# JOURNAL OF THE Electrochemical Society

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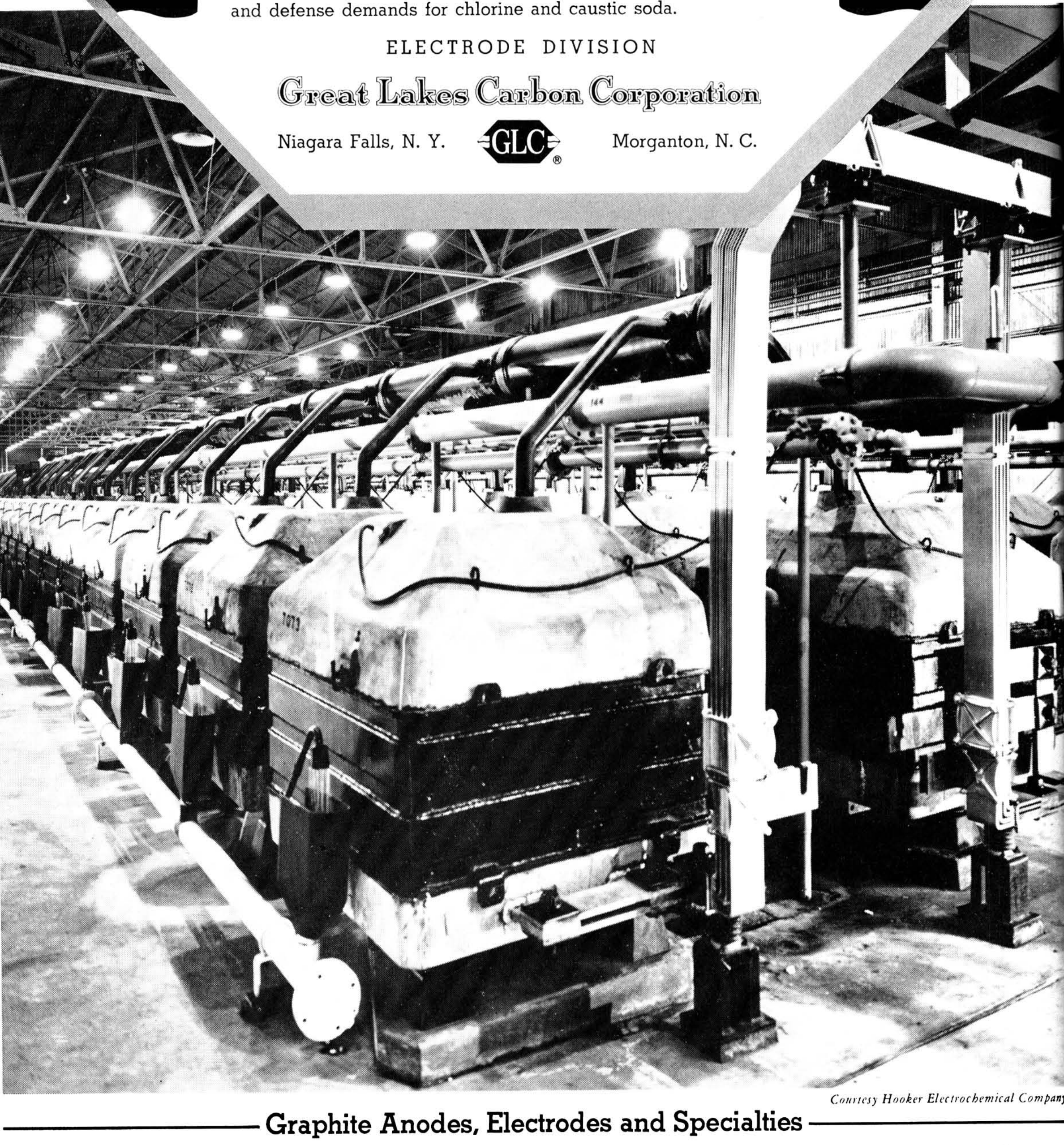
June, 1953

S. Thomas

ELECTROCHEMICAL INDUSTRY

The Pacific Northwest



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## CONTENTS

### *Editorials*

The Pacific Northwest. *Joseph Schulein* .................. 139*C*
The Astin Incident .................. 140*C*

### *Regional Feature*

Electrochemistry in the Pacific Northwest. *Joseph Schulein* .. 143*C*

### *Technical Papers*

Corrosion of Heating Electrodes in Molten Chloride Baths. *H. R. Copson* .................. 257
The Electric Strength of Sulfur Hexafluoride at Radio Frequencies. *John W. Gibson and C. Frank Miller* .................. 265
Preparation and Properties of Iodide Vanadium. *Julian W. Nash, H. R. Ogden, Richard E. Durtschi, and I. E. Campbell* 272
Electroplating on Beryllium. *John G. Beach and Charles L. Faust* .................. 276
Copper-Activated Zinc Sulfide Phosphors with Yellow and Red Emission. *H. C. Froelich* .................. 280
Electroplating on Zirconium. *W. C. Schickner, J. G. Beach, and C. L. Faust* .................. 289

### *Technical Review*

Review of Articles on Luminescence for 1951–1952. *Gorton R. Fonda* .................. 155*C*

### *Current Affairs*

Electrochemical Society Condemns Astin Dismissal .......... 159*C*
High Registration, Varied Symposia Score Success at N. Y. Meeting .................. 160*C*
Industrial Progress in Canada—1952 .................. 162*C*
Division News .......... 164*C*
Section News .......... 164*C*
Personals .......... 166*C*
New Members .......... 167*C*
New Products .......... 168*C*
Employment Situations .. 168*C*

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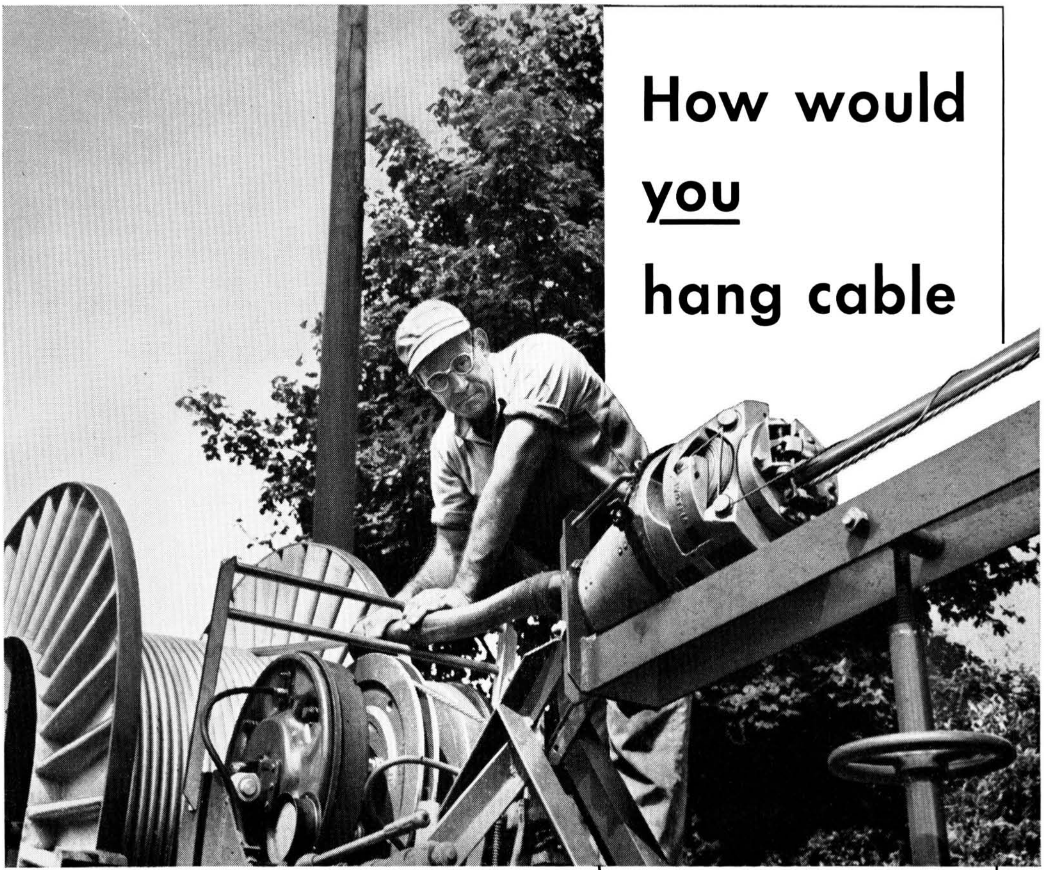

# How would *you* hang cable ...by the mile?

*Cable lasher appears to right of workman. As the cable and supporting strand feed through, the machine rotates, binding them together with steel lashing wire. Meanwhile, a winch hauls the lashed cable into position.*

IT IS a job your telephone company faces every day. Thousands of miles of cable go up each year—all secured to steel strand running from pole to pole. The best way to secure cable is to *lash* it to the strand with a spiral binding of wire.

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# Editorial

## The Pacific Northwest

POWER, power, everywhere, but not a watt to sell. That is the peculiar situation in the Pacific Northwest, a region undergoing a power shortage although it is one of the nation's greatest electricity producing areas. This situation has come about because of the rapid influx of great electrometallurgical industries into the area just as fast as the giant blocks of power became available; an influx so great, that within a few years the area has grown to where it now supplies nearly half of the country's aluminum, and uses electrical energy at a rate exceeding 30 billion kilowatt hours per year, with a foreseeable demand requiring three times that much within the next ten years.

That such a demand for power can be met from the region's resources is well established; however, the program under which the necessary facilities are to be constructed is not yet confirmed. Due to the magnitude of the undertaking, and the many interests involved other than power, the bulk of the program has of necessity fallen to the Federal Government, and has resulted in the creation of the Bonneville Power Administration as the marketing agent for all power produced by Federal facilities in the area. Much of this power, and that from private utilities and non-Federal public utilities, pours into a single system—the Northwest Power Pool, which binds together all the generating and transmitting facilities so as to serve an area running about 1000 miles from east to west, and some 700 miles from north to south.

How best to get more power, how best to allocate the uses of such power—these are problems of enormous import for the Pacific Northwest, and the Federal power policies in these matters are topics of continuous public interest, for the region realizes that here is the last stand of large-scale, low-cost hydroelectric energy; here is the vital "item" with which the area is to build new industry. What that industry will be, how it will change the area from dependence on forest-based products to an economy based on electro-produced products, and how it will affect the individual

*(Continued on next page)*

## Editorial (*continued*)

are so well visualized that the word "power" means much more to Pacific Northwest residents than to people in other sections.

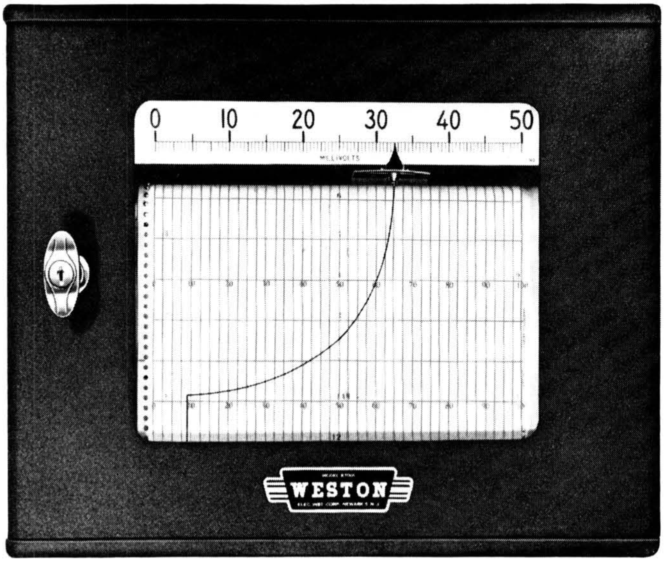
The review of Electrochemistry in the Pacific Northwest, appearing in this issue, is an attempt to assess the present electrochemical industry, and to indicate the factors affecting the future, in the nation's great green corner.

—JOSEPH SCHULEIN

## The Astin Incident

The unfortunate action of Secretary Weeks in demanding the resignation of Director Astin of the National Bureau of Standards was strongly condemned by the Society at its annual meeting, as described elsewhere in this issue. It is gratifying that this protest together with similar actions by other technical societies and the unanimous disapproval of an outraged engineering and scientific world led the Secretary to reverse his position and ask Dr. Astin to remain pending an investigation of the scientific facts in the case. This reversal and the denial by the Secretary that he intended to reflect upon the integrity of the Bureau or its director is welcome. It is to be feared, however, that the loss of public confidence in the Secretary will not be restored nor the damage done to the morale of government scientists and engineers repaired by this forced second thought. It is somewhat naive of the Secretary to assume as he does that it will be easy to find a qualified successor for Dr. Astin.

# THE Simplicity Features INSTRUMENT MEN PREFER



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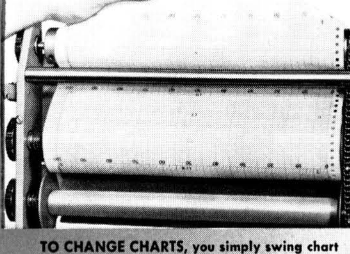
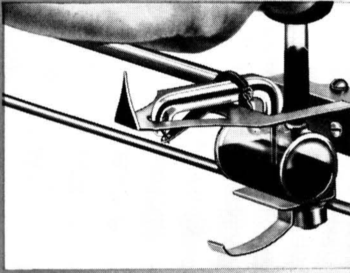


**TO CHANGE CHARTS,** you simply swing chart frame open a full 180°, insert chart and swing it over timing drum and across front of frame and fasten. No loose pieces to handle!



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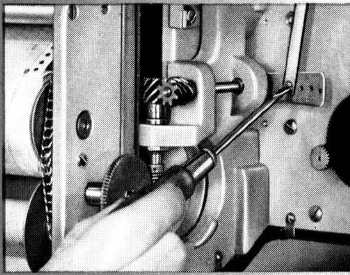
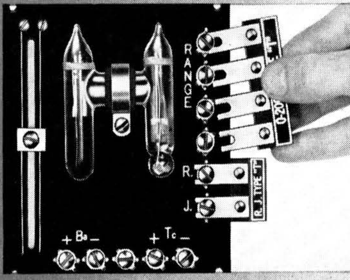


**TO CHANGE CHART SPEEDS,** a simple screwdriver adjustment gives you a choice of 5 different speeds. These speeds are doubled or quadrupled by changing one worm and gear assembly.



**TO CHANGE RANGES,** you simply substitute the desired range standard. The reference junction compensation is changed in like manner. No soldered connections to break!

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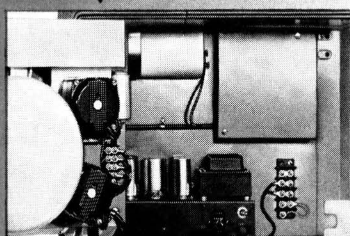

## WESTON *Instruments*

INDICATE — RECORD — CONTROL

# ELECTROCHEMISTRY IN THE PACIFIC NORTHWEST

*Joseph Schulein*[1]

The growth of electrochemistry in the Pacific Northwest parallels the development of the hydro resources of the area. Although there were some electrochemical plants operating in the area prior to 1940, the development of the original Federal hydro projects at Bonneville and Grand Coulee made available tremendous quantities of low cost energy just prior to World War II, and this situation greatly stimulated the growth of the electroprocess industries in the region.

Due to the very large growth of industry and population in the Pacific Northwest during the war period and in subsequent years, the power generating facilities of the area have not kept pace with the increasing demands for energy. As the Federal government has assumed the major responsibility for providing the hydroelectric facilities in multipurpose projects on the Columbia River and its tributaries, and although new Federal projects are under construction, as well as certain projects by private utilities, the availability of large blocks of power for new electrochemical plants depends on the completion rate of these new projects and other economic factors which will be treated in more detail later in this report. The major power use now in the area, of course, is in the production of primary aluminum.

## Aluminum

Primary aluminum is produced by the Aluminum Company of America at Vancouver and Wenatchee, Washington; by the Reynolds Metals Company at Longview, Washington, and Troutdale, Oregon; and by the Kaiser Aluminum and Chemical Corporation at Spokane and Tacoma, Washington.

### ALUMINUM COMPANY OF AMERICA

The Alcoa Pacific Northwest operation includes the manufacture of rod, wire, electrical conductor cable (aluminum cable, steel reinforced, known as ACSR), sheet ingot, extrusion ingot, and rod ingot, all produced at the Vancouver, Washington, plant in addition to the primary aluminum operation previously mentioned.

Installed capacity for primary metal production at Vancouver is 170,000,000 lb annually. The plant has prebaked type pots only in five pot lines. While the capacity is the figure before given, the output is, however, dependent upon the availability of power. The plant has 133,700 kw on firm power contract and 45,000 kw on an interruptible basis, all such power being furnished by the Bonneville Power Administration.

The Wenatchee plant also has an installed production capacity of 170,000,000 lb annually, with the same dependence on power availability as a limit on actual output. This new installation has 120,000 kw on firm contract, such power being furnished by the Chelan County Utility District, and 50,000 kw on an interruptible basis supplied by the Bonneville Power Administration.

Combined production of the two plants during 1952 was approximately 182,500,000 lb of primary aluminum. The Vancouver plant lost approximately one-fourth of its production capacity for four months and an additional 10 per cent of its remaining production capacity for two months, during the past winter season (1952–53) due to power cutbacks resulting from a severe regional water shortage. The new Wenatchee works began primary metal production on a small scale in June 1952. Operations continued at about one-fourth of production capacity until December 1952 when the second of the present four pot lines was activated. This pot line had operated briefly earlier in the year. Actual power delivered to Alcoa for the fiscal year ending June 30, 1952, was: Vancouver, 1,479,768,269 kwhr, and Wenatchee, 3,132,000 kwhr.

Heavy January 1953 precipitation brought an end to the hydro power shortage at about midmonth, permitting resumption of full operation in January. The Wenatchee plant's third pot line began producing metal the same month, and the fourth and final line was started in February 1953.

The Vancouver Fabricating Works of Alcoa, situated in buildings adjoining the smelter, has the capacity to produce 30,000,000 lb (aluminum weight) of electrical conductor cable (ACSR) annually. During 1952 the aluminum weight of electrical conductor, plus the weight of redraw rod shipped to other company plants and customers, totalled approximately 41,800,000 lb. Shipments of customer ingot totalled 41,400,000 lb.

Expected to go into operation in Vancouver this month will be a new facility which will have the capacity to produce approximately 6,000,000 lb per month of fabricating ingot. This product will take several forms: ingot for sheet; ingot for extrusion; and ingot for rolled rod. The product of this operation will be used by Alcoa either at Vancouver or other plants, or will be sold to customers.

The company does not produce any alumina in the Northwest but ships it all in from their other operations. They have extensively tested the ferruginous bauxites of this area and are reported to have developed processes for producing alumina from such materials, which are on the verge of becoming economic.

