>) corresponds to no more than that resulting from saturation of the solution with CaCO<sub>3</sub>. Additional amount of calcium salt would be expected to reduce attack still further.

Pitting attack was typical of specimens immersed in NaCl solutions, the maximum depth of pits in 0.01% NaCl after 7 days reaching several mils in absence of calcium, and several tenths mil in its presence. Pitting was not observed in chloride-free solutions. Formation of soluble or dispersed complexes of iron polyphosphates as a result of corrosion was evident from the transparent light yellow solutions of corrosion products, whereas in absence of polyphosphates insoluble rust flocs formed instead.

#### Potential and Polarization Measurements

Potentials of mild steel in contact with polyphosphate solutions were carried out to better understand the mechanism of inhibition. Time-potential curves were followed over a period of 48 hr in solutions containing (a) 60 ppm polyphosphate, and (b) the same solution with salts equivalent to 60 ppm Ca<sup>++</sup>, Mg<sup>++</sup>, or Na<sup>+</sup> added as chlorides. Three representative and convenient concentrations of

dissolved oxygen were selected, namely, deaerated, air-saturated, and oxygen-saturated.

The cell for potential determinations, as well as for subsequent polarization measurements, consisted of three compartments separated from each other by two sintered glass diaphragms. Mild steel specimens were placed in the central 1-liter compartment, and two platinum electrodes in the two outer smaller compartments. This arrangement provided for uniform current density of the mild steel electrode, and avoided contamination of anolyte with catholyte. All three compartments were kept saturated with appropriate gas by bubbling it through sealed-in dispersion tubes at the bottom of each compartment. Potentials were measured with respect to Ag-AgCl in 0.1*N* KCl, which made contact through a salt bridge filled with solution of the same composition as that in contact with mild steel. Because of the high resistance of solution and bridge, an electronic galvanometer was necessary for potential measurements used in conjunction with a precision potentiometer.

The steel electrode, measuring approximately 0.8 x 0.8 x 0.13 in. (2 x 2 x .33 cm), was mounted at the end of a glass tube enclosing a connecting wire. A Teflon washer, separating glass and the electrode, prevented solution coming into contact with metal other than the electrode itself. Surface preparation and composition of the electrode were the same as in the weight loss tests.

Fig. 8 shows that steady-state values of potential are achieved after several hours. Since the half-cell potential of 0.1*N* Ag-AgCl is 0.288 v, the potential of mild steel in deaerated sodium polyphosphate solution, neglecting a small liquid junction potential, is  $-0.62$  on the normal hydrogen scale. This can

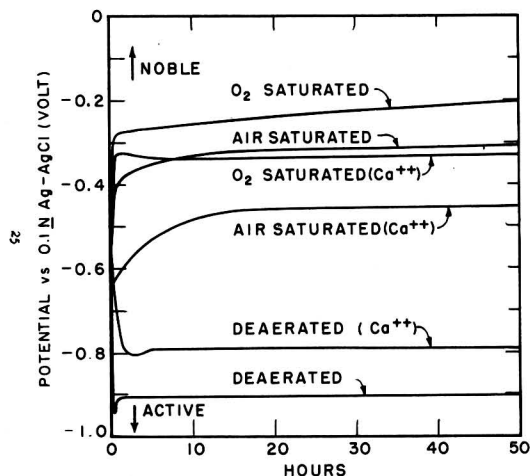


FIG. 8. Potential vs. time for mild steel in 60 ppm polyphosphate solutions in absence and presence of 60 ppm Ca<sup>++</sup>.

be compared with  $-0.54$  v for mild steel in deaerated 4% NaCl (16). The difference is ascribable to the complexing action of polyphosphate with iron salts, thereby reducing Fe<sup>++</sup> activity below the value associated with saturated hydrous ferrous oxide otherwise covering the metal surface. Complexing action shifts the potential in the active direction, in accord with the Nernst equation which expresses the potential of iron as a function of ferrous ion activity. Various soluble complexes of iron with sodium metaphosphate have been described in the literature (17-19).

Addition of calcium salts alters the potential in the noble direction by about 0.1 v, which may be evidence that Fe<sup>++</sup> is not complexed to the same extent by the calcium polyphosphate solution. Since it is always the corrosion potential that is observed and not the equilibrium potential, interpretation of the actual situation is complicated by change in corrosion rate brought about by Ca<sup>++</sup> and corresponding change in the anodic and cathodic polarization of local galvanic couples. Chloride ion associated with CaCl<sub>2</sub> is apparently not responsible for the shift in potential, because Ca(NO<sub>3</sub>)<sub>2</sub> was found to produce the same shift. By the same token, 60 ppm Na<sup>+</sup> as NaCl added to 60 ppm polyphosphate reproduced the potential behavior for deaerated polyphosphate solution in absence of Ca<sup>++</sup>. When, however, 60 ppm Mg<sup>++</sup> was added as chloride, the potential behavior was the same as that produced by Ca<sup>++</sup> addition.

Oxygen and air produce more noble potentials, the maximum change reaching a value as high as 0.7 v. This can be taken as true indication of passivity by Definition 1, according to the "Corrosion Handbook" (20), with oxygen as the passivator. Calcium ion, this time, alters the potential in the active direction, opposite to its effect in deaerated solutions, indicating increased polarization of the local action cathodes on the iron surface.

Polarization data were obtained with mild steel electrodes previously exposed to either aerated or deaerated solutions for 48 hr. Results are presented in Fig. 9 and 10. Data for oxygenated solutions were almost identical to those in aerated solutions and, hence, are not shown. The majority of measurements represent relatively steady-state values after about 3 to 5 min for each point. For anodic polarization in regions where the potential changed markedly, time to achieve steady state required as long as one hour.

In absence of calcium ions, it is obvious that anodic polarization is much more pronounced than is cathodic polarization, and that the situation reverses itself when calcium chloride is added. Furthermore, anodic polarization is much more pro-

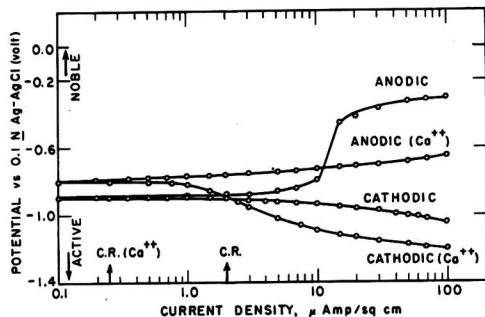


Fig. 9. Polarization curves for mild steel in deaerated 60 ppm polyphosphate solutions in absence and presence of 60 ppm  $\text{Ca}^{++}$ . C.R. = observed corrosion rate.

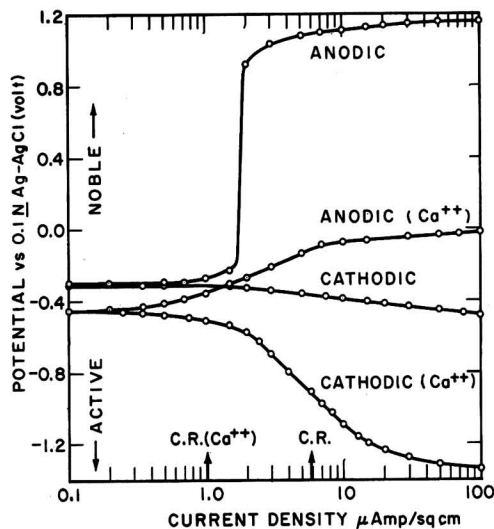


Fig. 10. Polarization curves for mild steel in aerated 60 ppm polyphosphate solutions in absence and presence of 60 ppm  $\text{Ca}^{++}$ . C.R. = observed corrosion rate.

nounced in presence of oxygen. Although pronounced cathodic polarization in presence of calcium chloride is undoubtedly associated with  $\text{Ca}^{++}$ , the parallel reduction of anodic polarization is caused instead by  $\text{Cl}^-$ . This was demonstrated by adding 60 ppm  $\text{Na}^+$  as  $\text{NaCl}$  to 60 ppm sodium polyphosphate and noting a similarly shaped curve. Magnesium chloride additions produced the same polarization curves as calcium chloride additions.

#### DISCUSSION

The data clearly show that sodium polyphosphates are effective corrosion inhibitors, provided the dissolved oxygen concentration is above a critical minimum. The lowest permissible concentration of oxygen is reduced by presence of calcium ions, and

the effect of dissolved oxygen, in general, is not so marked for solutions containing calcium. In solutions below the critical oxygen concentration, or in deaerated solutions, polyphosphates with or without calcium accelerate attack of steel rather than inhibit corrosion. The rate of attack with 60 ppm  $\text{Ca}^{++}$  added to deaerated 60 ppm polyphosphate solution is reduced to about  $\frac{1}{10}$ th the value for the sodium salt alone.

The beneficial effect of oxygen confirms in part the proposal by one of the authors (9) that inhibition by sodium metaphosphate, or better described as polyphosphates, results from passivation by oxygen. As Fig. 2 shows, oxygen in sufficiently high concentrations passivates iron even in absence of polyphosphates; but at lower concentrations (i.e., air saturation), all oxygen reaching the metal surface is reduced at cathodic areas, and oxygen correspondingly acts as a depolarizer. The corrosion rate for this situation is approximately proportional to oxygen concentration, since the amount of oxygen diffusing through the barrier surface film of hydrous  $\text{FeO}$  is also proportional to oxygen concentration. However, at high concentrations, more oxygen reaches the iron surface than can be cathodically reduced, whereupon excess oxygen is available to chemisorb on or passivate the metal, with attendant falling off of the corrosion rate and a change of potential in the noble direction. This mechanism of passivity is similar to that postulated for stainless steels (21). One might also hypothesize formation of an oxide film, but this is difficult to visualize in presence of soluble polyphosphate complexes. In fact, it is probably because the naturally formed barrier oxide film on iron is removed by reaction with polyphosphates to form soluble iron complexes that more oxygen can reach the metal surface for a given oxygen concentration in solution, and hence passivity is established at lower oxygen concentrations. This situation for aerated sodium polyphosphate solutions<sup>3</sup> accounts for reduced corrosion rates in Fig. 2.

But this model also predicts that, if oxygen concentration is sufficiently low, a value is eventually reached for which surface oxygen again acts as a depolarizer, and the corrosion rate should increase. This prediction is confirmed by the authors' data, and explains why sodium polyphosphates in solutions of low oxygen concentration are accelerators rather

<sup>3</sup> Dissolving the film in acid also accomplishes solution of the hydrous  $\text{FeO}$  film, except that in so doing more acid is brought to the surface, and ample adsorbed hydrogen is produced to react with the increased oxygen supply. With this state of affairs, corrosion always increases. At a neutral  $\text{pH}$ , as in the case of polyphosphate solutions, the concentration of hydrogen ions is much less.



than inhibitors of corrosion. In deaerated solutions, passivity by oxygen, of course, no longer applies, and corrosion is attended by evolution of hydrogen, the tendency to corrode (i.e., emf of local action cells) being increased by complexing of ferrous ions.

For oxygen concentrations within the region of marked passivity, presence of chloride ion is apt to cause pitting because of the well-known local breakdown of passivity caused by halogen ions. Pitting of stainless steels occurs for similar reasons (22). Local anodes are formed of restricted area where chloride ions competitively displace adsorbed oxygen, such areas being surrounded by broad areas of cathode (passive metal). The combination forms passive-active cells having high emf. Data of Fig. 8 indicate that potential differences inside (low  $O_2$ ) and outside (high  $O_2$ ) the pits may amount to about 0.6 v. Calcium ion reduces this potential difference, but does not eliminate it; hence, pitting may also be observed when calcium polyphosphates are used as inhibitors in aerated chloride solutions.

The important part played by calcium ions requires explanation over and above that given above for sodium polyphosphates, since both the present data and previously published observations indicate that the mechanism is quite different. Polarization and potential studies (Fig. 8, 9, 10) show that calcium salts increase cathodic polarization, and, hence, shift greater control of the corrosion rate to the cathode reaction. This fact was also pointed out by Hatch (9). Earlier, Mansa and Szybalski (23) reported that commercial polyphosphates increase polarization of cathodic areas. Experiments by Hatch indicated that relatively thick insoluble phosphate films are electrodeposited by the corrosion process on cathodic areas. The films were stated to contain calcium and to form on any conducting cathode, and not on iron alone. Lamb and Eliassen (24) using radioactive tracers, confirmed that phosphates are deposited on the cathode when current flows. Films so deposited are often thick enough to be visible, and presumably act as diffusion barrier layers impeding access of oxygen to the metal surface. In presence of such a protective barrier, dissolved oxygen has less effect on the over-all corrosion rate; however, oxygen concentration cells can still function, even though the potential difference of such cells is less.

Since there is pronounced inhibition in absence of both calcium salts and carbon dioxide, it is obvious that Raistrick's proposal is not tenable, namely that a protective film of calcium carbonate enters the mechanism of inhibition. Polyphosphates, as a matter of fact, would be expected to dissolve such films rather than to favor their formation.

The practical necessity of continuous flow when using polyphosphate-inhibited solutions is explained by the need to form a continuous protective cathode film over all the metal surface which, in turn, depends on a uniform corrosion rate. If corrosion currents are localized, as would be the tendency in stagnant solutions, obviously the cathode film would form in discontinuous patterns, with consequently lower level of protection. The present investigation indicates, in addition, that high surface oxygen concentrations, which motion of the liquid favors, are desirable from the standpoint of maintaining optimum passivity. Continuous agitation of solution is also necessary to avoid initiation of passive-active cells with attendant pitting. In presence of chlorides corresponding to over 0.01% NaCl, it is essential that calcium ions be present simultaneously, since, in this event, only the cathode diffusion barrier film retards corrosion, and passivity by oxygen is either spotty or does not occur at all. Similarly, adsorption and passivity by oxygen are not expected to function at elevated temperatures. It is the cathodic film that apparently accounts for temporary continuing inhibition in flowing systems after polyphosphate treatment is reduced or discontinued.

In deaerated solutions, the corrosion potential on the normal hydrogen scale ( $-0.62$  v) undoubtedly approximates the open circuit (O.C.) anodic potential (since the anode polarizes less than the cathode), and the cathodic O.C. potential equals  $-0.0592$  pH or  $-0.41$  v. With or without  $Ca^{++}$ , therefore, the reaction is cathodically controlled. In aerated solutions, on the other hand, considering the anodic

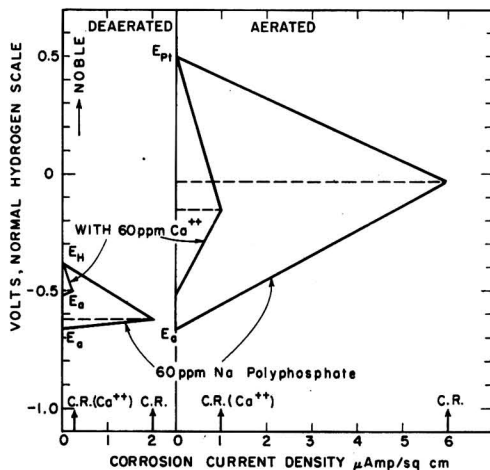


Fig. 11. Schematic polarization curves for equal anodic and cathodic areas on mild steel for deaerated and aerated solutions.

O.C. potential to remain the same, and the cathodic potential, 0.5 v, to be given by the measured potential of a platinum electrode in the same solution (the oxygen reversible potential is 0.81 v), an observed corrosion potential of  $-0.03$  v suggests mixed control (Fig. 11). In presence of calcium, a corrosion potential of  $-0.16$  v shifts control slightly in the anodic direction, but the over-all control is still mixed. Only at such time as the cathodic O.C. potential approaches the hydrogen potential accompanying total loss of passivity through presence of chloride ion or by some other factor, does corrosion control become largely cathodic. Schematic polarization diagrams depicting these relations are given in Fig. 10, with anode and cathode areas assumed equal, for sake of simplicity.

The present investigation, therefore, confirms that the mechanism of inhibition by calcium polyphosphates includes a diffusion barrier film on cathodic areas which increases cathodic polarization. In addition, passivation by dissolved oxygen occurs above a minimum partial pressure of oxygen, with consequent increased polarization of anodic areas. In presence of oxygen, corrosion control is mixed.

#### ACKNOWLEDGMENT

This research was supported by the Shell Companies of the U. S. to whom the authors express their appreciation. R. C. Lutton carried out valuable preliminary experiments.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

#### REFERENCES

1. G. B. HATCH AND O. RICE, *Ind. Eng. Chem.*, **32**, 1572 (1940).
2. *Ibid.*, **37**, 710 (1945).
3. *Ibid.*, **37**, 752 (1945).
4. M. COHEN, *Trans. Electrochem. Soc.*, **89**, 105 (1946).
5. P. PALLO, *J. Am. Water Works Assoc.*, **38**, 499 (1946).
6. O. RICE, *ibid.*, **39**, 552 (1947).
7. "Committee on Water Conditioning Methods to Inhibit Corrosion," *J. Am. Water Works Assoc.*, **34**, 1807 (1942).
8. B. RAISTRICK, *Chemistry & Industry*, **1952**, 408.
9. H. H. UHLIG, *Métaux et corrosion*, **22**, 204 (1947).
10. G. HATCH, *Ind. Eng. Chem.*, **44**, 1774 (1952).
11. R. MORGAN AND R. SWOPE, *ibid.*, **35**, 821 (1943).
12. R. C. LUTTON, M.S. Thesis, Massachusetts Institute of Technology, 1952.
13. M. PRYOR AND M. COHEN, *This Journal*, **100**, 203 (1953).
14. E. GROESBECK AND L. WALDRON, *Proc. Am. Soc. Testing Materials*, Part II, **31**, 279 (1931).
15. G. SCHIKORR, *Z. Elektrochem.*, **39**, 52 (1933).
16. H. H. UHLIG, N. CARR, AND P. SCHNEIDER, *Trans. Electrochem. Soc.*, **79**, 111 (1941).
17. O. SAMULSON, *Svensk. Kem. Tidskr.*, **56**, 277 (1944).
18. D. KANTZER, *Compt. rend.*, **220**, 661 (1945).
19. P. NAVET, *Tech. Eau*, Belgium, June 1947; *C.A.*, **41**, 6003 (1947).
20. H. H. UHLIG (Editor), "Corrosion Handbook," p. 21, John Wiley & Sons, Inc., New York (1948).
21. H. H. UHLIG, *Chem. Eng. News*, **24**, 3154 (1946); *This Journal*, **97**, 215C (1950).
22. H. H. UHLIG (Editor), "Corrosion Handbook," p. 165, John Wiley & Sons, Inc., New York (1948).
23. J. MANSA AND W. SZYBALSKI, *Acta Chem. Scand.*, **4**, 1275 (1950).
24. J. C. LAMB AND R. ELIASSEN, *J. Am. Water Works Assoc.*, **46**, 445 (1954).

# Solid Dielectric Breakdown Techniques<sup>1</sup>

J. J. CHAPMAN, L. J. FRISCO, AND J. S. SMITH

*Dielectrics Laboratory, The Johns Hopkins University, Baltimore, Maryland*

## ABSTRACT

Successful measurement of the breakdown strength of solid insulating materials is greatly dependent on the type of electrodes used. It was found, in studying materials over the frequency range from 60 cps to 100-megacycles/sec, that it was usually necessary to imbed the high voltage electrode.

A method is described that has proved widely applicable and free from compromising effects. Solder may be sprayed from a gun into a properly shaped cavity to form a perfectly imbedded electrode. Specimens that have been conditioned at high humidity may be equipped with such sprayed electrodes within a few minutes after removal from exposure. Tests were made over a temperature range from  $-55^{\circ}\text{C}$  to  $125^{\circ}\text{C}$ . The procedure, with minor variations, has been applied successfully to ceramic, laminated thermosetting, molded thermosetting, and rigid thermoplastic materials.

## INTRODUCTION

The ever increasing interest in the electrical properties of insulating materials has led to investigation of the dielectric strength of solid materials in the frequency range from 60 cycles to 100 megacycles. Results of these studies have shown that, without exception, the dielectric strength of solids decreases very drastically with increasing frequency.

Fig. 1 illustrates the effect of frequency on the dielectric strength of two commonly used materials. Similar data on many other materials raise interesting questions as to the mechanisms which are involved in the breakdown process. To the designer, however, data of this type are of immediate practical importance, even though the phenomena continues to be a matter of conjecture.

Most of the data on electrical properties of insulating materials which is available to the designer pertains to dielectric constant and dissipation factor as functions of frequency, but dielectric strength is usually stated with no reference to frequency or, at most, a note on the particular 60-cycle test which was applied. The 60-cycle values of dielectric strength not only fail to provide data which are applicable at the higher frequencies, but do not contain information which is required to establish an order of preference when comparing several materials.

In order to enhance the usefulness of high-frequency dielectric strength data it is important to discuss the techniques involved in the collection of such data. Since the usual problems associated with dielectric strength measurements become more critical with increasing frequency, the test methods, which can be used successfully at the higher fre-

quencies, afford improvements in conventional low-frequency techniques. Methods described herein have been used successfully at frequencies ranging from 60 cycles to 100 megacycles on a wide variety of solid materials. Apparatus developed for use in these investigations has been described in other publications (1-3).

## REQUIREMENTS OF A DIELECTRIC STRENGTH TEST

The primary requisite of a dielectric strength test is that the destructive effects of the field be limited to a volume within the specimen, bounded on opposite sides by the test electrodes. In other words, when failure occurs, it should not involve the medium in which the sample is immersed, nor should the breakdown path follow the surface of the specimen. This implies that prior to breakdown, as the voltage is being increased, there should be no evidence of incipient glow, or corona, in the immersion medium. Only when these conditions are met does the test indicate the dielectric strength of the specimen material, independent of the properties and the condition of the immersion medium.

In order to study solid breakdown it is necessary to eliminate the compromising effects which are often associated with dielectric strength tests. It is generally known that many spurious effects, such as corona, and accumulation of ionic impurities of the immersion medium in the neighborhood of the high voltage electrode, are time dependent. Therefore, it is always tempting to shorten the duration of a high voltage test and thereby avoid compromising phenomena that are impossible to evaluate.

Impulse studies constitute an important phase of dielectrics research but, in the case of solids, time dependent mechanisms are part of the chemical structure, and proper evaluation by the use of longer

<sup>1</sup> Manuscript received June 28, 1954.

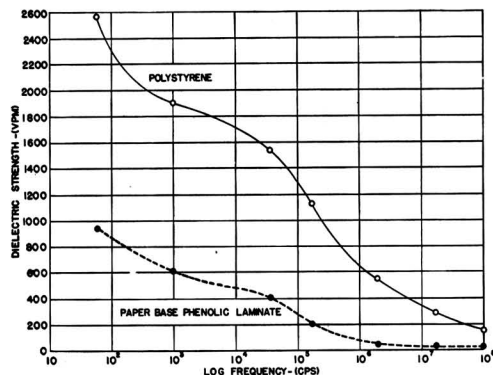


Fig. 1. Variation of dielectric strength with frequency for polystyrene and a paper base phenolic laminate.

time periods is a matter of theoretical and practical interest. To study slow mechanisms means that the specimen-electrode assembly must be electrically stable under longer periods of voltage application so that compromising effects do not enter into the tests. Since there are time-dependent mechanisms involved in the breakdown process, results which are obtained by impulse or pulsing techniques depend on pulse duration. Recourse to these methods has led to higher values of dielectric strength, and consequently has resulted in the use of the term "intrinsic breakdown." Although this may be a useful concept when agreement is reached on its definition and a method for its determination, it should not be implied that a breakdown which is accomplished in a relatively long period of time is not characteristic of the material. A breakdown which is the result of a gradual increase in voltage over a period of 1 min, if properly obtained, is as closely related to the inherent properties of a material, as one obtained with a 0.1  $\mu$ sec pulse. Naturally, the values are quite different since the mechanisms involved must necessarily respond in a different manner. The choice of time period depends on the information which is sought and the time-dependent mechanism to be studied.

The longer time period is more difficult experimentally, but ultimately one becomes interested in all mechanisms, even the very slowest, if they are inherent properties of the materials. It is possible to construct a composite dielectric, in a reproducible fashion, which consists of pure compounds. Such a material would exhibit time-dependent phenomena which arise at the interfaces; these phenomena would be inherent to the structure.

To satisfy current interest in the effects of frequency, temperature, moisture absorption, and irradiation on dielectric strength, it is injudicious to ascribe all anomalous behavior to the effect of "heat"

and thereby overlook important factors which influence the behavior of insulating materials. Although the basic structures of many commercial insulating materials appear to be simple, the distribution in chain length, plasticizer action, curing effects, etc., all lead away from precise description; however, these products are sufficiently uniform to be generally reproducible. Since such products represent the only solution to electrical design problems it is essential to evaluate their properties in such a manner that all of the inherent complexities which affect those properties are permitted to exert their influence. Some of the additives in a commercial material, from an electrical viewpoint, are "impurities." However, through them, desirable mechanical and thermal performance is obtained; thus, even from an electrical viewpoint they must be considered inherent to the composition. Tests described herein involve commercial materials which were tested by applying a voltage which was increased from zero to maximum in a period of approximately 40 sec.

Fig. 2 shows a cross-sectional view of the simplest specimen-electrode system, employing conventional electrodes. This arrangement is satisfactory for the very low strength materials at all frequencies up to 100 megacycles. Specimen and electrodes are immersed in transformer oil in order to increase the voltage level at which corona appears in the region around the high voltage electrode, where the electrode meets the surface of the specimen. At 60 cycles it is possible to use larger electrodes of smooth contour and thereby eliminate the troublesome effects of corona in the case of materials of moderate dielectric strength. However, larger electrodes cannot be used at high frequencies because the resulting specimen capacitance would normally be beyond the limit imposed by the requirements of the resonant test circuits which must be employed (1, 2). Moreover, at 60 cycles, recourse to such electrodes will not solve the corona problem for all materials; the very high dielectric strength plastics require a more perfect arrangement.

The limitation of this simple arrangement arises from the fact that often the liquid immersion medium has a lower dielectric strength and a lower dielectric constant than the material which is being tested.

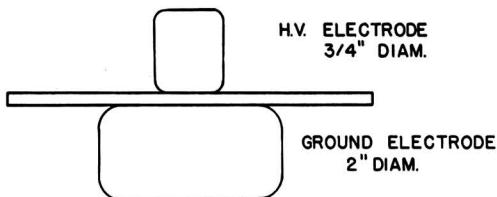


Fig. 2. Conventional electrode arrangement for low-frequency dielectric strength tests.

Two general methods can be used to overcome the difficulty; (a) use a semiconducting surface film in the critical region thus grading the field; and (b) fill the critical region with a material which can withstand the stress to which it will be subjected in the course of the test.

Both methods have been used with considerable success (1), although the former one is restricted to low-frequency investigations. At higher frequencies it proved necessary to use fillets of high dielectric strength material. However, where specimen thickness permitted, the use of recessed cavities to contain the high voltage electrode provided the most homogeneous and certain field configuration. Various types of recessed electrodes have been used by many investigators (1, 2, 4, 5). The fact that the preparation of such cavities for the purpose of careful research is difficult has caused the authors to seek improved techniques that would serve a wide range of practical materials as well as those most promising for theoretical study.

#### FURTHER DEVELOPMENT OF THE RECESSED BREAKDOWN ELECTRODE

Specimens described below were developed to serve a wide area of investigation involving a large variety of materials which were to be tested at several frequencies, after exposure to various conditions of temperature and humidity.

Fig. 3 shows a cross-sectional view of a specimen which can be drilled or molded in such a way that the cavity conforms to the shape of a  $\frac{3}{4}$  in. diameter cylindrical electrode. Intimate contact between the high voltage electrode and the specimen is accomplished by coating the cavity with a metallic film. A 2 in. diameter circular area on the bottom surface of the specimen is also coated to provide intimate contact with the ground electrode.

Commercially available silver paint was tried first (1) and proved satisfactory. However, a recent development is the prime reason for further reporting. It was found possible to apply solder film to the surface of solid insulating bodies in such a manner that the contact is intimate. The solder film has the advantages of no drying period and stability in the presence of solvents.

Various types of metal spray guns are available which can be used with many different metals. Since low melting point metals form excellent electrode surfaces, an inexpensive gun, designed to spray solder, does an excellent job.<sup>2</sup> The only auxiliary equipment required to operate this type of gun is a source of compressed air.

<sup>2</sup> The "Emess Hi-Heat Gun," manufactured by the Emess Tool and Chemical Corporation, has been used for this purpose with complete success.