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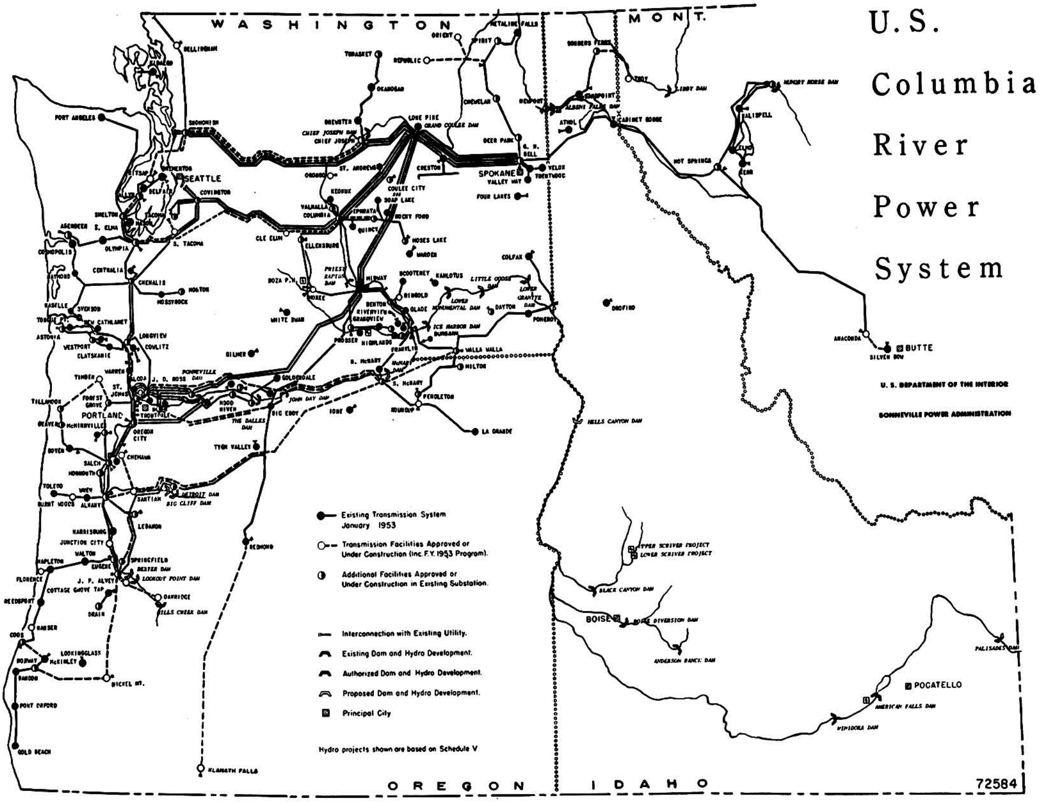

U. S. Department of the Interior, Bonneville Power Administration

Fig. 1. Map of the Pacific Northwest showing existing and proposed transmission systems, and existing, authorized, and proposed dam and hydro developments.

The company purchases about one-fourth of its raw materials (totalling approximately $14,000,000) in the Pacific Northwest. Plans for a substantial increase of cable-making capacity have been announced for Vancouver and construction is now underway on an expansion program estimated at $1,720,000. Work completion is scheduled for early 1954. The new facilities will be equipped to fabricate "expanded ACSR," a newly developed product designed to carry high voltage transmission loads. Additional expansion, now underway at an estimate of $2,700,000, calls for installation of extrusion presses for the production of strong alloy billets and extruded shapes in both strong and common alloys. Such alloy billets can be used for eventual production of rod, wire, and bar. The extruded shapes are to supply Pacific Northwest markets.

### Reynolds Metals Company

The Reynolds Metals Company operates a prebaked electrode type plant at Troutdale, Oregon, and a Soderberg electrode type plant at Longview, Washington. The Troutdale plant is a duplicate of the Alcoa plant at Vancouver except that it has four pot lines rather than five, and was constructed by Alcoa for the government during the war. It was later leased by, and then sold to, Reynolds by the government. Reynolds' Longview plant has recently had its capacity increased from 60,000,000 to approximately 100,000,000 lb annually, assuming that power is available. Reynolds has 202,100 kw on firm contract and 63,800 kw of interruptible power, all supplied by the Bonneville Power Administration. It is understood that the company operates their pots on a slightly different basis than Alcoa. On a basis of power availability, it is estimated that annual production of both plants, Troutdale and Longview, would be approximately 260,000,000 lb. Actual power deliveries for fiscal year 1951–52 were: Longview, 486,391,240 kwhr; and Troutdale, 1,358,422,548 kwhr.

The total production is primary aluminum and the plants operate on alumina shipped into the area. No plans have been announced for expansion of, or the integration of, either plant with production facilities for fabricated aluminum. The company's total raw material purchases are approximately the same as those given for the Aluminum Company of America of which a somewhat smaller percentage is purchased in the Northwest than the figure given for Alcoa.

### Kaiser Aluminum and Chemical Corporation

The Kaiser Aluminum and Chemical Corporation operates primary aluminum smelters at Tacoma and Mead (Spokane), Washington. The Tacoma plant has a capacity of approximately 60,000,000 lb per year produced in Soderberg type pots. An expansion project is just being completed at an estimated cost of $2,850,000 which will add more than 16,000,000 lb to the annual production of the Tacoma plant. Power is supplied by the Bonneville Power Administration and includes 50,000 kw of firm power and 17,000 kw of interruptible power. While the plant capacity at Tacoma is approximately as above given, actual production has been running closer to two-thirds.

The Mead plant operation at Spokane has a capacity of 324,000,000 lb of primary aluminum pig per year through the operation of eight pot lines, and is the largest single installation in the Pacific Northwest. Local purchases for this mill average about $5,000,000 annually.

The company operates a rolling mill at Trentwood (Spokane), Washington, which has a capacity of approximately 360,000,000 lb per year, and in itself takes the sizeable load of 35,000 kw of firm power and 4000 kw of interruptible power, all supplied by the Bonneville Power Administration.

At the Trentwood works, some of the sheet and plate is fabricated into final products such as aluminum clapboard house siding, aluminum roofing, and aluminum shade screen. Other products are semifabricated, such as aluminum circles for the pots and pans trade, and plate for aircraft structural members and other reinforcing purposes. This is the only mill in the Pacific Northwest producing aluminum sheet and plate. Local purchases for the Trentwood mill will also run approximately $5,000,000 per year. Power deliveries for the fiscal year 1951–52 were: Mead, 2,477,028,973 kwhr; Trentwood (fabricating) 225,287,505 kwhr; and Tacoma, 441,662,981 kwhr.

At each of the operating plants of all the concerns before mentioned, the electrode carbon requirements have been enormous, since for each pound of aluminum produced approximately two-thirds of a pound of carbon is consumed.

### HARVEY MACHINE COMPANY

The Harvey Machine Company of Torrance, California, has signed contracts with the Bonneville Power Administration for sufficient power for approximately 54,000,000 lb annually of aluminum production in a plant to be built at The Dalles, Oregon. Construction is expected to be started during 1953.

The Defense Production Administration has granted a certificate of necessity to the Harvey Company permitting Harvey to write off 85 per cent of the cost of the new plant and facilities over a period of five years. The certificate involves $65,250,000.

The company has also purchased a government surplus plant at Salem, Oregon, which had been constructed during the war in an attempt to produce alumina from clays of the area. The plant was never successful in producing such material in an economical manner, and it is presumed that Harvey's processing will be somewhat different from that originally proposed when the plant was first constructed.

It is understood that Harvey's primary aluminum production will be mainly for their own use in California, and, therefore, the same economic consideration in the production of alumina may not apply in full to their particular operation, especially since their smelter will be situated within a few miles of the dam and will be entitled to a preferential rate of 1.67 mills per kwhr (present base rate) as against the regular Bonneville power transmission line present base rate of 2 mills per kilowatt hour, which may thus help offset a part of the extra costs of producing alumina. It requires approximately 9 to 10 kwhr per pound to produce aluminum (over-all power). While no definite statement has been made at the time of this writing, it is thought that the Harvey smelter will utilize Soderberg type pots. Harvey is also planning a new rolling mill.

All of the aluminum companies which have operated in the Northwest have experienced difficulties through pollution of the atmosphere with fluorine-containing compounds. The results of such pollution have been particularily noticeable in areas given over to dairy farming and have resulted in heavy damages being paid, both voluntarily and after law suits. Each of the now operating concerns mentioned has invested heavily in fume control devices. Such installations have cost an average of approximately $1,500,000 per plant and have added several hundreds of thousands of dollars to the annual operating costs.

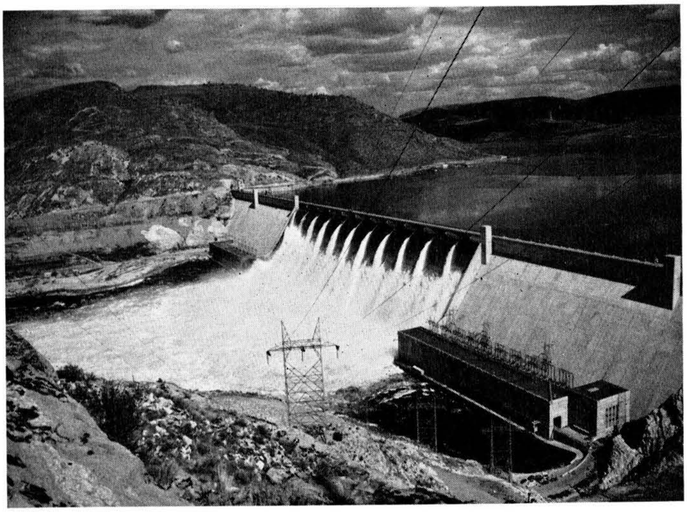

FIG. 2. Largest of the federal multipurpose dam projects in the Columbia river basin is Grand Coulee dam, completed by the Bureau of Reclamation. In addition to providing irrigation for thousands of acres of arid land, the power plant has a generating capacity of over 1,944,000 kw. Power from Grand Coulee flows to the industrial and load centers of western, central, and northeast Washington and northern Idaho.

These installations have, in general, consisted of various types of hooding devices to enclose the pots and aid in collection of the fume, which is then blown through baffled water-spray towers. The equipment seems quite effective in removing the gaseous compounds, but does pass some of the finer particulates.

Probably the efficiency of such fume control devices is now of the magnitude of 90 per cent, but whether or not this will be sufficient to protect the companies against further claims for damages in certain areas is a matter yet to be determined.

The public relations departments of these firms have done a remarkably good job in helping to overcome public prejudice arising through the air pollution problem, and any industry which has a fume problem and is contemplating establishing a plant in the Pacific Northwest would be well advised to have public relations counsel.

### Chlorine-Caustic Soda

There are two important producers of chlorine-caustic soda and related products in the Pacific Northwest. As the demand for these chemicals has been built mainly by the pulp industry, they are among the oldest, established electrochemical industries in the area.

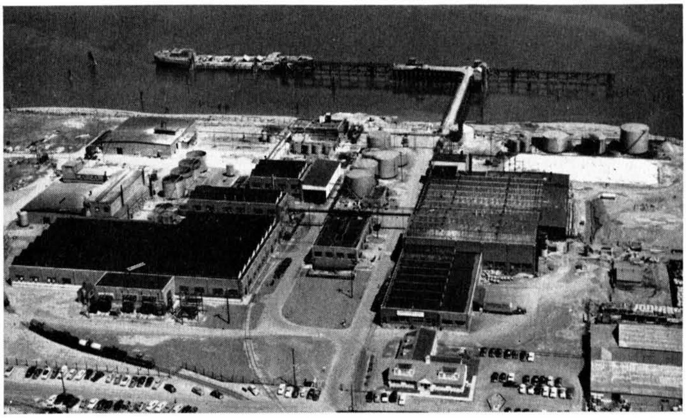

FIG. 3. Pennsylvania Salt Manufacturing Company, Portland, Oregon. Ship at Willamette River dock in background is used to store raw salt.

#### PENN SALT MANUFACTURING COMPANY

The Pennsylvania Salt Manufacturing Company of Washington, a wholly owned subsidiary of the Pennsylvania Salt Manufacturing Company, has long operated a chlorine-caustic plant at Tacoma, Washington, and since the early 40's has operated a second plant in Portland, Oregon. At Tacoma the principal products are chlorine and caustic soda, while the Portland plant produces chlorine, caustic soda, chlorates, DDT, insecticides, cleaners, and dry cleaning products. The company also produces some sodium hypochlorite, muriatic acid, and sodium arsenite. Statistics on the individual plants are not available, but for the combined operations the chlorine produced is approximately 7000 tons per year. Caustic soda production is approximately 4000 tons per year, chlorate 4000 tons per year, insecticides 5000 tons per year, and cleaners 2500 tons per year. The Tacoma plant operates on a firm power basis with power supplied by the Tacoma City Light Division, while the Portland plant is supplied by the Bonneville Power Administration and the Pacific Power and Light Company, with some power on an interruptible basis. The combined plant output of products has a total value of $15,000,000 per year and the company purchases approximately $1,650,000 worth of raw materials in the area (exclusive of power), and purchases approximately $1,850,000 worth of raw materials outside the area.

The company has not announced any plans for expansion, but has recently purchased an additional 22 acres adjoining the Portland operation, which plant increased its capacity 50 per cent in 1951 at an estimated cost of $6,000,000.

The principal raw material, salt, is brought up from California where it is produced by solar evaporation. Other chemicals purchased outside are MCB and BHC, while the principal purchases within the area are fuel oil, alcohol, arsenic, and sulfuric acid.

The plant operates a modified Vorce type of chlorine cell.

#### HOOKER ELECTROCHEMICAL COMPANY

The Hooker operation at Tacoma consists of the production of chlorine, caustic soda, anhydrous ammonia, trichlorethylene, and perchlorethylene. While admitted capacities are given only as "in excess of 300 tons per day of caustic soda and chlorine," it is estimated that actual production might be closer to 360 tons of caustic and 310 tons of chlorine. The admitted production of ammonia is "in excess of 40 tons daily," and it is estimated that the actual tonnage is probably close to 60. Muriatic acid tonnage is something over 10 tons per day. Hooker uses their own type cells.

Power is supplied on a firm contract by the Tacoma City Light Division, and it is anticipated that there will be a future plant expansion completed before the end of 1953.

The Hooker plant at Tacoma produces approximately 30 per cent of the more than $40,000,000, which constitutes the total sales value of the products produced by the Hooker Electrochemical Company.

The entry of this company into the production of anhydrous ammonia is of considerable interest since there is a possibility that a large use of such material will develop in the Northwest through the adoption of ammonia-base pulping by the pulp and paper industry. It is estimated that if such large-scale use actually develops there will be a demand for anhydrous ammonia to the extent of approximately 80 to 100 lb of ammonia per ton of pulp. Much of the hydrogen now being produced by the Pennsylvania Salt Manufacturing Company plant at Portland is being piped to the Portland Gas and Coke Company where it is used to enrich the Portland Gas supply. Whether this will be switched to ammonia or whether the area will await the coming of natural gas from Canadian sources has been a matter of much speculation.

### Calcium Carbide; Ferro Silicon; Acetylene; Magnesium

This group is listed together because of the overlapping of such products as produced by the companies now operating in the area.

#### PACIFIC CARBIDE AND ALLOYS COMPANY

The Pacific Carbide and Alloys Company operates a plant in Portland producing calcium carbide and acetylene. The plant operates on a firm power contract of 2000 kw and has an additional 3000 kw of interruptible power supplied by the Bonneville Power Administration. Annual production of calcium carbide is approximately 12,000 tons per year and acetylene runs approximately 6,000,000 ft$^3$ annually. The company buys approximately $350,000 worth of raw materials in the Pacific Northwest and about $50,000 worth outside the area. The total value of the products produced is in the neighborhood of $1,000,000. No plans for expansion have been announced to this date.

### Electro Metallurgical Company

The Electro Metallurgical Company, a division of Union Carbide and Carbon Corporation, produces calcium carbide, ferrosilicon, silicon, and ferromanganese in their Portland plant. No figures are available as to the exact amount of production, although the company reports it has recently doubled its capacity.

### Pacific Northwest Alloys

The Pacific Northwest Alloys, Inc., operates a plant at Spokane, Washington, which produces 75 per cent ferrosilicon and magnesium metal. Power is supplied by the Bonneville Power Administration on a firm contract of 13,000 kw and an interruptible contract of 47,000 kw. Pacific Northwest's capacity is 48,000,000 lb of ferrosilicon and 42,000,000 lb of magnesium, annually. The company purchases approximately $950,000 worth of raw materials annually in the Pacific Northwest and ships in another $880,000 worth.

### Keokuk Electro-Metals Company

The Wenatchee division of the Keokuk Electro-Metals Company produces ferrosilicon at Wenatchee, Washington. While production statistics are not available it is known that the plant does not produce other products and is operated on a firm power basis of 14,000 kw with an additional interruptible load of 7000 kw, furnished through the Bonneville Power Administration.

No information is available concerning the operation of the Ohio Ferro Alloys Company at Tacoma.

## Silicon Carbide

The Carborundum Company operates a plant at Vancouver, Washington, producing crude silicon carbide for abrasive and refractory use. Practically all of the raw materials used are purchased in the Pacific Northwest with production running approximately 1000 tons per month. The firm has 10,000 kw of firm power on contract supplied by the Bonneville Power Administration.

An expansion program now underway is expected to double the above capacity during 1953.

## Nickel

The Hanna Coal and Ore Corporation and the Hanna Nickel Smelting Company, both subsidiaries of the M. A. Hanna Company, Cleveland, Ohio, have contracted with the Defense Materials Procurement Agency to produce nickel from Nickel Mountain near Riddle, Douglas County, southwestern Oregon. The contract calls for the production of from 95,000,000 to 124,000,000 lb of nickel in ferronickel which will contain at least 25 per cent nickel and not more than 75 per cent iron. The Hanna Coal and Ore Corporation is to develop the mine on Nickel Mountain at its own expense at a cost of approximately $4,300,000. Ore from the deposit will be sold to the government at $6 per ton. In turn, the government will sell the ore to the Hanna Nickel Smelting Company at the same price, and the smelting company will treat the ore in an electric furnace plant to produce the ferronickel. This plant will be located about two miles down the mountain from the mine and it is reported that it will consist of four primary furnaces, one refining furnace, and two auxiliary furnaces. Contracts have been signed for 65,000 kw of firm power, and 10,000 kw of interruptible power.

The Hanna Smelting Company will use a patented process developed in France by the Societé D'Electro-Chimi, D'Electro Metallurgie et des Acieries Electrique D'Ugine. This process has been used in treating New Caledonia ores which are quite similar to the Oregon material, both being a nickel silicate. The first 5,000,000 lb of nickel produced in the ferroalloy will be sold at 79.39 cents per pound, with the price dropping to 60.5 cents per pound thereafter. A rapid write off has been agreed upon and the government is advancing $24,800,000 for the construction of the smelter. The Bechtel Corporation of San Francisco has been engaged to handle the design, engineering, and construction of the nickel smelting plant. The Oregon deposit on Nickel Mountain is by far the largest deposit of nickel ore known in the United States.

## Phosphorus

The availability of low cost power as an offset to higher cost rock, has brought three principal producers of phosphorus into the Pacific Northwest area.