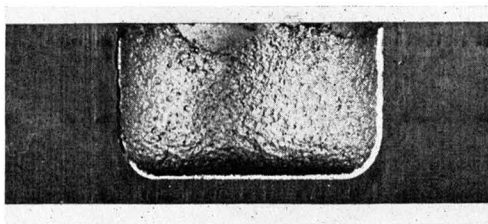


Fig. 3. Cross-sectional view of molded  $\frac{3}{4}$  in. diameter cavity coated with solder spray.

A masked sample can be sprayed quickly with the desired thickness of solder film. The solder solidifies immediately and very little heat is transferred to the specimen. The solder film makes perfect contact with the specimen and provides a surface of very high conductivity which the brass electrodes can engage. Since the cavity is coated with a metallic film it is not necessary for the brass electrode to make a perfect fit, because its only function is to engage the solder film. Any voids between the brass electrode and the solder film are in a field-free space, and consequently will not cause any compromising effects.

In order to prepare the surface to be sprayed it is necessary to remove the glaze usually present on most materials. This is accomplished by lightly sandblasting the area just enough to dull the surface finish. A small sandblasting machine<sup>3</sup> can be readily adapted to give excellent performance.

The sample shown in Fig. 3 is a cellulose-filled melamine molded material. In this case, the  $\frac{3}{4}$  in. diameter cavity was formed by the manufacturer during the molding process. The sample is  $\frac{1}{2}$  in. thick and the thickness of material directly under the cavity is approximately 60 mils. The cavity has been sprayed with 50/50 solder. It can be seen that the solder film forms a very rugged conductive surface, which was only slightly damaged in cutting the sample in half. A cavity of this shape can also be formed in most materials by the use of a special drill. In the case of the very hard materials the drill must have a carbide tip.

With some laminates, the mechanical stresses which attend the use of such a flat drill cause delaminations to occur. In order to overcome this difficulty a more practical tapered cavity was introduced, which has proven to have several advantages over the cylindrical cavity of Fig. 3.

Fig. 4 shows a tapered cavity which was drilled in a  $\frac{1}{2}$  in. thick glass silicone laminate specimens. A standard  $\frac{1}{2}$  in. diameter twist drill is used in this operation. The diameter of the flat section is usually

<sup>3</sup> A-C Spark Plug Cleaner, Model K.

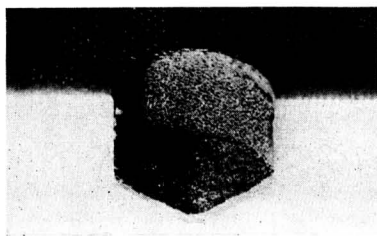


Fig. 4. Cross-sectional view of  $\frac{1}{2}$  in. diameter tapered cavity drilled in glass silicone laminate.

about twice as great as the thickness of the section directly under the center of the cavity. This configuration results in a very favorable field distribution, as evidenced by results which have been obtained with this type of specimen.

This type has proved successful with many types of materials. A commercially available carbide tipped drill is used with the hard materials. Some of the advantages of this type of specimen are:

(A) No special tools are required for its fabrication.

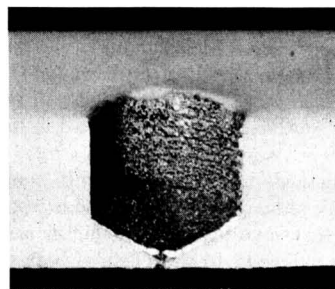
(B) In drilling the tapered cavity the material is not subjected to severe mechanical stresses which cause delaminations.

(C) The remaining section under the cavity is mechanically stronger than the section under a cylindrical cavity. This reduces the tendency for delamination and deformation during conditioning or handling of specimens.

A depth gauge is used to measure the thickness of the section under the cavity prior to testing. After the test has been completed the specimen is cut open and the breakdown distance is measured with a low power microscope. Assuming a uniform field distribution, the breakdown strength is computed by dividing the breakdown voltage by the distance in mils. Results obtained in this manner yield values of dielectric strength which are, in general, higher than those obtained with other methods. Since the tests are also more reproducible, it is felt that mechanical as well as electrical considerations have eliminated compromising effects.

#### PERFORMANCE TESTS

The values of dielectric strength shown in Fig. 1 were obtained with the  $\frac{1}{2}$  in. diameter tapered cavity. Measurements were made on unconditioned samples which were tested at room temperature. In the case of polystyrene the specimens were subjected to voltages as high as 60 kv, with no evidence of corona around the high voltage electrode. The thickness of the polystyrene section was 20 mils in the breakdown region.



A



B

Fig. 5. Cross-sectional view of tapered cavity after 60-cycle breakdown on (A) polytetrafluoroethylene, (B) paper base phenolic laminate.

The solder film performs satisfactorily over the temperature range from  $-55^{\circ}\text{C}$  to  $125^{\circ}\text{C}$  on numerous materials. At  $-55^{\circ}\text{C}$ , Varsol is used as the immersion medium. Although this liquid has the properties of kerosene, which would make its use at room temperature hazardous, it can be used safely at low temperatures.

Polystyrene is a material that exhibits higher dielectric strength than many others over the wide frequency range explored. Therefore, even with rather thin sections it is necessary to operate at a high voltage level in order to obtain puncture. This critical test on a strong material proved the merits of this type of electrode.

The numerical results obtained are of course the main objective of an investigation, but the descriptive phenomena is also important from the standpoint of both theory and practice.

Fig. 5 shows the typical failures that are obtained at 60 cycles with polytetrafluoroethylene and a paper base phenolic laminate. This pinpoint type of puncture is characteristic of most materials at low frequency. As the frequency is increased, however, the character of the failure changes in the case of some materials. The polytetrafluoroethylene fails in the same sharp manner that it did at low frequency.

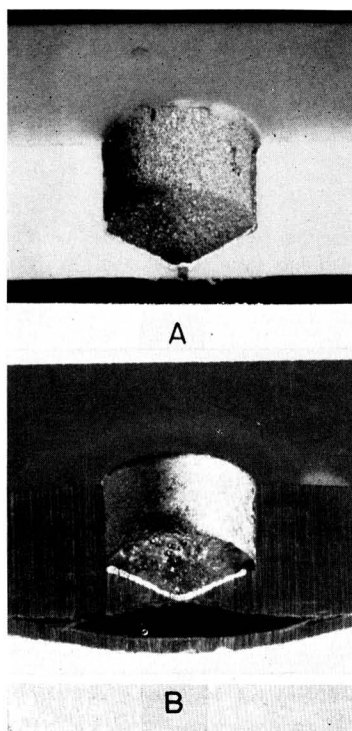


FIG. 6. Cross-sectional view of tapered cavity after 100 megacycle breakdown on (A) polytetrafluoroethylene, (B) paper base phenolic laminate.

The phenolic, however, exhibits a drastic change in behavior.

Polytetrafluoroethylene may be considered as one of the better dielectrics over the frequency range studied. The paper base phenolic laminate drops from a rather high dielectric strength value at low frequency to a quite poor performance at 100 megacycles. At this upper limit, the failure of this material is characterized by the formation of a large internal void, and the entire volume becomes quite hot. It is of further interest that monochlorotrifluoroethylene forms small voids within the failure region at 100 megacycles.

It would be premature to weigh the relative values of quantitative and descriptive observations of breakdown investigations at this time. However it does appear to the authors that, at low frequency, the character of the breakdown is sharp and clear but the numerical results show considerable spread. By contrast the high-frequency upper limit of strength is numerically well defined, but the character of the failure differs widely among materials and, in any particular case, the end point is apt to be decided to an important degree by effects that are not purely electrical.

TABLE I. Comparison tests with three types of electrodes\*

Material	Method	Voltage kv	Thickness mils	VPM	Remarks
Polyethylene	A	50.0	125	400	Value incorrect, edge glow
	B	50.0	38	1315	Definite puncture
	C	50.0	37	1350	Definite puncture
Polytetrafluoroethylene	A	70.8	125	566	Value incorrect, edge glow
	B	70.8	118	600	Definite puncture
	C	70.8	118	600	Definite puncture
Polystyrene	A	59.5	125	475	Value incorrect, edge glow
	B	59.5	31	1920	Definite puncture
	C	59.5	32	1860	Definite puncture
Paper base phenolic laminate	A	61.4	125	491	Value incorrect, edge glow
	B	61.4	68	902	Definite puncture
	C	61.4	69	888	Definite puncture
Glass silicone laminate	A	58.5	125	450	Value incorrect, edge glow
	B	58.5	98	587	Definite puncture
	C	58.5	146	400	Value incorrect, some specimens delaminated

Method A, ASTM electrodes.

Method B,  $\frac{1}{2}$  in. diameter tapered cavity (See Fig. 4).

Method C,  $\frac{3}{4}$  in. diameter cavity (See Fig. 3).

\* Tests conducted at 60 cps, voltage raised gradually over approximately 40 sec.

The importance of properly imbedded electrodes is illustrated by Table I. A comparison is made at 60 cycles among three types of electrodes namely, ASTM,  $\frac{1}{2}$  in. twist drill cavity, and  $\frac{3}{4}$  in. flat bottom cavity. The latter two give nearly identical performance, except that the flat bottom drill causes minute delaminations in materials such as glass silicone laminate. In the case of glass silicone laminate, the resulting low values of breakdown strength from such mechanical imperfections lower the mean value of volts per mil considerably. This mechanical difficulty does not accompany the other four materials listed; however, the flat bottom drill is always slower and less convenient to use than the standard twist drill. Comparison was made at a high level of voltage respective to each material, determined by use of the ASTM electrode and resulting in surface burning and failure. Data from voltage-thickness studies gave comparative points for the other two types of electrodes.

The ASTM tests were performed on  $\frac{1}{8}$  in. thick specimens and the values of breakdown strength obtained were all compromised by edge glow in the oil. In fact, unless the immersion oil is kept in excellent condition, the apparent values of breakdown

strength sometimes appear to be 20% lower. By contrast, the same voltage levels could be reached with thinner sections using the  $\frac{1}{2}$  in. twist drill cavity. In this case the value of volts per mil were valid and of higher magnitude. In spite of considerable edge glow, polytetrafluoroethylene and glass silicone laminate gave fair performance with the ASTM electrode; these materials are able to withstand considerable heating and arcing. At higher frequencies, corona may result in the dissipation of considerable energy and it is advisable to avoid it by use of an imbedded electrode.

#### CONCLUSIONS

1. Solder may be sprayed on plastic surfaces to gain intimate contact. Critical tests have proved that the conducting film thus formed is suitable for making breakdown measurements over a wide range of frequency.

2. The film may be applied to specimens that have been conditioned at high humidity. It also proves useful at low temperatures.

3. Results are reproducible under a variety of conditions of temperature, frequency, and choice of materials and may in time provide the synthetic chemist a new viewpoint in the development of materials. Spread in results has been reduced to that inherent to materials rather than method.

4. The performance of the  $\frac{1}{2}$  in. diameter cavity

formed with a standard drill is of extreme practical benefit.

5. Considerations of cavity shape and conducting film application are most timely in the large scale evaluation activities necessary to keep pace with new materials.

#### ACKNOWLEDGMENTS

The research concerning this method of obtaining breakdown has been of value in two contractual investigations. The authors have enjoyed the support of the Bureau of Ships and that of the Components and Materials Branch, Squier Signal Laboratory, SCEL, and therefore express their gratitude to both.

Further acknowledgment is made to Mr. Wilbur G. Baumann and Mr. Richard D. Picard whose careful specimen preparation and testing were an essential factor in the work

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

#### REFERENCES

1. J. J. CHAPMAN AND L. J. FRISCO, *Elec. Mfg.*, **53**, 136 (1954).
2. J. J. CHAPMAN, J. W. DZIMIANSKI, C. F. MILLER, AND R. K. WITT, *ibid.*, **48**, 107 (1951).
3. L. J. FRISCO AND J. J. CHAPMAN, *Rev. Sci. Instr.*, **25**, 8 (1954).
4. R. BECKER, *Archiv. Electrotech.*, **30**, 411 (1936).
5. A. VON HIPPLE AND R. S. ALGER, *Phys. Rev.*, **76**, 127 (1949).



# Nitrides of Chromium and Chromium-Titanium Alloys

## New Film-Type Resistance Elements<sup>1</sup>

E. R. OLSON, E. H. LAYER, AND A. E. MIDDLETON<sup>2</sup>

*Battelle Memorial Institute, Columbus, Ohio*

### ABSTRACT

Some electrical properties of nitrided Cr and nitrided Cr-Ti films are presented. Films of chromium and chromium-titanium alloys, deposited on ceramic bases by vacuum-evaporation methods, were nitrided to form electrical resistance elements. By varying thickness and nitriding conditions, the electrical properties of the films can be varied. Materials can be prepared with temperature coefficients of resistance less than 0.01%/°C. Resistors with resistances of from several hundred to several million ohms can be made. Resistance to environmental attack and other properties are also described.

### INTRODUCTION

There exists a need for new electrical-resistance materials suitable for high temperature-operating fixed resistors. A research program was undertaken to find and develop materials for such elements. In view of the potentialities of film-type elements, resistance materials in thin film form, which would be tightly adherent to an insulating supporting base, were chosen for study.

Early investigations were conducted by Campbell and coworkers (1) on the vapor-phase deposition of refractory materials. Also, studies of electron conduction in chemical compounds of this nature were made by von Meyer (2) and others (3). These studies prompted evaluation of alloy systems in the classes of materials referred to as nitrides, silicides, and borides.

### EXPERIMENTAL DETAILS

*Preliminary survey.*—A survey program was conducted to screen a large number of materials and to select those showing the most promise. Selection was made on the basis of several requirements which were considered necessary to meet the objectives. These requirements were:

1. Conduction must be electronic rather than ionic.

2. The materials must be of such a nature that they can be applied in thin, adherent, continuous films on a supporting, insulating base.

3. Effects of oxidation and water vapor on the electrical characteristics of the films must be very

<sup>1</sup> Manuscript received April 13, 1953. This paper was prepared for delivery before the New York Meeting, April 12 to 16, 1953.

<sup>2</sup> Present address: P. R. Mallory and Company, Inc., Indianapolis, Indiana.

small. Good chemical stability between 65° and 200°C was sought.

4. The resistivity must be of such a value that the temperature coefficient of resistance is near zero. This generally excludes materials whose resistivities are above 10<sup>-2</sup> ohm-cm.

5. Resistances in the order of 10 ohms per square<sup>3</sup> and 2000-5000 ohms per square should be obtainable with near-zero temperature coefficients of resistance. Specifically, resistances in the range 10 ohms to 10 megohms should be obtainable with temperature coefficients of resistance less than 0.01 %/°C.

6. Also required are: low voltage dependence; ability to undergo temporary electrical overload without permanent charge; ruggedness to sudden temperature change and to vibration.

Films were prepared by two processes. The first of these employed hydrogen reduction of halide vapors at temperatures high enough that the alloying constituents would codeposit on the ceramic base in adherent, continuous, crystalline films. This is the vapor-phase-decomposition method as described by Campbell (1). Borides and silicides were deposited by this process.

The second method involved thermal evaporation of metals in high vacuum, with subsequent conversion to the desired composition in an atmosphere

<sup>3</sup> The normal expression for electrical resistance of a conductor is

$$R = \frac{\rho \times l}{t \times w}$$

where  $R$  is resistance in ohms,  $\rho$  is resistivity in ohm-cm,  $l$ ,  $t$ , and  $w$  are the length, thickness, and width in cm, respectively. The value of the resistance of a film-type conductor of constant thickness, and with length and width equal, is known as the resistance per square. This resistance per square is numerically equal to the resistivity divided by the thickness.

containing the other constituent. This process was used chiefly to produce nitrides, although some silicides and borides were also produced.

From the standpoint of high temperature stability, films exhibiting the best properties were silicides of chromium and molybdenum. Several nitrides had good oxidation properties and could be produced with low temperature coefficients of resistance. In general, borides had poor oxidation resistance. Because film continuity, uniformity, and thickness were difficult to control for silicides and borides it was extremely difficult to obtain reproducible electrical properties in such films. In this respect the nitriding process was much more successful; therefore, most of the effort was concentrated on the systems Cr-N and Cr-Ti-N.

*Preparation of Cr-N and Cr-Ti-N films.*—Chromium and Cr-Ti alloys in solid form were thermally evaporated at a pressure of about  $10^{-4}$  mm Hg, and condensed on rotating ceramic rods. Mixtures of Cr and Ti powders were also used as the evaporation source. Source-to-rod distances were about 7 cm, and

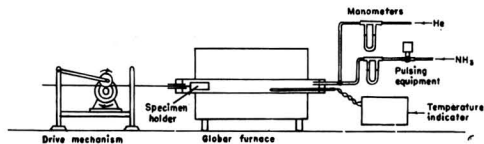


Fig. 1. Schematic diagram of nitriding apparatus

rod-rotation speeds of from 300 to 400 rpm were used. Certain zircons and high-alumina porcelains, detergent washed and rinsed in distilled water, were found to be suitable substrates, the two important properties being smooth, defect-free surfaces, and chemical inertness during the high temperature nitriding process.

The metallic films were nitrided in an ammonia atmosphere for a period of 10 min at various temperatures above  $800^{\circ}\text{C}$ . A schematic diagram of the nitriding apparatus is shown in Fig. 1. Flushing of the nitriding tube prior to introduction of ammonia gas was done with helium, while the metallized ceramic specimens were held in a quartz boat in the cold end of the tube. Either manual feed or mechanical feed was used to introduce the specimens to the hot zone of the nitriding furnace. After nitriding, resistors were cooled in helium at the position shown in the figure, and then removed from the furnace for further processing. Three to five minutes in the cooling zone was adequate.

The  $\frac{1}{4}$ -in. cylindrical coated rods were cut to 1-in. lengths and baked silver contact bands applied in  $\frac{1}{4}$ -in. widths circumferentially around the ends of the films. To complete the resistor assembly, silver-

plated end caps with tinned copper leads were pressure fitted over the ends of these contact bands.

## RESULTS AND DISCUSSION

### *Electrical and Structural Characteristics of Films in the Cr-N System*

Nitriding of chromium can occur at temperatures below  $800^{\circ}\text{C}$ , but Cr-N films with the most suitable electrical properties were formed at temperatures ranging from  $950^{\circ}$  to  $1250^{\circ}\text{C}$ . Results indicated that film resistivity at room temperature decreased with increasing nitriding temperature over this temperature range. X-ray and chemical analyses were made on powdered chromium samples nitrided at these temperatures. From these studies and published literature (4-6), information was obtained about the formation of the nitrides of chromium. Two known compounds, CrN and  $\text{Cr}_2\text{N}$ , are formed, the CrN having a cubic structure of the NaCl type, and the  $\text{Cr}_2\text{N}$  having the metal atoms arranged in a close-packed hexagonal structure. At the lower temperatures of nitriding  $950^{\circ}$  to  $1000^{\circ}\text{C}$ , the CrN predominates. At the higher temperatures of nitriding, more of the  $\text{Cr}_2\text{N}$  compound is formed. Decreasing resistivity over this temperature range suggests that  $\text{Cr}_2\text{N}$  has a lower resistivity than CrN.

If the thickness of the Cr films is varied to cover an extended range, the resulting Cr-N films, nitrided at any one temperature, will also exhibit a wide range of resistance per square, resistance decreasing with increasing thickness. The temperature coefficient of resistance of such films varies as a function of resistance per square such that, with increasing resistance (decreasing thickness), the temperature coefficient changes from positive to negative. This change in temperature coefficient from positive to negative occurs at different values of resistance per

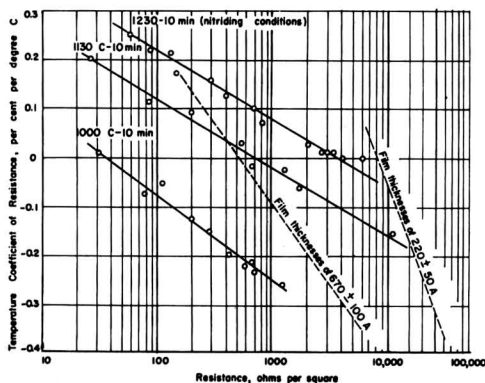


Fig. 2. Relationship between temperature coefficient of resistance and resistance for various values of nitriding and thickness parameters.

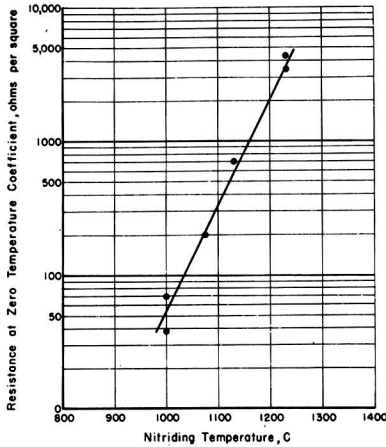


FIG. 3. Relationship between resistance at zero temperature coefficient and nitriding temperature for Cr-N films.

square, the particular value depending on the film thickness and the temperature at which the film is nitrided.

The effect of thickness and nitriding temperature on Cr-N films is shown in Fig. 2. These data were taken on chromium films ranging in thickness from 200 Å to 1500 Å, which were nitrided at temperatures of 1000°, 1130°, and 1230°C. Zircon ceramic was the base used for these films. The temperature coefficient of resistance at room temperature is plotted against resistance per square, the top curve representing results obtained for films nitrided at 1230°C and the lower curve representing the trend for films nitrided at 1000°C. The dotted lines represent approximately constant film thickness for the values indicated.

Resistances at which the temperature coefficients cross through zero are correlated with nitriding temperature in Fig. 3. It can be seen that the resistance at zero temperature coefficient increases with nitriding temperature and extends from about

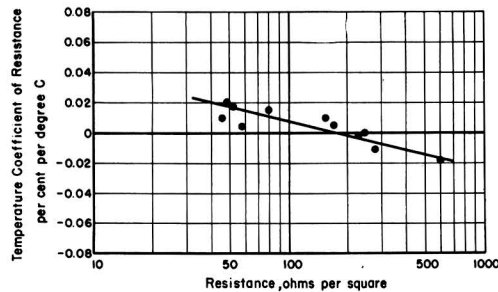


FIG. 4. Relationship between temperature coefficient of resistance and resistance for Cr-Ti-N films produced at 1230°C.

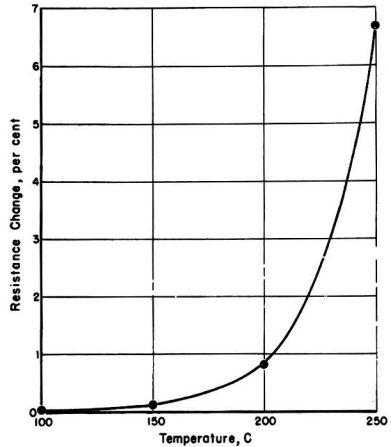


FIG. 5. Average change in resistance with temperature for Cr-Ti-N films heated in air for 200 hr.

50 ohms per square to 4000 ohms per square. This relationship is significant because it indicates essentially that a continuous series of fixed resistances can be produced over a wide resistance range with near-zero temperature coefficients. By altering the geometry of this low temperature coefficient conducting path, an even wider resistance range can be covered. For example, cylindrical resistors ¼ in. in diameter and 1 in. long have been produced over the range from 10 ohms to 10 megohms by employing the common practice of spiralling for extending the length of the conducting path.

Voltage coefficients of resistance of less than 0.02%/v were measured for the Cr-N films.

*Electrical Characteristics of Films in the Cr-Ti-N System*

Cr-Ti films nitrided in the temperature range 950–1250°C resulted in Cr-Ti-N films which have electrical properties differing somewhat from those of the Cr-N films.

First, the maximum resistance per square at low temperature coefficient was about 300 ohms per square as compared to 4000 ohms for the Cr-N films. Second, the nitriding temperature did not have

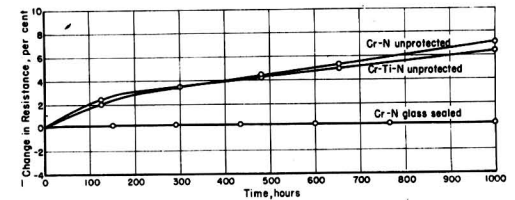


FIG. 6. Change in resistance with time for Cr-N and Cr-Ti-N resistors operating under 1-watt loads at 200°C ambient in air.

nearly so large an effect on the resistivity and temperature coefficient of the Cr-Ti-N films as in the case of the Cr-N films. As a result, small variations or fluctuations in nitriding temperature could be tolerated in the production of low temperature-coefficient Cr-Ti-N films. The third difference was that the temperature coefficient of resistance varied less as a function of resistance per square than in the case of the Cr-N system. This difference gives the Cr-Ti-N films an advantage over the Cr-N films. Fig. 4 shows the temperature coefficient and resistance per square relationship for Cr-Ti-N films produced at 1230°C. The range of resistances for temperature coefficients of less than 0.01 %/°C extended from 80 to 400 ohms per square for the Cr-Ti-N films as compared to the range of 3000 ohms to 5000 ohms per square for films of the Cr-N system nitrided at 1230°C. This meant that in laboratory production much better reproducibility of low temperature-coefficient films could be obtained with the Cr-Ti-N system than with the Cr-N system.

Voltage coefficients of resistance of Cr-Ti-N films were measured to be less than 0.02 %/v.

#### *Stability of Cr-N and Cr-Ti-N Resistors Subjected to Various Environmental Conditions*

Like chromium itself, nitrided chromium and nitrided Cr-Ti films exhibited fairly good resistance to oxidation. Fig. 5 shows the average change in resistance of groups of Cr-Ti-N films heated in air at temperatures ranging from 100° to 250°C under no-load conditions. Changes of 0.01 % at 100°C, 0.12 % at 150°C, 0.8 % at 200°C, and 6.7 % at 250°C were noted for 200 hr of test after an initial 150-hr pretreatment at 200°C. These films were exposed directly to the air while under test.

Typical load-life characteristics of Cr-N and Cr-Ti-N resistors are shown in Fig. 6. These resistors were operated for 1000 hr at 200°C ambient, with 1-watt leads. About 6.5 % increase was noted for the

Cr-N and the Cr-Ti-N resistors without protective coverings, as compared to 0.2 % for a glass-sealed Cr-N resistor.

Moisture resistance tests on both types of films, without protective coverings, have generally shown less than 3 % change in 500 hr. These tests were conducted at 95 % relative humidity, 75°C, and with ¼-watt d-c loads cycled 1½ hr on and ½ hr off.

Problems of reproducibility, particularly for the Cr-N resistors, are inherent because of the narrow usable resistance range for near-zero temperature coefficients for any given set of conditions. The necessity of careful control of evaporation conditions is imperative. Also, because of the thinness of the films, the slightest defect in the base can result in faulty performance of the resistor. Good contact termination is also necessary. These problems are still under investigation.

#### ACKNOWLEDGMENTS

This work was performed under Contract AF 33 (038)-8744 for the Wright Air Development Center. The authors express their appreciation to R. E. Miller of Battelle Memorial Institute for his technical assistance in the determination of the electrical properties of the resistive materials.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

#### REFERENCES

1. I. E. CAMPBELL, C. F. POWELL, D. H. NOWICKI, AND B. W. GONSER, *J. (and Trans.) Electrochem. Soc.*, **96**, 318 (1949).
2. W. VON MEYER, *Z. Elektrochem.*, **50**, 274 (1944).
3. C. AGTE AND K. MOERS, *Z. anorg. u. allgem. Chem.*, **198**, 233 (1931).
4. G. HÄGG, *Z. physik. Chem.*, **B12**, 33 (1931); *ibid.*, **B11**, 433 (1930).
5. R. BLIX, *Z. physik. Chem.*, **3**, 229 (1929).
6. K. SANO, *J. Chem. Soc. Japan*, **58**, 981 (1937).

# Electrolytic Preparation of Molybdenum from Fused Salts

## IV. Preparation of Reduced Molybdenum Chlorides from Molybdenite Concentrate<sup>1</sup>

SEYMOUR SENDEROFF AND ROGER J. LABRIE

National Bureau of Standards, Washington, D. C.