### Westvaco Division

The Westvaco Division of the Food Machinery and Chemical Corporation established the first electric furnace for phosphorus at Pocatello, Idaho, in 1949 and has added a furnace a year until they now operate four furnaces, with a combined capacity of 36,000 tons of phosphorus annually. Their power is supplied by the Idaho Power Company on both a firm and interruptible basis. Other products produced at Pocatello are ferrophosphate, slag, and precipitator dust. The phosphorus produced is shipped to other Westvaco plants at Carteret, New Jersey, Newark, California, and Lawrence, Kansas, the New Jersey plant being the largest. The Pocatello site provides Westvaco with power at an estimated 2.5 mill rate with a 35-year supply of rock within easy distance. Shipment of phosphorus in special tank cars under water has proven quite feasible and is commonly carried on by all producers. Freight rates on the yellow phosphorus is high because of its hazardous nature; if the railroads cannot be persuaded to go along with a lower rate, it is possible that consideration will be given to the conversion of yellow phosphorus into red phosphorus before shipment.

### Monsanto Chemical Company

The Monsanto Chemical Company reports that they are now operating, at Soda Springs, Idaho, the world's largest known electric furnace, having a capacity of 25,000 tons of phosphorus per year. The ore is mined in the hills surrounding the southeastern Idaho plant and the phosphorus is shipped to Monsanto processing plants at Trenton, Michigan, Carondelet, Missouri, Monsanto, Illinois, and Anniston, Alabama. Power is supplied by the Utah Power and Light Company which completed a new transmission system last year.

The company, which is the world's largest producer of phosphorus, started the Soda Springs operation this year, and the company has announced that more furnaces may be installed at the same location.

### VICTOR CHEMICAL COMPANY

While not in the exact area intended to be covered by this report, the Victor Chemical Company cannot be neglected in the phosphorus picture, since they process the sizeable amount of 28,000 tons of phosphorus per year through two electric furnaces at Silver Bow, Montana. Power to Victor is supplied by the Bonneville Power Administration and comes mainly from the Hungry Horse Dam. Victor has four processing plants located at Chicago Heights, Illinois, West Nashville, Tennessee, Morrisville, Pennsylvania, and the A. R. Maas Division at Southgate, California.

Power requirements for the three producers probably do not vary much on a tonnage basis, and is estimated to be approximately 12,000 kwhr per ton. The Idaho, Montana, and Wyoming phosphate rock deposits, estimated at nearly 8 billion tons, are the largest known reserves in the world, and apparently will be adequate for hundreds of years. Much of it is low grade, suitable only for electric furnace processing.

## Silumin

The National Metallurgical Corporation of Chicago has started construction of a plant at Springfield, Oregon, for the manufacture of silumin (a silicon-aluminum alloy) from clays. The newly formed company, which is jointly owned by the Apex Smelting Company of Chicago and the American Smelting and Refining Company on a fifty-fifty basis, has contracted for 10,000 kw of power. Operation is expected sometime during 1953. The process will be similar to one worked out by TVA during the war and the product will be used as deoxidizing and reducing agents, and as a basic raw material for high-aluminum alloy castings.

## Miscellaneous

### *Manganese Dioxide*

American Metallic Chemicals Corporation is producing electrolytic manganese dioxide in their Portland plant, which has a capacity of 20,000 lb per day of battery grade dioxide. It is understood that the process used is the conventional hot electrolytic oxidation of manganese solution. It is reported that this concern is also to make electrolytic perborate under license from Noury Van der Lande N. V. Deventer, Holland, covering a process which has been operated in Europe for more than ten years. AMC has sole license rights in the United States and Canada for all operations other than Noury.

### *Hydrogen Peroxide*

The Buffalo Electro-Chemical Company, a division of the Food Machinery and Chemical Corporation, is producing electrolytic hydrogen peroxide in a new plant at Vancouver, Washington. Since the company is one of two main producers of hydrogen peroxide in the country, details and statistics on their operations have not been made available. Power is supplied by the Clark County Public Utility District, the exact quantity again not being available. From the size of the plant, however, it is estimated that the production is appreciable. The Vancouver plant was built under a certificate of necessity authorizing accelerated amortization of 50 per cent. Hydrogen peroxide, Becco's principal product, is produced in four commercial grades, 27.5 per cent, 35 per cent, 50 per cent, and 90 per cent; it is presumed that Becco's Vancouver location, in addition to the availability of power, was selected because of the increasing growth of the use of peroxide for bleaching ground-wood pulp. At the present time, it is believed that much of the Vancouver output is being diverted to military uses.

### *Powdered Iron*

It is understood that the Tacoma Powdered Metal Company, Tacoma, Washington, is producing powdered iron, but no details are available.

### *Smelters*

The principal smelters of the area are those of the Bunker Hill & Sullivan Mining Company, Kellogg, Idaho, operating on lead-silver-zinc ore, the Sullivan Mining Company at Wallace, Idaho, also producing zinc, and the Tacoma, Washington, smelter of the American Smelting and Refining Company, operating mainly on copper.

### *Atomic Energy Installations*

The Atomic Energy Commission's major plant for the production of plutonium at Hanford, Washington, has been a substantial user of power supplied by the Bonneville Power Administration. While exact figures covering this use have never been made public, it is probable that the power requirement does not exceed approximately 900,000,000 kwhr per year. An expansion program now underway will undoubtedly materially increase the power demand.

The AEC installation at Arco is supplied by the Utah Power and Light Company and the Idaho Power Company. The load there, however, is relatively small and is not expected to be substantially increased.

### *Zirconium*

The Bureau of Mines Northwest Electro-Development Laboratory at Albany, Oregon, is producing a high grade zirconium by methods based on processes developed by Dr. William J. Kroll, of titanium fame. Exact production figures are not available but are estimated at more than 200 tons annually. The material has been going mainly to the AEC.

The Pacific Northwest area, of course, has the usual complement of small load users, and no attempt has been made to include them in this article.

## Power

During the winter of 1952–53 the Pacific Northwest experienced a serious power shortage following a prolonged drought in the preceding summer and fall. This was despite the fact that there has been an enormous expansion in the Columbia River Power System operated by the Federal Government, which has, in the last ten years, increased the annual output of such power from 2.4 billion to 18.6 billion kwhr, so that it now represents approximately 61 per cent of all the electric energy being used in the Pacific Northwest.

The large increase in population of the area, nearly 33 per cent in the last decade, plus the relatively rapid buildup of the electrochemical load, has called for much concerted study as to the proper development of the hydroelectric resources of the region, especially important since the Pacific Northwest has no oil, natural gas has not yet been brought to the area, and the coal resources are not too amenable to the production of low cost power.

The Columbia River System is particularly adapted to hydroelectric power production. It drains an area of a quarter of a million square miles and has an extremely high annual runoff, involving steep drops, within a relatively short distance, of clean water. Irrigation, navigation, flood control, and recreation are all elements that enter into the development of the river system for power. Since such a vast river can be best developed through the integrated operation of many power-and-storage dams, rather than through the operation of individual and isolated units, the very size of the complete development project has placed it in the hands of the Federal government. As marketing agent for the energy produced at the Federal dams, the Bonnevile Power Administration plays a most vital role in the Pacific Northwest power program, a role which, of necessity, places enormous power and responsibilities upon its administrators. The policy it is allowed to adopt will literally control the destiny of the Pacific Northwest.

The Bonneville Power Administration sells only at wholesale to private and publicly owned utilities for distribution to their customers, and markets at wholesale large blocks of power to industrial customers and Federal establishments within the area. In such operations, the Bonneville Administration builds, maintains, and operates a region-wide network of transmission lines and related facilities. The Bonneville network is the backbone of the Northwest Power Pool, which includes non-Federal as well as Federal facilities, and embraces the nation's largest transmission system, a 5,445-mile system designed to integrate the Federal plants with each other, and with other generating facilities in the region for the express purpose of: (*a*) making the fullest use of low cost hydroelectric power and increasing production through coordinated operation; (*b*) maintaining reservoir levels at non-Federal generating plants by using surplus stream-flow energy; (*c*) keeping the output of higher cost thermal electric energy to a minimum consistent with serving all loads; (*d*) permitting maximum use of the most efficient thermal plants when thermal generation is necessary; (*e*) increasing the reliability of service throughout the region by providing emergency connections between the Federal system and other utility systems.

It is evident that the nation as a whole has as much at stake in the future development of the Columbia River System as has the Pacific Northwest, since without the area's low cost power supply the many vital products produced in the area would have been less plentiful and considerably more expensive in the United States during the past decade. The Atomic Energy Commission's production of plutonium has also depended upon Columbia River Power. These materials have provided additional jobs in manufacturing, transportation, and marketing for thousands of people all over the nation.

The President's Materials Policy Commission has estimated that national power requirements will be 131 per cent larger in 1960 than in 1950. The Pacific Northwest, with an anticipated rate of population growth greatly exceeding the national average, and with greater dependence on hydro electric energy for industrial growth, will require a much larger proportionate expansion of such facilities than the country as a whole. During the last ten years, the average annual increase in power requirements in the area has been 14 per cent, which is at a rate 55 per cent greater than the national average rate. The region's energy requirement may reach 80 billion kwhr by 1960, some 206 per cent more than in 1950.

The growing dependence of industry in the Pacific Northwest on power is shown by the fact that in 1940 manufacturing plants purchased about 11,000 kwhr for each worker employed, and in 1950, 37,000 kwhr. Among the factors responsible for this trend are: (*a*) declining reliance on self-generated power (as from wood waste) and switching to purchased power; (*b*) technological advances requiring more energy, such as electrically operated saw mills and the hydraulic barker in pulp mills; (*c*) establishment of new electroprocess industries, which, it is estimated, could alone absorb as much as 3,000,000 additional kilowatts of power in the next ten years. Last year these industries required 1,400,000 kw, with an additional 270,000 kw committed to electroprocess plants under construction. These electroprocess industries accounted for 35 per cent of the total regional requirement for electricity. How the coming of such industries to the Northwest will ultimately affect the area is, of course, a matter of speculation, but it is highly probable that their very presence will result in a much greater utilization of the complex and low grade materials of the region, as is illustrated by the Hanna development of nickel previously mentioned, and thus revive the area as a potent source of mineral wealth which has lain untouched because of the lack of facilities for processing marginal deposits. This is particularly important in the area since the forest-based industries cannot possibly provide employment for the large number of people who are daily moving into the Pacific Northwest attracted by the favorable climate, topography, and recreational advantages.

FIG. 4. Tapping an electric furnace at the Pacific Carbide and Alloys Company, Portland, Oregon.

The Pacific Northwest is an area which must be seen to be appreciated, and contains many contradictions. As an example, the state of Oregon embraces approximately 100,000 square miles with a present population of about a million and a half. However, approximately one-third of these people live in the Portland area, and another third in the rich and fertile, but relatively small, Willamette Valley, which drifts southward from Portland, thus giving a state, which has some counties larger than the whole state of New Jersey, with only one metropolitan area.

Likewise the state of Washington can be said to have only two such areas: that around Seattle-Tacoma, and that around Spokane, the area of Vancouver being more correctly counted with the Portland area, thus, the requirement for the unusually long and diverse transmission system with all its attendent problems. The Pacific Northwest, in only a few years, has become the most electrified part of the United States and it will require the utmost cooperation between the Federal and private utilities to install generating and storage facilities rapidly enough to meet the growing requirements.

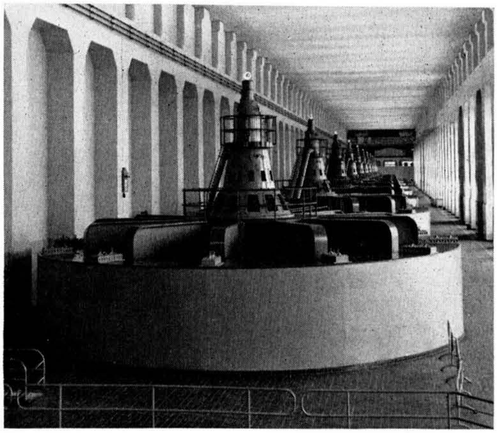

FIG. 5. Ten giant generators, each with a capacity of over 50,000 kw, at the Bonneville dam power house.

Residential and rural service average use per customer in the area in the calendar year 1951 was 5205 kwhr, as against a U.S. total average of 2137 kwhr. Despite the vastly increased generating capacity that will be provided by the projects now under construction indications are that additional developments must be immediately undertaken if the demands of the region and new industries are to be met. This will certainly require the construction of large multipurpose dams on the Columbia, which probably can only be undertaken by the Federal government. The development of facilities on the tributaries may, in many cases, be undertaken by the private utilities, possibly to the better development of the region if they are allowed to do so.

Electric requirements have more than doubled every ten years, not only in the Northwest, but throughout the nation. This same rate of increase has necessarily applied to investments in power plants and transmission lines. It is evident that the development of Columbia River Power at that pace is going to require such enormous funds in the future that serious consideration must be given to all plans for the development of the full potential of the region as to where the money is coming from. It may well be that a "clamp-down" by Congress on the spending spree of the last two decades will involve a putting off of the essential development of the river basin, so that the present proposed Federal program will have to be drastically modified.

The principal electric power need of the Pacific Northwest is in the development of generating and storage facilities with enough rapidity to meet the growing requirements. Many factors must be considered in developing a responsible program to this end. Since only the construction of large multipurpose dams on the Columbia and its tributaries will furnish a sufficient volume of power to meet the region's needs, new capacity must be added, not only at a rate consistent with load growth, but at locations where it will support the new demands with a minimum of transmission, as well as having storage projects and run-of-river plants in such a combination that they complement each other, making possible the fullest use of the available water resources. While power supply is of the main interest to the electroprocess industries, the dams must be correlated with other purposes, such as flood control, navigation, and irrigation, in order to satisfy full regional demands.

The Bonneville Power Administration, Bureau of Reclamation, and Corps of Engineers have all cooperated in recommending the Federal program. Projects now under construction are Hungry Horse, Albeni Falls, McNary, Big Cliff, Lookout Point, Dexter, Chandler, Chief Joseph, Palisades, and The Dalles. The first increments of storage in addition to Grand Coulee became available at Albeni Falls and Hungry Horse in mid-1952, and by the end of the year Hungry Horse was supplying 142,500 kw from its first two generators. During 1953 the first blocks of power will be coming from Detroit and McNary dams, and in 1954 will come the first power from Albeni Falls, Big Cliff, and Lookout Point; in 1955 from Dexter, Chandler, and Chief Joseph; in 1956 from Palisades; and in 1957 from The Dalles.

Authorized projects, not currently under construction, are expected to bring additions to the area's power supply in the following order: Roza, (see map), American Falls, Ice Harbor, Libby, Hills Creek, Lower Monumental, Little Goose, Priest Rapids, Lower Granite, and John Day. Projects recommended but not yet authorized are Upper Scriver Creek, Lower Scriver Creek, Hell's Canyon, and certain thermal plants. According to this schedule, new facilities at Federal hydroelectric projects would add more than 5,000,000 kw of prime power to the Federal Columbia River System in the next ten years under minimum hydroelectric conditions.

In addition, the Bonneville plan proposes constructing 400,000 kw of thermal electric plants and interconnecting the existing transmission facilities with adjacent systems in California and Idaho. The purpose of the thermal electric plants is to provide base energy at the time of limited stream flow, a plan which offers a relatively large addition to the system's prime power with a small average power cost, and a materially decreased transmission cost due to the feasibility of locating thermal plants near the load, which, of course, cannot be done with the hydropower since nature has placed practically all such power east of the rugged Cascade Range of mountains, while man has elected to locate, to a large degree, west of that range.

Mention was made before of the expansion of the Atomic Energy Commission's facilities at Hanford. How far this expansion may go in the future is probably unknown even to the AEC. There is no doubt, however, but that such expansion will require considerably more power, not only for the operation of the AEC installation, but also to serve the increasing population and service facilities which are rapidly building up in that area. Ice Harbor is in a location to best serve such a load, but until Ice Harbor, or equivalent facilities, are supplied, the additional Hanford needs will require the refusal of equivalent service to other new loads in the region.

The Columbia's flow characteristics are such that the average high flow comes in the summer when power loads are lowest. The power system's capability can only be sustained by constructing upstream reservoirs that will store water when stream flows are high, for release during the winter to supplement low flows. Such dams, installed or proposed, are Hungry Horse, Albeni Falls, Grand Coulee, Libby, and Hell's Canyon.

Run-of-river projects with storage only for peaking purposes are Bonneville, The Dalles, John Day, McNary, Priest Rapids, and Chief Joseph on the Columbia, and Ice Harbor, Lower Monumental, Little Goose, and Lower Granite on the Snake.

The five primary storage reservoirs—Grand Coulee, Hungry Horse, Albeni Falls, Hell's Canyon, and Libby—will provide flood control benefits and store water for power from snow melt so that while the reservoirs are refilling, for later power production, flood crests will be reduced at downstream points. Generators will be installed at all storage dams, but the Bonneville Power Administration regards their major contributions to the Columbia River power supply as their ability to regulate the release of stored waters for use at downstream plants. Detroit and Lookout Point will furnish further flood control protection, and the plans for Priest Rapids and John Day incorporate emergency storage of flood waters. Grand Coulee has the largest irrigation facilities although some of the others will aid by reducing pumping heads or furnishing pumping power. Below Chief Joseph on the Columbia and Hell's Canyon on the Snake the dams are designed to provide for preservation of fish runs.

In addition to the Federal interest, the private utilities of the Northwest have always been aware of their obligation to their consumers, and in combination with the non-Federal public owned utilities, have projects underway which will add 604,000 kw of prime power and more than twice that amount of peaking capability under minimum year water conditions in the next three years. These projects now under construction are Ross by the city of Seattle; installation of additional generators at Rock Island by the Chelan County PUD; Box Canyon by the Pend Orielle PUD; Cabinet Gorge by the Washington Water Power Company; Station "B" additions by the Portland General Electric Company; Clearwater Plants No. 1 and No. 2 on the Umpqua by the California-Oregon Power Company; and additions to the Kerr Plant of the Montana Power Company. Scheduled additions not yet under construction are Mayfield and Mossyrock by the city of Tacoma; Guffey and Dike by the Idaho Power Company; Lemolo Plants No. 1 and No. 2 by the California-Oregon Power Company; and Pelton and Round Butte by the Portland General Electric Company; some of which plants are currently being delayed by legal actions.

1955 is the latest date included in the above definitely scheduled non-Federal projects. Others, however, are being considered to the possible extent of an additional 573,000 kw. These possible facilities are Swift Creek and Muddy Fork by the Pacific Power & Light Company; Noxon Rapids by the Washington Water Power Company; Trout Creek by the Montana Power Company and Big Bend Nos. 1, 2, and 3, Salt Caves; and Keno by the California-Oregon Power Company.

Beginning with 1955–56, the Bonneville Power Administration will have increasing amounts of firm power for new electroprocess plants providing the proposed schedule is fulfilled. However, since nonindustrial demands on the Federal system beginning in 1961–62 will absorb all the increase in generating capacity now scheduled for those years, no additional firm power will be available for electroprocess plants unless facilities not now scheduled are brought into production. Table I is of interest in this regard. It should be pointed out that an industry which is willing to take a "calculated risk" on interruptible power may find it very favorable to consider entering the area at an earlier date.