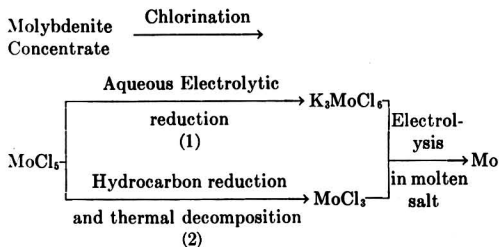
### ABSTRACT

Commercial molybdenite concentrates are chlorinated to produce molybdenum pentachloride and sulfur chlorides. Sulfur chlorides are removed and molybdenum pentachloride is reduced either electrolytically in aqueous solution or by reaction with a hydrocarbon in a nonaqueous system. The aqueous reduction product is recovered as potassium hexachloromolybdate (III),  $K_2MoCl_6$ , and the hydrocarbon reduction product is recovered, after heating, as molybdenum trichloride. Either of these salts may be dissolved in alkali halides and electrolyzed to deposit molybdenum metal at the cathode.

### INTRODUCTION

In earlier papers of this series, a process was described by which pure molybdenum may be obtained by the electrolytic reduction of a complex trivalent molybdenum halide dissolved in molten alkali halides (1). It was also shown that the presence of oxygen, moisture, and oxygen-containing compounds was harmful to the process (2). The potassium hexachloromolybdate (III),  $K_2MoCl_6$ , used for electrolysis, when prepared by electrolytic reduction of an aqueous molybdate solution (3), was rather difficult to free from the last traces of moisture and oxycompounds.

The present paper describes the preparation of a salt suitable for use in the electrolytic bath by starting from a concentrate of molybdenite, the most commonly occurring ore of molybdenum, and treating it by water-free and "oxygen-free" methods only, in order to obtain the desired reduced molybdenum halide. The process which was developed may be summarized as follows:



Steps 1 and 2 are alternative methods of reduction of the molybdenum pentachloride, but step 2 is

<sup>1</sup> Manuscript received June 11, 1954. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954.

preferred since it does not require an aqueous system.

The molybdenite concentrate<sup>2</sup> contained about 80% molybdenum disulfide and about 5% each of water and mineral oil as residues from the flotation operation, with the balance mainly silica. Significant metallic impurities are aluminum, magnesium, calcium, copper, and iron (see Table I).

Molybdenum disulfide is exceedingly inert toward most chemical reagents except strong oxidizing agents and, even with these, elevated temperatures are usually required for reaction to occur at a satisfactory rate. A preliminary study of the common reactions of molybdenum disulfide indicated that the most promising reaction for the authors' purpose might be chlorination.

### PREPARATION OF MOLYBDENUM PENTACHLORIDE

It was necessary first to dry the molybdenite concentrate by heating at 300°C in an inert atmosphere for several hours in a large round-bottom flask, the neck of which was tilted downward to drain off oil and water which distilled out. The dried molybdenum disulfide remained as a very fine, free-flowing, dark gray powder similar in appearance and texture to graphite.

The dried molybdenite concentrate was charged into the Pyrex reaction tower shown in Fig. 1. In order to remove air from the tower and thus prevent formation of oxychlorides during chlorination, helium was passed into the system from the bottom of the reaction tube, and heating was begun. When the charge reached a temperature of 550°C, chlorine was passed through the system at a rate of about 0.5 l/min. Chlorine was mixed with about 15% of

<sup>2</sup> Supplied by Climax Molybdenum Company.

TABLE I. Spectrochemical analysis of molybdenum compounds

Element	Molybdenite concentrate	MoCl <sub>5</sub>	Mo powder from MoCl <sub>5</sub>	K <sub>2</sub> MoCl <sub>6</sub>	Unreacted residue from chlorination
Ag	VW	—	—	FT	W
Al	M	W	M	VW	S
Ba	T	—	—	—	VW
Bi	W	—	—	—	—
Ca	M	FT	—	VW	M
Cu	W	VW	T	T	M
Fe	W	VW	W	T	W
K	—	—	—	VS	—
Mg	M	VW	T	W	S
Mn	VW	T	—	FT	W
Mo	VS	VS	VS	VS	S
Ni	—	—	VW	—	T
Pb	VW	T	VW	FT	W
Si	S	W	W	W	VS
Sr	T	—	—	—	VW

VS = greater than 10%.      VW = 0.001–0.01%.  
 S = 1–10%.                      T = 0.0001–0.001%.  
 M = 0.1–1.0%.                  FT = less than 0.0001%.  
 W = 0.01–0.1%.

helium to maintain a sufficient flow of gas through the system so that air would not enter. In order to prevent blocking of the apparatus by the molybdenum pentachloride and sulfur chlorides which were collected in the receiver, the connecting tube between the receiver and reaction tower was wrapped with heating tape and kept at 350°C. When about half of the charge had reacted, the plug at the top of the reaction tube was removed, molybdenite concentrate added, and the plug quickly replaced before an appreciable amount of air could enter.

When the receiver containing the molybdenum pentachloride and the sulfur chlorides was full it was taken off and stoppered quickly. The products were transferred to a distilling flask in an inert atmosphere, and the sulfur chlorides were removed by distillation. Most of the SCl<sub>2</sub> was removed at room temperature by vacuum distillation. The remainder, together with the S<sub>2</sub>Cl<sub>2</sub>, was then removed by warming the flask under reduced pressure. The mixed sulfur chlorides consisted of about 80% SCl<sub>2</sub> and 20% S<sub>2</sub>Cl<sub>2</sub>. Molybdenum pentachloride remained as a black powder in the flask.

The process would be more economical with respect to chlorine consumption if more S<sub>2</sub>Cl<sub>2</sub> and less SCl<sub>2</sub> were produced. Since SCl<sub>2</sub> is known to dissociate (4), it is possible that other conditions of temperature, flow, etc., and apparatus design may be found which would favor formation of S<sub>2</sub>Cl<sub>2</sub>.

Seven hundred grams of molybdenum pentachloride was produced during a 20-hr run in which 450 g of dried molybdenite concentrate was added to the reaction tower. Molybdenum pentachloride

produced in this manner is essentially free of the original contaminants of the ore. Most of the silica remained in the reaction tower in the unreacted residue which comprised about 7% of the total charge. Metallic impurities, such as aluminum, magnesium, copper, and iron, also were concentrated in the unreacted residue. In Table I are shown the spectrochemical analyses of the molybdenite concentrate (column 2), the molybdenum pentachloride (column 3), and the unreacted residue (column 6). Comparison of concentrations of impurities in these three materials clearly shows the degree of purification achieved as a result of the chlorination of the ore concentrate. Chemical tests showed, however, that the molybdenum pentachloride contained a trace of sulfur.

Reaction rates at various temperatures were determined by placing porcelain boats containing molybdenum disulfide in a horizontal Vycor tube and heating them for 2 hr under chlorine flowing at 50 ml/min. The weight loss at the end of the run was taken as an indication of the amount of reaction. Approximate relative rates at various temperatures are shown in Table II.

At 1050°C the reaction was nearly quantitative, based on the amount of chlorine passed through. The temperature of 550°C used in the preparation de-

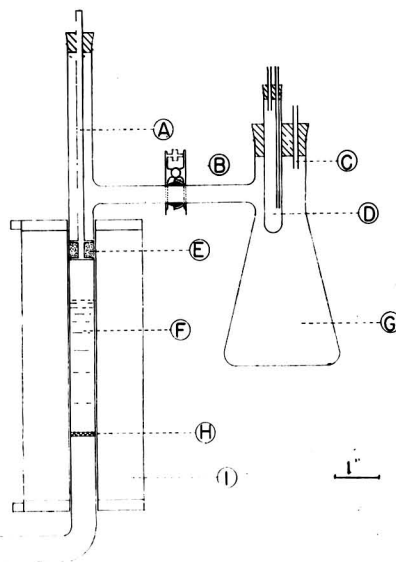


FIG. 1. Apparatus for chlorination of molybdenite concentrate. (A) Glass rod with flanges; (B) 35/20 ball joint with spring clamp; (C) gas outlet tube; (D) water-cooled cold-finger; (E) glass wool plug wound between flanges; (F) molybdenite charge in reaction tower; (G) receiving flask; (H) coarse fritted Pyrex disk sealed in reaction tower; (I) hinged tube furnace.

scribed above was close to the upper limit permissible for the Pyrex equipment that was used. A higher temperature would clearly be desirable when a higher reaction rate is required, and it might also favor the production of  $S_2Cl_2$  rather than  $SCl_2$ . Purification, however, might be less at higher temperatures since it was found that the unreacted residue remaining after exhaustive chlorination at  $900^\circ C$  was 5.3% of the total charge, and at  $550^\circ C$  it was 6.7% of the total charge.

TABLE II. Rate of chlorination of molybdenum disulfide at various temperatures

Temp, °C	Relative rate
800	1
550	0.3
300	0

#### PREPARATION OF MOLYBDENUM TRICHLORIDE

In an attempt to find a suitable solvent for the reduction of molybdenum pentachloride it was observed that this compound reacts with cetane and higher paraffin hydrocarbons. Hydrogen chloride is liberated during the reaction, and the reduced molybdenum halide precipitates. Organic products, which might include chloro-alkanes, polymers, or unsaturated products, have not been studied. Because molybdenum compounds are sensitive to moisture, all operations must be performed in an inert atmosphere and all reagents and solvents thoroughly dried. The reaction has been run with cetane and with molten paraffin wax.

About 300 g of paraffin wax (M. P. =  $56^\circ-58^\circ$ ) is heated to  $145^\circ C$ . About 150 g of molybdenum pentachloride (ground to about No. 80 mesh) is added rapidly and with stirring. Stirring and heating is continued (for about 20 min) until the reddish color disappears and the rate of gas evolution decreases. At this point the level of the liquid drops somewhat and the mixture takes on a green-black color instead of the previous red-brown. The hot mixture is poured onto a coarse fritted glass Buchner funnel and filtered. The solid product is washed further with paraffin wax at about  $145^\circ C$ . It is then washed with dry benzene and finally with dry petroleum ether, and dried. If cetane is used in place of paraffin wax, this reaction is best carried out at a somewhat higher temperature, about  $160^\circ C$ .

A representative batch contained 4.1% water-insoluble material, the composition of which was not determined. The Cl:Mo<sup>w</sup> ratio in the water-soluble remainder was 1.55 compared to the calculated value of 1.48 for  $MoCl_4$ . Unfortunately, this product could not be purified by recrystallization because no suitable solvent could be found.

$$\frac{142}{95.95} = 1.48$$

Preliminary experiments have shown that tungsten hexachloride undergoes a similar reaction at a slightly higher temperature to form, mostly, tungsten pentachloride.

The product of the reaction with the paraffin, the analysis of which corresponds closely to  $MoCl_4$ , is a very fine black powder that reacts with moist air and must be handled in an inert atmosphere. When heated at  $300^\circ C$  in a stream of helium, it disproportionates slowly to form molybdenum trichloride and molybdenum pentachloride; the latter can be recycled in the process. The Cl:Mo<sup>w</sup> ratio in the  $MoCl_4$  so produced was 1.11, which agrees, within the limits of accuracy of the analysis, to the calculated value for this compound. The material contained a small amount of carbonaceous residue from the original reaction.

#### PREPARATION OF POTASSIUM HEXACHLOROMOLYBDATE (III)

Since  $K_3MoCl_6$  has proved useful as an electrolyte for producing molybdenum, its preparation from molybdenum pentachloride obtained by chlorination of the molybdenite concentrate was investigated. The method described previously (3) used the

TABLE III. Reduction of molybdenum pentachloride

Reducing agent	Conditions	Remarks
Na	In bomb above $400^\circ C$	Explosive reaction to produce mixture of reduced halide and fine molybdenum powder.
High surface sodium* (Na dispersed on NaCl)	$180^\circ C$	Smooth reaction to form reduced halides which are difficult to separate from carrier on which Na was dispersed.
$H_2$	1 atm $350^\circ-850^\circ C$	Mixtures of halides and Mo metal.
Al powder	(a) $MoCl_5$ and Al powder heated in a sealed tube (b) $MoCl_5$ vapors passed over Al powder at $350^\circ C$	Either incomplete reaction or explosive reaction.
Electrolysis	Sealed cell, $300^\circ C$ , with a trace of KF or LiCl.	No reaction observed at cathode.
Thermal decomposition	$MoCl_5$ + helium, $1200^\circ C$ , 1 atm.	No visible reaction.

\* Described in bulletin entitled "High Surface Sodium," issued in 1953 by U. S. Industrial Chemicals Company, 120 Broadway, New York 5, N. Y.

hexavalent potassium molybdate as a starting material. Electrolytic reduction of the pentachloride, containing pentavalent instead of hexavalent molybdenum, to the trivalent compound would result in a saving of about  $\frac{1}{3}$  of the electricity required, and it may have other advantages in cost and solubility.

One hundred and forty g of potassium carbonate and 275 g of molybdenum pentachloride were dissolved in a solution containing 500 ml of concentrated hydrochloric acid and 600 ml of water. A higher acid concentration gave a precipitate of potassium chloride. This solution was electrolyzed as described previously (3), saturated with hydrogen chloride, and the precipitated  $K_2MoCl_6$  was washed and filtered. About 200 g of  $K_2MoCl_6$  was obtained, which represents a yield of 70% based on the  $MoCl_5$  used. The spectrochemical analysis of this product is shown in column 5 of Table I, from which it is clear that further removal of impurities from the  $MoCl_5$  was accomplished by electrolytic reduction.

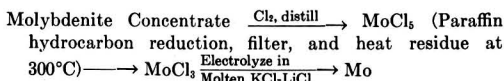
It is interesting to note that molybdenum trichloride prepared by hydrocarbon reduction forms the same trivalent hexachloromolybdate anion when it is added to the eutectic mixture of potassium chloride and lithium chloride and the mixture melted in an inert atmosphere. A 4 mole% solution of molybdenum trichloride in the alkali chlorides was prepared in this manner by heating to 600°C. On cooling, a homogeneous pink melt, having the characteristic appearance of a fused mixture of  $K_2MoCl_6$  and alkali chlorides, was obtained. The molten mixture,  $MoCl_3 - KCl - LiCl$ , was electrolyzed in a divided cell with a graphite anode and molybdenum deposited at the cathode. The analysis of the molybdenum powder thus produced is shown in column 4 of Table I.

#### MISCELLANEOUS REDUCTIONS OF MOLYBDENUM PENTACHLORIDE

Other methods of obtaining reduced molybdenum compounds were tried, but were not found to be suitable for the authors' purpose. Results of attempted reductions of  $MoCl_5$  are shown in Table III.

#### SUMMARY

The following procedure for reduction of molybdenite concentrate to molybdenum metal has been shown to be feasible:



Raw materials are molybdenite ore, chlorine, and paraffin hydrocarbon; by-products are sulfur chlorides and anhydrous hydrogen chloride.

Work is now in progress on the electrolysis of the  $MoCl_3$  thus produced.

#### ACKNOWLEDGMENT

The authors express their appreciation to A. Brenner, National Bureau of Standards, for his guidance and suggestions throughout the course of the investigation, and to the Bureau of Ordnance, Department of the Navy, for financial support.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

#### REFERENCES

1. S. SENDEROFF AND A. BRENNER, *This Journal*, **101**, 16 (1954).
2. S. SENDEROFF AND A. BRENNER, *ibid.*, **101**, 31 (1954).
3. S. SENDEROFF AND A. BRENNER, *ibid.*, **101**, 28 (1954).
4. J. W. MELLOR, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 10, p. 645, Longmans, Green, London (1930).



# Deposition of Titanium Coatings from Pyrosols<sup>1</sup>

A. W. SCHLECHTEN, M. E. STRAUMANIS, AND C. B. GILL

*Department of Metallurgical Engineering, University of Missouri, School of Mines and Metallurgy, Rolla, Missouri*

## ABSTRACT

It has been found that titanium dispersed in fused salts can be deposited on other metals, especially on copper and iron. For example, if a piece of copper sheet is placed in close proximity to a titanium sheet (but not in actual contact) and then the whole is immersed into a fused salt, preferably NaCl or KCl, titanium will transfer to the copper sheet. The thickness of the titanium layer on the copper increases with temperature and time, approaching a maximum thickness of 0.001–0.007 in. (0.025–0.178 mm). Titanium forms a coherent layer on the metals mentioned and protects them from corrosion. The substrate can be dissolved from the reverse side (Fe in FeCl<sub>3</sub>, Cu in HNO<sub>3</sub>); the titanium coating remains.

The mechanism of titanium transfer is thought to consist of, first, a titanium pyrosol formation, and then the deposition of these titanium particles upon the other metals forming a titanium rich alloy. Similar behavior has been observed for other metals.

## INTRODUCTION

The excellent resistance of titanium to corrosion, particularly against nitric acid, has given great incentive to the search for a method of coating cheaper metals with titanium. As far as is known by the authors, no successful method exists for electroplating titanium from aqueous or organic solutions. Titanium can be electrodeposited from fused salt baths (1) chiefly in the form of powder and flakes; sometimes a thin diffusion coating of titanium is obtained on the cathode. Fused salt electrolysis requires materials of high purity and a protective atmosphere of helium or argon.

Attempts to obtain titanium coatings by cementation or treatment in TiCl<sub>4</sub> have been summarized by Chapin and Hayward (2); none of these yielded corrosion resistant coatings. Alexander (3) has patented a process which consists of heating titanium hydride on a copper surface; an alloy of eutectic composition is formed which flows and coats the surface. This type of coating is of limited application for corrosion resistance.

The process described in this paper was the outgrowth of previous experiments on corrosion (4) which showed that titanium is severely attacked when immersed in molten chlorides or fluorides exposed to air. The corrosion products, particularly in chloride baths, are to a great extent finely divided titanium and resemble the "metal fogs" or "pyrosols" described by Lorenz and Eitel (5). It was observed

that the walls of the porcelain crucibles used for corrosion tests were covered below the salt level with a layer which was largely titanium. A series of tests were made to determine if such coatings could be obtained on other surfaces.

As a result of these experiments, it was discovered that objects of copper, iron, or other metals, immersed in the salt bath where there was a high concentration of the titanium pyrosol, were covered with a coating of high titanium content.

In order to achieve the necessary high pyrosol concentration, the object to be plated is placed in close proximity to the titanium source which is corroding, but preferably not in contact with it. Thus, flat surfaces may be plated by placing them parallel to sheets of titanium, and irregular objects can be imbedded in titanium powder or cuttings.

The resulting coatings form a coherent layer that protects the underlying metal from corrosion. For example, copper and iron objects coated by this process can be immersed in nitric acid solutions with no evidence of attack.

Experiments are described which demonstrate the variation of the coating process with time and temperature of treatment, composition of bath, and other factors.

## EXPERIMENTAL PROCEDURE

Small disks of copper or iron about 2 cm in diameter and 1 mm thick were fastened parallel to pieces of titanium sheet which were slightly larger in diameter; pieces of 0.5 mm wire were used as spacers between the two metals. The assemblage was placed in a small porcelain crucible, covered with salt, and heated in a resistance muffle furnace for several hours at a temperature above the melting point of the salt.

<sup>1</sup> Manuscript received May 4, 1954. This paper was prepared for delivery before the Chicago Meeting, May 2 to 6, 1954, and is based on a portion of the work carried out at the Missouri School of Mines and Metallurgy for the Wright Air Development Center under Contract No. AF 33(616)-75.

After heating, the crucible was removed from the furnace, allowed to cool, and placed in a beaker of water heated to digest the salt. In some experiments, the salt was melted before the object to be plated and the titanium source were placed in the crucible. In other experiments, the assemblage was removed from the molten salt as soon as the crucible was taken from the furnace; there was enough salt adhering to the plated object to prevent any appreciable oxidation of the titanium coating. These variations in procedure had no detectable influence on the results.

After the salt had been dissolved, it was necessary to rub or brush away the dark corrosion residue to expose the metallic titanium coating on the disk.

The weight of the coating was calculated from the increase of weight of the plated disk, or better yet, by dissolving the iron or copper away from the coating, which could then be weighed. The average thickness of the coating was calculated from the weight and density of titanium, and was checked by measuring a cross section under the microscope.

Irregular objects were plated by imbedding them in titanium powder or cuttings on the bottom of the crucible, filling up the crucible with salt, and proceeding as before. Titanium hydride powder was also successfully used in the same way as a source of the titanium pyrosol. Powdered ferrotitanium was tried, but did not give a coating.

A variety of salts were tried for the fused bath; a number of addition agents to regular NaCl or KCl baths were tested. The effect of time and temperature was investigated, as well as the influence of stirring the bath, or applying an external emf.

## RESULTS

*Metals that can be coated.*—Copper, iron, and low carbon steel objects were plated in most of the experiments, but it was found that nickel, cobalt, and nickel-copper alloys were also readily coated with a titanium layer. Medium and high carbon steels, as well as cast iron, were coated only with difficulty, and a relatively thin and patchy titanium layer was observed. Aluminum could not be coated because it was badly corroded in the molten chloride bath.

*Arrangement of titanium source and object to be plated.*—Flat surfaces to be plated were placed as close as possible to the titanium sheet serving as a source without actually having them touch; usually a 0.5–1 mm diameter wire of chrome-nickel, titanium, or copper was used as a spacer. It is not desirable to have the object and the titanium touch because at the points of contact actual cementation occurs, and when the metals are separated the desired coating may be broken at these points.

If titanium powder is packed around the object to be plated, some small particles of titanium will be cemented to the coating, which will then be rougher than the coating obtained wholly from the pyrosol. Coarse cuttings of titanium, such as come from a hacksaw, give better coatings than powder, because the cuttings do not stick to the plated surface as readily, and seem to allow freer circulation of the pyrosol-bearing molten electrolyte.

Titanium hydride powder, as well as metal powder, served as a source of titanium pyrosol; no particular advantage or disadvantage could be claimed for it.

Tests with a low carbon and a high carbon titanium ferrochrome, containing 24% and 34% titanium, respectively, as a source material, were entirely unsuccessful.

On the theory that plating from the pyrosol is the most desirable method, a piece of titanium metal was heated in a mixture of NaCl and KCl at 850°C for 4 hr. The severely corroded metal was then removed leaving the corrosion products, much of which was the black pyrosol, in the salt in the crucible. Next, a piece of copper was placed in the mixture in the crucible and heated. A very thin and patchy coating was obtained on the copper, indicating that the effectiveness of the pyrosol degenerates rapidly.

In an attempt to plate irregular objects, several experiments were made in which, first, a piece of titanium acting as a source was revolved in the bath with the object to be coated held stationary; next, the object was revolved with the titanium stationary; finally, they were both revolved. Only fragmentary coatings were obtained. This seemed to show that dispersal of the pyrosol by stirring was undesirable.

As mentioned before, coatings obtained from titanium powder are rough, so it was thought that stirring or agitation would be beneficial. However, as the titanium powder partially sinters and agglomerates in the salt bath, all attempts at stirring, agitation, or tumbling of a closed container failed. The powder and the object all moved together as one piece.

*Composition of bath.*—NaCl, KCl, LiCl, and mixtures of all proportions appeared to be equally effective. Eutectic mixtures of NaCl and KCl had the advantage of a lower melting point. The still lower melting mixtures (around 400°C) using LiCl were not warranted because no coating could be obtained at such low temperature.

Thin unsatisfactory coatings were obtained in  $K_2TiF_6$ , NaOH, and KOH. No coatings were obtained in NaCN, KCN, or a variety of sulfates.

A number of experiments were made in which NaI, KI, NaBr, KBr,  $K_2TiF_6$ , or NaF, were added in amounts varying from 1 to 15% to NaCl or KCl baths. It was thought that these additions would

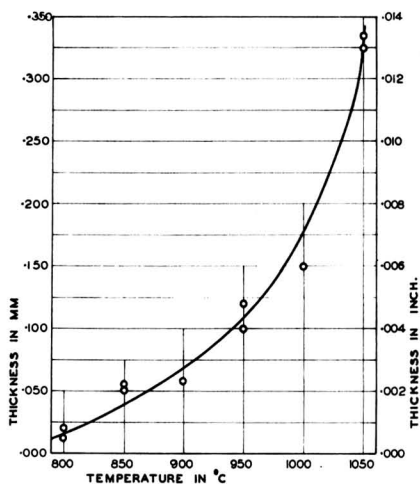


FIG. 1. Thickness of titanium coatings on iron; 7-hr deposition time in a KCl-NaCl bath.

hasten corrosion of the titanium source and, hence, increase the rate of plating. None of the additions was beneficial; the plating obtained with these additions was less than that with baths of only NaCl, KCl, or a mixture of the two. It is evident that for plating purposes it is not only the amount but the nature of titanium corrosion products that must be considered.

*Effect of temperature.*—Disks of low carbon steel were plated on one side from titanium sheet using a bath of 50-50 mole % of NaCl and KCl, and 7 hr plating time. Iron was then dissolved by heating the sample at 60°-80°C in a saturated solution of ferric chloride. Final traces of iron on the titanium were removed with 1-4 nitric acid. The deposit was washed, dried, weighed, and analyzed for iron and titanium.

Fig. 1 shows how the thickness of the titanium coating increases with the increased temperature of the bath. The thickness was calculated from the weight.

The temperature range for coating copper is more

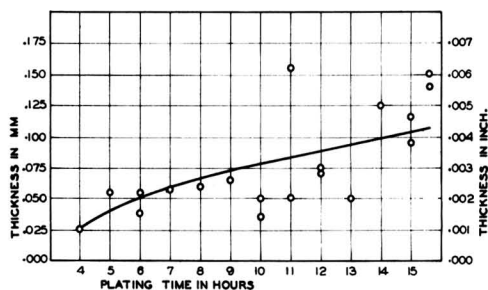


FIG. 2. Thickness of titanium coatings on iron; KCl-NaCl bath at 900°C.

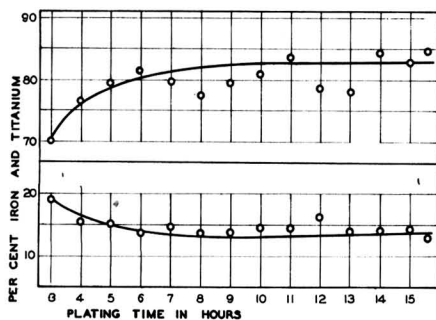


FIG. 3. Titanium and iron contents of titanium coatings vs. coating time; KCl-NaCl bath at 900°C.

limited. Below 800°C very little coating is obtained, and the upper limit is set by the copper-titanium eutectic temperature of about 878°C. If this temperature is exceeded, the sample and the titanium source form a molten alloy. Several tests were made to plate titanium on copper in KCl-LiCl baths at temperatures lower than those reported above. No coating was visible after 4 hr at 450°C and less than 0.0001 in. was obtained at 600°C and 4 hr plating time.

*Effect of time.*—Using a procedure similar to that described in the previous section, iron samples were coated at 900°C for times varying from 1 to 16 hr. Very little titanium was deposited until after 3 hr plating time. Fig. 2 shows the results of this series of tests.

It can be seen that the thickness of the coating increases with time, but that there is much variation. This lack of reproducibility, especially when longer times are used, is related to the deterioration of the plating power of the bath. Undoubtedly, the pyrosol becomes oxidized in the open crucibles and loses its ability to form a coating, and the rate of oxidation is not the same in successive experiments.

*Composition of titanium coatings.*—Titanium coatings

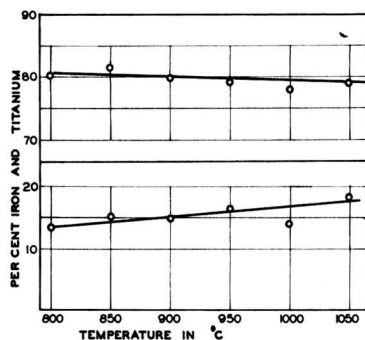


FIG. 4. Titanium and iron contents of titanium coatings vs. temperature; KCl-NaCl bath for 7 hr.

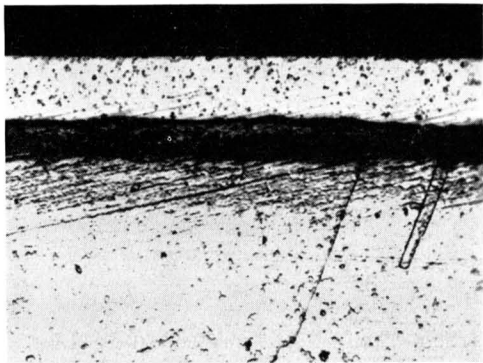


FIG. 5. Titanium coating on copper showing two layers; deposited in KCl at 850°C for 8½ hr; etched in 50% NH<sub>4</sub>OH + 50% H<sub>2</sub>O + few drops H<sub>2</sub>O<sub>2</sub>. 500X.

from experiments reported in the previous two sections were analyzed for titanium and iron by colorimetric methods. The determination of titanium was made using hydrogen peroxide as a reagent (Weller's method); iron was determined by the method of Moss and Mellon (6). Results are shown in Fig. 3 and 4.

It can be seen that there is no great variation of composition with time of coating, and only a slight trend toward higher iron content with higher temperatures of treatment. The sum of iron plus titanium is in the neighborhood of 95% for all samples; the remaining 5% is probably oxygen, although this has not been proved by analysis.

Photomicrographs, such as the one shown in Fig. 5, reveal that the coating on copper consists of an outer layer and an intermediate layer of approximately the same thickness which has a dark appearance in the photograph. This same phenomenon has been reported by Steinberg, Sibert, and Wainer (7) for zirconium electrodeposits on copper. Titanium coatings on iron also show two layers, but the intermediate layer, presumably higher in iron, is not more than one tenth the thickness of the outside layer (see Fig. 6).

*Application of outside emf.*—An experiment was made in which direct current was passed through the salt bath, with a piece of titanium as the anode and a piece of copper as the cathode; no plating was obtained on the cathode. Titanium and copper were in close proximity so that, in the absence of current, a coating would have been obtained on the copper; thus, the current was detrimental in this arrangement. Examination of the bath showed that titanium had gone into the bath as ions of lower valence, giving the salt a purple color. Without the current, the bath would have been gray-black from the finely divided pyrosol.

Several tests were made in which 60-cycle current

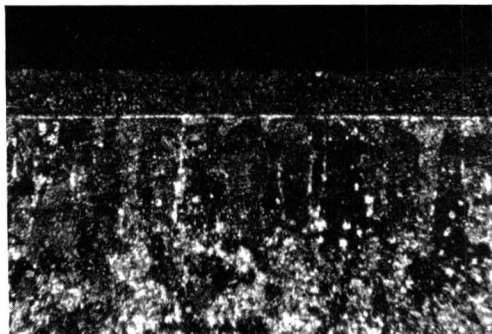


FIG. 6. Titanium coating on iron showing two layers; deposited in NaCl at 950°C for 6 hr. 100X under polarized light.

was passed into the bath through two titanium electrodes. It was hoped that this would hasten the formation of titanium pyrosol, but no advantage could be observed.

#### DISCUSSION AND CONCLUSIONS

Some aspects of the procedures described in this paper are similar to the process patented by Lauenstein and Ulmer (8) wherein iron castings are packed in powdered ferrochrome or ferromanganese and common salt in a crucible and heated for approximately 3 hr at 1600°–2000°F (871°–1093°C). This procedure results in alloying and coating of the iron surface with chromium or manganese; the inventors claim that the salt is decomposed to yield sodium which acts as a reducing agent for the manganese or chromium chloride formed from the ferroalloy.

The authors' experiments with titanium show that its chief corrosion product in chloride salt baths is in the form of finely divided particles which are not ions (4), and that this material can be used in a practical way to coat iron, copper, and other metal surfaces with a high titanium alloy. Whether this pyrosol acts directly to form a diffusion coating on the base metal, or whether there is an intermediate reaction to form a lower chloride of titanium which

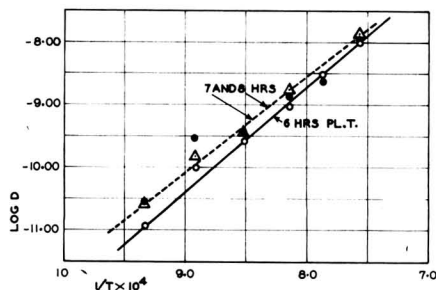


FIG. 7. Log diffusion constant,  $D$ , for titanium on iron vs. reciprocal of absolute temperature.

in turn is decomposed to produce the coating is not clear from the present experiments. Analogy with chromizing is not helpful because chromium coatings on iron can be obtained either by packing the iron in metallic chromium powder or by submerging it in salt baths containing chromous chloride.

Using the equation,  $x^2/4Dt = K$ , where  $x$  is the thickness of the coating,  $t$  is the time, and  $K$  is assumed to be one, values were calculated for  $D$ , the diffusion constant, using the data of thickness vs. time and temperature reported in a previous section. The results in Fig. 7 show the expected relationship between  $D$  and temperature for a diffusion process.

From a practical standpoint the process will produce a coherent substantial coating high in titanium and suffers only from those drawbacks common to chromizing, siliconizing, and other comparable processes. In a similar fashion coatings have been made of zirconium, hafnium, uranium, and manganese on iron and copper.

#### ACKNOWLEDGMENTS

The authors are grateful to the Wright Air Development Center for support of this work and permission to publish the results obtained. Valuable

contributions to this investigation have been made by Dr. T. M. Morris, Dr. W. H. Webb, and Professor A. Legsdin.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

#### REFERENCES

1. G. D. P. CORDNER AND H. W. WORNER, *Australian J. Appl. Sci.*, **2**, 358 (1951).
2. E. J. CHAPIN AND C. R. HAYWARD, *Trans. Am. Soc. Metals*, **38**, 909 (1947).
3. P. P. ALEXANDER, U. S. Pat. 2,351,798, June 20, 1944; U. S. Pat. 2,512,455, June 20, 1950.
4. C. B. GILL, M. E. STRAUMANIS, AND A. W. SCHLECHTEN, *This Journal*, **102**, 42 (1955).
5. R. LORENZ AND W. EITEL, "Pyrosol," Akad. Verlagsges, Leipzig, (1926); R. LORENZ in J. ALEXANDER'S "Colloid Chemistry," Vol. I, pp. 681-706, Reinhold Publishing Co., New York (1926).
6. M. L. MOSS AND M. G. MELLON, *Ind. Eng. Chem., Anal. Ed.*, **14**, 862 (1942).
7. M. A. STEINBERG, M. E. SIBERT, AND E. WAINER, "Zirconium and Zirconium Alloys," p. 37, American Society for Metals, Cleveland, Ohio (1953). See also, *This Journal*, **101**, 63 (1954).
8. C. F. LAUENSTEIN AND P. F. ULMER, U. S. Pat. 2,046,638, July 7, 1936; U. S. Pat. 2,102,539, Dec. 14, 1937.

# The Crystallographic Dependence of the Oxidation Potential of Solid Copper<sup>1</sup>

W. E. TRAGERT AND W. D. ROBERTSON

*Yale University, New Haven, Connecticut*

## ABSTRACT

Oxidation potentials of solid copper crystals have been evaluated for the isolated crystallographic planes (111), (110), (100), (210). It has been demonstrated that the only stable surface configuration of atoms is that of the close-packed octahedral plane and, accordingly, only this plane on the electrode surface produces a reversible cell. The significance of potentials obtained with other forms of electrodes has been interpreted on the basis of the observed crystallographic requirement for equilibrium.

## INTRODUCTION

The electrochemical anisotropy of crystalline solids has been qualitatively established by several investigators. Following early work on rates of solution of ionic crystals (1-3), studies were made of solution rates and chemical reactivity of metallic single crystals as a function of lattice orientation. Glauner and Glocker (4), working with electrolytic copper crystals, surveyed the basic stereographic triangle with respect to rate of solution in 20 different organic and inorganic solutions. The results they obtained in acetic acid, for example, showed relative solution rates parallel to (111), (100), (110), and (210) directions to be 1.2:1:0.56:0.31, with seven selected orientations completely describing all maxima and minima. Aminoff (5) and Straumanis (6) both observed the stability of the basal plane in zinc relative to the pyramidal and prism planes as indicated by oxidation, vaporization, and solution rates. The latter authors suggested that the stability of a crystal plane could be directly associated with the atomic configuration in that plane, with higher atomic density corresponding to greater stability. More recently, Leidheiser and Gwathmey (7) studied the variation in electrochemical properties of the surface of a copper single crystal as a function of orientation. Their experiments included a measurement of the potential difference between the cube and octahedral planes in an acid  $\text{CuSO}_4$  electrolyte; it was determined that the magnitude of the potential difference was dependent on the presence or absence of air in the electrolyte and that the sign of the potential could be reversed by a hydrogen atmosphere anneal of the specimens.

Experimental results cited above indicate that the crystallographic dependence of electrochemical phenomena is real and that specific observations were at least qualitatively reproducible within the rather arbitrary limits of individual experiments. The fact that apparently complementary measurements yielded contradictory results can be directly attributed to the dynamic nature of the experiments. Nonequilibrium conditions, unknown or unrecognized side reactions, chemical impurity and inhomogeneity of the metal crystals, and inadequate control of physical parameters appear to preclude quantitative interpretation of these investigations.

With respect to thermodynamic treatment, the history of the determination of the standard potential of copper may be described in terms of attempts to define a standard form of electrode. Lewis and Lacey (8) attributed the scatter in values obtained from a number of coherently electroplated copper electrodes to surface strains; to eliminate strain they used a copper sponge electrode which they found to be constant and reproducible to 0.0001 v. Neilsen and Brown (9), however, found that values obtained with a copper sponge varied and that reproducibility could only be achieved with a 2-phase copper amalgam electrode. Subsequently, the amalgam electrode was utilized by several other investigators (10-13), all of whom corroborated the experience of Neilsen and Brown. Getman (13) also investigated the potential of an unamalgamated single crystal of copper which he considered to be incapable of supporting significant stress and thus less liable to exhibit the erratic behavior of the massive polycrystalline copper electrodes previously employed. The copper single crystal, in the form of a cylindrical rod of undetermined crystallographic orientation, gave results which were 0.0035 v higher than those obtained with the amalgam but which, in contrast to unamalgamated electrodes previously employed, were re-

<sup>1</sup> Manuscript received July 12, 1954. This paper is taken from a thesis submitted by W. E. Tragert to the Faculty of the School of Engineering, Yale University, in partial fulfillment of the requirements for the degree of Doctor of Engineering.

producible and constant to 0.0001 v. Recently, Wetmore and Gordon (14) obtained results with amalgam electrodes that agree substantially with those obtained by Nielsen and Brown and with the amalgamated polycrystalline electrodes used by Getman.

It is evident from both equilibrium and non-equilibrium experiments that electrochemical potential measurements involving reactions at a metal surface depend on crystallography. In this connection, two significant and related problems require quantitative evaluation: (a) the magnitude of this crystallographic dependence and its relation to the principal crystallographic directions; and (b) the significance of crystallography with respect to the standard oxidation potential of a metal.

The experiments described below consist of a number of measurements designed to determine the magnitude and significance of potential differences between four low index crystal planes of copper as a function of electrolyte concentration and temperature. The cell chosen for the purpose was Cu; CuSO<sub>4</sub>; Hg<sub>2</sub>SO<sub>4</sub>; Hg. The crystal planes were (111), (110), (100), and (210).

#### EXPERIMENTAL PROCEDURE

All experiments were conducted in a water thermostat completely covered by a black felt hood. Temperature was controlled to  $\pm 0.005^\circ\text{C}$  by high sensitivity mercury switches controlling a small fraction of the required heat input. Temperature was measured with a Beckman thermometer calibrated against a standard platinum resistance thermometer before the series of measurements were made. Potentials were measured with a precision potentiometer in conjunction with a galvanometer of 0.0006  $\mu$  amp/mm sensitivity.

All cells were operated under water-pumped nitrogen, deoxidized by passage through a tower containing copper powder at  $400^\circ\text{C}$ ; the finely divided powder copper was previously deposited on glass wool by hydrogen reduction of cuprous oxide.

The electrolyte was prepared by dilution of approximately 1.0M stock solution of doubly recrystallized reagent grade copper sulfate. Prior to each run, solutions were deaerated by vigorous boiling and cooling under pure nitrogen; they were then equilibrated with copper chips and reagent grade mercurous sulfate at the temperature of the run for 12 hr. Quantitative determination of concentration was made by standard electrodeposition analysis subsequent to each experiment.

The crystals from which electrodes were cut were grown by the standard Bridgman method in high purity graphite molds from polycrystalline copper rod. Preliminary measurements were made using

crystals of 99.95% Cu (0.04P) and 99.97% Cu (0.02Zn) and final determinations were made with 99.999% copper electrodes. The latter measured 0.30 in. in diameter by 3 in. long; the others were  $\frac{1}{2}$  in. by 5 in. The orientation of each crystal was determined by the Laue back reflection technique at two points  $90^\circ$  apart on the circumference and  $\frac{1}{2}$  in. from opposite ends. The crystal was then mounted in a goniometer vise with the clamped portion wrapped in a  $\frac{1}{16}$  in. thickness of stiff paper to avoid deformation; successive cuts were made with a jeweler's saw running in a steel miter parallel to each of the planes mentioned above. The crystal specimens, each approximately  $\frac{3}{4}$  in. long, were etched in 50% HNO<sub>3</sub> until etch pits developed on the cut surfaces. The crystal orientation normal to the end surface, which was to serve as the electrode area on each piece, was then obtained by a back reflection photogram, from which the accuracy of the cut was determined. From the small degree of austeration of the spots on the film the etching operation was judged to be effective in removing the heavily deformed material adjacent to the cut. The surfaces were mechanically abraded on 1/0 emery paper to correct errors in the initial cutting and to bring the desired crystal plane to within  $2^\circ$  of coincidence with the surface. Usually 3 or 4 successive cycles of polishing, etching, and orientation determination were required to produce the desired surface orientation. X-ray photograms of the final test surfaces indicated a lineage of less than  $\frac{1}{2}^\circ$ .

Final specimen preparation consisted of abrasion on 3/0 and 4/0 emery paper followed by electropolishing for approximately 70 min in a 40% orthophosphoric acid electrolyte at the optimum point on the current-voltage curve as described by Jacquet (15). In order to facilitate handling during the electropolishing operation and subsequently in the cells, a 6-in. length of 18-gauge copper wire was soldered to each specimen at the end opposite the experimental surface. Solder connections and supporting wires were coated with a mixture of 70% beeswax: 30% paraffin after mechanical abrasion had been completed, and the cylindrical surfaces were masked out after 1 hr of electropolishing. Final test surfaces were specular and free from pits. Specimens were electropolished successively and, as each electrode was removed from the polishing cell, it was rinsed thoroughly with deaerated distilled water and allowed to dry in a stream of dry, purified nitrogen. At the same time, a warm copper wire was run along the edge of the masking wax around the test surface to permit the wax to flow over the area which had been undercut in the final 30 min of electropolishing. The specimen was then placed in a nitrogen filled storage flask; the supporting wire was sealed with

wax into a hole previously cut in a large rubber stopper which served to hold the specimens and to seal the flask.

The procedure finally adopted, after the preliminary experiments described below, was the following. When all of the electrodes were in the storage flask, a 50%  $\text{HgNO}_3$  solution was introduced under nitrogen pressure to produce simultaneous amalgamation. The order in which electrodes were prepared proved to have no measurable effect on subsequently measured potentials and it was concluded that this technique produced electrodes essentially free from surface films. The assembly of amalgamated specimens in the rubber stopper was removed from the mercurous nitrate solution, rinsed in distilled water and two portions of  $\text{CuSO}_4$  solution identical with that in the cell, and then transferred to the cell. Potentiometer leads were immediately soldered to the ends of the electrode support wires. The total time that the wet electrodes were exposed to air during the transfer operation did not exceed 3 or 4 sec and it was estimated that this interval was too short for appreciable oxygen absorption to occur.

Two types of cells were utilized: an H-cell with a fritted glass disk in the connecting arm, and a straight tube cell. Both were equipped with a platinum-in-glass contact for the mercurous half-cell and were sealed with a large, wax coated rubber stopper. Preparation consisted, first, of adding redistilled mercury sufficient to cover the platinum contact and, then, mercurous sulfate which had been thoroughly washed with copper sulfate solution of the same concentration as would subsequently be used in the particular run. Cells were placed in the thermostat, evacuated, flushed with nitrogen, and held under a slow stream of nitrogen for 12 hr prior to introduction of electrodes and the electrolyte. In the case of the H-cell, electrolyte portions for each of the half-cells were separately equilibrated with respect to cupric and mercurous ion, care being taken to maintain a solution head in the copper half-cell during the filling operation to insure exclusion of mercurous ion. Filling was accomplished by transferring the solutions under nitrogen pressure from reservoirs in the water bath. With the straight tube cell this procedure was altered, the electrolyte being siphoned from the equilibration flask. In either case, upon introducing the electrodes the cell was evacuated to boiling of the electrolyte and flushed with nitrogen in order to remove any air carried in with the electrode assembly.

Since the same set of electrodes was used repeatedly during any particular phase of the experiment, it appeared desirable to devise some simple method for removing liquid mercury and the solid phase copper-mercury alloy from test surfaces prior

to reparation of the electrodes between runs. This was accomplished by mounting the electrodes individually in a polishing cell, with a copper wire counter-electrode. Each electrode was first connected as the cathode and a loose copper deposit was formed at low current density on the mercury coated surface. The specimen was removed from the cell and the surface rubbed with tissue paper, causing the deposited copper to amalgamate and thus remove the liquid mercury as the amalgamated sludge was washed away with distilled water. It was usually necessary to repeat this process several times to produce the desired result. The specimen was then connected as the anode and polished for about 1 min at a current density sufficiently high to cause strong anodic gas evolution. This operation served to remove the last traces of amalgam from the surface and left the specimens ready for final preparation in the manner described above.

#### PRELIMINARY INVESTIGATION

Preliminary measurements were made using an H-cell, unamalgamated crystal electrodes, and an electrolyte concentration of approximately 0.5M. Under these conditions two runs were made, each involving a set of electrodes prepared from one of the two lower purity crystals. In each case, readings were taken over an 8-day period at a temperature of 24.48°C. This arrangement yielded values which fluctuated during a 6-hr interval, then decreased slowly in absolute potential for the remainder of the run. At the beginning of the period of fluctuation, the electrodes maintained relative potential differences of the order of 4.5 mv between the (111) (most noble) and the (110) (least noble) with the (100) value intermediate but closer to (110). The differences decreased proportionately and within minutes settled at about 2 mv maximum after which they diminished very slowly to 1.5 mv at the end of the run. The (210) was not included in these runs. After the first day, the specimens exhibited a photosensitivity which increased with time in an apparently exponential fashion. Upon removal from the cell, specimens were found to be covered with a reddish crystalline deposit, previously discussed by Newbery (16), which was heaviest on the (100) and (110) surfaces. Growth spirals were observed on some of the superficial crystals and a microscopic study of the crystal forms indicated that they were of cubic symmetry. Simple mineralogical tests (fracture, streak, solubility) lead to the tentative identification of the crystalline deposit as cuprite,  $\text{Cu}_2\text{O}$ . On the basis of this assumption, more rigorous precautions were taken to remove and exclude air from the system.

The effectiveness of the exclusion of mercury from



the electrode surface was checked by immersing a polycrystalline copper rod in the cell for one week under operating conditions. Upon removal, approximately 0.005 in. was machined off the surface. The chips were spectrographically analyzed for mercury; none was detected. However, since the electropolished copper surface might be expected to be extremely sensitive to minute quantities of adsorbed substances, it was decided to amalgamate the test surfaces. This arrangement also served to eliminate practical difficulties involved in keeping copper electrodes free of mercury. The amalgamation procedure which was adopted is that described in the previous section.

The amalgamated electrodes, (111), (110), and (100), were mounted in the H-cell and potentials were measured over a period of 20 days. Following an initial interval of transient values, the potentials appeared to stabilize and, in the case of the (110) and (100) planes, remained constant for approximately 9 hr and then tended to approach the (111) value which remained constant to  $\pm 0.00006$  v during the period of the run. Upon removal from the cell, the (100) and (110) electrode surfaces were found to be covered in patches with a crystalline deposit having the color of mercury and the physical properties of an intermetallic compound. The (111) surface was free of any film deposit. The electrodes were thoroughly washed and held in a flask open to atmosphere for two weeks. Most of the liquid mercury evaporated and it was then possible to examine the surface and solid residue. The surfaces of the active electrodes, (110) and (100), had been eroded by the development of fine convolutions, and a profusion of superficial crystallites was in evidence. The (111) electrode was relatively unaltered and only one or two microscopic crystallites were present on the surface. In every instance, there was no observable variation in behavior between the two sets of lower purity crystals.

Reference to the copper-mercury phase diagram (17) shows that, at the temperatures here employed, the solubility of copper in liquid mercury is approximately 0.003%, the almost vertical liquidus line giving a very small solubility temperature coefficient. At temperatures below 96°C the liquid solution is in equilibrium with the intermetallic compound CuHg at 50 atom % mercury. On this basis, the crystallites described above were presumed to be CuHg.

Since the necessity for maintaining the surrounding electrolyte free of mercurous ion was eliminated by prior amalgamation of the electrodes, the final preliminary run was conducted with a straight tube cell and electrodes prepared from 99.999% copper. This run was characterized by an

initial period of fluctuation of only 45 min, followed by stable values for a period of 6 hr. At this point, the temperature of the water bath was lowered to 17.2°C and again raised to the reference temperature, 24.48°C. The potentials then measured agreed with those of the stable period to within 0.02 mv. A similar cycle through 34.4°C was performed and identical results were obtained, substantiating the reversible character of the cell.

As a check on the reproducibility of the mercurous sulfate electrodes, a cell was made up of two such electrodes in opposition, and over a period of 3 days the variation from zero potential did not exceed 0.03 mv.

#### EXPERIMENTAL RESULTS

The final potential values which were obtained are recorded in Table I as a function of crystal surface orientation, electrolyte concentration, and temperature (columns 1-4). Measurements at 25.0°C were corrected from 24.48°C by interpolation based on the observed temperature coefficients for individual concentrations. Each value represents the mean of at least 12 readings taken, in general, at 15-min intervals with an average deviation of 0.04 mv as can be seen in Table II which records a typical run. At the lowest concentration the error in the

TABLE I

M	Temp. °C	Crystal plane	E, v	-log $\gamma$	E $_{cell}^{\circ}$ v	$\frac{\Delta E}{v \times 10^{-3}}$	$\frac{dE_{cell}^{\circ}}{dT} \times 10^{-4}$
0.01447	17.2	111	0.41113	0.445	0.2797	—	8.1
		110	0.41495	—	—	3.8	
		100	0.41483	—	—	3.7	
		210	0.41497	—	—	3.8	
	25.0	111	0.40890	0.455	0.2733	—	
		110	0.41273	—	—	3.8	
		100	0.41262	—	—	3.7	
		210	0.41236	—	—	3.5	
	34.7	111	0.40645	0.467	0.2656	—	
		110	0.41012	—	—	3.7	
		100	0.41002	—	—	3.6	
		210	0.40978	—	—	3.3	
0.05395	25.0	111	0.38835	0.677	0.2733	—	
		110	0.39294	—	—	4.6	
		100	0.39293	—	—	4.6	
		210	0.39287	—	—	4.5	
0.4829	17.2	111	0.36418	1.152	0.2796	—	8.1
		110	0.36847	—	—	4.3	
		100	0.36837	—	—	4.2	
		210	0.36848	—	—	4.3	
	25.0	111	0.36094	1.165	0.2733	—	
		110	0.36491	—	—	4.0	
		100	0.36491	—	—	4.0	
		210	0.36501	—	—	4.1	
	34.7	111	0.35697	1.181	0.2655	—	
		110	0.36056	—	—	3.6	
		100	0.36092	—	—	4.0	
		210	0.36106	—	—	4.1	

TABLE II.  $T = 24.48^\circ\text{C}$ ;  $M = 0.4771$ 

Time $\left\{ \begin{array}{l} \text{hr} \\ \text{min} \end{array} \right\}$	(111)	(110)	(100)	(210)
Cell assembled				
:15	0.36118	0.36562	0.36551	0.36557
:30	0.36121	0.36560	0.36555	0.36563
:45	0.36125	0.36565	0.36559	0.36569
1:00	0.36125	0.36569	0.36559	0.36567
1:15	0.36118	0.36574	0.36560	0.36568
1:30	0.36117	0.36569	0.36559	0.36566
1:45	0.36116	0.36567	0.36561	0.36566
2:00	0.36117	0.36566	0.36559	0.36567
2:15	0.36116	0.36565	0.36561	0.36568
2:30	0.36115	0.36566	0.36555	0.36568
2:45	0.36118	0.36566	0.36563	0.36563
3:00	0.36113	0.36565	0.36551	0.36566
7:00	0.36113	0.36564	0.36553	0.36553
7:15	0.36114	0.36562	0.36550	0.36549

potential values due to the solubility of mercurous sulfate probably does not exceed the limit of uncertainty of the measurement and can accordingly be disregarded.

The standard cell potential was evaluated using the relationship  $E = E_{\text{cell}}^0 - (\nu RT/nF) \cdot \ln m \gamma$ . Because of the inherent unreliability of emf measurements at low electrolyte concentrations, highly dilute solutions were not used in this experiment and the Lewis and Randall (18) method of extrapolating a function of  $E$  to infinite dilution to obtain the standard potential was not employed. It appeared that the value of the normal potential could be derived most satisfactorily from freezing point depression measurements (19), and relative partial molar heat content values (20) in the manner outlined by Wetmore and Gordon (21). The assumption was made that a function which empirically represented the freezing point data,  $j = Amx$ , where  $x = 0.423$  and  $A = 1.718$ , could be extended without significant error to include 0.01447M, the lowest concentration. The corresponding  $\ln \gamma$  was calculated and then corrected to 298.2°K using the appropriate  $\bar{L}_2$  and considering  $(\bar{C}_{p2} - \bar{C}_{p2}^0)$  to be negligible (22). The result of this calculation,  $\log \gamma = -0.455$ , permitted the direct evaluation of  $E_{\text{cell}}^0$  for the (111) electrode in the most dilute electrolyte. This choice of electrode surface was made because of typical stability of the (111) potential with time in every cell which was observed. Potential differences, listed in column 7, Table I, are thus simply the arithmetic differences in measured potential relative to the standard, (111). Taking the normal potential of the mercurous sulfate electrode (23) as  $-0.6152$  at  $25^\circ\text{C}$ , the standard potential of the amalgamated copper crystal electrode is  $-0.3419$  v. Activity coefficients at two other temperatures,  $17.2^\circ$  and  $34.7^\circ\text{C}$ , were calculated from the activity coefficient at the freezing point and the value of  $\bar{L}_2$ , and cor-

responding  $E_{\text{cell}}^0$  values were obtained directly. These results are entered in Table I, columns 5 and 6. At other electrolyte concentrations the value of the activity coefficient was similarly based upon the  $E_{\text{cell}}^0$  corresponding to the (111) electrode.

Since a single set of high purity crystal electrodes was used throughout the final measurements, it appeared desirable to establish the fact that strain had not been anisotropically introduced during the original cutting operation. Although the maximum residual stress remaining in any one specimen would not be expected, on a bulk thermodynamic basis, to affect the potential within the limits of the present experimental error, strain might conceivably exert a disproportionate influence on surface properties, thus constituting the source of the potential differences. Specimens were prepared, accordingly, as for a potential run, then stripped of wax and solder and heated in vacuo at the rate of  $10^\circ\text{C}/\text{hr}$  to  $250^\circ\text{C}$ , and furnace cooled. There was no visual evidence of recrystallization after brief etching in 25%  $\text{HNO}_3$ . Test surfaces were repolished electrolytically and the specimens mounted in a 0.01447M cell. Observed potential differences were identical with those previously obtained.

To facilitate direct comparison of the single crystal electrodes with a polycrystalline electrode, an annealed 0.25-in. diameter rod of 99.999% copper having a small grain size was electropolished, amalgamated, and placed in a 0.4829M cell. The measured potential, which initially remained constant for 6 hr at 0.05 mv below the value of the (110) electrode in the same cell, decreased continuously for about 40 hr and finally stabilized at a value 0.5 mv higher than the (111). At this point the surface was examined microscopically. Nonuniform surface alteration was observed, certain grains having been deeply eroded, others less, and some apparently not at all. Grain boundaries were similarly affected, the extent of erosion presumably being a function of boundary angle. CuHg crystallites were in evidence on the surface; apparently their distribution was related directly to the extent of localized erosion.

To determine the rate of precipitation of CuHg from a homogeneous solution of copper in mercury, a 5% copper amalgam was prepared electrolytically and stored under an acidified  $\text{CuSO}_4$  solution for one week. The presence of solid phase CuHg in detectable amounts was not observed until the second day. After the third day, the volume of CuHg appeared to remain constant, indicating that phase equilibrium had been established within two days.