### Transmission

During the next ten years the Federal grid will be extended more rapidly than before. By 1965 its peak capability is scheduled to total better than 9,000,000 kw. Although the prime purpose of the transmission grid is to deliver the output of Federal plants to the Bonneville Power Administration's load centers throughout the region, it is also utilized to integrate the operation of Federal power plants with non-Federal facilities, and to achieve benefits by tie-ins with areas adjacent to the Columbia Basin region. It is evident that transmission lines must keep pace with the increase in generation facilities to bring energy from new dams to markets.

The proposed transmission program has been divided into two phases. The first has received engineering study and is to be completed by January 1957. The second phase, covering the period from January 1957 to 1963, while not yet specific, is fairly definite as to the pattern that such transmission system expansion must follow.

Under the first phase, three major transmission lines are under construction (see map). A 300,000-kw, 300-kv circuit, to be completed this year, will connect Grand Coulee to the Bonneville Power Administration's Olympia Substation, and is the first line in the area carrying voltage in excess of 230

TABLE I. *U. S. Columbia River Power System. Existing and potential large electroprocess industrial requirements*
1953–54—1962–63
(Thousands of kw) Average over the storage release season

| | 1953–54 | 1954–55 | 1955–56 | 1956–57 | 1957–58 | 1958–59 | 1959–60 | 1960–61 | 1961–62 | 1962–63 |
|---|---|---|---|---|---|---|---|---|---|---|
| Alumina | 0 | 20 | 20 | 20 | 28 | 28 | 28 | 28 | 32 | 32 |
| Light metals primary production* | 1030 | 1380 | 1516 | 1617 | 1872 | 2111 | 2161 | 2338 | 2580 | 2714 |
| Light metals fabrication | 32 | 44 | 44 | 62 | 68 | 70 | 81 | 83 | 86 | 98 |
| Ferroalloys | 97 | 148 | 169 | 230 | 230 | 239 | 315 | 363 | 381 | 396 |
| Phosphate industry | 47 | 140 | 215 | 239 | 239 | 292 | 344 | 368 | 398 | 474 |
| Chlorine, chlorates, caustic soda | 36 | 46 | 62 | 67 | 70 | 84 | 87 | 92 | 97 | 110 |
| Calcium carbide | 24 | 29 | 53 | 63 | 67 | 67 | 87 | 87 | 106 | 120 |
| Abrasives | 31 | 40 | 50 | 55 | 65 | 75 | 84 | 94 | 94 | 94 |
| Ammonia | 22 | 42 | 70 | 70 | 88 | 88 | 122 | 122 | 122 | 132 |
| Other† | 97 | 228 | 273 | 349 | 388 | 418 | 484 | 507 | 537 | 569 |
| Grand Total | 1416 | 2117 | 2472 | 2772 | 3115 | 3472 | 3793 | 4082 | 4433 | 4739 |
| Existing‡ | 1213 | 1480 | 1544 | 1577 | 1607 | 1607 | 1607 | 1607 | 1607 | 1607 |
| Potential new industrial | 203 | 637 | 928 | 1195 | 1508 | 1865 | 2186 | 2475 | 2826 | 3132 |

* Includes aluminum, magnesium, and titanium.

† Includes carbon, graphite, glass, hydrogen peroxide, iron, lead, manganese dioxide, cellulose products, synthetic fibers, zinc, lithium, methanol, and other chemicals.

‡ Includes BPA commitments, agreements, and reservations as of December 1, 1952.

kv. Two circuits to be completed by the end of 1955 will connect the Chief Joseph Dam to the Snohomish Substation. These lines are being designed for future conversion to 345 kv service—the highest voltage, highest capacity circuits in the country, and will deliver 500,000 kw at that voltage. A 230-kv submarine cable across Puget Sound to serve the Bremerton area and the Olympic Penninsula is scheduled for 115-kv energizing in late 1954, with conversion to 230 kv two years later.

By 1957 four new circuits will be bringing McNary Dam power westward to market. Two of these circuits will bring the power to a new Santiam substation, with 230-kv lines extending to Chemawa, Albany, and the J. P. Alvey substation. From Alvey, circuits will be built to supply the Nickel Mountain load, previously mentioned, and continuing westward to Coos Bay. One of the remaining two circuits will consist of the McNary-Big Eddy-Troutdale circuit, to be in operation by 1954, and the other will be the McNary-Ross Substation circuit, scheduled for late 1955 completion.

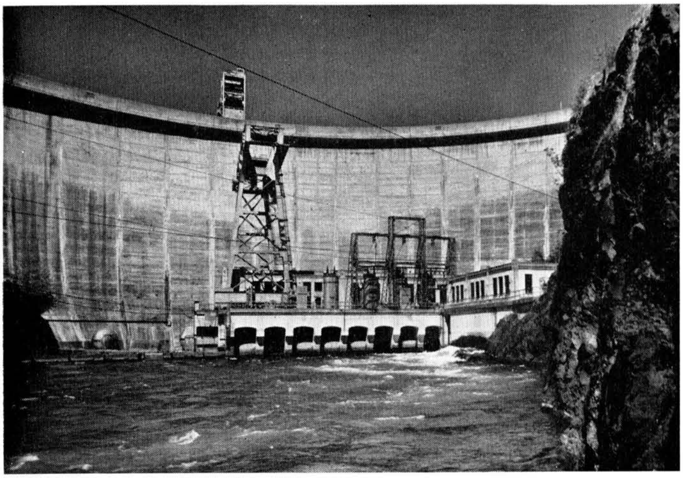

FIG. 6. Merwin Hydroelectric Project, Pacific Power & Light Company, Lewis River, Washington—100,000 kw.

230-kv facilities now run as far south as Redmond, Oregon, and by the end of the present year will be extended to Klamath Falls, where it is proposed that the interconnection be made with the northern California circuits.

Central Washington will be served by a new 230-kv circuit from McNary to Walla Walla, to be completed in late 1955, and the present 115-kv system in the vicinity of Pasco will be reinforced because of the heavy load requirement due to the AEC expansion at Hanford.

The transmission of power in the Pacific Northwest cannot be properly compared with power transmission elsewhere in the United States since many miles of high voltage, high capacity circuits must be built through very difficult terrain, resulting in average transmission distances of about 160 miles—much longer than for any other U. S. system—and covering a vast area with parts of the circuits inaccessible due to heavy rainfall and snow. The resulting construction necessary to insure continuity of service, at the lowest possible cost, requires continuous development and adoption of new engineering designs.

The Bonneville Power Administration power contracts all provide that adjustments may be made in wholesale rates every five years. The next adjustment date is December 1954. Since the cost of new facilities expected to be added to the Federal Columbia River Power System before 1959 will be substantially higher than the costs incurred in the construction of Bonneville and Grand Coulee, it is anticipated that some increase may be required at the December 1954 adjustment date. Probably the present basic rate of $17.50 per kilowatt year will be raised to approximately $20 per kilowatt year or possibly as high $22.50. But even at that level, power from the U. S. Columbia River System will be lower in cost than power available elsewhere in this country, and no difficulty in selling it is foreseen.

### Power Policies

The program as presented represents an estimated cost of nearly four and one half billions of dollars.

The immensity of this proposed undertaking, plus the past concentration of power in the hands of a Federal bureau, has given much cause for thought to the people of the Pacific Northwest area. The Bonneville Power Administration is not an autonomous "authority" such as the TVA, but is rather a marketing agency under the Department of the Interior. To many in the Northwest region, Bonneville appears to have too much power over the life of the area. This is because of its marketing control and its potent force in the ability to allocate the area's energy almost in any way it desires. Many are convinced that the Bonneville Administration has used its great power in a socialistic manner, backing the PUD's in a plan to destroy private utilities. PUD's generally operate on a county-wide basis; but in the state of Washington, they have been extended the power of joining together so as to exercise their rights of eminent domain outside their normal area to the extent that they may condemn and purchase all, or any part, of the facilities of private firms. This has led to considerable internal fighting between PUD's and private power companies in that state. Washington has some 20 PUD's operating, whereas Oregon, which does not extend such broad power to the PUD's, has only two.

The private utilities, which have been able to buy power from the Bonneville Power Administration for transmission to their customers, have become largely dependent upon it for their energy; however, this has been on Bonneville's terms, which to many in the private utility field, are intolerable since the private utilities feel that the people they serve are the established residents of the area, and the small and medium businesses which furnish the livelihood for so many people. They feel that it has been unfair of Bonneville to arbitrarily split its available energy on the present basis of approximately 60 per cent to large industries and 40 per cent to the general public. They point to the tight power situation of the past several years as an indication that the power needs of the general public have not been given the priority over large new firm commitments to high load factor industries that they believe should have been given.

The people of the Northwest in general are independent in nature. They "pioneered" the area, and cast a jaundiced eye at paternalism. To more than just a voluble few, the Bonneville colossus is beginning to appear menacing and a definite reversion to the "states rights" idea is rapidly developing. With the recent change in national administration the proponents of such views have taken heart and there will undoubtedly be considerable opposition to the enactment of the whole proposed river-system development plan as previously discussed. The private utilities feel that the government has no place in the building of hydroelectric power projects which the utilities are ready and able to take on when the demand is apparent, and feel that the Federal policies should be to limit Federal construction to those projects involving irrigation, flood control, etc., to a large degree.

There has been practically no complaint in the area as to the technical phases of the system. The Northwest power pool, for instance, to which Bonneville supplies approximately 85 per cent of the net energy requirements, has been a marvelous thing for the area. It is only at the policy making level that dissatisfaction starts. As an example of the intense feeling developing in the area, the Washington state legislature has recently provided for a state power commission having the authority to acquire facilities, or build them, and to negotiate with the government, Canada, any other state or public power agencies, this as part of the regional effort to recover a maximum of local level authority.

It is unfortunate that in an article of this type political policies have to be brought in, but at the present time the future of the electrochemical industry in the Pacific Northwest rests, to a great extent, on the final resolving of such energy distribution policies by the Federal government.

Due to the rapidly growing feeling about local control, and the developing uncertainties as to the adoption of the proposed Federal program, the larger utilities, public as well as private, are looking more and more toward the independent construction of necessary generating plants on an individual or joint basis. Such plans by private companies bring out many conflicts, such as the controversy raging between the Idaho Power Company and the Federal bureaus for the development of the Snake River, wherein the Idaho Power Company desires to make further construction at the Oxbow site, whereas the Reclamation Bureau's viewpoint is that this would prevent construction of the proposed multipurpose Hell's Canyon project. Some of the suggestions of the private utilities even include the non-Federal construction of the power features of multiple purpose government projects. Whether such proposals will have a deterrent effect upon congressional authorization of the now unauthorized portion of the Columbia River Plan, cannot be foretold. The general feeling in the area is that some modifications are going to be made. Whether or not such modifications will seriously affect the rate at which the electroprocess industries can expect to enter the Pacific Northwest on a firm power basis is likewise unpredictable. In the meantime, opportunity does exist to utilize interruptible power, either through the Bonneville Power Administration, or through the non-Federal and the private utilities.

**Acknowledgment**

Data concerning industry have been obtained from such concerns wherever definite figures are given, and from miscellaneous sources wherever such figures are given as estimates.

Much of the information concerning the present and proposed Power program has come from various publications of the Bonneville Administration, which also supplied the map.

## MANUSCRIPTS AND ABSTRACTS FOR FALL MEETING

Manuscripts are now being received for the Fall Meeting of the Society, to be held at the Ocean Terrace Hotel in Wrightsville Beach, N. C., September 13, 14, 15, and 16, 1953. Subjects to be covered at the technical sessions will be Battery, Corrosion, and Electrodeposition.

To be considered for this meeting, triplicate copies of manuscripts or abstracts (not to exceed 75 words in length) must be received at Society headquarters, 235 West 102nd Street, New York 25, N. Y., *not later than July 1, 1953.*

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Yardney Electric Corp., New York, N. Y.

# Corrosion of Heating Electrodes in Molten Chloride Baths[1]

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## ABSTRACT

Alternating current between immersed electrodes is used to heat sodium-potassium chloride heat-treating salt baths to temperatures around 1500°F. The corrosive conditions to which the electrodes are exposed were simulated in laboratory tests. It was found that under certain conditions the electrodes wasted away or "pencilled" rapidly. This pencilling was due to metal dissolving during the anodic part of the a-c cycle and plating back as a nonadherent powder during the cathodic part of the cycle. Whether or not pencilling occurred depended upon the condition of the protective oxide coating on the electrodes, which in turn was controlled by the composition of the neutral salt bath. Oxidizing constituents in the bath kept the oxide film in repair. Alkalinity in the bath was necessary for film breakdown and pencilling. No pencilling occurred in fresh pure salt. Pencilling increased rapidly with current density.

## INTRODUCTION

Molten salt baths have been developed to carry out practically all the heat-treating operations which may be required in handling metals. There are many types of salts and many types of furnaces (1). A convenient and economical means of supplying heat to the bath, particularly in the higher temperature ranges, is by means of alternating current passed through the bath between immersed electrodes (2). For long life such electrodes are made of some heat-resisting alloy. As might be expected, the life of the electrodes depends in large part on the composition of the salt bath and the conditions of operation. Generally the corrosive action is most severe at the liquid line.

On the other hand the attack has sometimes occurred beneath the liquid line with a smooth wasting away or "pencilling" of the electrodes. Fig. 1 shows such a pencilled electrode. Such thinning is always much more pronounced on the facing surfaces of a pair of electrodes, and is evidently associated with the passage of the alternating current. This type of attack has been sporadic with many electrodes showing no effect of the passage of current.

It was decided to study the phenomenon of pencilling on a laboratory scale. For this purpose a particular salt composition and a particular electrode material were selected. The electrode material was Inconel of the following composition: 77.51% nickel, 14.40% chromium, 7.40% iron, 0.08% carbon, 0.10% silicon, 0.16% manganese, 0.009% sulfur, and 0.23% copper. The salt bath selected was a common neutral chloride bath containing 56 parts of potassium chloride and 44 parts of sodium chloride (3). This bath is used in the temperature range of 1350° to 1650°F. It is neither carburizing nor decarburizing to steel and hence is called neutral.

## METHODS AND RESULTS

### *Experimental Procedure*

The laboratory setup was intended to reproduce commercial conditions on a small scale. A small scale meant that at the same current density on the electrodes there was less heat input into the salt, the heat input being roughly proportional to the square of the current multiplied by the resistance of the salt. This meant that auxiliary heat was required to keep the salt molten. Auxiliary heat was supplied by a gas furnace. The apparatus was surrounded by a hood to remove fumes.

While as described below there were some variations in procedure, the general conditions were as follows. A weight of 3½ lb of C.P. salt mixture was melted in cast metal pots, 6 in. in diameter and 5 in. deep, and the temperature of the furnace was set for 1500°F. A pair of electrodes, ½ x ½ x 8 in. in size, were spaced ½ in. apart and lowered into the center of the fused salt to a depth of 1 to 2½ in. Low voltage alternating current (0 to 6 volts) was applied across the electrodes and a current of 0 to 130 amp allowed to flow. Generally the current was adjusted to 20 amp/in.$^2$ of immersed electrode area. Usually an experiment was continued for about 18 hours. Then the electrodes were removed, cleaned, and weighed. The weight loss was confined principally to the immersed portion and was calculated as grams per square inch of immersed area per day. The depth of penetration on each surface was measured also.

During a run the salt level dropped about ⅓ in. due to volatilization and creeping. Accordingly, the

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[1] Manuscript received October 14, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

immersed area was estimated at the start, at the end, and averaged. As the salt level dropped, the resistance between the electrodes increased and the current dropped. Fortunately the decrease in immersed area and the decrease in current compensated for each other and the current density remained substantially constant. As the current decreased the heat input from this source dropped, and the temperature dropped somewhat. However, the downward drift in temperature was not large, and the temperature was controlled within ±30° of 1500°F.

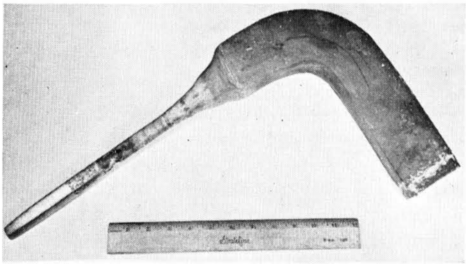

FIG. 1. Commerical electrode showing severe thinning beneath the liquid line.

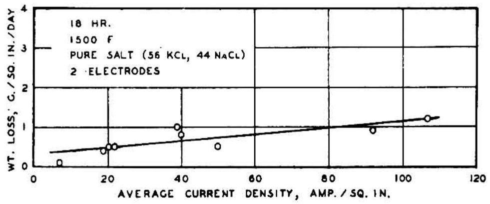

FIG. 2. Effect of current density in pure salt

With the setup described the current distribution on the electrodes was not uniform. Obviously there was more current on the facing surfaces of the electrodes than on their backs, and more current on the corners than on the flat surfaces. Consequently the average current density should be interpreted with caution. In a few runs the current distribution was made more uniform by placing one experimental electrode in the center of the salt pot and using the pot as the other electrode.

### *Electrode Behavior in Pure Salt*

No pencilling was ever obtained in experiments starting with fresh pure salt despite variations in temperature and current density. To obtain high current densities the cross sections of the electrodes were cut down. In one run such high currents were imposed on small electrodes that they became much hotter than the salt (2200°F at a guess) and caused the salt to boil where in contact with the electrodes.

The effect of current density on weight loss is shown in Fig. 2. The weight loss increased slightly with current density, but even exceedingly high currents produced nothing resembling pencilling. There were some small scattered pits 0.01 to 0.02 in. deep, and these were more numerous on the facing surfaces. Analysis of the salt showed no appreciable change in composition during these runs.

### *Electrode Behavior in Alkaline Salt*

Fused chloride salt baths are not completely stable at high temperatures, but gradually react with moisture and air to form oxides and carbonates. A water solution of such a salt is alkaline, and hence the fused salt itself is often said to be alkaline. To simulate this decomposition, the salt bath was made alkaline at the start by the addition of small amounts of sodium hydroxide or sodium carbonate. It made little difference which was added because under the conditions existing in the gas furnace the hydroxide was rapidly converted to carbonate. Under these alkaline conditions the electrodes pencilled.

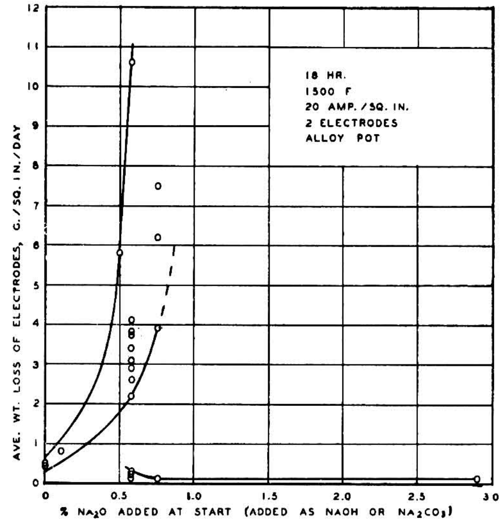

FIG. 3. Effect of alkalinity

Fig. 3 shows the weight loss plotted against the calculated amount of $Na_2O$ added at the start. The weight loss increased rapidly with $Na_2O$ content up to 0.58 to 0.77 per cent. The data show some scatter for reasons which are described below. The curves in the left portion of the figure indicate the range of scatter. The bottom curve in Fig. 3 is discussed further below.

In Fig. 4 the center electrode illustrates the typical appearance of electrodes showing pencilling at a current density of about 20 amp/in.$^2$, average. This electrode was exposed to salt with 0.58 per cent $Na_2O$ present at the start (added as sodium carbonate) and had an average weight loss on the immersed portion of 3.7 g/in.$^2$/day. However, as can be seen in the figure the attack was confined to the facing surface and to the edges and bottom, manifestly regions of high current density. The depth of attack on the facing surface was about 0.05 in. The attacked portions were smooth and bright, whereas the rest of the immersed area was dull gray. The gray portions were strongly magnetic and appeared on magnification as though built up with an electrodeposit. Measurements with a micrometer showed an increase in thickness of several thousandths of an inch, particularly near the liquid line.

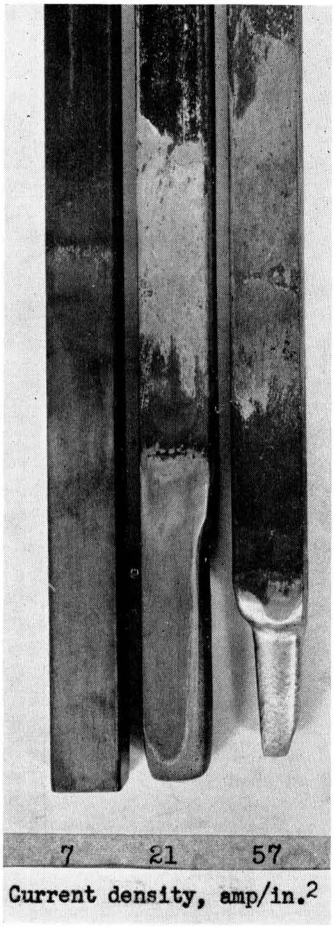

FIG. 4. Side view of electrodes exposed for 18 hr at 1500°F in bath with 1% sodium carbonate added at the start. Natural size.

Microexamination of cross sections through pencilled electrodes confirmed the presence of a deposit on the back and sides. The deposit is shown in Fig. 5. It had a nodular growth characteristic of electrodeposits. The specimen in Fig. 5 was copper plated to protect the edges during polishing. The fact that the deposit readily took the copper plate tends to prove that it was metallic. The deposit was not adherent and could be flaked and powdered off.

When pencilling occurred a powdery, black, magnetic sludge accumulated beneath the electrodes. Occasionally bubbles could be seen rising to the surface and sometimes these burst into flame, probably indicating the presence of carbon monoxide. Upon solidifying the solid salt was white in color although sometimes it had a bluish tint.

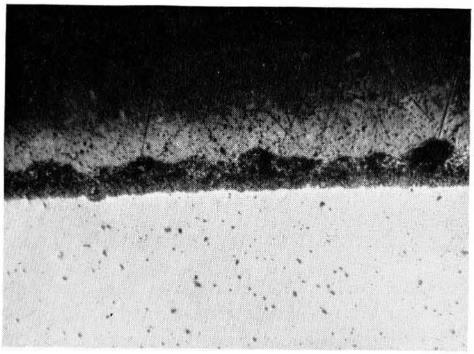

FIG. 5. Cross section of pencilled electrode showing deposit on back surface. Specimen copper plated. 25×

### *Electrode Behavior in Oxidizing Salt*

When large amounts of alkaline materials were added there was no attack of the electrodes whatsoever (Fig. 3). In such cases the salt acquired a yellow color and was found to have become high in chromate. These runs were made in nickel-chromium-iron heat-resisting alloy pots, and it is believed the high alkalinity attacked the oxides on the surface of the pots. Sodium chromite was probable carried to the surface of the salt bath and there oxidized to chromate. This mechanism tended to be confirmed by the fact that the electrodes showed a small encrustation of yellow alkaline salt at the liquid line 2 or 3 inches above the salt level even when the rest of the salt was white. That chromium was lost from the pots was shown by chemical analyses of layers removed from their cleaned surfaces. In one case the chromium content of the pot was reduced after several runs from an initial value of 20 per cent to 6.4 per cent at the surface. The "dechromizing" effect extended to considerable depth with a layer of metal removed some distance beneath the surface analyzing 13.2 per cent chromium.

The chromate contents of strongly alkaline salt baths built up to as high as 1.1 per cent chromate in solution. Whenever much chromate was present there was no pencilling. The immersed portion of the electrode acquired a thin adherent black coating. Apparently chromate in solution acted as an oxidizing agent to put a protective oxide coating on the electrodes.

To avoid the complication of chromate build-up in the salt, five runs were made in a nickel pot. The results are given in Table I. There was no sharp break in the rate of pencilling as in Fig. 3, but again the rate of pencilling passed through a maximum. This occurred somewhere between 1 and 5 per cent of added sodium carbonate. Above 5 per cent the attack decreased, and with 25 per cent added sodium carbonate it was less than in pure salt. The electrodes in this last run acquired a thin uniform black oxide coating. This shows that carbonate is oxidizing toward the electrodes, and, in sufficient concentration, can prevent pencilling by forming a protection oxide coating. Presumably other oxidizing agents besides chromate and carbonate would prevent pencilling.

TABLE I. *Electrode behavior in alkaline salt in nickel pot*

Time: 18 hr; Temp: 1500°F; Current density: 20 amp/in.$^2$; 2 electrodes; Nickel pot.

| Run | Composition of salt at start, % | | | Wt loss of electrodes g/in.$^2$/day |
|---|---|---|---|---|
| | $Na_2CO_3$ | KCl | NaCl | |
| 25 | 0.0 | 56.0 | 44.0 | 0.4 |
| 37 | 1.0 | 55.5 | 43.5 | 1.6 |
| 36 | 5.0 | 53.2 | 41.8 | 2.9 |
| 44 | 10.0 | 50.4 | 39.6 | 1.6 |
| 43 | 25.0 | 42.0 | 33.0 | 0.2 |

### *Effect of Adding Chromate to the Salt*

Once it was observed that accumulations of chromate in alkaline salt prevented pencilling, deliberate additions of potassium chromate were tried. Analyses of the salts at the ends of the runs showed that the chromate content of the salt was not constant, but might either increase or decrease. Apparently, once sufficient chromate was present to prevent pencilling the chromate content of the salt tended to build up even higher. On the other hand, once pencilling started, the chromate content dropped to very low values, probably through reaction with the electrode sludge with its large surface area. It was found that the chromate content of the salt could be estimated very accurately from the yellow color of the solid salt in comparison with known standards.

For convenience the chromate content at the start and at the end of the runs was averaged. In Fig. 6 the weight losses of the electrodes are plotted against the average chromate contents of the alkaline salt baths (one per cent of sodium hydroxide or sodium carbonate added at the start). The figure shows that pencilling never occurred with average chromate contents above about 0.045 per cent, equivalent to 450 ppm of chromate. Below 0.045 per cent some pencilling might occur with maximum rate increasing with decreasing chromate content.

In practice it might take some watching to maintain the chromate content of neutral chloride baths around 0.05 per cent. A large area of work passing through the bath would lower the chromate content. Normally, oxidizing constituents cannot be tolerated in the bath because they decarburize steel. However, 0.05 per cent of chromate would be small enough to have no significant effect in this respect, although larger amounts would be expected to cause some decarburization.

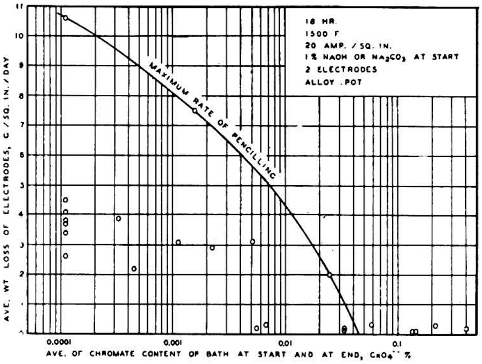

FIG. 6. Effect of chromate on pencilling in alkaline salt

### *Changes in Salt Composition*

It had become apparent that the composition of the salt baths with added alkali was not remaining constant. Accordingly some baths were analyzed after different times, the $Na_2O$ content being determined by titration, and the $CO_2$ content by evolution. The results are shown in Fig. 7. It was found that both these constituents were being lost from the baths, and at different rates. After a short time there was a small excess of alkalinity. During these runs the chromate content increased from zero at the start to 0.0085 per cent at 6 hours and then decreased to negligible values again. This would mean that some of the average chromate contents in Fig. 6 were incorrect, but not sufficiently so to change the general picture. While Fig. 7 is considered typical there was undoubtedly considerable variation between runs. As already noted, it made little difference whether sodium hydroxide or sodium carbonate was added at the start because the hydroxide was converted to the carbonate within the first hour.

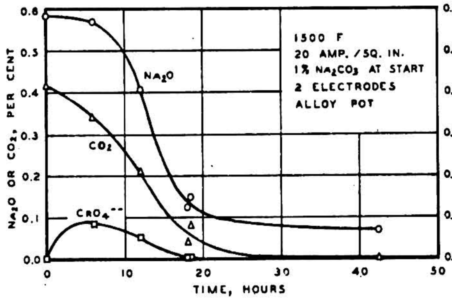

FIG. 7. Changes in salt composition with time

TABLE II. *Interrelation of chromate, carbonate, and alkalinity on pencilling*

Time: 18 hr; Temp: 1500°F; Current density: 20 amp/in.$^2$; 1% $Na_2CO_3$ at start; 2 electrodes; 50 Ni, 20 Cr alloy pot.

| Run* | Salt composition at end | | | Wt loss of electrodes g/in.$^2$/day |
|---|---|---|---|---|
| | Sodium carbonate $Na_2CO_3$ | Excess alkalinity $Na_2O$ | Chromate $CrO_4$ | |
| | % | % | % | |
| 79 | 0.337 | 0.013 | 0.011 | 0.2 |
| 80 | 0.169 | 0.041 | 0.002 | 3.1 |
| 81 | 0.265 | 0.015 | 0.013 | 0.3 |
| 82 | 0.024 | 0.024 | 0.001 | 2.2 |

* Runs in old alloy pot with partial cleaning of pot between runs.

TABLE III. *Effect of age of alloy pot on salt composition*

Time: 18 hr; Temp: 1500°F; Current density: 20 amp/in.$^2$; 1% $Na_2CO_3$ at start; 2 electrodes; 35 Ni, 15 Cr alloy pot.

| Run* | Salt composition at end | | | Wt loss of electrodes g/in.$^2$/day |
|---|---|---|---|---|
| | $Na_2O$ | $CO_2$ | $CrO_4$ | |
| | % | % | % | |
| 58 | 0.15 | 0.07 | 0.0002 | 3.8 |
| 59 | 0.35 | 0.20 | 0.0002 | 3.7 |
| 60 | 0.38 | 0.23 | 0.0002 | 2.6 |
| 61 | 0.39 | 0.29 | 0.0002 | 3.4 |

* Successive runs in a new alloy pot with no cleaning between runs.

During these experiments the rate of pencilling was not constant with time. There was a period at the start when there was little or no attack on the electrodes. Pencilling started at a slow rate and gradually increased in severity up to 18 hours at least. Sometime after 18 hours pencilling slowed down again but did not stop.

Perhaps the interrelation of carbonate, excess alkalinity, and chromate is made clearer by the data in Table II. No pencilling occurred in runs 79 and 81 where the chromate and carbonate were relatively high. However, it did occur in run 80 where the chromate was low and the excess alkalinity high, and in run 82 where the chromate and carbonate were both very low.

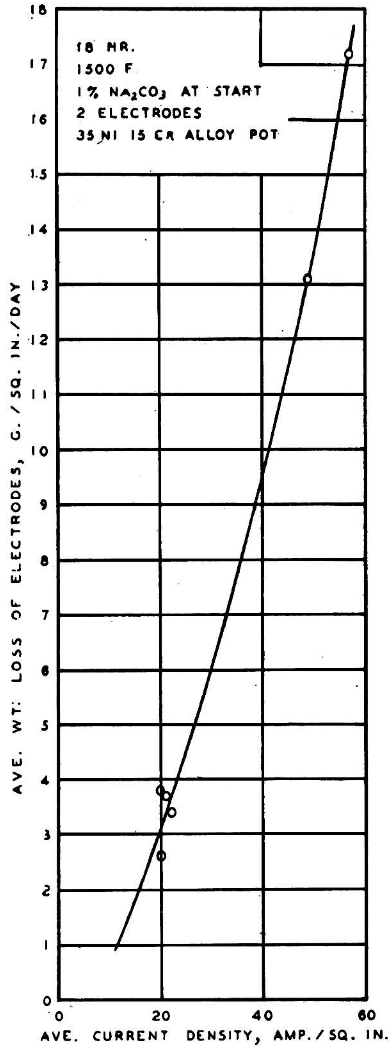

FIG. 8. Effect of current density in alkaline salt as determined on two closely spaced square electrodes.

The rate of change in composition of the salt bath was affected by everything coming in contact with the salt, such as the atmosphere above the salt, the salt pot, the thermocouple protection tube, the electrodes, and the sludge from pencilling electrodes.

Commercially there would be still other factors affecting the composition, although a large volume of salt would tend to make conditions more stable. The effect of the alloy salt pots did not remain constant but changed with the age of the pot, presumably due to the accumulation of an oxide coating and to chromium depletion. This is illustrated in Table III for the first four runs in a new alloy pot containing nominally 35 per cent nickel, 15 per cent chromium, balance iron. It would have been desirable to have had better control of salt composition.

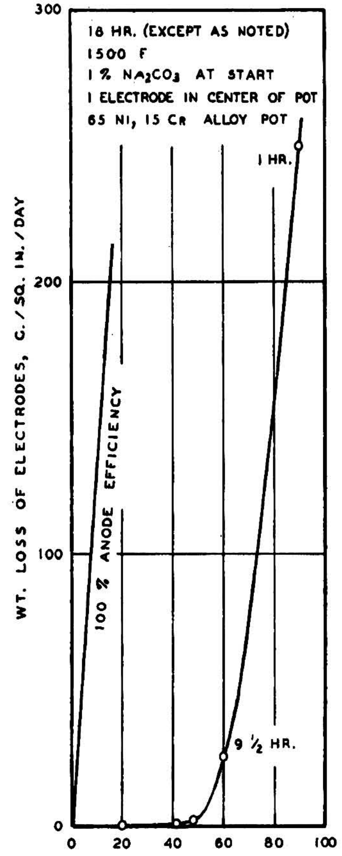

FIG. 9. Effect of current density in alkaline salt as determined on one electrode in center of circular pot.

### *Effect of Current Density*

Contrary to the behavior in pure salt, current density was of the utmost importance in alkaline salt. Some typical results are plotted in Fig. 8. Weight loss increased rapidly with current density.

Fig. 4 shows the effect of increasing current density on appearance. The electrode tested at 7 amp/in.$^2$, average, showed no weight loss and acquired a dark, uniform, good looking coating. This run was made in a nickel pot. The electrode tested at 21 amp/in.$^2$, average, showed pencilling on the facing surface and was representative of the many electrodes showing attack at this current density. The electrode tested at 57 amp/in.$^2$, average, was severely pencilled on all surfaces. This electrode was shortened about 0.15 inch by the pencilling.

It was found that the pot composition had some effect on the rate of pencilling, particularly at the higher current densities. The lowest rates of pencilling were obtained in nickel pots, intermediate rates in a 35 per cent Ni, 15 per cent Cr, balance Fe pot, and the highest rates in a 50 per cent Ni, 20 per cent Cr, balance Fe pot. Thus a weight loss of 7.3 g/in.$^2$/day was obtained in a nickel pot at 43.5 amp/in.$^2$, average, and in a 50 per cent Ni, 20 per cent Cr pot at 22.5 amp/in.$^2$, average. The rate of pencilling increased with the chromium content of the pot. Undoubtedly this was due to the influence of the pot on the salt bath composition. The effect might be due to chromium in the pot tending to remove oxidizing constituents from the bath.

As already pointed out, the current distribution around two closely spaced square electrodes was far from uniform. To obtain a more uniform current density one electrode was placed in the center of an alloy pot and the pot made the other electrode. The effect of increasing current density under these conditions is shown in Fig. 9. There is an inflection point in the curve at 50 to 54 amp/in.$^2$ Most of the laboratory weight losses plotted along this inflection point. In other words, an average current density between two electrodes of 20 amp/in.$^2$ produced the same weight loss as a uniform current density of 52 amp/in.$^2$ This gives an indication of the extent of concentration of current on the facing surfaces of the electrodes, but should not be regarded as exact. In Fig. 9 there is plotted the weight losses for 100 per cent anode efficiency. Under the severest conditions shown at 90 amp/in.$^2$ the pencilling was equivalent to an anode efficiency of 21 per cent.

Fig. 8 and Fig. 9 leave no doubt of the benefit to be gained by decreasing the current density. With two electrodes the attack was negligible below an average current density of about 7 amp/in.$^2$ Higher currents could be tolerated with more uniform current distribution. By way of emphasis it might be remarked that in none of these laboratory experiments did the Inconel thermocouple protection tube at zero current density ever show any attack.

### *Sludge from Electrodes*

Whenever pencilling occurred, a black sludge accumulated beneath the electrodes. After letting the salt bath solidify, lumps of this sludge were chipped out. Chemical analysis showed that the ratios of nickel to iron to chromium in the sludge were 78.1 to 7.6 to 14.3 as compared with 78.0 to 7.5 to 14.5 in the electrodes. Hence there was no question but that the sludge came from the electrodes.

The lumps of sludge obtained were always contaminated with lots of salt. This salt could be washed away, leaving behind a fine, dark, magnetic powder which would conduct current. Titrating the washings brought out the significant point that more alkalinity was always present than in the salt bath proper. In one case where 5 per cent sodium carbonate had been added, the salt bath at the end titrated 2.57 per cent $Na_2O$, whereas water extracts from the lumps of sludge showed 3.90 per cent $Na_2O$ in this material. Knowing that the lumps contained a total of 15.80 per cent of nickel, chromium, and iron, that they were 81.83 per cent soluble, and that in this run the electrodes lost 17.4 grams, it was possible to calculate that this extra alkalinity was sufficient to tie up all the chromium in the sludge as sodium and potassium chromites, and most of the iron as sodium and potassium ferrites. Practically all the nickel seemed to be present as metal powder. A little nickel oxide and iron oxide were probably present also.

The calculated composition corresponded to the known properties of the sludge. Washing with water would decompose the chromites and ferrites and dissolve the $Na_2O$. Treating the sludge with 5 per cent hydrochloric acid dissolved practically all the nickel and iron, but none of the chromium, as would be expected. On standing in aerated water the sludge produced no rust, which would have occurred if much metallic iron was present. The large amount of metallic nickel accounts for the magnetic and current conducting properties of the sludge.