## DISCUSSION

Data and calculated values obtained in the present investigation are in substantial agreement with those

in the literature. A direct comparison of the authors' data with that obtained by Wetmore and Gordon (14), Getman (13), and Neilsen and Brown (9) is shown in Fig. 1 where the quantity  $E^{0'}$ , defined by the relationship

$$E^{0'} \equiv E + \frac{\nu RT}{nF} \ln m = E^0 - \frac{\nu RT}{nF} \ln \gamma$$

is plotted against  $m^{1/2}$ . It can be seen that values derived from saturated amalgam electrodes, with and without massive copper present, approximate a curve which defines the lower limit of all data represented. The curve which represents Getman's single crystal data is roughly 3.5 mv above the lower curve, while a third curve, about 5 mv above the amalgam curve, contains potential values typical of the authors' most active crystal plane electrodes. The positive drift in their values at the lowest concentration is ascribed to chemical factors associated with more dilute solutions, since the potential differences are consistent with those observed at other concentrations.

A comparison of the authors' values for  $\log \gamma$ , based on  $E(111)$ , with those of Wetmore and Gordon shows a definite deviation. This is related to the deviation in observed  $E$  mentioned above. Inasmuch as the same extrapolation function of the freezing point data of Hovorka and Rodebush (19) was used in both instances, identical values of  $\log \gamma$  are obtained up to the limits of the extrapolation. At 0.01447M the observed  $E$  yields a value of  $E^0$  (0.2733 v) approximately 3 mv higher than Wetmore and Gordon's value (0.2702 v) at 0.02024M. Correspondingly, at 0.05395M and 0.4289M, the authors'  $E^0$  and the observed potentials give  $\log \gamma$  values greater than those calculated by the above investigators in the same concentration range. If  $E^0 = 0.2702$  v is assumed to be consistent with solutions

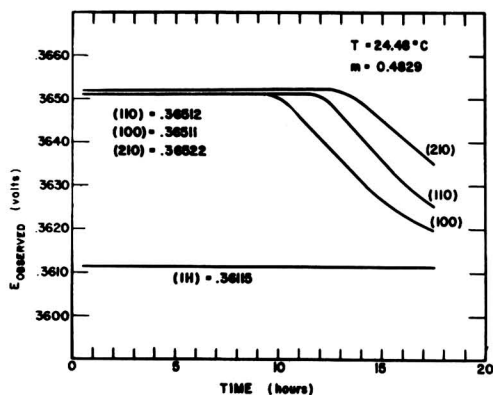


FIG. 1. Potentials of single crystal plane electrodes recorded during a typical determination.

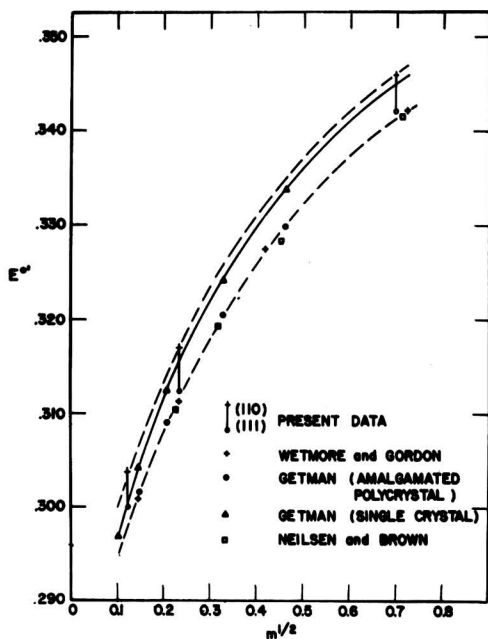


FIG. 2. Crystal plane potentials plotted together with other electrode values.

more concentrated than approximately 0.02M, and is accordingly used with the authors' observed potentials, the resulting values for  $\log \gamma$  are in good agreement with those of Wetmore and Gordon. In fact, using this  $E^0$ , the activity coefficients do not differ significantly when calculated from any of the data that define the amalgam curve (Fig 2.).

The absolute value of  $E^0$  thus appears to be susceptible to evaluation from data obtained either with an equilibrium two-phase amalgam or with a critically oriented single crystal surface as is discussed presently. It is immediately apparent, however, that considerable difficulty is involved in the experimental realization of the crystal electrode with respect to both preparation and prevention of surface film formation. On this basis, the electrolytic amalgam appears to offer the most convenient form of reversible electrode.

Single crystal electrodes having a given lattice plane lying in the surface exhibit potentials which may be classified as stable and metastable, constancy in time being the criterion for such designation. The (111) surface appears to yield the stable potential in the system under consideration. Metastable surfaces yield potentials approximately 4.5 mv above the value characteristic of the (111) plane. In copper sulfate solutions, using unamalgamated electrodes, this potential difference deteriorates within minutes to about 2 mv, then more slowly to

1.5 mv at the end of eight days. Amalgamated crystal electrodes, however, give cell potentials which retain the initial 4.5 mv differences for 10–15 hr and approach the (111) value as shown in Fig. 1. In neither case can potential differences be considered quantitative in the sense of providing a direct measure of variation of surface activity with orientation because a reversible cell is obtained only with the (111) electrode.

The single crystal potential values reported by Getman and plotted in Fig. 2 may be interpreted as representing metastable potentials intermediate to values derived in this investigation. Since the crystal was utilized without regard to crystallographic orientation, it must, of necessity, have presented a variety of surface configurations to the electrolyte. In the absence of mercury on the surface (the crystal was unamalgamated), any surface alteration toward a stable configuration was rendered impossible, at least in the time required for the potential measurements.

Behavior of amalgamated crystal electrodes may be interpreted in terms of the following facts: all surfaces except (111) show attack and deposited CuHg; a finite time of the order observed for constant potential difference is required to nucleate and form solid CuHg from supersaturated liquid solution (24). Upon amalgamation, the mercury covering the metastable faces becomes supersaturated with the copper removed from these faces in an attempt to reach a stable crystallographic configuration by the development of etch facets. On the other hand, copper is removed from the stable (111) face to saturate liquid mercury at a concentration consistent with the activity of copper in the close-packed face and without crystallographically altering the exposed face except possibly to the extent required by inaccuracies of preparation. In fact, no macroscopic changes of the surface of this electrode were ever observed and the potential is definite and constant for prolonged periods of time, the equilibrium value having been recorded for 17 days in one instance.

Observed, initial, potential differences between planes represent potentials corresponding to different concentrations of copper homogeneously dissolved in mercury. The small differences between the metastable planes may be attributed to the fact that the amount of copper removed from the different planes to approximate a (111) configuration does not vary greatly between the low index planes. The higher potential associated with supersaturated mercury persists during the induction period characteristic of the nucleation of CuHg, after which the growth of CuHg depletes the solution of excess copper and the potential approaches the value of the

amalgam in equilibrium with the stable (111) surface.

If the electrode is prepared by the amalgamation of massive polycrystalline copper, the initial potential is characteristic of the degree of supersaturation of copper in mercury as derived from those copper crystallites whose surface orientations represent other than the most stable atomic configuration. In time, the potential decreases with the progressive formation of CuHg. The final surface is comprised of regions defined by areas of individual crystallites which have been more or less altered, depending on their initial orientation. The final potential is very nearly (0.5 mv) that of the electrolytic amalgam or the stable (111) amalgamated face; a small disparity is to be expected as a result of the continued presence of higher activity surface areas and grain boundaries which mark the lines of geometric transition between stable regions. If a sufficient volume of liquid mercury is not available for the equilibrating process to proceed to completion, the terminal emf would be expected to be somewhat above the proposed most stable value. That Getman's amalgamated polycrystal values are in good agreement with the electrolytic amalgam data would appear to be a consequence of the above described process having been completed while the electrode was stored for some considerable time under liquid mercury prior to immersion in the cell. The position of the authors' most stable crystal potentials, generally above the amalgam curve, is attributable to a slight convexity of the test area resulting from electropolishing, and to the small change in surface orientation attendant to the preparation of electrodes for successive runs. These factors would not be expected to influence seriously the behavior of the more active electrodes if one considers the observed potential to vary rather slowly as a function of orientation except near the (111) surface configuration. On this basis, surface convexity and error in gross orientation of the (111) electrode would serve to alter its potential rather sharply and in the more active direction, as indicated in Fig. 2. The relatively small scatter of values about the amalgam curve may, in general, be attributed to the varying degree of control of physical and chemical parameters in the several investigations considered.

Reference to Table I, column 7, shows that the potential differences between crystal electrodes varied in successive runs by about 0.5 mv. Since measurements were first made at the highest electrolyte concentration and then, in turn, at the intermediate and lowest concentrations, the variation appears not to be systematic but rather a function of surface preparation between runs. Accordingly,

potential differences are probably characteristic of the amalgamated copper crystals and are independent of the electrolyte concentration.

Variation of potential differences with temperature is, on the other hand, not indicative of any intrinsic property of the crystal faces, but is probably related to the differing proportions of copper in the four amalgams. The temperature-potential relationship was determined by making the measurements at 17.2°, 24.48°, and 34.7°C in that order, followed by return to 24.48°C. In terms of the phase diagram, such temperature changes require an increased equilibrium concentration of copper in liquid mercury. On the basis of the previously stated mechanism, metastable electrode amalgams contain an excess of copper relative to the equilibrium concentration at any of these temperatures and so would not be expected to dissolve additional copper from the crystal surfaces upon temperature increase. The (111) amalgam, however, would become progressively richer in copper in accordance with the requirements of phase equilibrium and its potential would thus approach those of the metastable electrodes. This process would lead to a diminution of potential differences upon increasing temperature, which is, in fact, indicated by present data. Presence of the minute quantity of CuHg which has been observed on the amalgamated (111) surface may, in part, be attributed to the slight supersaturation which resulted from the return of the electrode to 24.48°C subsequent to the 34.7°C measurements.

The temperature coefficient of the cell,  $-8.1 \times 10^{-4}$ , again calculated for the (111) electrode, is slightly greater than the value of  $-7.6 \times 10^{-4}$  obtained by Wetmore and Gordon. It may be pointed out, however, that the higher value is in better agreement with the temperature coefficient of the cell as calculated from available entropy data (25). Unfortunately, the greatest uncertainty among the individual entropy values employed exists for the oxidation of copper to cupric ion, the reaction pertinent to this discussion. The authors' temperature coefficient yields a calculated entropy for cupric ion of  $-22.6$  eu, the  $dE/dT$  value of  $-7.6 \times 10^{-4}$  yields an entropy of  $-20.4$  eu, and the reference literature value is  $-25.9 \pm 3$  eu.

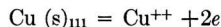
Oku (26) has measured the potential between a saturated electrolytic amalgam and an electrodeposited copper sludge and reports a value of 5 mv which can also be considered to define the difference between the lowest and highest curves of Fig. 2.

The 5 mv difference measured by Oku can be explained in the following manner. The electrodeposited copper sludge consisted of extremely small copper crystals, whose predominating surfaces were

different from the (111) orientation. The potential of this electrode would thus be less noble than the equilibrium amalgam and would constitute a compromise value for the higher activity crystal faces exposed on the surfaces of the particles. In addition, the size of particles may have given rise to a second contribution to the potential on the basis of the increase of solubility with decrease in radius, as defined by the Gibbs adsorption equation. Since the size of the particles which comprised the sludge is not known, it is impossible to evaluate the latter factor. It appears, then, that Oku's value for copper, relative to the amalgam, does not represent a reversible potential and, consequently, should not be added to amalgam values to obtain the oxidation potential of crystalline copper.

#### SUMMARY

1. The oxidation potential of solid copper, and presumably other metals, is dependent on the crystallographic configuration of atoms in the surface.
2. The only stable plane of the face-centered cubic system is the close-packed octahedral plane and, accordingly, only this plane produces a reversible cell. The electrode reaction may thus be written



3. All other crystal plane surfaces are metastable and approach the (111) configuration in time.
4. Polycrystalline electrodes approach the stable state providing sufficient time is allowed for the establishment of the stable crystallographic configuration.

#### ACKNOWLEDGMENTS

The authors wish to express their thanks to the Office of Naval Research for financial support of these experiments under Contract Nonr 305(00), and to the American Smelting and Refining Company for supplying the high purity copper.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

#### REFERENCES

1. D. N. ARTEMIEV, *Z. Krist.*, **48**, 415 (1910).
2. W. SCHNORR, *ibid.*, **54**, 289 (1914).
3. W. SCHNORR, *ibid.*, **68**, 1 (1928).
4. H. GLAUNER AND R. GLOCKER, *ibid.*, **80**, 377 (1931).
5. G. AMINOFF, *ibid.*, **65**, 23 (1927).
6. M. STRAUMANIS, *Z. physik. Chem.*, **147**, 161 (1930).
7. H. LEIDHEISER, JR., AND A. T. GWATHMEY, *Trans. Electrochem. Soc.*, **91**, 97 (1947).
8. G. N. LEWIS AND W. LACEY, *J. Am. Chem. Soc.*, **36**, 804 (1914).
9. R. NIELSEN AND D. BROWN, *ibid.*, **49**, 2423 (1927).

10. E. COHEN, F. CHATTAWAY, AND W. TOMBROCK, *Z. physik. Chem.*, **60**, 706 (1907).
11. M. OBATA, *Proc. Phys. Math. Soc. Japan*, **2**, 223 (1920).
12. M. QUINTIN, *Compt. rend.*, **196**, 473, 538 (1933).
13. F. GETMAN, *J. Phys. Chem.*, **34**, 1454 (1930).
14. F. WETMORE AND A. GORDON, *J. Chem. Phys.*, **5**, 60 (1937).
15. P. JACQUET, *Metal Finishing*, **47**, (5), 48 (1949).
16. E. NEWBERRY, *J. Am. Chem. Soc.*, **51**, 1315 (1929).
17. M. HANSEN, "Der Aufbau der Zweistofflegierungen," p. 565, Springer, Berlin (1936).
18. G. N. LEWIS AND M. RANDALL, "Thermodynamics," p. 286, McGraw-Hill Book Co., New York (1923).
19. F. HOVORKA AND W. RODEBUSH, *J. Am. Chem. Soc.*, **47**, 1614 (1925).
20. E. LANGE, J. MONHEIM, AND A. ROBINSON, *ibid.*, **55**, 4733 (1933).
21. F. WETMORE AND A. GORDON, *loc. cit.*
22. *International Critical Tables*, Vol. V, p. 122.
23. H. S. HARNED AND B. B. OWEN, "The Physical Chemistry of Electrolytic Solutions," p. 439, Reinhold Publishing Corp., New York (1950).
24. H. TERREY AND C. WRIGHT, *Phil. Mag.*, *Bd. 6*, 1055 (1928).
25. K. K. KELLEY, *U. S. Bur. Mines Bulletin* 477.
26. M. OKU, *Sci. Rep. Tohoku Imp. Univ.*, **22**, 288 (1933).

# Polarographic Investigation of Organic and Inorganic Compounds in an Ammonia-Ammonium Nitrate Solvent<sup>1</sup>

GUY WILLIAM LEONARD, JR., AND DOUGLAS E. SELLERS

*Department of Chemistry, Kansas State College, Manhattan, Kansas*

## ABSTRACT

Precision polarography is applied to the study of organic and inorganic compounds in Divers' solution. The lead-lead nitrate cell serves satisfactorily in Divers' solution as a reference electrode. Although the measured half-wave potentials are shown to be shifted by the addition of water to the solvent, values for the half-wave potential reproducible within  $\pm 0.003$  v can be obtained. Well formed polarograms are obtained for which the diffusion current is proportional to the concentration, and the half-wave potential is dependent on the species being reduced.

## INTRODUCTION

During recent years an increasing number of polarographic studies have been carried out in non-aqueous solvents. Among the solvents studied, the ammonia-ammonium nitrate system (1) appears to have a distinct advantage over other nonaqueous solvents, for no supporting electrolyte is needed since the solvent is an excellent conductor. This solvent (2), which is often called Divers' solution, is formed by passing anhydrous ammonia gas over ammonium nitrate at 0°C. Ammonium nitrate takes up sufficient ammonia gas to form a saturated solution whose ammonia vapor pressure is reduced to such an extent that the solution can exist at room temperature.

Since the chief difficulties encountered in the use of organic solvents are the high resistance of the solution and the necessity of finding a suitable supporting electrolyte, the present investigation was undertaken to determine the possible use of Divers' solution for the polarographic study of organic compounds as well as to extend the investigation of the polarographic behavior of inorganic compounds in this solvent.

## EXPERIMENTAL

*Chemicals.*—Reagent grade chemicals were used without further purification except for certain salts which were prepared in this laboratory. The anhydrous ammonia was purchased in 50 lb tanks from Armour.

*Apparatus.*—A Sargent-Heyrovsky Polarograph Model XII was used with a wave spreader (3). A Rubicon Portable Potentiometer was used to measure the applied potential at the beginning and at the

end of the polarogram. Calibration points were marked on the photographic record by adjusting the galvanometer to 20 and opening the shutter at each point. The reference electrode was a lead-lead nitrate electrode (4). The electrolysis cell was of the H-type. The resistance of the cell circuit as measured by an Industrial Instruments Conductivity Bridge Model RC was 31 ohms.

*Procedure.*—A weighed amount of previously dried ammonium nitrate was placed in one arm of the H-cell and an approximately equal amount was placed in the other half of the cell. The cell was then placed in a constant temperature bath maintained at 0°C by melting ice. Anhydrous ammonia was simultaneously passed through each cell until the system reached vapor pressure equilibrium with 1 atm ammonia at 0°C. The obtaining of equilibrium was indicated by the total dissolution of ammonium nitrate. Under these conditions, the resulting solution contained approximately three moles of ammonia per mole of ammonium nitrate. After equilibrium was established, the reference cell was saturated with lead nitrate, the lead electrode placed in the solution, and a weighed amount of sample placed in the sample compartment. Ammonia was again bubbled through both cells for about ten minutes to insure thorough mixing. The polarograms were then taken with a span of 0.2 v.

## RESULTS AND DISCUSSION

A preliminary investigation, using a mercury pool as the reference electrode, revealed that the potential of the reference electrode was dependent on the length of time the mercury had been in contact with the solution. Since equilibrium conditions could not be obtained readily, and since reproducible measurements of half-wave potentials could not be obtained,

<sup>1</sup> Manuscript received July 12, 1954.

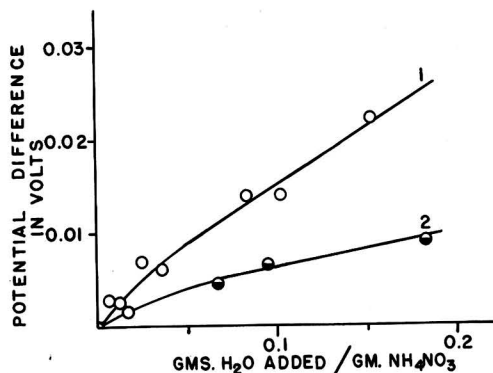


FIG. 1. Effect of moisture content upon half-wave potentials. Curve 1, change of half-wave potential for the lead system; curve 2, change of half-wave potential for the diphenyl thiocarbazon system. Potential difference =  $E \frac{1}{2}$  without added water— $E \frac{1}{2}$  with given amount of water added.

the mercury pool was replaced with the lead-lead nitrate reference cell. The lead-lead nitrate reference cell gave results which could be reproduced within  $\pm 0.003$  v. The polarographic investigation of a sample could be completed before detectable amounts of lead diffused from the reference cell into the working cell.

The influence of moisture contamination upon the half-wave potential is shown in Fig. 1. The half-wave potential of the  $Pb^{++} + 2e^- = Pb$  couple was shifted toward more positive potentials as the amount of water contamination was increased in the working cell. No water was added to the reference cell. A similar dependency upon moisture content was found for the half-wave potentials of diphenyl thiocarbazon (curve 2, Fig. 1); however, the shift in the half-wave potentials was much less than that for the lead couple. Although there is a change in the half-wave potential accompanying a change in the water content, as is shown in Fig. 1, reproducible results for the half-wave potentials could be obtained.

Table I shows the typical compounds that were

TABLE I. Inorganic and organic compounds which are soluble in Divers' solution at 0°C

As <sub>2</sub> O <sub>3</sub>	Hg(SCN) <sub>2</sub>	Nicotinic acid
BaO	CdSO <sub>4</sub>	Aspartic acid
HgO	Cu(NH <sub>3</sub> ) <sub>4</sub> (SCN) <sub>2</sub>	Thiourea
PbO	Co(NH <sub>3</sub> ) <sub>6</sub> (NO <sub>3</sub> ) <sub>2</sub>	Maleic anhydride
PbBr <sub>2</sub>	<i>m</i> -Nitroaniline	Benzil
PbI <sub>2</sub>	Diphenyl thiocarbazon	Azobenzene
Pb(NO <sub>3</sub> ) <sub>2</sub>	Benzoic acid	1 Naphthol-5-sulfonic acid
AgSCN		

TABLE II. Inorganic and organic compounds which are insoluble in Divers' solution at 0°C

Al <sub>2</sub> O <sub>3</sub>	TeO <sub>2</sub>	Ni(CN) <sub>2</sub>
CuO	TiO <sub>2</sub>	<i>p</i> -Hydroxybenzophenone
Fe <sub>2</sub> O <sub>3</sub>	Co(CN) <sub>2</sub>	Phenyl- $\alpha$ -chloroisobutyrate
MgO	Ni(NH <sub>3</sub> ) <sub>6</sub> Br <sub>2</sub>	Benzoyl peroxide
Sb <sub>2</sub> O <sub>5</sub>	Benzophenone	Phthalic anhydride
SeO <sub>2</sub>		

found to be soluble in Divers' solution, while Table II shows those that were found to be insoluble. Not all of the compounds shown in Table I gave polarographic waves falling within the useable voltage span of the ammonia-ammonium nitrate electrolyte against the lead-lead nitrate reference cell, i.e., + 0.4 to -0.8 volt. Table III lists the compounds that gave well-defined polarographic waves. Copper, cobalt, and cadmium compounds were prepared and purified according to recommended procedures (5-7). A plot of  $\log [i/(i_d - i)]$  against  $E$  gave straight lines with very little scatter of points. Slopes of the plots for lead, cadmium, and cobalt were, respectively, 0.0289, 0.031, 0.105, indicating that lead and cadmium gave reversible reactions corresponding to a two-electron change, while the cobalt reduction was irreversible. The copper compound formed two reversible waves each representing a one-electron change which corresponds to the reduction of cupric to cuprous and then cuprous to copper as indicated by a slope of 0.0562 and 0.068. Some of the compounds formed a maximum in the polarogram, but the maximum was easily suppressed by the addition of gelatin. Since gelatin is just slightly soluble in Divers' solution, a saturated solution was prepared by adding a few grains of gelatin to the solution and bubbling ammonia through it for five minutes to assure thorough mixing. The diffusion current was found to be propor-

TABLE III. Half-wave potentials and diffusion current constants for various inorganic and organic compounds

Compound	$E \frac{1}{2}$ in volts vs. the lead-lead nitrate reference electrode	$i_d$ cm <sup>2</sup> /3 t <sup>1/2</sup> /6
PbO	+0.019	10.9
Cu(NH <sub>3</sub> ) <sub>4</sub> (SCN) <sub>2</sub> *	+0.185	4.04
Cu(NH <sub>3</sub> ) <sub>4</sub> (SCN) <sub>2</sub> *	-0.026	4.04
Co(NH <sub>3</sub> ) <sub>6</sub> (NO <sub>3</sub> ) <sub>2</sub>	+0.191	†
CdSO <sub>4</sub>	-0.387	14.9
<i>m</i> -Nitroaniline*	-0.034	48.8
Diphenyl thiocarbazon	+0.173	0.536
Benzil*	+0.088	†
Azobenzene	+0.196	†

\* Gelatin added to suppress the maximum.

† Low solubility.

$m \frac{2}{3} t \frac{1}{2}$  equaled 1.97 a at potential of 0.4769 vs. the lead-lead nitrate electrode.  $c$  is expressed in mg/g of NH<sub>4</sub>NO<sub>3</sub>.



tional to the concentration of reducible material, and the half-wave potential was found to be dependent upon the species present.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1955 JOURNAL.

## REFERENCES

1. E. VECCHI, *Atti acad. Nazl. Lincei, Rend., Classe sci. fis., mat. e nat.*, **14**, 290 (1953).
2. E. DIVERS, *Proc. Roy. Soc.*, **21**, 109 (1875).
3. D. N. HUME AND T. W. GILBERT, *Anal. Chem.*, **24**, 431 (1952).
4. V. A. PLESKOV AND A. M. MONOSSON, *J. Phys. Chem. (U.S.S.R.)*, **4**, 696 (1933).
5. T. W. RICHARDS AND B. S. MERIGOLD, *Z. anorg. Chem.*, **17**, 245 (1898).
6. W. C. FERNELIUS, Editor, "Inorganic Syntheses," 1st ed., Vol. II, p. 218, McGraw-Hill Book Co., New York (1946).
7. A. DE SCHULTEN, *Compt. rend.*, **107**, 405 (1888).

# FUTURE MEETINGS OF The Electrochemical Society



Cincinnati, May 1, 2, 3, 4, and 5, 1955

Sessions will be scheduled on

Electric Insulation, Electronics, Electrothermics  
and Metallurgy, Industrial Electrolytics, Theo-  
retical Electrochemistry

Headquarters at the Sheraton-Gibson Hotel

★ ★ ★

Pittsburgh, October 9, 10, 11, 12, and 13, 1955

Headquarters at the William Penn Hotel

★ ★ ★

San Francisco, April 29 and 30, and May 1, 2, and 3, 1956

Headquarters at the Mark-Hopkins Hotel

★ ★ ★

Cleveland, October 28, 29, 30, and 31, and November 1, 1956

Headquarters at the Statler Hotel

★ ★ ★

Washington, D. C., May 12, 13, 14, 15, and 16, 1957

Headquarters at the Statler Hotel

★ ★ ★

Buffalo, October 6, 7, 8, 9, and 10, 1957



## Society Plans Spring Meeting in Cincinnati



Meeting of some members of the Cincinnati Convention Committee. *Left to right:* Carl L. Taglauer, R. S. Good, L. M. Lederer, Roy O. McDuffie, and William J. Schreiner.

The 1955 Spring Meeting of the Society will be held in Cincinnati, Ohio, May 1-5, at the Sheraton-Gibson Hotel. The 107th Meeting will feature sessions on Electric Insulation; Electronics, including Luminescence, Phosphor Applications, and Semiconductors; Electrothermics and Metallurgy, Industrial Electrolytics, and Theoretical Electrochemistry.

Roy O. McDuffie, Professor of Metallurgical Engineering, University of Cincinnati, General Chairman of the Convention, has appointed local committees to arrange for the meeting. The committees are as follows:

### *Meeting Arrangements*

Robert Price, University of Cincinnati, *Chairman*

Joseph Sausville, University of Cincinnati

### *Registration and Hotels*

Ezra Blount, *Products Finishing Magazine, Chairman*

John W. Magly, Consulting Engineer

Joseph H. Creevy, Newport Steel Company

### *Plant Trips*

Richard Rolfes, Emery Industries, *Chairman*

### *Finance*

L. M. Lederer, Innertank Lining Company, *Chairman*

### *Entertainment*

Carl Taglauer, Harshaw Chemical Company, *Chairman*

William J. Ehlen, Consulting Engineer

Robert Miller, Electric Autolite Company

### *Publicity*

William J. Schreiner, Cincinnati Gas & Electric Company, *Chairman*

### *Ladies' Entertainment*

Mrs. W. J. Schreiner, *Chairman*

Mrs. Roy O. McDuffie  
Mrs. Milton J. Pfeiffer  
Mrs. Carl Taglauer  
Mrs. William J. Ehlen  
Mrs. Robert Miller  
Mrs. Robert Price  
Mrs. Joseph Sausville  
Mrs. Ezra Blount  
Mrs. Joseph H. Creevy  
Mrs. Richard Rolfes  
Mrs. L. M. Lederer

Details of the program are being worked out by the committees and will be announced later.

---

## DIVISION NEWS

---

Proposed Bylaws  
of the

ELECTROTHERMICS AND METALLURGY DIVISION  
of

The Electrochemical Society, Inc.

### Article I

#### NAME AND OBJECT

Section 1. This organization shall be known as The Electrothermics and Metallurgy Division (hereinafter referred to as the Division) of The Electrochemical Society, Inc. (hereinafter referred to as the Society). The Division shall consist of those members of the Society who are interested in one or more phases of the fields of electrothermics and/or metallurgy.