## MECHANISM OF PENCILLING

The pencilling of the electrodes appeared to be controlled by the presence or absence of a protective oxide coating. In some cases this oxide coating was thick enough to be seen. In the presence of the protective coating the electrodes behaved like inert or passive material and were unaffected by the passage of current. In the absence of a protective coating the electrodes dissolved during the anodic part of the a-c cycle. The metal ions formed plated out during the cathodic part of the cycle as a nonadherent powder most of which settled to the bottom of the pot. The salt still carried a good portion of the current, so that the sludge was formed at low current efficiency.

Pencilling was caused by anything leading to film breakdown. Alkalinity tended to remove iron and chromium oxides from the surface by forming ferrites and chromites. In the absence of current this did no particular harm. In the presence of current pencilling occurred under these conditions and the sludge was contaminated with chromite and ferrite. The mere fact of pencilling would tend to prevent film repair. The continuous formation of fresh quantities of sludge with its large surface area would remove oxidizing constituents from the bath and thus prevent film repair. High current density was definitely a factor in promoting pencilling under alkaline conditions.

Pencilling was prevented by anything leading to film formation or repair. In pure salt there apparently was enough oxidizing power to maintain a protective film. Chromates and carbonates were film formers. It is interesting that high alkalinity favored the acquisition of both carbonate and chromate by the salt bath.

The interrelation of alkalinity and oxidizing power of the salt was complex. Some $Na_2O$ was necessary to break down the protection film on the electrodes. However, the rate of pencilling did not increase steadily with $Na_2O$ content because as the alkalinity increased the oxidizing power of the bath increased due to the accumulation of both chromate and carbonate. In the laboratory setup high $Na_2O$ contents were always accompanied by a comparatively high oxidizing power in the salt.

Pencilling was favored by anything tending to remove or prevent the accumulation of chromate. This might be accomplished by work passing through the bath. All exposed metal tended to react with the chromate and reduce it. In the case of the metal pots this tendency increased with the chromium content of the alloy in accord with the known affinity of chromium for oxygen. On the other hand, the presence of large amounts of chromic oxide, such as existed on used metal pots, tended to promote the formation of chromate. Thus chromium in the alloy pot was harmful, but chromate in solution was beneficial.

## DISCUSSION

In the commercial operation of salt baths the primary object is to turn out the work in good condition. The effect of the salt on the electrodes is a secondary matter. Nevertheless it is evident that the composition of the salt controls the life of the electrodes. No pencilling ever occurred in pure salt or in strongly oxidizing salt. Normally, strongly oxidizing conditions cannot be tolerated because of their action on the work. An ideal situation would be one where the bath was just oxidizing enough to protect the electrodes, but not oxidizing enough to harm the work. Such a condition could be achieved by maintaining about 0.05 per cent chromate in the bath (4).

During operation, neutral salt baths tend to become alkaline and to pick up carbonates. In this condition they are decarburizing to steel. Where this cannot be tolerated "rectifiers" are added to the bath. The rectifiers may be of many types. Where the rectifiers function only to maintain the hardness of the steel surface they might have little effect on pencilling. However, where the rectifiers function to remove the alkalinity or to restore the bath to its initial condition, they should be an effective means of preventing pencilling.

A third method of preventing or reducing pencilling is to maintain a low current density on the electrodes. This is largely a matter of furnace design and operation. In the case of electrodes immersed from the top of the bath merely maintaining a sufficient depth of salt might prevent pencilling.

## SUMMARY

Laboratory tests using Inconel electrodes and a sodium chloride, potassium chloride salt bath at 1500°F showed that pencilling is an electrochemical phenomenon, and is controlled by a protective oxide film on the electrodes. Under conditions of film breakdown the electrodes dissolve during the anodic part of the a-c cycle. The metal ions formed plate back during the cathodic part of the cycle as a nonadherent powder which settles out.

No pencilling ever occurred in fresh pure salt. Apparently there was enough oxidizing power in fresh salt to maintain a protective film on the electrodes. Alkalinity in the salt attacked the protective film and removed iron and chromium oxides from the surface by forming chromites and ferrites. In the presence of current the film damage in alkaline salt led to pencilling. In alkaline salt pencilling increased rapidly and at an increasing rate with current density.

In alkaline salt the presence of oxidizing agents such as carbonate and chromate acted to repair film damage and prevented pencilling. The presence of 0.05 per cent chromate was sufficient to prevent pencilling. Under the small scale laboratory conditions the salt composition changed rapidly with time as regards constituents important to pencilling. The composition and condition of the metal pots used as containers influenced these changes.

Three methods of preventing pencilling involved the use of rectifiers to remove alkalinity, the use of oxidizing agents to maintain a protective film on the electrodes, and the use of low current density.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the JOURNAL.

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# The Electric Strength of Sulfur Hexafluoride at Radio Frequencies[1]

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## ABSTRACT

**The electric strength of $SF_6$ in uniform fields has been measured at 60 cps and in the radio frequency range 2–16 megacycles per second at gauge pressures of 5, 10, 15, and 20 lb/in.$^2$ The electric strength of $SF_6$ was found to be essentially the same at 16 megacycles per second as at 60 cps. At 16 megacycles per second, the electric strength exceeded that of polystyrene or polyethylene even at low pressures. The voltage required to break down a given configuration depends upon electrode material and irradiation.**

## INTRODUCTION

The superior insulating performance of sulfur hexafluoride, as compared to air or nitrogen, results from both the relatively large collision cross section of such molecules which extract energy from the free electron in the field and from the tendency of such molecules or their dissociation products to attach electrons and form impotent negative ions (1). Thus the effect of electronegative gases is to capture free electrons and reduce the efficiency of the ionization process.

The purpose of the present investigation was to study sulfur hexafluoride in the range of radio frequencies between 2 megacycles per second and 16 megacycles per second in order to determine the breakdown strength as a function of frequency, and to provide engineering data on the electric strength of this important gaseous insulating medium.

It was found that the electric strength of sulfur hexafluoride was essentially independent of frequency in a uniform field up to 16 megacycles per second.

During the course of the investigation, it was determined that cathode material and the introduction of irradiation had a relatively large effect upon the breakdown potential. The same cathode materials and irradiation level had no detectable effect on the electric strength of air. This was attributed to the fact that $\alpha$ (the first Townsend coefficient) is smaller for sulfur hexafluoride than for air.

## EXPERIMENTAL WORK

### *Test Cell*

Spheres were chosen as electrodes because the gradient at any point between two spheres may be calculated (2). In order that objects near the sphere gap have a negligible effect on the electric field between the spheres, certain precautions must be taken. The effect of nearby objects is to increase the electric field at the surface of the spheres and thereby lower the breakdown voltage. No insulating body should be nearer to the sphere gap than one sphere diameter, and the sphere shanks should not be greater in diameter than one-fifth the sphere diameter if field distortion is to be avoided (3).

The test cell consists of a 6-in. inside diameter cylinder whose length is 6 in. One end plate is made of glass silicone laminate and supports the ungrounded sphere. This plastic was selected because of its high mechanical strength and its low loss at radio frequencies. The other end plate is made of brass and supports the mechanism by which the gap is adjusted. The end plates are each secured with eight bolts.

A port was cut in the cylinder wall, and a special ultraviolet transmitting window sealed in the port to permit irradiation of the gap and observation of the interior.

The high potential sphere is fixed while motion of the grounded one is permitted by means of a copper bellows pressure seal. Rectilinear motion of the movable sphere is maintained by four precision pilot pins and a long central sphere-shank bearing. Actual motion of the movable electrode is accomplished with a hand screw in the axis of the electrodes. A vernier micrometer head permits the gap setting to be read to a tenth of a mil (0.0001 in.). To produce a given gap setting, the grounded sphere is moved in until an ohmmeter indicates contact; it is then backed out to give the desired separation.

Neoprene gaskets were used for the end plate and window-seals. A polyethylene gasket was used as a pressure-vacuum seal at the high voltage bushing because of the high electric stress. The cell is gas tight when cycled between a 3-micron vacuum to an internal pressure of 40 lb/in.$^2$ (gauge).

Spheres of brass, aluminum, zinc, copper, and chromium plated brass were employed in various

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phases of the work. The sphere diameter was 0.786 in. (2 cm) ±0.001 in. in all cases.

The silicone laminate end plate was capable of withstanding 40 kv (rms) at 60 cps and 20 kv (rms) at 20 megacycles per second.

In order to determine the proximity effects of the structure on the gap field, the breakdown curve was determined for air at 60 cps and found to agree within one per cent with results for spheres in free space for separations up to 0.2 in. after appropriate air density corrections were made. Since the maximum gap spacing used in this work did not exceed 0.06 in., one may conclude that the field distortion introduced by the cell structure was quite small.

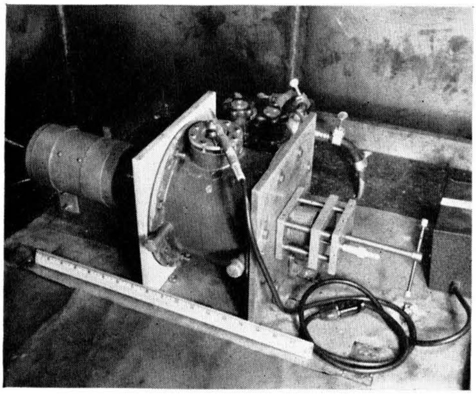

FIG. 1. Cell and associated equipment used in the determination of the electric strength of sulfur hexafluoride.

The gas cell assembly is shown in cross section in Fig. 2.

### *Voltage Sources*

Tests were conducted at frequencies of 60 cps, 2, 4.8, 9.8, and 16 megacycles per second. The 60-cycle voltage was obtained from a high voltage transformer capable of supplying 70 kv (rms). The voltage was varied by a Variac in the primary side.

A Navy type TDH-4 transmitter with a power capability of 3 to 5 kw over the frequency range of 2–18 megacycles per second was used as the primary source of radio frequency test voltages. The output voltage of this transmitter was stepped up by tuned radio frequency transformers to a maximum of 20 kv (rms). The secondary of the selected transformer is tuned by the capacitance of the test cell in parallel with a motor-driven variable liquid capacitor.[2] The magnitude of the test voltage is controlled by a Variac which changes the rectified and filtered plate voltage on the final amplifier of the transmitter. A schematic diagram of the radio frequency system is shown in Fig. 3.

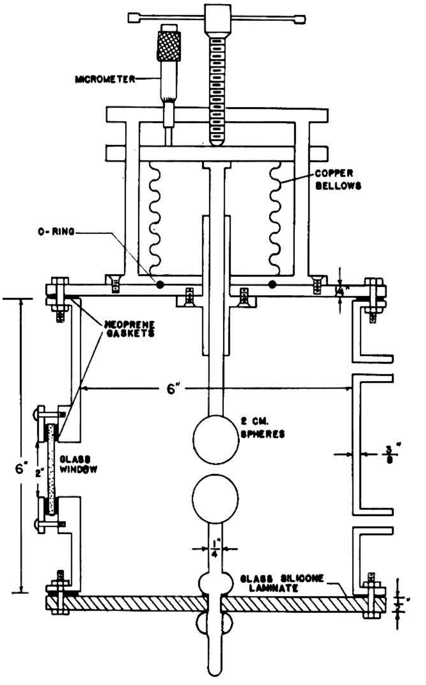

FIG. 2. Cross section of the gas cell

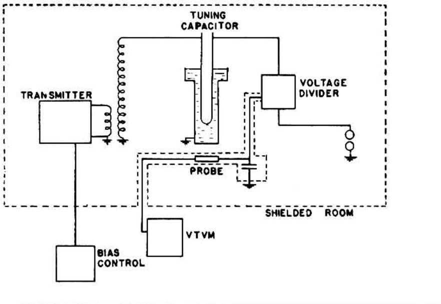

FIG. 3. Schematic of the radio frequency circuit

### *Voltage Measurement*

At 60 cps the voltage was measured at the sphere gap by means of a voltage divider and vacuum tube voltmeter. The vacuum tube voltmeter was a Hickock model 209-A with abnormally long scale so that the voltage could be read to a high degree of ac-

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[2] Further details of the radio frequency supply are given in reference (4).

curacy. This system was calibrated both by sphere gaps and an electrostatic voltmeter substituted for the test cell. These two calibrations were found to be identical.

The measurement of high voltage at radio frequencies is more difficult and was accomplished by using a capacitance voltage divider and a Sylvania low-voltage, radio frequency, vacuum tube voltmeter. This combination was calibrated against an RCA Type MI-13533A radio frequency voltmeter used as standard. Calibration was accomplished at each frequency used because the capacitance of the nominal 2500 $\mu\mu$fd end of the voltage divider was a function of frequency.

As a check on the RCA meter used as a standard, the following test was performed: a 70 $\mu\mu$fd capacitor was connected from the probe electrode of the divider to ground so that the resulting divider had a division ratio of approximately 100:1. A radio frequency voltage of roughly 150 volts was applied to the high voltage lead; this voltage and the quotient voltage were measured by a General Radio type 1800A radio frequency voltmeter. This established the division ratio at this frequency. The RCA standard was then connected to the high voltage lead and the General Radio meter was connected to read the quotient voltage. Results of this test showed that the RCA meter reading and the measured divider ratio times the General Radio meter reading differed by only one per cent.

The capacitance divider was connected as closely as possible to the test cell so that there would be a minimum of impedance between the sphere gap and the point at which the high voltage was measured.

### *Irradiation*

The source of radiation was a mercury arc lamp with a quartz envelope. This lamp was mounted on the cylinder and the ultraviolet light was transmitted through the special glass window. The irradiation was maintained constant throughout the experiment since the position of the source was fixed.

### *Associated Equipment*

A Cenco Hyvac vacuum pump was used to evacuate the test cell. This pump was shock mounted on the bottom of the equipment table and was connected to the apparatus by a large copper tube. The vacuum was measured by a vacuum thermocouple gauge which was calibrated against a McLeod gauge.

The sulfur hexafluoride was supplied in a gas cylinder at a gauge pressure of 250 lb/in.$^2$ This pressure was reduced to the range 0–20 lb/in.$^2$ by a standard gas regulator.

Other investigators (3) have shown that the lower valence fluorides of sulfur and fluorides of metals used in the construction of the apparatus may be effectively removed by activated alumina. The sulfur hexafluoride was filtered through a two-foot column of activated alumina before passing into the test cell.

The pressure was measured by a standard bourdon-type gauge which was calibrated against a standard gauge.

### *Measuring Procedure*

In order to remove as much air as possible the pressure system, which had been previously evacuated and filled with sulfur hexafluoride, was closed off and the cell was evacuated to a pressure of 3 microns. The cell was then flushed with sulfur hexafluoride and again evacuated to a pressure of 3 microns. The vacuum system was then closed off and sulfur hexafluoride was admitted to the test cell. The pressure was adjusted by means of a conventional type pressure regulator. Several cell volumes of gas were allowed to pass through the cell before it was sealed.

The movable sphere was adjusted to touch the other sphere to establish the zero for the micrometer. The gap separation was then set at the desired value by the adjusting screw and the micrometer.

The ultraviolet source was turned on and the voltage raised until a breakdown occurred. The breakdown was detected by observing the voltmeter in the measuring circuit. The breakdown caused the voltage across the gap to drop and at this time the voltage source was manually de-energized.

Preliminary tests showed that the breakdown did not contaminate the gas by the formation of byproducts to any appreciable extent. Thus it was not necessary to introduce a new sample of gas for each breakdown. Since the voltage was removed quickly after each spark, the electrodes remained unpitted for many breakdowns. When a breakdown caused surface damage, it resulted in an apparent reduction in breakdown strength of the sulfur hexafluoride and was then obvious to the operator.

At each frequency the breakdown voltage was measured for various gap settings at a specific pressure. Gas was then admitted or released to establish a different pressure and the process repeated. For each gap setting and pressure three breakdowns were observed (using the same sample of gas), and the maximum deviation was found to be less than ±2 per cent in all cases. The spheres were then changed and the entire process repeated twice. Thus, nine values of breakdown voltage were obtained for each pd (pressure × gap length) values. The maximum deviation in these nine values was found to be less than ±3 per cent.

## EXPERIMENTAL RESULTS

In a preliminary study, spheres of brass, copper, aluminum, zinc, and chromium plated brass were employed. All of these, with the exception of the plated spheres, were found to be satisfactory. After 20 breakdowns the surfaces were unpitted, and there was no evidence of any chemical reaction with the sulfur hexafluoride. The chromium plated spheres were unsatisfactory because the plating ruptured after a few breakdowns. This was probably due to the different rates of expansion of the brass and chromium.

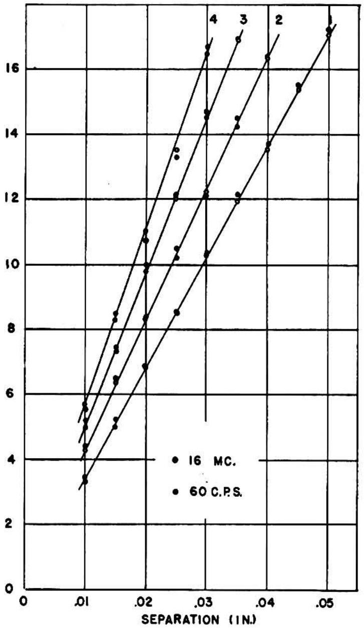

FIG. 4. Electric strength of $SF_6$ between 2 cm diameter brass spheres at gauge pressures of: 1–5 psi; 2–10 psi; 3–15 psi; and 4–20 psi.

The breakdown strength of sulfur hexafluoride was found to be the same, within the experimental accuracy of ±3 per cent, for all of the frequencies tested. For this reason the 60-cycle and 16-megacycle data are only plotted in the curves of Fig. 4. Plots of these same data showing the effect of pressure on the breakdown voltage for three different gap separations are shown in Fig. 5.

The effect of irradiation and cathode material on the breakdown strength of sulfur hexafluoride at 60 cps and 5 lb/in.$^2$ (gauge) pressure is shown by the curves of Fig. 6. The same level of irradiation when applied to the sphere gap with air as an insulator did not lower the breakdown voltage. However, irradiation did reduce the statistical time lag for air. If a gap in air failed at a certain potential $V_s$ with irradiation, when the irradiation was turned off and the voltage brought up to $V_s$, the gap would again

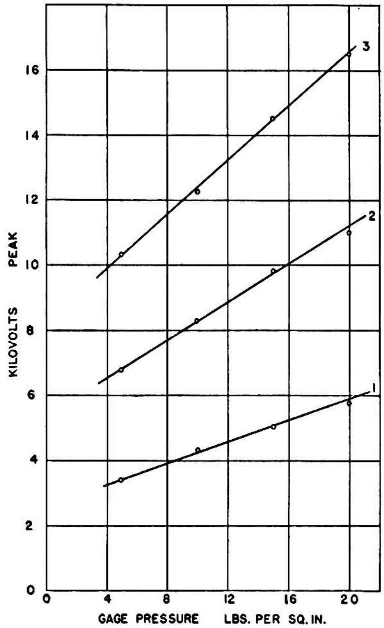

FIG. 5. Electric strength of $SF_6$ between 2 cm diameter brass spheres at separations of: 1–0.01 in.; 2–0.02 in.; and 3–0.03 in.