Section 2. The Division shall function as a nonprofit organization in a manner consistent with the laws, rules, and regulations of the Society.

Section 3. The purpose of the Division is to aid and encourage the advancement of science and industry which are concerned with the fields of electrothermics and metallurgy. Among the means to this end shall be the holding of meetings for the reading and discussion of professional and scientific papers on these subjects, the publication of such papers, discussions, and communications as may seem expedient, and cooperation with chemical, electrical, and other scientific and technical societies.

Section 4. More specifically, the Division is primarily interested in high temperature materials, methods, and measurements, the preparation, recovery, use, or execution of which involves electrical



Some of the members of the Ladies' Entertainment Committee. *Left to right:* Mesdames Taglauer, Blount, Price, McDuffie, Good, Rolfes, and Schreiner.

energy or electrochemical processing or is of importance to the electrochemical industries. In the metallurgical field, the Division is particularly interested in those metals referred to in the past as rare metals.

## Article II

### MEMBERSHIP

Section 1. The membership of the Division shall consist of those members of the Society who register their desire to be members of the Division with the Secretary-Treasurer of the Division and who pay Division dues if such be established.

## Article III

### DUES

Section 1. Annual dues, if any, shall be fixed by the Executive Committee of the Division subject to a two-thirds vote of the membership of the Division.

Section 2. Any Division dues established according to Section 1 shall be collected by the Secretary-Treasurer of the Division.

## Article IV

### OFFICERS AND EXECUTIVE COMMITTEE

Section 1. The officers of the Division shall be a Chairman, two Vice-Chairmen, and a Secretary-Treasurer.

Section 2. The governing body of the Division shall be an Executive Committee, consisting of the four officers and four Members-at-Large, plus the immediate past Chairman of the Division.

## Article V

### ELECTION OF OFFICERS AND MEMBERS-AT-LARGE

Section 1. The officers and Members-at-Large of the Division shall be elected biennially by a majority vote of the members present at the business meeting of the Division during the Spring Convention of the Society in odd-numbered years, and shall take office immediately after adjournment of the meeting in which they are elected.

Section 2. The term of office of the officers and Members-at-Large shall be two years. Officers and Members-at-Large shall be eligible for re-election but for not more than two successive terms.

Section 3. The Chairman of the Division shall appoint, at least five months prior to the Spring Convention at which an election is to be held, a Nominating Committee of three members of the Division to make nominations for officers and Members-at-Large, and he shall notify the Secretary of the Society of these appointments.

Section 4. The nominees selected by the Nominating Committee shall be members in good standing of the Division who after being informed of the duties of office have agreed to serve, if elected.

Section 5. The report of the Nominating Committee shall be submitted in writing to the Executive Committee of the Division for approval, and to the Secretary of the Society at least three months before the meeting at which the election is to be held. The Secretary-Treasurer of the Division shall have the report published in the JOURNAL of the Society prior to the election.

Section 6. At the time of election the report of the Nominating Committee shall be presented to the members

present, after which the election shall proceed.

Section 7. Nominations may also be made from the floor by qualified members of the Division at the time of the election.

Section 8. If the Chairman should fail to appoint the Nominating Committee as provided in Section 3, the Executive Committee of the Division or the Board of Directors of the Society may instruct the Vice-Chairman or another member of the Executive Committee to do so.

Section 9. In the event there is no election when one is due, the President of the Society shall appoint officers and Members-at-Large from the membership of the Division to serve until the next regular election date.

Section 10. If the office of Chairman should become vacant during his term of office, the Executive Committee, excluding the two Vice-Chairmen, shall elect one of the two Vice-Chairmen to the office of Chairman. The Chairman shall fill any other vacancies by appointment, subject to the approval of the majority of the members of the Executive Committee remaining in office.

## Article VI

### DUTIES OF OFFICERS

Section 1. The Chairman shall have the following duties: (a) To preside at all meetings of the Division and of its Executive Committee, and to perform such other duties as are required by these Bylaws or by action of the Executive Committee or as may be appropriate to his office. (b) To represent the Division on the Board of Directors of the Society as provided in the Bylaws of the Society. If he is unable to be present, he shall appoint a proxy.

Section 2. (a) The Vice-Chairmen shall assist the Chairman in his duties and assume the duties of the Chairman in his absence. (b) The Vice-Chairmen shall be responsible for the organization of the technical sessions of the Division at the National Meetings.

Section 3. The Secretary-Treasurer shall have the following duties: (a) To keep an accurate record of all proceedings of the Division and its Executive Committee, and to keep a list of the members of the Division. (b) To collect any dues that may be assessed by the Division. (c) To have custody of funds of the Division and keep a record of all receipts and expenditures of such funds. Expenditure of funds by the Secretary-Treasurer of the Division shall be subject to approval by the Executive Committee of the Division. Said approval consisting of a two-thirds vote taken at a formal meeting of the Committee, or if a meeting has not been scheduled, the vote must be in writing, all members of the Committee having been notified. (d) Withdrawals of the Division's funds, approved in accordance with the foregoing, must be countersigned by the Chairman. The bank account(s) must be designed accordingly. (e) To present an annual report, including a financial statement, to the members of the Division at the annual business meeting, and to file a copy of this report with the Board of Directors of the Society.

## Article VII

### DUTIES OF THE EXECUTIVE COMMITTEE

Section 1. The Executive Committee shall be the governing body of the Division and shall determine its policies.

Section 2. The Executive Committee

may propose to the Division amendments or revisions of these Bylaws.

Section 3. The Executive Committee shall, through the Division Chairman, bring before the Board of Directors of the Society such recommendations on matters concerning the Society as may be proper for Board action.

Section 4. The Executive Committee shall have jurisdiction over the safekeeping, investment, and disposition of all funds or other property of the Division.

Section 5. The Executive Committee shall be responsible for any Technical Sessions and shall choose adequate subject matter.

Section 6. The Executive Committee shall have jurisdiction over any special publication which this Division may sponsor, subject to such approval as may be required by the Constitution and Bylaws of the Society.

## Article VIII

### MEETINGS

Section 1. The Division shall hold one business meeting annually, presided over by Division officers or other members designated by the Executive Committee of the Division at the Spring Convention of the Society.

Section 2. The Division each year shall, if possible, hold at least one technical session in each of its two major fields of interest, namely: electrothermics and metallurgy.

Section 3. Meetings of the Executive Committee may be called at the discretion of the Chairman, or by request of three members of the Executive Committee.

## Article IX

### QUORUM

Section 1. Thirty members of the Division, present in person or by proxy, shall constitute a quorum for the transaction of all business at an annual meeting of the Division.

Section 2. Five members of the Executive Committee, present in person or by proxy, shall constitute a quorum for the transaction of all business at a meeting of the Executive Committee.

## Article X

### AMENDMENTS

Section 1. Amendments to these Bylaws may be proposed either by a majority vote of the Executive Committee, or by written request of ten members of the Division.

Section 2. The text of a proposed amendment shall be published in the JOURNAL of the Society at least two months before it is submitted to a vote unless the Board of Directors of the Society shall approve the amendment without publication.

Section 3. To be adopted, proposed amendments shall either be approved by a two-thirds vote at a business meeting of the Division, a quorum being present, or, if the Executive Committee deems it preferable, the proposed amendment may be submitted to all the members of the Division by mail, the favorable vote of two-thirds of those replying within one month being required for adoption.

\* \* \*

---



---

## SECTION NEWS

---



---

### New York Metropolitan Section

The Metropolitan Section held its regular meeting on November 17, 1954, with Dr. Seymour Senderoff of the Bureau of Standards as guest speaker. The subject of Dr. Senderoff's talk was "The Electrochemistry of the Refractory Metals," and covered processes for electrowinning, electrorefining, and electroplating of chromium, molybdenum, tungsten, titanium, and zirconium.

The electroplating of chromium from the chromic acid bath is an old and well-established art. The electrowinning of chromium in a bath of mixed bivalent and trivalent sulfates is in commercial operation but baths of this type have not been successfully developed for plating.

With the exception of chromium, successful electrodeposits of this group of metals have only been obtained from fused salt electrolytes. No commercial processes are in operation for the electrowinning of the refractory metals although considerable research work is being carried on in this field.

Laboratory scale studies on a molten electrolyte containing  $K_2MoCl_6$  have given promising results for electrodepositing molybdenum both as powder and as coherent plate. Various laboratories have and are studying the deposition of titanium and zirconium from molten baths of complex halides. The use of a fluotitanate bath has shown some promise, while baths containing chlorides have suffered from difficulties due to the high vapor pressure of the chlorides.

Some measurements of polarization and equilibrium potentials in molten salts were described which indicated that oxycompounds in the molybdenum bath depolarized the electrode and resulted in the deposition of oxides. Other interesting conclusions from these measurements concerned the conditions for the existence of complex compounds in molten salts.

The lecture was concluded with a discussion of the need for theoretical studies of the physical chemistry of molten electrolytes, electrode mechanisms and crystal growth in electrolysis of molten salts, and investigations of material for crucibles, diaphragms,

and other special equipment required in this work.

KENNETH B. MCCAIN,  
*Secretary-Treasurer*

### Pacific Northwest Section

The Pacific Northwest Section sponsored a dinner meeting on November 10, 1954, at Wright's Diner in Spokane, Wash. The meeting was held jointly with the Spokane Section of the American Chemical Society. An audience of 45 persons, representing approximately equal numbers of Electrochemical Society members, American Chemical Society members, and guests, was privileged to hear an address by Mr. R. E. Brown, Head, Earth Sciences Unit at General Electric Company's Hanford Atomic Products Operation. Mr. Brown's topic was "Central Oregon, Its Volcanoes and Its Quicksilver."

Mr. Brown asserted that "... the sudden upsurge in the price of quicksilver to an all-time high has created a new 'metal-of-the-hour.' Quicksilver lacks the glamour of uranium, yet provides even better opportunities for profitable, small-scale operations. The Ochoco district of Central Oregon offers excellent opportunities for prospecting and exploration, for the district is large, the deposits are well distributed, and past prospecting has not been guided by known geologic conditions. Large areas with considerable promise remain unexplored." Mr. Brown illustrated his talk with a series of colored slides which explained the geology of the district, the distribution and general occurrence of the ores, and the relationship of ore deposits to volcanic rocks and probable volcanoes. Most promising prospects for cinnabar deposits are to be found associated with large intrusive masses of biotite rhyolite or basaltic and andesite, often noted to be hydrothermally decomposed to such an extent that the intrusive plugs have been reduced to basins rather than to appear as local prominences.

Mr. Brown's activities in the Ochoco district as a member of the U. S. Geological Survey have given him a keen insight into the geological aspects of the region, as well as into the operating histories of the many mines in the district. The latter histories provided many interesting and amusing sidelights which Mr. Brown used to good advantage in his talk.

The Local Section has embarked upon a membership drive, which, at time of writing, has netted four applications. Although this number is small,

it represents an increase of some 10% in the local membership. A Membership Committee and a Nominating Committee have been appointed as follows:

*Membership Committee*—Dr. E. C. Pitzer, General Electric Co., Richland, Wash.; Dr. M. J. Pryor, Kaiser Aluminum and Chemical Corp., Spokane, Wash.; and Mr. Joseph B. Heitman, Pennsylvania Salt Manufacturing Co. of Washington, Tacoma, Wash.

*Nominating Committee*—Dr. R. L. Dillon, General Electric Co., Richland, Wash.; Mr. Glen C. Ware, Portland, Ore.; and Mr. Henry J. Wittrock, Kaiser Aluminum and Chemical Corp., Spokane, Wash.  
K. L. SANBORN, *Secretary-Treasurer*

### Philadelphia Section

At the meeting of the Philadelphia Section on November 3, 1954, Dr. Lewis G. Longworth, of the Rockefeller Institute for Medical Research, was the speaker. After dinner at the Lenape Club, members and guests assembled in the John Harrison Laboratory to hear Dr. Longworth speak on "Diffusion in Liquids."

Dr. Longworth commenced by pointing out that in recent years measurements of diffusion coefficients in liquids could be made with much greater precision owing to the development of more accurate techniques, for example, the use of optical interferometry. As a result, the re-examination of some prevalent ideas based on older results has become necessary, and the increased accuracy of the newer techniques opens up the possibility of studying such problems as the concentration dependence of diffusion coefficients, the diffusion of isomers, and the relation between diffusion coefficient and molecular structure.

The speaker then went on to discuss the limitations of the Stokes-Einstein relationship in terms of the effects of molecular asymmetry and solvation; the factor  $6\pi$  in this relationship probably tends to about  $3\pi$  when the dimensions of the diffusing entity approach those of the solvent. For larger particles, the apparent applicability of the Stokes-Einstein equation doubtless results, he said, from a compensation of asymmetry and hydration on the one hand and a numerical factor less than  $6\pi$  on the other.

Dr. Longworth then described some interesting results with certain groups of isomers, some of which were dipolar,

having zwitterion structure, while others were relatively nonpolar. In a number of cases, the difference of diffusion coefficients among the isomers could be explained in terms of the stronger solvation of the dipolar isomers. However, a number of interesting anomalies exist which must be explained by a combination of effects of shape, volume, polarity, and solvent interaction.

From the temperature dependence of diffusion coefficients, Dr. Longworth said, it was possible to derive both the effect of temperature on the Stokes radius and also the energy of activation for the diffusion process. He then discussed some interesting comparisons between the values of these parameters for ions and nonelectrolytes.

Dr. Longworth concluded his lecture with a discussion of experimental problems in liquid diffusion and pointed out that one of the most important problems at the present is to increase the precision of tracer methods. A number of stimulating questions were asked and the meeting was concluded with a vote of thanks which was heartily endorsed by all present.

G. W. BODAMER, *Secretary*

### Washington-Baltimore Section

The Washington-Baltimore Section met on November 18, 1954, at the National Bureau of Standards. The speaker of the evening was Milton Janes of National Carbon Company, Research Laboratories, whose subject was "The Electrochemistry of Carbon."

Mr. Janes described the physical and chemical properties of carbon and graphite that render it of particular interest to the electrochemical industry. Its high strength at high temperatures makes it uniquely useful in arcs, furnaces, and atomic piles. Its relatively high conductivity and inert chemical activity render it suitable for many interesting electrochemical applications. Mr. Janes described the use of carbon and graphite anodes in aqueous and nonaqueous electrolysis for production of caustic, elementary halogens, aluminum, magnesium, beryllium, cerium, and other rare earths.

Its use in such processes testifies to its distinctly inert nature, thus of particular interest was the description of the deterioration of the graphitic anode in such processes. In addition to the formation of the gaseous oxides, these carbonaceous anodes are attacked with the formation of a complex quinoic

acid, a so-called "graphitic oxide" that bridges the gap between organic and inorganic chemistry, and with the formation of laminal compounds constituting interstitial solution of ions that cause unidirectional expansion of the graphite lattice.

The discussion period was followed by an enjoyable social hour.

JEANNE BURBANK, *Secretary*

Dr. H. A. Laitinen, University of Illinois, was the speaker at the December 16 meeting of the Washington-Baltimore Section held at the National Bureau of Standards. Dr. Laitinen's topic was The Kinetics of Rapid Electrode Reactions. In his talk, Dr. Laitinen described some of the highlights of the development of the theory of electrode kinetics that has evolved over the past fifty years into the treatments of Grahame in this country and Randles in England. This development has been concerned with the establishment of equivalent electrical circuits that adequately express the behavior observed at electrodes.

Dr. Laitinen briefly described an a-c bridge circuit used in his investigations, and showed some experimental results. These results indicated that adsorption of ionic species plays a part in the reaction of the cobaltamine diamine complexes. Electrocapillary measurements were used to verify the adsorption of these ions at electrode surfaces. The studies resulted in a modification of the equivalent circuit to allow for adsorption effects.

More recently Dr. Laitinen has been investigating electrode reactions in fused salts. These systems have the advantage that the electrode processes studied have shown essentially true reversibility. Oxidation-reduction reactions were studied for platinum and nickel ions in the potassium chloride, lithium chloride eutectic. An interesting discussion period concluded the meeting.

JEANNE BURBANK, *Secretary*

---

## NEWS ITEMS

---

### New Titanium Casting Furnace in Operation

National Research Corporation, Cambridge, Mass., has added a new titanium casting furnace to the facilities of its Metallurgical Research Department.

This new furnace is an arc-melting

vacuum skull furnace capable of pouring 50 pounds of titanium per charge. It was designed and built by The Equipment Division for use with the NRC Titanium Shape Casting Process or for remelting of titanium scrap.

The new and larger size of this furnace makes possible the production of large castings, or several small parts at once, with important cost reductions. Sound castings are being made with the following typical interstitials content: carbon less than 0.02% by weight, oxygen less than 0.06% by weight, hydrogen less than 0.01% by weight.

As part of the facilities of the NRC Metallurgical Department, it is being used for further development of titanium melting and casting techniques. National Research is also prepared to produce evaluation quantities of a variety of types of castings such as valve bodies, cover plates, gyro parts, turbine parts, compressor parts, or physical test specimens precision cast to tolerances which make further machining unnecessary in many cases.

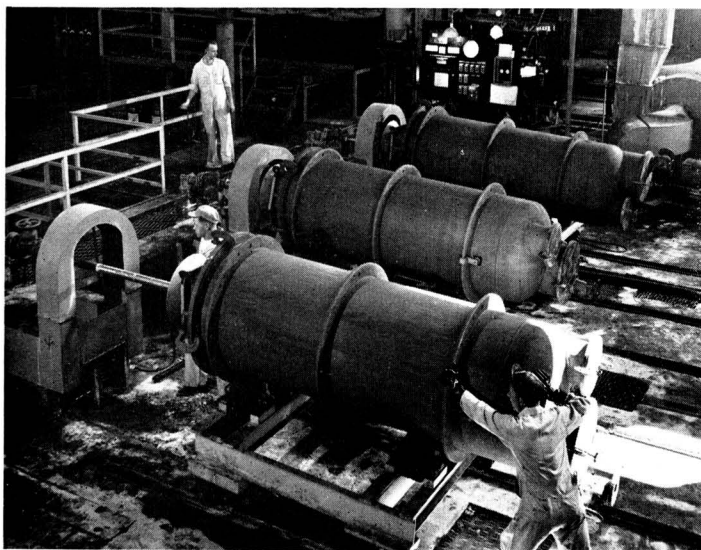
The NRC Titanium Shape Casting Process permits the production of sound castings of titanium and titanium alloys with a finish equivalent to that of good sand castings. An important feature of this process is a mold material which withstands the action of molten titanium. National Research is licensing this process on a nonexclusive basis; its first licensee is Titanium Casting Corporation, division of Howard Foundry Company, Chicago, Ill.

### Dow Forms New Market Research Group

Formation of a research development section in the Market Research Department of The Dow Chemical Company has been announced.

The group's primary responsibility will be to analyze specific industrial fields as a means of forecasting long-range trends and needs of various industries. It will then present such information to Dow research and development groups for use in developing ideas for new company products. The unit will also exchange ideas with development people in the industries being studied.

Heading the new section's activities, now under way in two major fields, are Dr. E. R. Boedeker who will handle the petroleum industry, and T. E. Werkema who will devote his efforts to the construction industry.



An unplated vessel being pushed into position for closed-cycle chemical nickel plating.

### Chemical Nickel Plating

The American Locomotive Company has announced new facilities for producing metal coatings at their Dunkirk, N. Y., plant. The coating, called "Alco-plate," is essentially nickel but contains about 7% phosphorus and has much the same corrosion properties as commercial nickel. This is a full scale application, using 3500 gallons of solution, of the "Kanigen" process recently patented and announced by General American Transportation Corporation and based on the "Electroless" process patented at the Bureau of Standards by Abner Brenner. Deposits are produced on metal surfaces by the interaction of nickel sulfate and sodium hypophosphite.

American Locomotive is currently using the process as modified by recent researches for plating inside surfaces of heavy steel vessels, typical of which are cylindrical shapes 6-12 feet long, 2-3 feet in diameter, with domed heads, manholes, and flanged and threaded fittings. The coating closely follows all surface contours, including protrusions, as well as depressions and crevices which would not be practical to electroplate. It is dense and very hard, about 49 Rockwell C, and ductility is said by the producer to be good in proportion to the high hardness.

Some 200,000 mil ft<sup>2</sup> of coating has been produced to strict A.E.C. specifications in the last several months. Vessels to be coated inside are now conveniently used as self-containers for the plating

solution during processing, and tank facilities are being added as containers for outside and simultaneous inside and outside coating of vessels and tubes. American Locomotive expects the new process to extend the use of nickel coatings into types of equipment in chemical and electrochemical industries where it has not been used in the past.

### Stackpole Electronic Components Available

For the first time in 48 years of manufacturing, many favorite electronic components made by the Stackpole Carbon Company, St. Marys, Pa., will now be made available at attractive prices through selected electronic parts distributors all over the country.

Under a new policy outlined by company president Lyle G. Hall, "Stackpole is taking this step in order to better serve its many industrial and military customers who often find it convenient to purchase Stackpole components in quantities up to 1000 units and in recognition of the growing importance of the electronic parts distributor plays in the industrial market. Moreover, this move will enable service technicians for the first time to obtain for replacement uses the same high quality Stackpole components that have been first choice of leading set and equipment manufacturers since the 'knee pants' days of radio."

Stackpole fixed composition resistors will be available in 1/2-, 1-, and 2-watt sizes in all RETMA "preferred" values

with standard tolerances of 5, 10, and 20%. Electrical performance, dimensions, and color coding are designed to RETMA and military specifications.

Tiny, low-cost, Stackpole slide switches—widely used in many portable radios, appliances, toys, and small motors—will also be available in a variety of U.L. Approved 1-, 2-, and 3-pole types.

Also included in the Stackpole line for distributors will be a completely new series of "Engineered Economy" powdered iron cores. These easily stocked, "preferred-type" cores cover a big percentage of modern engineering requirements and have the advantage of low price because of their standardization.

A forthcoming Stackpole development includes replacement Add-a-shaft variable resistors (volume and tone controls, etc.). Plug-in shafts will enable service technicians to meet an extremely high percentage of all replacement needs with a modest stock of basic Stackpole variable resistor types.

The name and address of the nearest distributor stocking Stackpole electronic components is available on request to the Distributor's Division, Stackpole Carbon Company, 26 Rittenhouse Place, Ardmore, Pa.

### G. E. Increases Life of Coil Insulation

A completely new coil insulation with 50% longer life than conventional systems is now becoming available on General Electric induction motors of 100 to 3000 hp rating, according to the company's Medium Induction Motor Department. Described by G. E. engineers as the most significant development in form-wound insulation in 50 years, the new Polyex insulation increases dielectric strength by 50% and mechanical strength by 600%.

For the first time, the materials in an insulation system are natural insulators in themselves. Previous systems have had cotton or paper bases, which in themselves are not insulating materials.

Utilizing Mylar (DuPont trademark), Dacron, and synthetic hydrocarbon resin, Polyex insulation is the first complete change in large motor insulation since the turn of the century. At that time, the insulation acted only as a spacer to form a dielectric air space between coils. Later improvements included soaking the spacer material in linseed oil, adding insulating ma-

terials, and finally the development of cambic cloth, which still utilizes non-dielectric materials.

Heat aging tests of the new insulation show large increases in mechanical and dielectric strength. Resistance to contaminants, shown by salt water immersion tests, is at least twice that of conventional insulation.

In one of the most exacting tests, coil power factor of Polyex insulated coils was substantially lower than coils insulated by conventional systems, because of the tighter, more homogeneous character of the new insulation.

### Industrial Scientists Meet "Old Masters"

Rare paintings and engravings tracing the evolution of industrial science from the alchemist's household laboratory to the Atomic Age highlighted the open house held by Fisher Scientific Company on November 5, 1954, for 1500 researchers at the debut of the new Chicago plant.

Overnight, the huge office was turned into an art gallery, with velvet-hung aluminum walls erected where teletypes and desks had been shortly before; and on the walls were 100 pictures, from an old wood-cut of the father of alchemy "Wei Po-Yang" (142 A.D.) to the Curies, and finally an abstract painting by top abstractionist Russell Twiggs, "symbolizing the impersonality of quantum mathematics."

The alchemist portrayed in such great detail and diversity in the pictures of the Fisher Collection is of unusual interest to scientists because (a) he was the predecessor of today's highly-esteemed chemist and (b) his contribution to scientific knowledge laid the foundation of modern chemistry, pharmacology, and medicine.

Frequently the alchemist was employed by a government to produce gold—and thereby power for armies. To this end he used every conceivable means at his command. Sometimes he would "seed" the crucible with a real piece of gold in order to "attract" the precious metal. At other times, he performed his chemical operations and resorted to poetry, music, or religion as a "catalyst" hoping it would accelerate the desired reaction.

As Chester G. Fisher, Board Chairman of Fisher Scientific, pointed out to his "open house" guests, "Where the alchemist made only a good start, the modern scientist has succeeded. Today's chemist has 'transmuted' basic materials into the gold of commerce and, in fact, has

changed one element into another with the tremendous release of atomic energy. Furthermore, he has conquered disease to such an extent that Americans have a harbinger of a true Elixir of Life—their life span now exceeds the Biblical three score and ten."

The Fisher Collection of Alchemical and Historical Pictures has been gathered together from all parts of the world, principally Europe, by Mr. Fisher. Begun as a hobby more than 30 years ago, the Collection now is the largest of its kind in the world. It is often consulted by chemists, educators, and historians, and frequently is the source for textbook, historical, and commemorative illustrations.

The present Fisher Collection consists of about 40 oil paintings (some 300 years old), about 500 original engravings and etchings, and several hundred photographs and copies. It is on permanent display at the Company offices, 717 Forbes Street, Pittsburgh.

Forming a dramatic background for several hundred thousand dollars worth of Art was a modern version of Science, in the form of the technical service and demonstration laboratories of the new plant, where visitors saw the latest in electronic instrumentation; the 37,000 square-foot warehouse, so completely integrated by pneumatic and conveyor systems that ten men handle the stock of over 16,123 different items of apparatus and several thousand different reagent chemicals; and the modern office facilities.

As added dividends, the Company transplanted, intact from Pittsburgh, its "Pasteur Memorial U.S.A.," the largest collection of Pasteur portraits and manuscripts and original letters in this country, and the 18-ton Fisher Mobilab, a complete lab-on-wheels.

### New Olin Packaging Plant

Production of Olin polyethylene packaging film and tubing began late in November 1954 in a newly completed addition to the Pisgah Forest, N. C., plant of Ecusta Paper Corporation at which Olin cellophane is manufactured. Ecusta is a subsidiary of Olin Mathieson Chemical Corporation.

Simultaneously, production of the Olin Film Division's "Dura-clear" polyethylene by the Harwid Company plant at Cambridge, Mass., was discontinued.

The production of Olin polyethylene and cellophane at Pisgah Forest gives both films the advantage of the most

modern equipment, rigid quality control, and combines at one location the Olin Film Division's experience in the manufacture of the two packaging films.

### Neely Represents Sanborn Industrial Division on West Coast

Since October 1, 1954, the Industrial Division of Sanborn Company, Cambridge, Mass., manufacturers of oscillographic recording systems, has been represented by Neely Enterprises in California, Nevada, Arizona, and New Mexico.

Neely's main office is in Los Angeles with branches in San Francisco, Sacramento, San Diego, Phoenix, and Albuquerque.

### J. W. Gartland Awarded Certificate of Merit Posthumously

Joseph W. Gartland, long a member of the Cleveland Section of The Electrochemical Society, was posthumously awarded a Certificate of Merit in recognition of his outstanding work in the field of chemistry and also for his active participation in furthering the chemical profession. This award, which was accepted by Mrs. Gartland, was presented at the Sixth Annual Chemical Profession Dinner held on November 3, 1954. The Cleveland Section is one of six participating professional groups sponsoring this event which was attended by some 400 members of the chemical profession in Cleveland.

Speaker at the meeting was Mr. Ivor Griffith, President of the Philadelphia College of Pharmacy and Science. In his address, entitled "Live Long and Like It," Mr. Griffith pointed out the need for recreation, relaxation, and moderation, in addition to an active interest in a variety of endeavors.

Mr. Gartland's research contributions did much to advance the science underlying the manufacture of carbon and graphite products. Of particular importance were his discoveries of the profound influence of variations in types of raw materials on the properties of carbon and graphite electrodes for electrothermic applications. This work led to an extensive study, by x-ray diffraction techniques, of the crystal-line structure of carbonaceous materials and the degree of crystal ordering resulting from thermal treatments. The development of a practical laboratory carbon tube furnace for use at tempera-



tures up to 3000°C was a further result of these studies.