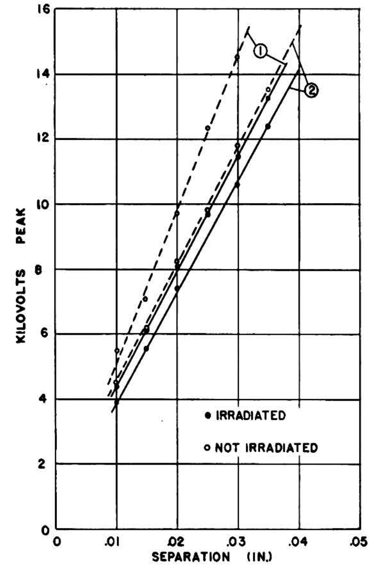

FIG. 6. Electric strength of sulfur hexafluoride at 60 cps using: 1—copper electrodes, and 2—zinc or aluminum electrodes. These data correspond to a pressure of 5 lb/in.$^2$ gauge.

fail, but in some cases the voltage $V_s$ had to be maintained for half a minute or longer before failure occurred.

## DISCUSSION OF RESULTS

For the brass spheres and irradiation level used the electric breakdown strength of sulfur hexafluoride was found to be essentially independent of frequency. As has been suggested by Bright (6) the negative ions formed tend to balance out the field due to the positive ions.

It is of interest to calculate the value of $E/p$ (volts/cm/mm of Hg) at which breakdown occurs. Since the spheres have a radius of 0.394 in. and the maximum separation is 0.05 in. the maximum field intensity, which occurs at the surfaces, is 8 per cent greater than voltage applied to the spheres divided by the minimum separation between the two spheres. For a separation of 0.010 in., the deviation from the average field is only 1 per cent. Assuming a uniform field, the breakdown curve at a gauge pressure of 5 lb/in.$^2$ corresponds to an $E/p$ of 130, for the curve at 10 lb/in.$^2$, 125, for 15 lb/in.$^2$, 125, and for the 20 lb/in.$^2$ curve $E/p$ is 121.

Although an analysis of the ions formed was not undertaken in this investigation, other investigators (7) have analyzed the ionization of $C\ Cl_2F_2$ and found both $F^+$ and $F^-$ ions. The probability of the formation of $F^+$ and the probability of the formation of $F^-$ are both functions of $E/p$, although the exact forms of these functions are not known. At a value of $E/p$ of approximately 125 the difference in the probabilities must allow a space charge to build up and initiate the breakdown. Loeb (2) has shown that negative ions in oxygen lose their electrons in fields in the region of $E/p$ equal to 90 volts/cm/mm. Mohr and Weissler (8) believed that negative ions in $CF_2Cl_2$ could be stable up to $E/p$ greater than 200.

The variation of sparking potential with pressure is a straight line up to a gauge pressure of 20 lb/in.$^2$, as shown in Fig. 5. This is the same result obtained by Chapman and Camilli (9). There are no other data available for the breakdown strength of sulfur hexafluoride in uniform fields at the separation used. A rough correlation may be obtained by comparing the results of this investigation with the breakdown strength of nitrogen as published by Bright (6). The results of this investigation show that the breakdown strength of sulfur hexafluoride is approximately 1.64 times the strength of nitrogen. The results of Chapman and Camilli (9) show the electric strength of sulfur hexafluoride to be 1.57–1.76 times the electric strength of nitrogen in uniform fields. Both of these results are lower than the ratio of the electric strength of sulfur hexafluoride compared to nitrogen of 2.3–2.5 as published by Hockberg (5).

The quartz mercury arc is not considered an intense source of radiation and its effect on breakdown in air is only to reduce the statistical time lag of breakdown (2). This agrees with the results of the present investigation as the source of radiation was not found to lower the breakdown voltages in air.

However, the fact that this same value of irradiation in sulfur hexafluoride causes a reduction in breakdown voltage of approximately nine per cent suggests that some mechanism is active in the electronegative gas which does not take place in air.

When photons collide with atoms they produce results analogous to those caused by electrons of equivalent energy; the equivalent energy being given by the relation $hV = \frac{1}{2} mv^2$. There are, however, important differences between collision processes involving photons and those involving electrons, as might be expected, owing to the fact that a photon has no "rest mass" and possesses no electrical charge. A photon can generally only excite an atom when it has exactly the required excitation energy, whereas an electron may cause excitation when it has any energy greater than the critical energy (10).

The ionization potential of air, if taken as that of nitrogen, is 15.57 volts. Photons having wavelengths in excess of 792 Å will not have sufficient energy to effect photoionization. Sulfur hexafluoride has an ionization potential of 19.3 volts which corresponds to an even shorter photon wavelength. The window used in the test cell employed in these experiments was opaque to radiation wavelength below 2,000 Å. Thus, one would not expect irradiation transmitted by the window to ionize the contents of the test cell directly, whether air or sulfur hexafluoride.

The high electrical breakdown strength of sulfur hexafluoride resides in its ability to trap or attack electrons to form less mobile negative ions. A mechanism which would detach these electrons and put them "back in circulation" would weaken this gas as a dielectric. The absorption of light has been suggested as a possible method of detachment of electrons from negative ions (11). The removal of the electron from a negative ion of fluorine is possible under the conditions of this test since the electron affinity of the fluorine ion is only four volts (corresponding to a photon wavelength of 3084 Å). However, this mechanism, since active only in the gas, should not be affected by the cathode material. Under the conditions of these tests the breakdown strength of sulfur hexafluoride was found to be higher for copper than for aluminum or zinc electrodes. One is therefore led to suspect photoelectric emission at the electrodes or the enhancement of the photocurrent resulting therefrom as causing the observed effects of cathode material and irradiation level.

In the discussion which follows it should be pointed out that the curve marked "Not Irradiated" in Figure 6 is a curve showing data which were taken with the irradiation window exposed to the ambient illumination of the laboratory.

The photoelectric work functions of the materials used as electrodes are: copper (4.5–4.1), aluminum (2.5–3.6), and zinc (3.68–3.32) (3). The reason for this range in the value of the work function of a material is apparent if one reviews the work of Hardy and Craggs (12). These investigators have shown that the photoelectric current from a surface depends on the surface conditions as well as the previous irradiation of the surface. Then a quantitative computation of the relative number of electrons produced by different materials when exposed to the same irradiation would be meaningless.

From the results of Hardy and Craggs and the published work function values, one may conclude that for a given intensity of ultraviolet irradiation copper would emit fewer electrons than would zinc or aluminum. This suggests that the observed reduction in breakdown voltage with materials of low work function depends on the initial photoelectric current.

According to the Townsend mechanism of the spark, the current is given by:

$$i = \frac{i_o(\alpha - \beta)e^{(\alpha-\beta)\chi}}{\alpha - \beta e^{(\alpha-\beta)\chi}}$$

where: $\alpha$ = first Townsend coefficient; $\beta$ = second Townsend coefficient; $\chi$ = gap separation; $i_o$ = photoelectric electron current; neglecting $\beta$ in comparison to $\alpha$ this equation becomes:

$$i = \frac{i_o \alpha e^{\alpha\chi}}{\alpha - \beta e^{\alpha\chi}}.$$

When the denominator of this equation approaches zero the current $i$ becomes infinitely large irrespective of the value $i_o$. Townsend in 1902 interpreted this as representing the condition for the initiation of a spark. For a time experiment appeared to bear out this conclusion, and $V_s$ was found in a limited range of values of $i_o$ to be independent of $i_o$. In 1934, White (13) discovered that when $i_o$ was increased $10^5$ times, by using a spark for an ultraviolet source instead of a quartz Hg lamp, the value of $V_s$ was reduced about 10 per cent.

Loeb (2) suggests that the Townsend equation is a steady-state equation and was never intended to be a condition for a transient phenomenon such as a spark. He also states that the correct criterion for a spark is that $i$ increases to some value $i_1$ which marks the beginning of current instability. At this current, $i_1$, space charge accumulations suddenly develop, or existing ones alter, so that for a constant potential applied, $i$ changes abruptly to some larger value and continues at this value in absence of $i_o$. It is this abrupt transition that defines the spark in its broader aspect.

White (13) suggests essentially the same criterion, that when the number of positive ions in the gap reaches a certain value, breakdown occurs. In the explanation of the reduction of the sparking potential by 10 per cent with intense illumination, the following analysis is offered (13). The number of positive ions ($N$) or electrons produced by collision ionization is given by $N = N_o e^{\alpha d}$. One may write $N_o = e^{\gamma d}$ so that $N = e^{(\alpha+\gamma)d}$. Then for small illumination intensities $N_o$ will be small, and consequently $\gamma$ will be negligible compared to $\alpha$. However, for larger illumination, $N_o$ will be large and $\gamma$ will be comparable to $\alpha$. The smaller intensities affect only the time lag of the spark.

In the case of electronegative gases, the formation of negative ions and the relatively inelastic electron impacts tend to decrease materially the first Townsend coefficient (8). Since $\alpha$ is small, one might expect that $\gamma$ will be comparable to $\alpha$, and the effect of irradiation will be to reduce the sparking potential. This is then somewhat analogous to the case where $\alpha$ is large, compared to the $\alpha$ of electronegative gases, but $\gamma$ is made comparable to $\alpha$ by increasing the irradiation to very high levels.

TABLE I

| Material | 60 cps volts (rms)/mil | 18 megacycles/sec volts (rms)/mil |
|---|---|---|
| Glass silicone laminate | 468 | 71.2 |
| Polystyrene | 2275 | 150.5 |
| Polyethylene | 1338 | 205.0 |
| Paper phenolic laminate | 729 | 18.3 |
| Glass | 306 | 27.4 |

## CONCLUSIONS

At low frequencies, sulfur hexafluoride does not have a breakdown strength comparable to the best solid insulators. At a gauge pressure of 20 lb/in.², the electric strength was found to be 390 volts (rms) per mil and this value was constant in a uniform field up to a frequency of 16 megacycles per second. In the radio frequency range the value of 390 volts (rms) per mil exceeds the strength of most solids. As a means of comparison Table I shows the electric breakdown strength of some solid insulators (4).

## ACKNOWLEDGMENTS

The authors wish to thank The Pennsylvania Salt Manufacturing Company for supplying the sulfur hexafluoride without charge. It is desired also to express gratitude to Dr. R. K. Witt and Dr. J. J. Chapman for helpful suggestions, and for use of research facilities under their direction.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1953 issue of the JOURNAL.

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# Preparation and Properties of Iodide Vanadium[1,2]

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## ABSTRACT

Massive vanadium was prepared by the hot-wire reduction of vanadium iodide vapor by both the Van Arkel-de Boer method and a straight-flow process.

The iodide decomposition provides an excellent method of obtaining small quantities of vanadium exceptionally low in nonmetallic impurities. Metal prepared by the straight-flow process could be worked directly, but specimens prepared by the Van Arkel-de Boer process were not satisfactory for direct fabrications and were arc melted prior to a determination of their mechanical properties.

Iodide vanadium has excellent ductility, moderate strength, and a high modulus of elasticity. The cold workability of iodide vanadium was evaluated by the use of cold rolling and flow-curve data. The metal was found to have a high capacity for cold work and could be cold rolled to give a ninety per cent reduction without intermediate annealing.

## INTRODUCTION

In 1801 Von Humbolt (1) announced the discovery of a new metal associated with the lead ores of Mexico, but the identity of the metal now known to be vanadium was not clearly established. About 30 years later, Wöhler (2) succeeded in isolating the metal from an iron ore found in Taberg, Sweden. It was named vanadium from the Scandinavian goddess, Vanadin.

For over a hundred years, investigators attempted by various methods and techniques to prepare the pure metal. Practically all attempts proved unsuccessful, and one worker concluded his investigations by saying that he knew of no metal more difficult to prepare in the pure state than vanadium.

The first successful attempt to produce ductile vanadium was reported by Van Arkel (3), who used the iodide decomposition process previously used by Van Arkel and de Boer to prepare high purity zirconium and titanium. Since that time, a number of processes have been developed for the preparation of ductile vanadium. McKechnie and Seybolt (4) have reported the preparation of ductile metal by calcium reduction of the trioxide in the presence of iodine. Lilliendahl (5) and coworkers fabricated ductile rod, wire, and sheet from a powder produced by calcium reduction of vanadium trioxide. Relatively pure metal which is suitable for working or remelting has been produced (6). Facilities for producing 100 pounds of massive ductile vanadium per day are reported with indications that any reasonable demand in the near future can be met.

Despite all the progress which has been made, however, the iodide process still offers the best method of obtaining metal of high purity in small quantities. Other methods require the use of either powder metallurgy or fusion techniques to consolidate the metal, and this leads to further contamination during processing.

The purpose of the work reported here was to prepare a quantity of high purity metal for a fundamental study of the physical properties of vanadium. This paper describes the process and presents data on some of the physical properties and working characteristics of the metal.

## DISCUSSION OF DEPOSITION PROCESS

In the method as used initially by de Boer, crude metal is reacted with iodine in an evacuated vessel to form volatile iodides which are decomposed on a heated filament to form a coherent deposit of high purity metal. The liberated iodine then resumes its function as a carrier. The successs of this process in producing pure metal from crude metal containing large quantities of oxygen and nitrogen lies in the fact that neither the nitrides nor the oxides are attacked appreciably by iodine under the conditions of operation and, hence, oxygen and nitrogen are transferred only to a very limited extent.

When the conventional de Boer bulb was used to prepare vanadium, the final product was loosely knit and the crystals were nonuniform in size. They consisted of a number of spines or acicular-like crystals which projected from a core of varying cross sections, as shown in Fig. 1. A deposit of this type is not satisfactory if the as-deposited rod is to be fabricated directly. However, such a deposit can be fabricated readily after it has been consolidated by melting.

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[1] Manuscript received August 12, 1952. This paper was prepared for presentation before the Philadelphia Meeting, May 4 to 8, 1952.

[2] This research was carried out under Contract No. W-7405-eng 92 with the Atomic Energy Commission.

The cause of the uneven deposits was unknown, but seemed related to the instability of the iodides. Vanadium diiodide must be heated to 800°–900°C to obtain satisfactory rates of sublimation, but in this temperature range, the diiodide unfortunately tends to dissociate.

It was felt that operation at reduced pressure would give a better opportunity for obtaining a coherent deposit. The de Boer process was, therefore, abandoned, and provision was made for the continual draw-off of iodine, rather than permitting it to function as a carrier. For such a straight-flow process, a separate vaporizer would normally be used, but this proved to be unsatisfactory for vanadium because of the low volatility of the diiodide and its tendency to disproportionate. It was therefore decided to prepare the diiodide, in place, in close proximity to the filament, and to continually remove the liberated iodine under high vacuum during the deposition process.

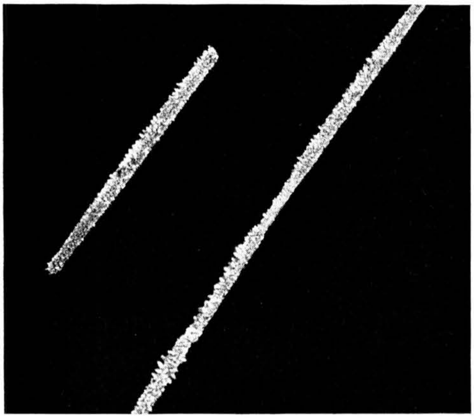

FIG. 1. Coarse crystalline deposit of vanadium

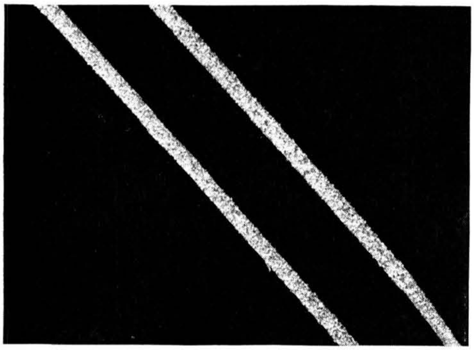

FIG. 2. Smooth deposit of vanadium

This straight-flow process gave a relatively smooth, uniform deposit of high purity, as shown in Fig. 2.

## EQUIPMENT AND PROCEDURE

The bulbs were charged with ¼-in. lumps of crude vanadium, placed on ledges around the outside of a perforated molybdenum can. Approximately two pounds of crude metal were required to charge a 100-mm Vycor bulb. The flat Vycor cap was equipped with two ¼-in. tungsten electrodes with a uranium glass-tungsten seal. After the bulb was charged, the cap was sealed to the bulb and the unit was tested for leaks.

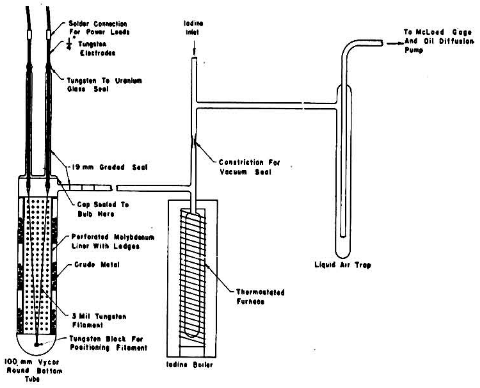

FIG. 3. Schematic design of equipment used in producing iodide vanadium.

An iodine boiler made of Pyrex and large enough to hold approximately two pounds of iodine was sealed to the bulb. The entire assembly was positioned, sealed to the vacuum system, evacuated, and the bulb heated to 900°C to outgas the unit. The outgassing was continued until a vacuum of the order of $10^{-4}$ mm or better was maintained. The bulb was then cooled to room temperature, and sufficient argon was admitted through a liquid-air trap to bring the pressure to one atmosphere.

A weighed quantity of iodine (600–900 grams) was then added to the boiler while a counterflow of argon was maintained. The iodine inlet to the boiler was sealed off, and the assembly evacuated to $10^{-4}$ mm. The boiler was then isolated from the vacuum system by sealing the constriction, as shown in the schematic drawing, Fig. 3.

The bulb was heated to 900°C and the iodine vaporized slowly into the bulb where it combined with the crude vanadium to form the diiodide. Overnight heating was required to insure maximum reaction between iodine and crude metal. When the iodination reaction was complete, the bulb assembly was

TABLE I. *Chemical and spectrographic analysis*

| Constituents | As-received[a] % | As-deposited[b] % | As-received[c] % | As-deposited[b] % |
|---|---|---|---|---|
| Vanadium | 91.45 | — | 99.7 | — |
| Iron | 2.05 | 3.48 | 0.01–0.05 | 0.07 |
| Aluminum | 1.00 | 0.01 | 0.01–0.05 | 0.005 trace |
| Silicon | 0.90 | 0.03 | 0.05–0.1 | 0.002 |
| Chromium | — | — | 0.001–0.005 | 0.002 trace |
| Sulfur | 0.08 | — | — | — |
| Phosphorus | 0.02 | — | — | — |
| Manganese | 0.04 | 0.01 | 0.001 | Not detected |
| Molybdenum | — | — | 0.003–0.008 | 0.005 |
| Oxygen | 4.36 chiefly oxygen | 0.015 | 0.033 | 0.012 |
| Nitrogen | — | 0.0007 | 0.7 | 0.008 |
| Hydrogen | — | 0.005 | 0.007 | 0.005 |
| Hardness, Vickers | 350 | 144.5 | 431 | 84 |
| Ductile | No | Yes | No | Yes |

[a] Analysis by Vanadium Corporation of America.