Mr. Gartland was an active and contributing member of his profession. As educational adviser for the Cleveland alumni organization of M.I.T., he devoted much of his time to the encouragement and guidance of young men interested in technical careers. He held memberships in the American Chemical Society, the American Petroleum Institute, the Society for Experimental Stress Analysis, and The Electrochemical Society. As a member of the local section of The Electrochemical Society, he did much to foster its development. He served on the Acheson Medal Committee and on many local section committees. He was chairman of the section in 1947-1948, and had recently been appointed Chairman of the Committee in Charge of the National Society Meeting to be held in Cleveland in the fall of 1956.

Joseph Gartland was always willing to share his wealth of experience in all phases of carbon technology. He was an inspiring guide to younger technical men working in this field, and his keen analysis of research problems was of inestimable value to all his associates.

---

## PERSONALS

---

FRANK H. RIDDLE, vice-president, Champion Spark Plug Company, Detroit, Mich., has been named the 1955 recipient of the Albert Victor Bleininger Award. The announcement was made at the December 10th meeting of the Pittsburgh Section of the American Ceramic Society. The award is the highest honor conferred in this country for distinguished achievement in the field of ceramics and is given annually by the Pittsburgh Section. The medal and scroll representing the award will be presented to Mr. Riddle at the Bleininger Award Dinner to be held in March at the Hotel Schenley, Pittsburgh.

CLYDE WILLIAMS, director, Battelle Memorial Institute, Columbus, Ohio, has been added to the Board of Governors of the International Science Foundation. The newly established International Science Foundation sponsors the operation of international science centers at the California Academy of Sciences and the New York Academy of Sciences. These centers provide facilities for visiting engineers

and scientists who desire to develop informal working relationships with professional personnel in the area they serve. Other centers are in the planning stage and will be activated as industry support becomes available.

ROBERT S. DALRYMPLE, formerly with the General Electric Company at Richland, Wash., has joined the staff of the Reynolds Aluminum Company in Louisville, Ky.

J. O'M. Bockris has informed us that S. E. EL WAKKAD, Reader in Chemistry at the University of Cairo, has recently taken up a research fellowship in the Chemistry Department of the University of Pennsylvania. Dr. El Wakkad has become well known recently for his outstanding work on the values of the electrode potentials of metals in equilibrium with their salts. By showing that the values generally accepted have been affected by the presence of oxide films, he has led to important revisions of these values which have a very general significance. Dr. El Wakkad has also carried out a large number of other studies on fundamental electrode processes and has published some 25 papers. It occurs to Dr. Bockris that a number of electrochemists in the United States might be eager to meet and talk to Dr. El Wakkad about his work, and it would be useful to them if they could know that he is available in Philadelphia. His research fellowship will keep him here until the end of August 1955.

---

## NEW MEMBERS

---

In December 1954 the following were approved for membership in The Electrochemical Society by the Membership Qualifications Committee:

### Active Members

PETER PAUL BENO, R. B. MacMullin Associates, Mail add: 130 Kelvin Dr., Buffalo 23, N. Y. (Industrial Electrolytic)

ALDO S. BERCHIELLI, Yardney Laboratories, Inc., Mail add: 192-10B-64th Ave., Fresh Meadows 65, N. Y. (Battery, Electrodeposition, Industrial Electrolytic, Theoretical Electrochemistry)

JAMES D. BUHLER, Kaiser Aluminum and Chemical Corp., Mail add: 1924 Broadway, Oakland, Calif. (Electro-

thermics and Metallurgy, Industrial Electrolytic)

JOHN CONVEY, Dept. of Mines & Technical Surveys, Canadian Govt., 568 Booth St., Ottawa, Canada (Electrothermics and Metallurgy)

CLYDE C. CUPPS, Standard Steel Spring Division, Rockwell Spring & Axle Co., Mail add: 43 Bridge St., Newton Falls, Ohio (Electrodeposition)

RONALD F. DICKERSON, Battelle Memorial Institute, 505 King Ave., Columbus, Ohio (Electrothermics and Metallurgy)

WILFRED GEORGE DICKS, Canadian Industries (1954) Ltd., Central Research Laboratories, McMasterville, Quebec, Canada (Industrial Electrolytic)

NICHOLAS FATICA, Harshaw Chemical Co., Mail add: 15709 Halliday Ave., Cleveland 10, Ohio (Electrodeposition)

RALPH M. FOEKING, National Carbon Company, Division of Union Carbide and Carbon Corp., 3709 Warren Rd., Cleveland 11, Ohio (Battery)

ROBERT GRAHAM, Shell Petroleum Co., Ltd., Thornton Research Centre, P.O. Box 1, Chester, England (Corrosion)

JACK HALPERN, Dept. of Metallurgy, University of British Columbia, Vancouver, B. C., Canada (Theoretical Electrochemistry)

WILLIAM HENRY HOWELL, Electric Storage Battery Co., Mail add: 98 Riverview Circle, Fairfield, Conn. (Battery)

MAX L. HOLLANDER, American Smelting and Refining Co., Mail add: 1338 E. 7th St., Plainfield, N. J. (Industrial Electrolytic)

HENRY FRANKLIN IVEY, Lamp Division, Westinghouse Electric Corp., Research Dept., Bloomfield, N. J. (Electronics)

JACOB HYNER, Whyco Chromium Co., Inc., Thomaston, Conn. (Electrodeposition)

MARK MARTIN JONES, University of Illinois, 353 Noyes Laboratory, Urbana, Ill. (Electrodeposition, Theoretical Electrochemistry)

RALPH W. KRUEGER, National Carbon Co., Mail add: 19733 Riverwood Ave., Rocky River, Ohio (Battery)

KARL E. KUNKEL, Niagara Alkali Co., Mail add: 55 Wallace Dr., Grand Island, N. Y. (Industrial Electrolytic)

GERARDO A. LORDI, General Electric Co., General Engineering Laboratory, Schenectady N. Y. (Electric Insulation, Electrodeposition)

## ECS Membership Statistics

The following two tables give breakdown of membership as of Jan. 1, 1955. July 1954 figures included delinquents; January 1, 1955 figures exclude them. The Secretary's Office feels that a regular accounting of membership will be very stimulating to membership committee activities. In Table I it should be noted that the totals appearing in

the right-hand column are *not* the sums of the figures in that line since members belong to more than one Division. But the totals listed are the total membership in each Section, with the exception that Sustaining Memberships are not broken down by Sections or Divisions. Since Sustaining Members are not broken down by Sections or Divisions, the total listed in Table I will be less than the total in Table II, the difference being the total number of Sustaining Memberships.

TABLE I. *ECS Membership by Sections and Divisions*

Section	Division												
	Battery	Corrosion	Electric Insulation	Electrodeposition	Electronics	Electro-Organic	Electrothermics & Met.	Industrial Electrolytics	Theoretical	No Division	Totals as of 1/1/55	Totals as of 7/1/54	Net Change
Chicago	10	31	33	47	11	8	9	8	18	10	102	104	-2
Cleveland	37	33	4	46	33	7	18	24	40	8	150	153	-3
Detroit	4	18	6	34	5	7	5	4	21	11	67	65	+2
India	4	1	1	9	2	3	3	9	5	4	23	33	-10
Midland	6	13	0	5	1	2	6	14	6	3	36	35	+1
New York	56	98	16	122	62	28	44	50	73	55	374	404	-30
Niagara Falls	5	17	0	15	2	6	40	38	11	13	105	109	-4
Pacific Northwest	5	11	0	6	1	2	4	12	9	5	29	31	-2
Philadelphia	17	26	6	34	38	16	16	13	43	23	144	153	-9
Pittsburgh	3	26	4	17	7	5	18	13	23	10	69	69	0
San Francisco	5	8	1	13	6	2	6	15	10	3	38	39	-1
Washington-Baltimore	34	35	11	30	15	3	12	11	27	9	104	99	+5
Ontario-Quebec	6	11	0	11	0	2	14	18	5	12	43		
U. S. Nonsection	65	150	24	154	77	54	88	95	134	78	581	622	-41
Foreign Nonsection	24	38	6	47	16	24	27	50	50	62	176	185	-9
Total as of 1/1/55	281	516	81	590	276	169	309	374	460	306	2041		
Total as of 7/1/54	299	533	88	621	299	178	326	397	478	318		2148	
Net Change	-18	-17	-7	-31	-23	-9	-17	-23	-18	-12			

CARL LAVERNE MCHATTIE, National Electric Products Corp., Mail add: 515 Burkhart Ave., Baden, Pa. (Electrodeposition)

GEORGE THEODORE MILLER, Hooker Electrochemical Co., Mail add: Jarrett Dr., Lewiston, N. Y. (Industrial Electrolytic)

GERALD LEROY MORAN, Sylvania Electric Products Inc., Towanda, Pa. (Electronics)

GLORIA S. MURPHY, Kaiser Aluminum & Chemical Corp., Dept. of Metallurgical Research, Spokane 69, Wash. (Theoretical Electrochemistry)

ERNEST PASKELL, Battelle Memorial Institute, 505 King Ave., Columbus, Ohio (Electronics)

R. V. PAULSON, Kaiser Aluminum & Chemical Corp., Dept. of Metallurgical Research, Spokane 69, Wash. (Theoretical Electrochemistry)

HENRY W. RAHN, Columbia-Southern Chemical Corp., Corpus Christie, Texas (Industrial Electrolytic)

WALTER EDWARD REID, JR., National Bureau of Standards, Mail add: Apt. 32, 4910 Ft. Totten Dr. N.E., Washington, D. C. (Electrodeposition)

HUGH F. SCHAEFER, National Carbon Co., Mail add: 1472 Cohasset Ave., Cleveland 7, Ohio (Battery)

PAUL FELIX GUSTAV SCHMIDT, Philco Corporation, Mail add: 5254 N. Howard St., Philadelphia 20, Pa. (Electrodeposition)

FRANK J. SEVERIN, Western Electric Co., Mail add: P.O. Box V, Salem Depot, N. H. (Electrodeposition)

N. R. SRINIVASAN, Indian Institute of Science, Dept. of Metallurgy, Bangalore 3, India (Corrosion, Industrial Electrolytic)

ROBERT ARTHUR STANFORTH, Monsanto Chemical Co., 710 N. Twelfth Blvd., St. Louis 1, Mo. (Electrothermics and Metallurgy)

JAMES BARRY TROUT, Navy Dept., Bureau of Ships, Mail add: 406 Plum St., Vienna, Va. (Battery)

RICHARD A. WILLIAMS, Philco Corp., Research Division, Mail add: 11 Harding Terrace, Collingswood, N. J. (Electrodeposition)

### Associate Member

ROBERT EDWIN DE LA RUE, JR., Stanford Research Institute, Mail add: 622 Enright Ave., Santa Clara, Calif. (Industrial Electrolytic)

### Student Associate Members

RALPH SHERMAN COOPER, Physics Dept., University of Illinois, Urbana,

### III. (Theoretical Electrochemistry)

ARTHUR CONSTANTINOS DOUMAS, Virginia Polytechnic Institute, Mail add: Box 3650, Virginia Tech Station, Blacksburg, Va. (Electrodeposition)

PAUL EDWIN GRUBB, Columbia University, Mail add: 39 Warner Ave., Jersey City 5, N. J.

HAROLD O. STRANGE, University of Pennsylvania, Harrison Laboratory, 34th & Spruce Sts., Philadelphia 4, Pa. (Theoretical Electrochemistry)

WATT W. WEBB, Massachusetts Institute of Technology, Room 8-111, Dept. of Metallurgy, Cambridge 39, Mass. (Theoretical Electrochemistry)

PERRY NIEL YOCUM, University of Illinois, Mail add: 606 W. Ohio St., Urbana, Ill. (Electric Insulation, Electronics, Industrial Electrolytic)

### Transfers to Active

LEE JOHN DROEGE, March Engineering Corp., Mail add: 7943 Haskell Ave.,

TABLE II. *ECS Membership by Grade*

	Total As of 7/1/54	Total As of 1/1/55	Net Change
Active	1895	1880	-6
Life	14	14	0
Emeritus	34	39	+5
Associate	73	63	-10
Student	37	31	-6
Honorary	5	5	0
Sustaining	103	100	-3
Total	2251	2141	-20

Van Nuys, Calif. (Corrosion, Electrodeposition, Theoretical Electrochemistry)

WOODWARD G. EICKE, JR., National Bureau of Standards, Mail add: 10212 Parkwood Dr., Kensington, Md. (Battery)

ARTHUR LAFOND GEARY, Metals Research Laboratories, Electro Metallurgical Co., Niagara Falls, N. Y.

(Corrosion, Theoretical Electrochemistry)

RICHARD LOWELL NOLDER, Kaiser Aluminum and Chemical Corp., Dept. of Metallurgical Research, Spokane 69, Wash. (Electrodeposition)

ARNOLD OTTO RATHJE, General Electric Co., Mail add: 834 Nelaview Ave., Cleveland Heights 12, Ohio (Electronics)

EDWARD V. RAYMOND, Metals Section, Transformer Laboratories, General Electric Co., Pittsfield, Mass. (Corrosion, Electrodeposition)

#### Active Reinstatement

CLAUDIUS NIELSEN, Nielco Laboratories, Mail add: P.O. Box 4703, Detroit 19, Mich. (Corrosion)

---

## MEETINGS OF OTHER ORGANIZATIONS

---

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS, including Institute of Metals Division, Conrad-Hilton Hotel, Chicago, Feb. 13-17.

TULSA SECTION, NATIONAL ASSOCIATION OF CORROSION ENGINEERS, Sixth Annual Corrosion Short Course for Pipeliners, Mayo Hotel, Feb. 16-18.

NATIONAL SOCIETY OF PROFESSIONAL ENGINEERS, annual spring meeting, Hotel Charlotte, Charlotte, N. C., Feb. 18-19.

JOINT WESTERN COMPUTER CONFERENCE AND EXHIBIT, sponsored by the IRE, AIEE, and Association for Computing Machinery, Statler Hotel, Los Angeles, March 1-3. For further information write to: William Gunning, Conference Secretary, International Telemetering Corp., 2000 Stoner Ave., Los Angeles 25, Calif.

CHEMICAL INSTITUTE OF CANADA, 5th Divisional Conference of the Chemical Engineering Division, Ottawa, Ont., March 7-9. One of the features will be a trip on March 9 to the Chalk River Plant of Atomic Energy of Canada Ltd. by a limited number of people. A security clearance is required of all taking the trip; all inquiries should be sent to: Dr. W. M. Campbell, Box 323, Deep River, Ontario.

NATIONAL ASSOCIATION OF CORROSION ENGINEERS, Eleventh Annual Conference and Exhibition, Palmer House, Chicago, March 7-11.

AIEE, Electrical Utilization of Aluminum Conference, William Penn Hotel, Pittsburgh, March 15-17.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, Louisville, Ky., March 20-23.

AIEE, Materials Handling Conference, Hotel Cleveland, Cleveland, March 28-29.

AMERICAN SOCIETY FOR METALS, Western Metal Congress and Exposition, Los Angeles, March 28-April 1.

AMERICAN ASSOCIATION OF SPECTROGRAPHERS is planning its 6th Annual Conference in Chicago, May 6, on the subject "Industrial Applications of Spectroscopy." Contributed papers in the fields of Emission, X-Ray Fluorescence, or Absorption Spectroscopy as applied to industry are invited. *Abstracts must be submitted by March 1, 1955.* Please address all inquiries to: F. E. Stedman or E. E. Stilson, Co-Chairmen, Engineering Research Laboratory, Bendix Products Division, Bendix Aviation Corp., 401 North Bendix Drive, South Bend 20, Ind.

AIEE, Committee on Technical Operations, Southern District Meeting, St. Petersburg, Fla., April 13-15.

---

## LETTERS TO THE EDITOR

---

Dear Sir:

Congratulations on your editorial on "The Crisis in Science Teaching" in the November 1954 JOURNAL. Good work.

HUGH S. TAYLOR  
Princeton, N. J.

Dear Sir:

Your editorial in the November 1954 issue of the JOURNAL touches on a timely and important topic.

I have felt for a long time that industrial laboratories, as well as technical societies, have a responsibility to discharge, i.e., that of helping to develop interest in careers in science in the minds

of school children, both elementary and secondary. To start my own laboratory along these lines on a continuing basis, I have sent copies of your editorial to my boss and several of my colleagues with the suggestion that we consider ways of implementing some of your suggestions. Should anything come of it, I will inform you.

H. BANDES  
Flushing, N. Y.

Dear Sir:

I enjoyed your fine editorial on "The Crisis in Science Teaching" in the November 1954 JOURNAL. In your position as Chairman of the Editorial Staff, you have certainly done a distinguished job in giving the Journal the proper tone, and we all are certainly indebted to you for the trouble and care which you take in your editorials.

ALLAN T. GWATHMEY  
Charlottesville, Va.

Dear Sir:

As usual, your editorials are a gem of clear thinking on a timely subject. I have reference to your editorial on "The Crisis in Science Teaching" in the November 1954 JOURNAL.

If our societies would properly investigate and appraise the condition of the teaching profession and advise the schools of the proper qualifications for science teachers, they would do the schools an immeasurable amount of good. We set our standards high for new members of our societies and it seems to me that many of the teachers of science in secondary schools would be unable to meet these requirements.

Our societies have a degree of responsibility in informing the schools as to what is expected of them in the education of the students, especially where the caliber of the teachers is involved.

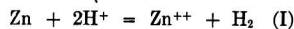
H. ROBERT SCHOENFELDT  
Cleveland, Ohio

### Oxidation Affinities, Reduction Affinities, and Electrode Potentials

Dear Sir:

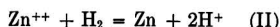
The recent Letter to the Editor by A. J. de Béthune<sup>1</sup> offers a method of establishing potential values with the so-called "European" signs from the free enthalpy changes of reactions such as

<sup>1</sup> A. J. DE BÉTHUNE, *This Journal*, 101, 252C (1954).



through the simple device of dividing these free enthalpy changes by the charge transferred by the reaction, i.e., two Faradays in the above case. The method, however, does not explain that these potentials with European signs give the correct polarity of the electrodes versus the hydrogen electrode.

If we consider the  $-\Delta G$  (using the recommended notation  $G$  for free enthalpy and thereby avoiding confusion with the Faraday  $F$ ) of reaction (I) as the De Donder affinity<sup>2</sup>  $A_{\text{oxid}}$  of this oxidation reaction of Zn by  $\text{H}^+$ , division of  $A_{\text{oxid}}$  by the reaction charge gives a potential with the so-called "American" sign or an "oxidation potential." Conversely, the affinity  $A_{\text{red}}$  of the reduction of  $\text{Zn}^{++}$  by  $\text{H}_2$ :



divided by the reaction charge will give a potential with the "European" sign or a "reduction potential." Oxidation potentials are thus oxidation affinities by  $\text{H}^+$  per Faraday and reduction potentials are reduction affinities by  $\text{H}_2$  per Faraday. That the latter potentials have the correct signs to determine the polarity of the corresponding electrodes vs. the hydrogen electrode and vs. one another is easily seen on the basis of the fact that an electrode at which reduction occurs must receive electrons from the outside circuit, the positive current thus leaving this electrode as it enters the outside circuit.

When the cell corresponding to reactions (I) or (II) is balanced by means of a suitable potentiometric circuit, we have the electrochemical equilibrium condition

$$A_{\text{oxid}} + 2F(\varphi_{\text{Zn}} - \varphi_{\text{Pt}}) = 0 \quad (\text{III})$$

or, alternatively,

$$A_{\text{red}} + 2F(\varphi_{\text{Pt}} - \varphi_{\text{Zn}}) = 0 \quad (\text{IV})$$

formulas in which  $\varphi_{\text{Zn}}$  and  $\varphi_{\text{Pt}}$  are the electric potentials of the leads (both of copper, for instance) connected with, respectively, the zinc and the hydrogen electrode. We easily find

$$\varphi_{\text{Zn}} - \varphi_{\text{Pt}} = -\frac{A_{\text{oxid}}}{2F} = +\frac{A_{\text{red}}}{2F} \quad (\text{V})$$

At the 1953 meeting of the International Union of Pure and Applied

<sup>2</sup> TH. DE DONDER AND P. VAN RYSELBERGHE, "Thermodynamic Theory of Affinity," Stanford University Press (1936).

## Members: Please Check Your Code Numbers

JOURNAL mailing wrappers are now being addressed at Society Headquarters. The code number appears at the right of your name and address.

Please check the wrapper to be sure your code is correct. For instance, 6 B

means Active Member, New York Section, Corrosion Division.

A complete explanation of the code is printed below. In order to keep the records up to date, members are kindly requested to check the code numbers on recent mail from the Society and, if incorrect, please send the corrected code number to The Electrochemical Society, Inc., 216 West 102nd Street, New York 25, N. Y.

Membership Classifications	SECTIONS		Division Classification
	No.	City	
1 Active Member	1	Chicago	A Battery
2 Honorary	2	Cleveland	B Corrosion
3 Sustaining	3	Detroit	C Electric Insulation
4 Associate Member	4	India	D Electrodeposition
5 Student Associate	5	Midland	E Electronics
6 Subscriber	6	New York	F Electro-Organic
7 Emeritus	7	Niagara Falls	G Electrothermics and Metallurgy
8 Life	8	Pacific Northwest	H Industrial Electrolytic
9 D. B. G.	9	Philadelphia	I Theoretical Electrochemistry
10 Faraday	10	Pittsburgh	
	11	San Francisco	
	12	Washington-Baltimore	
	13	Ontario-Quebec	
	—	No Section	

Chemistry in Stockholm<sup>3</sup> the recommendation was made that the differences  $\varphi_{\text{Zn}} - \varphi_{\text{Pt}}$ , i.e., our reduction affinities per Faraday, could be called *relative electrode potentials* (or, in abbreviated form, *electrode potentials*), but that the differences  $\varphi_{\text{Pt}} - \varphi_{\text{Zn}}$ , i.e., our oxidation affinities per Faraday, should not be called electrode potentials.

If we consider the ratio  $A_{\text{oxid}}/2F$  as the electromotive force of the cell reaction, we see that the relative electrode potential of the zinc electrode is equal to minus this electromotive force. The state of electrochemical equilibrium thus appears as one of balance between a chemical force (electromotive force or oxidation potential or oxidation affinity per Faraday) and an electric force (relative electrode potential). In French and German one would say that chemical and electric tensions balance each other.

<sup>3</sup> J. A. CHRISTIANSEN AND M. POURBAIX, "Conventions concerning the signs of electromotive forces and electrode potentials" in "Comptes Rendus de la dix-septième conférence" of IUPAC, Paris, Maison de la Chimie, pp. 82-84 (1954).

These considerations are similar to those of MacDougall.<sup>4</sup> This and connected matters are thoroughly discussed in a series of reports of the Commission of Electrochemical Nomenclature and Definitions of the International Committee of Electrochemical Thermodynamics and Kinetics (CITCE).<sup>5</sup>

It is to be hoped that the regrettable confusion which has existed in this field for so long and has uselessly irritated so many chemists will soon be a matter of mere historical interest.

PIERRE VAN RYSELBERGHE  
Department of Chemistry  
University of Oregon  
Eugene, Ore.

<sup>4</sup> F. H. MACDOUGALL, "Physical Chemistry," 3rd ed., Chapter XVIII, pp. 575-641, Macmillan Co., New York (1952).

<sup>5</sup> P. VAN RYSELBERGHE, Comité international. thermodynam. et cinét. électrochim., Compt. rend. réunion 1950, 287 (1951), and Compt. rend. réunion 1951, 409 (1952).

P. VAN RYSELBERGHE, *Z. Elektrochem.*, **58**, 530 (1954).

## RECENT PATENTS

Selected by Fred. W. Dodson, Chairman of the Patent Committee, from the Official Gazette.

November 2, 1954

- Snavely, C. A., Faust, C. L., and Bride, J. E., 2,693,444, Electrodeposition of Chromium and Alloys Thereof  
 Howell, W. N., and Hill, H., 2,693,445, Electrolytic Method for Production of Fluorine  
 Van Krevelen, D. W., 2,693,446, Process for the Elimination of Oxygen from Gases  
 Penberthy, H. L., 2,693,498, Electrode Assembly for Glass Furnaces  
 Neumann, G., 2,693,499, Storage Battery Cell

November 9, 1954

- Reschan, R. R., and Krieg, A., 2,694,017, Process of Chemical Nickel Plating of Aluminum and Its Alloys and Baths Therefor  
 Gutzeit, G., 2,694,019, Processes of Chemical Nickel Plating and Baths Therefor  
 Davis, G. W., and Waltz, M. C., 2,694,040, Methods of Selectively Plating *p*-Type Material of a Semiconductor Containing a *p-n* Junction  
 Brown, H., 2,694,041, Electrodeposition of Nickel  
 Collin, F. C., 2,694,097, Electric Smelting Equipment and Method of Using Same  
 Leins, O. J., 2,694,098, Thermoelectric Generator and Method for Production of Same  
 Zahn, H. E., 2,694,099, Lead-Acid Battery Grid  
 Zahn, H. E., 2,694,100, Alkaline Battery Grid

November 16, 1954

- Tanczyn, H., 2,694,626, Stainless Steels  
 Ostrow, B. D., 2,694,677, Bright Copper Plating Bath  
 McLeod, H. G., and Wernlund, C. J., 2,694,678, Electropolishing Process and Composition  
 Holland, A. J., Boxer, G. E., and Rickards, J. C., 2,694,679, Preparing Vitamin B<sub>12</sub> Analogs  
 Katz, W. E., and Rosenberg, N. W., 2,694,680, Transfer of Electrolytes in Solution  
 Lang, K. A., 2,694,740, Pot Type Furnace for Molten Metal

## Support Our Advertisers

Since advertisers in the JOURNAL are investing money in our publication, members of the Society have a great opportunity to cooperate in the mutual success of the project. For instance, Society members buy large quantities of products, instruments, and equipment. Whenever an advertiser's products meet company specifications, readers are urged to give preference in their purchases to JOURNAL advertisers.

Rice, E. E., and Foley, M. J., 2,694,741, Electrically Heated Annealing Furnace Base

- ✓ Harding, M. S., 2,694,742, Battery  
 ✓ Ruskin, S. L., and Bakst, A., 2,694,743, Polystyrene Grid and Separator for Electric Batteries  
 ✓ Tamburini, B., 2,694,744, Process for Making Separators for Electric Storage Batteries and Product Obtained Thereby  
 ✓ Kennedy, H. A., and Remus, F., 2,694,745, Storage Battery  
 ✓ Evers, B. C., 2,694,746, Battery Contact Support

November 23, 1954

- Peck, A. C., and Thompson, W. S., 2,695,216, Method of Operating a Nitrogen Fixation Furnace  
 Sheridan, C. M., and Benzer, W. C., 2,695,229, Chrome-Nickel Hardenable Stainless Steel  
 Wright, C. A. H., 2,695,268, Process for the Concentration of Isotopes  
 De Witz, A. E. E., and Roy, F. P., 2,695,269, Apparatus for Electroplating Wire  
 Mayer, S. E., and Sterling, H. F., 2,695,380, Electric Current Rectifier

November 30, 1954

- Espy, R. H., 2,695,872, Electrolytic Polishing Method  
 Loverde, A., 2,695,873, Process for Chlorinating Methyl Aromatic Compounds  
 Zdansky, E. A., 2,695,874, Pressure Regulating Device for Electrolytic Gas Generating Diaphragm Cells

Matejka, J., 2,695,922, Carbon Depositing Furnace

## ANNOUNCEMENT FROM PUBLISHER

NUCLEAR GEOLOGY edited by Henry Faul. Published by John Wiley & Sons, 1954. 414 pages, \$7.00.

Subtitled "A Symposium of Nuclear Phenomena in the Earth Sciences," the book covers questions of theory, methods, and latest developments.

## BOOK REVIEWS

STATISTICAL ANALYSIS IN CHEMISTRY AND THE CHEMICAL INDUSTRY by C. A. Bennett and N. L. Franklin. Published by John Wiley & Sons, Inc., New York, and Chapman and Hall, Ltd., London, 1954. 724 pages, \$8.00.

Under the aegis of the Committee on Applied Mathematical Statistics of the National Research Council, this comprehensive book on modern statistics was written with the examples chosen from the several branches of chemistry. The level of mathematical sophistication was deliberately equated to the general level of a graduate chemist or engineer. As a single volume this book succeeds quite well in so present-

ing basic fundamental theory, formal methods of analysis of data, and appropriate scheduling of experiments that the professional should be able to use the statistical approach to research or production.

The basic theory is presented in the first five chapters. The next four chapters are devoted to the statistical design of an experiment and the analysis of data resulting therefrom. Chapter Ten treats control charts not only from the production aspect but also as an analytical tool for the researcher. The

final chapter treats of several techniques for examining admissibility of data.

Undoubtedly this volume will become a standard reference book as it is exceedingly well written as to methodology. It is unfortunate that not all the confusing notation has been expunged and that the mathematics is overcumbersome. The chapter on control charts seems to suffer from a failure either to introduce the midrange and median or to discuss chart analysis of data from complex experiments. The treatment of tolerance limits, components of

variance, and multiple comparisons leaves much to be desired.

However, in the main, solutions are given to the most vexing statistics problems of the chemist.

M. E. TERRY

**NEW INSTRUMENTAL METHODS IN ELECTROCHEMISTRY** by Paul Delahay. Published by Interscience Publishers, Inc., New York, 1954. xvii + 437 pages, \$11.50.

Since the end of World War II, a new approach to the study of electrochemical processes has been developed by making use of constant potential or constant current techniques. The literature in this field has grown to the extent that a comprehensive and critical review is needed. Dr. Delahay's book has fulfilled this need and, as he is one of the leading workers in this field of electrochemistry, he is well qualified to prepare such a monograph.

The book is divided into four parts. Part one, entitled "Voltammetric and Related Methods," embodies the principal part of the book. Chapter one introduces the subsequent subject matter with an excellent review of electrochemical methods. Voltammetry is concerned with the study of the current-voltage characteristics of an electrochemical cell and one distinguishes between voltammetry at controlled potential and voltammetry at controlled current. Polarography is an example of voltammetry at a controlled potential. Potential-time curves obtained at a controlled current have applications in chemical analysis and also in the study of electrochemical kinetics. Each chapter is introduced with a theoretical analysis of the electrochemical process under consideration. Mathematical details are omitted in case of boundary value problems because of the limited interest to chemists. Solutions of some of the boundary value problems, however, are given in an appendix.

Part Two deals with coulometry, electrolysis at controlled potential, and related methods. The subject matter is of interest to analytical chemists primarily; however several physicochemical applications are cited as well.

Part Three is devoted to high-frequency methods of analysis and was written by Dr. C. N. Reilley. While this topic is timely and represents a new instrumental method in electrochemistry in keeping with the title of the book, it seems out of place in a

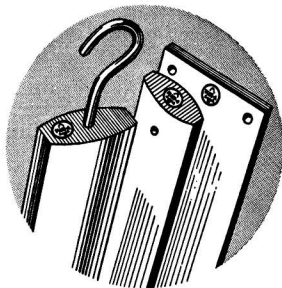
# NOW! GET 10% TO 15% MORE ANODE MILEAGE WITH . . .

**NEW ANACONDA**

## "PLUS-4" ANODES\*

(PHOSPHORIZED COPPER)

- + 1 Freedom from anode sludge—no "bagging" or diaphragms required.
- + 2 No copper build-up in solution.
- + 3 Exceptionally smooth, heavy cathode deposits.
- + 4 10% to 15% more cathode deposits per pound of anode.



It has been discovered that carefully controlled amounts of phosphorus, together with minute amounts of other elements in electrolytic copper, make anodes of vastly superior quality for acid plating. ANACONDA "PLUS-4" Anodes are available in all the standard sizes and forms at no increase in cost over ordinary anodes. Look for the stamp "PLUS-4" on the anodes you buy.

We'll be glad to supply additional information, in detail, without obligation. Just write to: The American Brass Company, Waterbury 20, Connecticut.

\*For use under Patent No. 2,689,216

54156

**ANACONDA®** "PLUS-4" ANODES  
made by THE AMERICAN BRASS COMPANY

monograph concerned primarily with voltammetry and coulometry. The principal advantage of the high-frequency method is that conductometric titrations may be made with the electrodes outside the cell. This "electrodeless" type of analysis can be of the condenser type or the coil type. More information is available on the former.

"Instrumentation" is the title of Part Four. It discusses the apparatus used in all phases of voltammetry and coulometry. The book is similar in many respects to a recent book by J. J. Lingane entitled "Electroanalytical Chemistry," also published by Interscience Publishers, Inc. While Dr. Lingane's book is more complete in its discussion of instrumental apparatus it is written primarily for the analytical chemist. Dr. Delahay's discussion of the instrumental methods is quite adequate, however, even though it was purposely limited. He has sought to describe these instruments in terms that are understandable to chemists with no special training in electronics. Block diagrams are used to a large extent.

The book includes two appendixes, an author and a subject index, and a good number of illustrations and references. It represents an invaluable source book to everyone concerned with electrochemistry or electrochemical methods.

D. R. TURNER

## LITERATURE FROM INDUSTRY

**INSULATED "ALLIGATOR" ELECTRIC TEST CLIPS.** Circular describes and illustrates the free, uninhibited use in compacted equipment of new Mueller Insulated Alligator test clips, made possible by their slim shape and complete covering of high dielectric vinyl. It shows how "lip action" of slotted insulator permits clip to "bite" terminal without exposing metal clip. Mueller Electric Co. P-266

**PLASTIC COATINGS.** A basic technique manual for spraying Cocoon® plastic coatings is offered. The main subjects of the booklet include discussions of the spray gun, air pressures, width of spray fan, thickness of film, number of coats, spraying technique, direction of spray, motion of the spray gun, and general suggestions. Cocoon is a sprayable vinyl plastic consisting

of a synthetic resin combination carried in volatile solvents. The manual reviews the various methods of spraying and their effects on Cocoon coatings. R. M. Hollingshead Corp. P-267

**POROUS FLUOROCARBON FILTER.** Properties of Porous "Kel-F" plastic, design and performance data on complete filters equipped with this new filter media, are now available. Porous fluorocarbon plastics with controlled porosity are produced by the company's exclusive process and fabricated into filters with extreme chemical resistance. The new brochure describes several basic types of newly developed filters, gives data on pore size, particle size removal, and flow capacity. In addition to data on porous fluorocarbon media and filters, information is presented on the company's engineering and application services and other plastics in controlled porosity form. Porous Plastic Filter Co. P-268

**MOLYBDENUM COMPOUNDS.** New technical bulletin collects and summarizes thermodynamic values for molybdenum and its more important compounds. It is based on a search of the literature (including the reports of original in-

vestigations as well as compilations of data) for the last 20 years. This should assure virtually complete coverage of all available, pertinent data. Copies available on request. Climax Molybdenum Co. P-269

**POROUS STAINLESS STEEL, ALLOYS.** Types, performance, and application data for stainless steel and other metals with controlled porosity are now available in a new brochure. Properties of available porous metals, including Type 304 and 316 stainless steels, nickel, monel, stellites, and other alloys are presented in the new 45-page booklet. Included also are data on the various porous stainless steel filter elements and containers—some with filter areas up to 1000 square feet—and their laboratory- and plant-scale application. Eight types of complete filter units for immediate pipeline service are described. Design and engineering services offered by the company in the application of these unique materials are outlined. Micro Metallic Corp. P-270

**"ALODINE" 1000.** Illustrated folder describes "Alodine" 1000, the new finish which provides invisible protection for aluminum and its alloys. The

## A CAREER OPPORTUNITY

with

# DU PONT

For an Experienced

## Engineering Materials Engineer

A unique career opportunity is now available in our Engineering Department to a graduate metallurgist or metallurgical engineer (advanced degree desirable) whose education included a minor in physical chemistry, engineering materials, or corrosion engineering. Experience should include evaluation, selection, specification, and use of materials of construction, both metallic and non-metallic, for process equipment. This should include both corrosion properties and fabrication procedures, including forming, welding, stress relieving, heat treating, and inspection.

The successful applicant will provide consulting service to operating plants and to the Engineering Department on problems in the above engineering materials fields. Problems in plant operations will include evaluation of performance of materials in process equipment to prevent product contamination and to reduce maintenance to a minimum. This provides an extremely wide field of application in a great variety of processes.

Please send complete resume, including details of education and experience, to:

Mr. J. C. Costello, Jr.

Engineering Dept., Personnel Section

## E. I. du Pont de Nemours & Co., Inc.

Wilmington 98 Delaware

following are some of the typical surface characteristics of aluminum Alodized with "Alodine" No. 1000: composition—amorphous, mixed metallic oxides and chromates; color—invisible, no change in appearance of the metal; thickness—not measurable; weight—less than 10 mg/ft<sup>2</sup>; solubility—in-soluble in alcohol, water, solvents, gasoline, and other petroleum products, soluble in strong alkalis and acids; electrical properties—surface is electrically conductive and can be welded; heat stability—unaffected at moderate temperatures, corrosion resistance lowered by long exposure to high temperatures. American Chemical Paint Co.

P-271

**COLEMAN TOOLS FOR SCIENCE.** New manual brings together the pertinent facts about the modern instruments and accessories offered by Coleman Instruments Inc., along with brief discussions of the analytical sciences which they serve. The purpose of the manual is to acquaint the reader with Coleman products, their characteristics, and their particular merits. For clarification and easy reference, instrument descriptions are grouped in accordance with the analytical systems to which they are applied. A bibliography of textbooks giving more complete information on analytical principles appears at the back of the book. Coleman Instruments Inc.

P-272

---

## NEW PRODUCTS

---

**CORROSION RESISTANT PRIMER.** Lock-Prime, a corrosion resistant liquid primer for new or corroded steel surfaces, has been developed. "Applied by brush or roller directly from the can, Lock-Prime offers excellent resistance to under-cutting by corrosion when cover coats are mechanically damaged." On either sandblasted new steel or wire-brushed rusted steel, Lock-Prime forms a tight adherent bond to the surface and provides excellent adhesion for

To receive further information on any New Product or Literature from Industry listed above, send inquiry, with key number, to JOURNAL of The Electrochemical Society, 216 West 102nd Street, New York 25, N. Y.

Please print your name and address plainly.

following top coats of Pennsalt NeoCoat (liquid neoprene) or Pennsalt Thick-coat, a chlorinated aliphatic hydrocarbon. Equally effective in acidic and organic atmospheres. Applicable to all ferrous metal surfaces. Specifications and directions upon request. Pennsylvania Salt Manufacturing Co. N-141

**ANTI-STATIC AGENT.** A new anti-static agent called Cationic SP (stearamidopropyl dimethyl -  $\beta$  - hydroxyethyl ammonium phosphate) has been announced. Small amounts will effectively control static charge accumulation on a wide variety of materials such as textiles, plastics, paper, waxes, and polishes. It can be applied externally to textile fabrics by brush, pad, or spray of dilute aqueous solution, or incorporated into the rinse water after washing. Inclusion of Cationic SP in textile lubricants, such as coning oils, helps keep fibers static free during processing. Permanent static control of plastics is accomplished by adding Cationic SP to the resin before molding, or including it in the emulsion or slurry polymerization recipe. Samples and technical data available on a 35% solution of Cationic SP in an isopropanol-water mixture. American Cyanamid Co.

N-142

**VOLTAGE REGULATED D-C POWER SUPPLY.** Economical, voltage regulated, d-c power supply has been designed for general laboratory and production line use and to provide power for low voltage klystrons. Designated PRD Type 807, it features a wider than usual output range with a B supply ranging from 0 to +600 v, 0 to 200 ma, and a C supply from 0 to -250 v, 0 to 5 ma. It offers an additional fixed voltage of -250 v, 0 to 50 ma, derived from the C supply, and an unregulated 6.3 v, 10 amp, center tapped, filament supply. It will provide klystrons with up to -600 v cathode voltage and an additional 0 to -250 v for the reflector. Higher voltages may be obtained through "stacking" two or more units because none of the supply voltages are grounded to the chassis. Polytechnic Research & Development Co., Inc.

N-143

**PORCELAIN SUPPORT STAND.** For chemists engaged in one-burette titrations with hard-to-see, fugitive end-points, Fisher has a sparkling white porcelain support stand designed especially for their needs. The new square (9 in. x 9 in.) stand is an ideal background for viewing the first fleeting

---

## ADVERTISERS' INDEX

American Brass Company . . . .	46C
Enthone, Incorporated . . . .	Cover 4
Fisher Scientific Company . . . .	26C
Great Lakes Carbon Corporation . . . . .	Cover 2
National Carbon Company . . . .	31C
Rapid Electric Company . . . .	29C
E. H. Sargent & Company . . . .	28C
Stackpole Carbon Company . . . .	30C
Sylvania Electric Products Inc. . . .	27C
Weston Electrical Instrument Corporation . . . . .	32C
John Wiley & Sons, Inc. . . . .	34C

---

change in an indicator. In addition, the new square unit offers ample space for aluminum support rod to front, for convenient single titrations. There are almost 7 inches between the aluminum rod and the front of the base; there is now no danger of a vessel's teetering on the rim of the titration stand. The square shape and concentration of weight in the base give the stand greater stability than before: the center of gravity of the load is directly over the middle. Fisher Scientific Co. N-144

---

## EMPLOYMENT SITUATIONS

---

Please address replies to box shown, % The Electrochemical Society, Inc., 216 W. 102nd St., New York 25, N. Y.

### Position Wanted

CHEMIST, 36, experienced in batteries, electroplating, general physical and chemical commercial testing, seeks South Jersey position. *Reply to Box 356.*

### Positions Available

METALLURGICAL CHEMIST, ELECTROCHEMIST, ANALYTICAL CHEMIST. Un-usual opportunities for men with graduate training and experience qualifying them to do research on the chemistry and metallurgy of Nickel and Cobalt. The program includes the hydrometallurgical extraction and refining of these metals, and the development of related analytical methods. Send full resume, salary, to: Director, Research and Development Division, Nickel Processing Corporation, Subsidiary of National Lead Company, 4 Cherry Street, Montclair, New Jersey.





# The Electrochemical Society

## INSTRUCTIONS TO AUTHORS OF PAPERS

Address all correspondence to the Editor,  
JOURNAL OF THE ELECTROCHEMICAL SOCIETY,  
216 W. 102nd St., New York 25, N. Y.

FORM

**Manuscripts** submitted for publication should be in triplicate to expedite review. They should be typewritten, double-spaced, with 2½–4 cm (1–1½ in.) margins.

**Title** should be brief, followed by the author's name and his business or university connection.

**Abstract** of about 100 words should state the scope of the paper and give a brief summary of results.

ILLUSTRATIONS

**Drawings** will be reduced to column width, 8 cm (3½ in.), and after reduction should have lettering at least 0.15 cm (⅙ in.) high. Original drawings in India ink on tracing cloth or white paper are preferred. Curves may be drawn on coordinate paper only if the paper is ruled in blue. All lettering must be of lettering-guide quality. See sample drawing on reverse page.

**Photographs** must be glossy prints and mounted flat.

**Captions** for all figures must be included on a separate sheet. Captions and figure numbers should not appear in the body of the figure.

**General**—Figures should be used only when necessary. Omit drawings or photographs of familiar equipment. Figures from other publications are to be used only when the publication is not readily available, and should always be accompanied with written permission for reprinting.

REFERENCES

Literature and patent references should be listed at the end of the paper on a separate sheet, in the order in which they are cited. They should be given in the style adopted by *Chemical Abstracts*. For example:

R. Freas, *Trans. Electrochem. Soc.*, **40**, 109 (1921).

H. T. S. Britton, "Hydrogen Ions," Vol. **1**, p. 309, D. Van Nostrand Co., New York (1943).

H. F. Weiss (To Wood Conversion Co.), U. S. Pat. 1,695,445, Dec. 18, 1928.

UNITS OF MEASUREMENT

Metric units should be used throughout but, where desirable, English units may be given in parentheses.

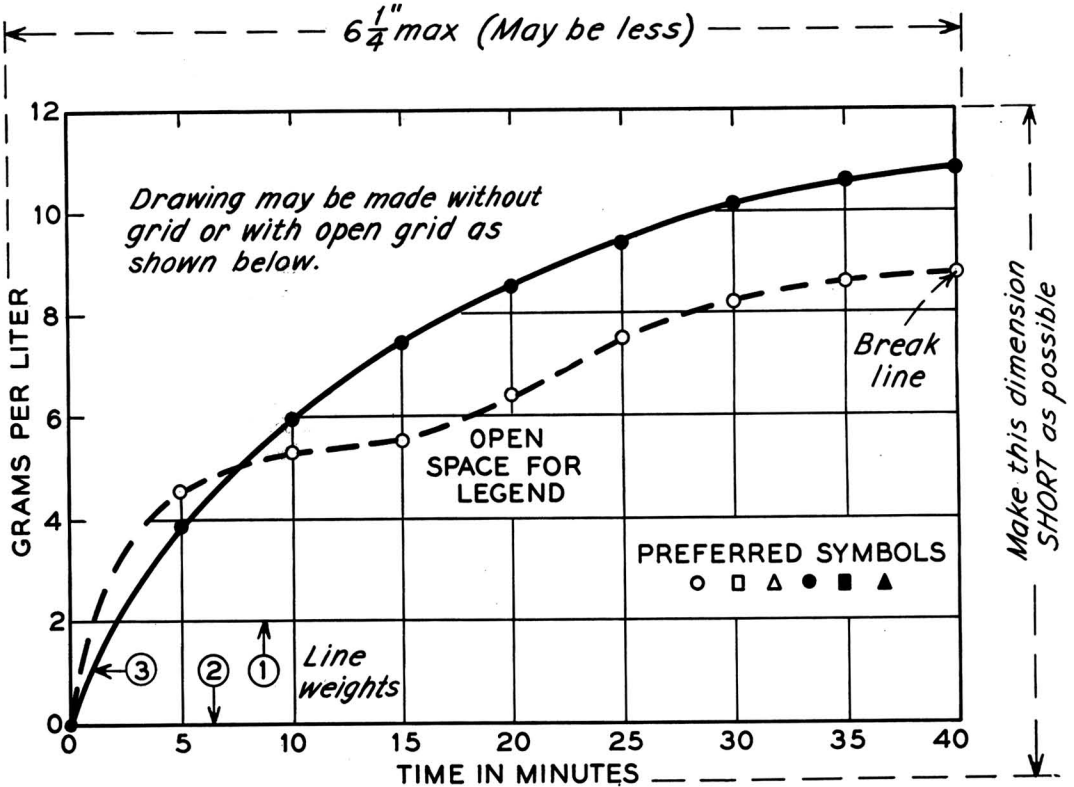
Corrosion rates in the metric system should preferably be expressed as milligrams per square decimeter per day (mdd), and in the English system as inches penetration per year (ipy).

As regards algebraic signs of potentials, the standard electrode potential for  $\text{Zn} \rightarrow \text{Zn}^{++} + 2e$  is negative; for  $\text{Cu} \rightarrow \text{Cu}^{++} + 2e$ , positive.

Abbreviations should conform with the American Standards Association's list of "Abbreviations for Scientific and Engineering Terms."

Authors should be as brief as is consistent with clarity, and must omit all material which can be regarded as familiar to specialists in the particular field.

The use of proprietary names, trade-marks, and trade names should be avoided if possible. If used, these should be capitalized so that the owner's legal rights are not jeopardized.



Remarks: Line weight ② is used for borders and zero lines. When several curves are shown, each may be numbered and described in the caption. Lettering is approx.  $\frac{1}{8}''$ .

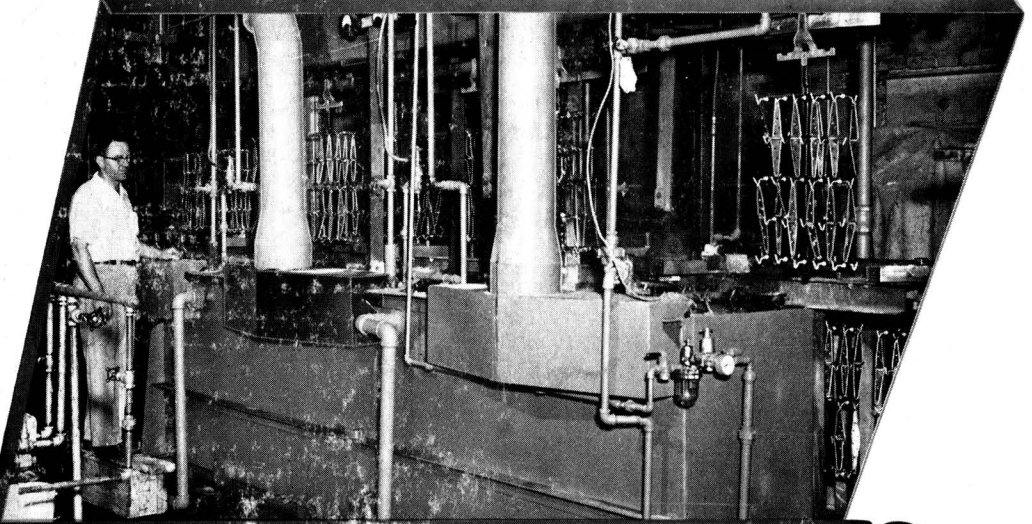
SAMPLE CURVE DRAWING FOR REDUCTION TO  $\frac{1}{2}$  SIZE

# Sustaining Members of The Electrochemical Society

- Air Reduction Company, Inc., New York, N. Y.  
Ajax Electro Metallurgical Corporation, Philadelphia, Pa.  
Alloy Steel Products Company, Inc., Linden, N. J.  
Aluminum Company of America, New Kensington, Pa.  
Aluminum Company of Canada, Ltd., Montreal, Canada  
American Machine & Foundry Co., Raleigh, N. C.  
American Platinum Works, Newark, N. J. (2 memberships)  
American Potash & Chemical Corp., Los Angeles, Calif.  
American Zinc, Lead and Smelting Company, St. Louis, Mo.  
Armour Research Foundation, Chicago, Ill.  
Auto City Plating Company Foundation, Detroit, Mich.  
Bart Manufacturing Company, Bellville, N. J.  
Bell Telephone Laboratories, Inc., New York, N. Y.  
Bethlehem Steel Company, Bethlehem, Pa. (2 memberships)  
Buffalo Electro-Chemical Company, Buffalo, N. Y.  
Burgess Battery Company, Freeport, Ill. (4 memberships)  
Canadian Industries Limited, Montreal, Canada  
Chrysler Corporation, Detroit, Mich.  
Columbia-Southern Chemical Corporation, Pittsburgh, Pa.  
Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B.C. (2 memberships)  
Corning Glass Works, Corning, N. Y.  
Crane Company, Chicago, Ill.  
Diamond Alkali Company, Pittsburgh, Pa. (2 memberships)  
Dow Chemical Company, Midland, Mich.  
Wilbur B. Driver Company, Newark, N. J.  
E. I. du Pont de Nemours & Company, Inc., Wilmington, Del.  
Eagle-Picher Company, Joplin, Mo.  
Eaton Manufacturing Company, Stamping Div., Cleveland, Ohio  
Electric Auto-Lite Company, Toledo, Ohio  
Electric Storage Battery Company, Philadelphia, Pa.  
The Eppley Laboratory, Newport, R. I.  
Ford Motor Company, Dearborn, Mich.  
General Chemical Division, Allied Chemical & Dye Corporation, New York, N. Y.  
General Electric Company, Schenectady, N. Y.  
General Motors Corporation, Research Laboratories Division, Detroit, Mich.  
Gould-National Batteries, Inc., Depew, N. Y.  
Graham, Crowley & Associates, Inc., Chicago, Ill.  
Great Lakes Carbon Corporation, Niagara Falls, N. Y.  
Hanson - Van Winkle - Munning Company, Matawan, N. J. (2 memberships)  
Harshaw Chemical Company, Cleveland, Ohio (2 memberships)  
Hooker Electrochemical Company, Niagara Falls, N. Y. (3 memberships)  
Houdaille-Hershey Corporation, Detroit, Mich.  
International Graphite & Electrode Div., Speer Carbon Company, St. Marys, Pa. (2 memberships)  
International Minerals & Chemical Corporation, Chicago, Ill.  
International Nickel Company, Inc., New York, N. Y. (2 memberships)  
Kaiser Aluminum & Chemical Corporation, Division of Metallurgical Research, Spokane, Wash.  
Mathieson Chemical Corporation, Niagara Falls, N. Y. (4 memberships)  
McGean Chemical Company, Cleveland, Ohio  
Merck & Company, Inc., Rahway, N. J.  
Metal & Thermit Corporation, New York, N. Y.  
Monsanto Chemical Company, St. Louis, Mo.  
National Carbon Division, Union Carbide and Carbon Corporation, New York, N. Y. (2 memberships)  
National Cash Register Company, Dayton, Ohio  
National Research Corporation, Cambridge, Mass.  
Niagara Alkali Company, Niagara Falls, N. Y.  
Norton Company, Worcester, Mass.  
Pennsylvania Salt Manufacturing Company, Philadelphia, Pa. (2 memberships)  
Philco Corporation, Lansdale, Pa.  
Philips Laboratories, Inc., Irvington-on-Hudson, N. Y.  
Potash Company of America, Carlsbad, N. Mex.  
Promat Division, Poor & Company, Waukegan, Ill.  
Ray-O-Vac Company, Madison, Wis.  
RCA Victor Division, Radio Corporation of America, Harrison, N. J.  
Rockwell Spring and Axle Company, Coraopolis, Pa.  
Solvay Process Division, Allied Chemical & Dye Corporation, Syracuse, N. Y. (3 memberships)  
Stackpole Carbon Company, St. Marys, Pa.  
Standard Steel Spring Division of the Rockwell Spring and Axle Company, Coraopolis, Pa.  
Stauffer Chemical Company, San Francisco, Calif.  
Sylvania Electric Products Inc., Bayside, N. Y. (2 memberships)  
Sarkes Tarzian, Inc., Bloomington, Ind.  
Tennessee Products & Chemical Corporation, Nashville, Tenn.  
Udylite Corporation, Detroit, Mich. (2 memberships)  
Union Carbide Company, Electrometallurgical Division, New York, N. Y.  
United Chromium, Inc., New York, N. Y.  
Vanadium Corporation of America, New York, N. Y.  
Victor Chemical Works, Mt. Pleasant, Tenn.  
Wagner Brothers, Inc., Detroit, Mich.  
Western Electric Company, Inc., Chicago, Ill.  
Western Electrochemical Company, Los Angeles, Calif.  
Westinghouse Electric Corporation, E. Pittsburgh, Pa.  
Willard Storage Battery Company, Cleveland, Ohio.  
Wyandotte Chemicals Corporation, Wyandotte, Mich.  
Yardney Electric Corporation, New York, N. Y.

*Entholics*<sup>\*</sup>

AT WORK at C. HAGER & SONS HINGE MFG. CO.



WHEN IMPROVED PRE-PLATING  
PROCESSES HINGED ON ENTHONE

**Alka-Deox compound 134**

supplied the cost cutting answer!

C. Hager & Sons Hinge Manufacturing Company, St. Louis were experiencing periodic rejects due to incomplete cleaning and pickling in the pre-plating processes employing alkali cleaning and acid pickling.

Enthone's chemists and metallurgists applied *Entholics* to the problem. The answer was the use of Alka-Deox Compound 134 in place of the acid dip in three fully-automatic plating machines.

**THE RESULTS?** Using the Alka-Deox process, Hager reported: "Soak cleaning and cyanide dip completely eliminated . . . Flash rust no longer a problem

. . . Laboratory analysis cut to one a month . . . Solution operating-life of 5 months—and more—compared with the former use of 6 carboys of muriatic acid each week . . . Annual materials-cost savings of \$391.50 on just three machines . . . Labor and maintenance savings . . . Reduced down time . . . And the complete elimination of plating rejects due to incomplete cleaning and/or pickling!"

*Entholics at work* has proved its value to Hager. And if production improvements in your plant hinge on improved metal-pre-plating processes, contact Enthone's Research Department—today! Why not put *Entholics* to work for you?

*\*The Scientific Solution of Metal Finishing Problems.*

METAL FINISHING PROCESSES

442 ELM STREET, NEW HAVEN 11, CONNECTICUT

ELECTROPLATING CHEMICALS

**ENTHONE**  
INCORPORATED

Service Representatives and Stock Points: BINGHAMTON, N. Y., Austin F. Fletcher, Inc.; CHICAGO, Arlco, Inc.; CLEVELAND, R. O. Hull & Co. DALLAS, Weaver Engineering & Supply Co., Inc.; LOS ANGELES, L. H. Butcher Co.