[b] Analysis by Battelle Memorial Institute.

[c] Analysis by Carbide and Carbon Chemicals Corporation.

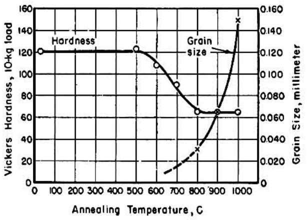

FIG. 4. Effect of annealing temperature on the hardness and grain size of high purity vanadium cold rolled 90 per cent. (Annealed for 1 hour at temperature.)

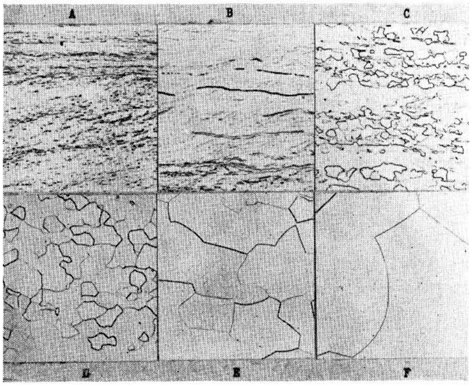

FIG. 5. Microstructures of high purity vanadium annealed 1 hour at temperature after cold rolling 90 per cent reduction. (Etched in 1 part $HNO_3$, 1 part HF, and 2 parts water.) (A) 1 hr at 500°C; (B) 1 hr at 600°C; (C) 1 hr at 700°C; (D) 1 hr at 800°C; (E) 1 hr at 900°C; (F) 1 hr at 1000°C.

cooled to room temperature, the iodine boiler removed from the assembly, and the amount of diiodide formed was calculated from the quantity of iodine reacted.

TABLE II. *Mechanical properties of high purity vanadium cold rolled 90 per cent, followed by annealing for 1 hour at 800°C*

| | |
|---|---|
| Modulus of elasticity, psi | 20,100,000 |
| Proportional limit, psi | 12,200 |
| 0.1% offset, yield strength, psi | 15,300 |
| 0.2% offset, yield strength, psi | 16,700 |
| Ultimate strength, psi | 31,600 |
| Elongation, % in 1 in. | 17* |
| Reduction in area, % | 75 |
| Minimum bend radius | OT (through 180° angle) |
| Vickers hardness | 64 |

* Broke outside the gauge marks; uniform elongation reported.

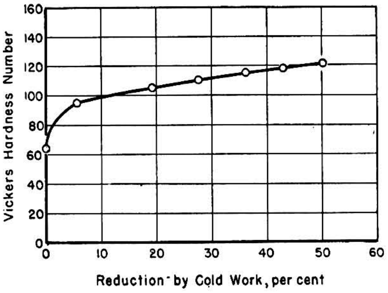

FIG. 6. Effect of cold work on the hardness of annealed high purity vanadium.

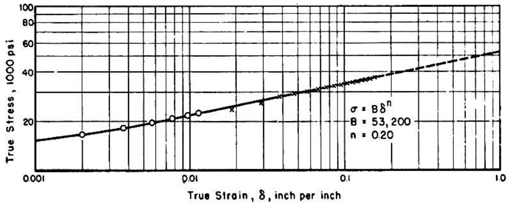

FIG. 7. Flow curve for high purity vanadium

The bulb was then connected to the vacuum system, evacuated to $10^{-4}$ mm, and heated slowly to 800° to 900°C. The filament was then heated to approximately 1400°C, as determined by an optical pyrometer, to initiate deposition.

A variable-voltage transformer was used to control the filament current which must be carefully regulated at the outset in order that a uniform deposit may be obtained. The rate of the deposition was controlled within limits by regulating the filament temperature. This was done by periodic adjustment of the applied voltage on the observed temperatures as read with the optical pyrometer.

Although normally the voltage was gradually diminished, it was occasionally necessary to boost the voltage in order to continue the deposition. The initial and final filament voltages and currents in a typical reaction ranged from 0.6 amp at 12 volts to 82 amp at 8.5 volts. A typical deposit weighed approximately 50 grams.

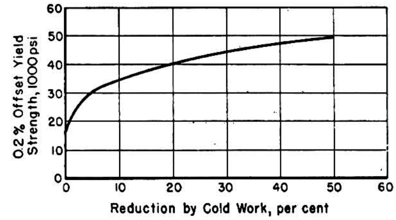

FIG. 8. Effect of cold work on the yield strength of high purity vanadium as predicted from true stress-strain data.

## MECHANICAL PROPERTIES OF HIGH PURITY VANADIUM

A complete analysis of the as-deposited metal used for this study is given in Table I.

*Melting and fabrication.*—Twelve grams of vanadium were arc melted in a water-cooled copper hearth under 10 cm of Hg pressure of high purity argon (99.92% argon). The Vickers hardness of the arc-melted ingot was 70.

After melting, the ingot was cold rolled to 0.040-in. sheet, a total reduction of 90 per cent, with no intermediate anneals. The Vickers hardness of the cold-rolled vanadium was 120. Prior to annealing the cold-rolled sheet, a study of the recrystallization temperature and grain growth was made. Samples of the cold-rolled material were annealed in an argon-atmosphere furnace for one hour at temperatures of 500° to 1000°C and quenched in water. The effect of annealing temperature on the Vickers hardness and grain size is shown in Fig. 4. The microstructures at each annealing temperature are shown in Fig. 5. From these data, an annealing treatment at one hour at 800°C was chosen as the condition for producing the vanadium in a fine-grained, equiaxed form for testing.

*Mechanical properties.*—The conventional tensile properties, bend ductility, and hardness values of the annealed vanadium are given in Table II. The modulus of elasticity, proportional limit, and yield-strength values were calculated from the load-elongation data obtained by using electrical strain gauges. The specimen broke outside the gauge marks, and no total elongation could be obtained. However, the high reduction in area is indicative of the high degree of ductility that can be obtained with high purity vanadium. The bend radius was obtained using a set of dies with radii ranging from ¼ in. to a sharp edge. The specimen was bent through an angle of 105° using the sharp-radius die. It was then removed from the die and bent flat, or through an angle of 180°.

*Cold-working characteristics.*—Two methods were used for determining the cold-working characteristics of vanadium. A cold-work vs. hardness curve was obtained by measuring the hardness at every 10 per cent reduction during a cold-rolling test. These data are given in Fig. 6. The other method consisted of plotting a true stress-strain curve from data obtained during the tension test. These data not only provide information on the flow characteristics of a metal, but also can be used to predict what the yield strength of that metal will be for any given reduction by cold work. The true stress-strain curve for vanadium is given in Fig. 7, and the yield strength vs. cold-work curve derived from the true stress-strain data is given in Fig. 8. From the effect of cold work on both the hardness and yield strength, a prediction can be made of the relationship between hardness and yield strength of cold-worked vanadium. This relationship is shown in Fig. 9.

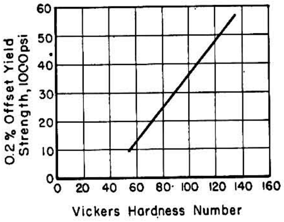

FIG. 9. Correlation of Vickers hardness and yield strength for cold-worked high purity vanadium.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the JOURNAL.

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# Electroplating on Beryllium[1,2]

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## ABSTRACT

Two methods for electroplating on beryllium are discussed; one method involves electrochemical and chemical activation of the beryllium for direct plating with other metals, and the other involves an intermediate replacement zinc film on the beryllium surface. Chemical polishing of beryllium is described. Alloying of the beryllium with the deposited metals and its effect on the as-plated adhesion are also discussed.

## INTRODUCTION

Beryllium is a light, hard, brittle metal. It is lighter than aluminum and heavier than magnesium. Metallurgical and mechanical fabrication of beryllium are complicated by its brittleness, and, as one machinist emphasized: "Treat the stuff as glass." Chemically and electrochemically, beryllium is similar to aluminum, zinc, and magnesium. Therefore, methods for plating on these metals (1) were considered.

Reduction of metal iodides and carbonyls on beryllium surfaces had been explored, but not pursued, because of the greater ease of electroplating metals. The work of Kolodney [reported (2) at a later date] describes a method for electroplating on beryllium. Comparison of the above process with the one reported herein for direct plating on beryllium was made. Although both processes are satisfactory for thin electrodeposits ($<1$ mil), heavy electrodeposits such as silver ($>2$ mils) on beryllium using Kolodney's process could be peeled, whereas comparable electrodeposits using the process reported herein could not be peeled.

## METHODS FOR PLATING ON BERYLLIUM

### *General Comments*

Some plating baths will attack beryllium and prevent satisfactory electrodeposition of another metal. For example, high acid baths containing sulfate, chloride, fluoborate, or fluoride chemically attack an active beryllium surface. Chromic acid solutions passivate beryllium surfaces and prevent the direct deposition of adherent chromium.

The flowsheet in Fig. 1 shows the over-all operations used to electroplate on beryllium. Eight variations in the preliminary preparation were used without noticeable effect on the adhesion. The recommended procedure contains several precautionary operations that have not been fully evaluated.

The plating methods were used for the preparation of beryllium samples for testing and were proven adequate. Study of varying the operations has been limited.

### *Preliminary Surface Preparation*

*Descaling.*—Heat-treating, extrusion, and rolling scales (oxides and/or nitrides) generally are not removed uniformly chemically. Since machining operations probably would precede any electroplating operation, scale removal was not considered a problem.

*Cleaning.*—Greases and oils are best removed by organic-solvent degreasing (vapor or contact). Residual dirt is removed by cathodic cleaning in a caustic solution (e.g., 25 to 75 amp/ft$^2$ in 50 to 100 g/l NaOH or KOH at room temperature). Although solvent degreasing is generally sufficient, alkaline cleaning would be recommended when a number of parts are to be processed.

*Chemical polishing.*—Chemical polishing to remove the as-machined beryllium surface was studied to provide uniformly sound metal for electrocladding. The following solution and conditions were used: 5% $H_2SO_4$, 75% $H_3PO_4$, 7% $CrO_3$, balance water; 120°F (49°C), 1 mil removed in 20 minutes.

Since chemical polishing preferentially dissolves impurities and opens subsurface porosity, its use was limited to that of an inspection tool for machine damage.

To determine if chemical polishing was causing or propagating cracks, a 1-in. diameter, as-extruded, beryllium rod (apparently free of cracks) was alternately cylindrically ground and chemically polished successively with the following observation: (*a*) As extruded, crack free; (*b*) Chemical polish, crack free; (*c*) Grind to true bar, no cracks apparent; (*d*) Chemical polish, circumferential cracks over length; (*e*) Grind (−20 mils), no cracks apparent; (*f*) Chemical polish, fewer cracks; (*g*) Grind (−20 mils), no ap-

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[1] Manuscript received January 15, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

[2] Based on work performed under AEC Contract No. 7405-eng-92.

parent cracks; (*h*) Chemical polish, remaining cracks concentrated at center ends of bar. These results preclude cracking by chemical polishing, and apparently cracks, once formed, can be removed by further machining. Cracking was attributed to a flexing stress during the first, cylindrical-grinding operation.

*Activating pickle.* — Chemical polishing leaves a semipassive surface film, presumed to be beryllium oxide or chromate. Although this film is generally dissolved during subsequent operations, its removal in room-temperature sulfuric acid solutions is preferred so as to more uniformly activate beryllium surface. Pickling for ¼ to ½ minute in 10 per cent (by volume) of concentrated sulfuric acid at 80 ± 10°F (25°C) has been satisfactory.

### *Direct Plating Method*

The following steps are used for adherent electroplating directly onto beryllium surfaces (approximately 0.5 mil of the beryllium surface is dissolved).

(*a*) *Anodic pickle:* 10 volume per cent of 85% $H_3PO_4$; 2 volume per cent of 38% HCl; balance—water; 80 ± 10°F (25°C); 100 ± 50 amp/ft$^2$; 2 minutes.

(*b*) *Chemical pickle:* concentrated nitric acid (70% $HNO_3$); 80 ± 10°F (25°C); 2 minutes.

(*c*) *Water rinse.*

(*d*) *Acid dip:* (for plating from alkaline baths) 100 g/l ammonium sulfate $(NH_4)_2SO_4$; $p$H 2 with $H_2SO_4$; balance—water; 80 ± 10°F (25°C); ½ to 1 minute.

(*e*) *Water rinse.*

(*f*) *Electroplate:* aluminum, copper (baths I or II), nickel (baths I plus II), iron, and zinc (bath I) can be adherently electrodeposited after step (*c*). Presumably, the sulfate, citrate, or tartrate inhibits the precipitation of beryllium hydroxide at the interface.

To electroplate metals such as silver or tin from highly alkaline solution, steps (*d*) and (*e*) are included. Again the sulfate inhibits the formation of beryllium hydroxide at the interface.

An advantage of this method is direct application of most of the electrodepositable metals. A disadvantage is the preferential dissolution of inclusions (such as extrusion stringers, etc.) during anodic pickling, resulting in voids which are difficult or impossible to bridge.

### *Zinc-Immersion Methods*

This method is similar to those used to electroplate on aluminum and magnesium and depends on the application of an adherent, immersion-zinc film onto the beryllium surface. Since the zinc film is chemically active, the initial electroplate must be from a bath usable for plating on zinc. The following steps were used to electroplate copper plus chromium on beryllium:

(*a*) *Zinc immersion:* 120 g/l—$Na_4P_2O_7$; 40 g/l—$ZnSO_4 \cdot 7H_2O$; 7.5 g/l—NaF; 5 g/l—$K_2CO_3$; $p$H 7.5 to 8.0—$H_2SO_4$ and $H_3PO_4$; 180$^+$°F (82$^+$°C) 5 minutes' immersion.

(*b*) *Cold water rinse.*

(*c*) *Copper plate* (bath III).

(*d*) *Water rinse.*

(*e*) *Outgas:* heat for 30$^+$ minutes in boiling water.

(*f*) *Cyanide dip:* 45 g/l—NaCN; 80 ± 10°F (25°C) —½ to 1 minute.

(*g*) *Water rinse.*

(*h*) *Acid dip:* dip in 3$N$ sulfuric acid at room temperature (80 ± 10°F) (25°C).

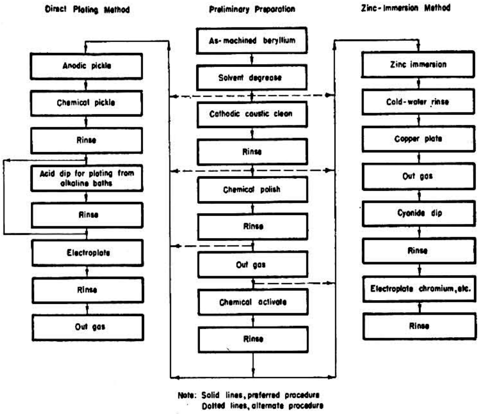

FIG. 1. Flowsheet of the operations used to electroplate on beryllium.

(*i*) *Water rinse.*

(*j*) *Chromium plate.*

The copper plate (step *c*) is to protect the zinc film during subsequent chromium plating. Nickel (bath I), iron, and zinc can also be plated directly over the zinc film.

Outgassing (step *e*) prevents blistering of the copper.

An advantage of this method is the formation of a more uniform surface for plating. A disadvantage might be the required zinc film.

### *Plating Baths*

*Aluminum.*—Aluminum can be plated directly on pretreated beryllium from a nonaqueous (organic) electrolyte composed of ethyl pyridinium bromide-aluminum chloride eutectic (3). After anodic and chemical activation, the beryllium was rinsed and dried with alcohol, then immersed in benzene before plating. The aluminum (1 mil) could not be peeled or cut off at the aluminum-beryllium interface.

*Chromium.*—Chromic acid solutions passivate beryllium surfaces. Therefore, chromium is plated over another intermediate metal on beryllium. In this work, copper over immersion-zinc film was used as a basis for chromium plating. Chromium was plated from a standard chromic acid bath (400 g/l $CrO_3$, 4 g/l $H_2SO_4$, balance—water) using 110 amp/ft$^2$ at 113°F (45°C) or 220 amp/ft$^2$ at 130°F (54°C).

*Copper.*—Copper can be plated directly on beryllium (baths I and II) and on the immersion-zinc film (bath III). Acid, copper sulfate, plating baths chemically attack beryllium and zinc, preventing satisfactory deposition, unless preceded by a strike plate.

I. Copper pyrophosphate bath: "Unichrome" process, United Chromium Corporation; *p*H 8.5; 140°F (60°C); 40 amp/ft$^2$.

II. Cyanide bath: 30 g/l NaCN; 22.5 g/l CuCN; 15 g/l $NaCO_3$; 0.5 g/l $Na_2S_2O_3$; *p*H 9 with tartaric acid; 120°F (49°C); 25 amp/ft$^2$.

III. Cyanide bath: 46 g/l NaCN; 26 g/l CuCN; 15 g/l $K_2CO_3$; 7.5 g/l KOH; 22.5 g/l NaF; *p*H 13.2 ± 0.1; 130°F (54°C); 30 amp/ft$^2$ 1 minute, 15 amp/ft$^2$ thereafter.

*Iron.*—Attempts to plate iron directly on beryllium using iron-plating methods reported in the literature were unsuccessful. The baths attacked the beryllium and/or produced pitted deposits.

Iron was plated directly on beryllium using a modified bath: 300 g/l $FeSO_4 \cdot 7H_2O$; 42 g/l $FeCl_2 \cdot 4H_2O$; 35 g/l $H_3BO_3$; 15 g/l NaCOOH; 15 g/l $(NH_4)_2SO_4$; 1 g/l Duponol ME; *p*H 4.0; 140°F (60°C); 40 amp/ft$^2$.

The bath is also suitable for plating over zinc.

*Nickel.* — Nickel can be plated on beryllium directly and after immersion-zinc coating. A strike nickel plate (bath I) is required to protect the beryllium and/or the zinc from chemical attack.

I. Strike nickel bath: 143 g/l $NiSO_4 \cdot 7H_2O$; 75 g/l $MgSO_4 \cdot 7H_2O$; 15 g/l $NH_4Cl$; 15 g/l $H_3BO_3$; 20 ml/l XXXD[3]; *p*H 5.5 ± 0.1; 90°F (32°C); 15 amp/ft$^2$.

The thickness of the strike nickel plate required to protect the beryllium and/or the zinc will vary with the characteristics of the beryllium surface. In this work, 0.3 to 0.4 mil (30 minutes at 15 amp/ft$^2$) was used on beryllium. Thicker deposits were built up in the following bath:

II. Nickel-plating bath: 300 g/l $NiSO_4 \cdot 7H_2O$; 50 g/l $NiCl_2 \cdot 6H_2O$; 35 g/l $H_3BO_3$; 15 g/l NaCOOH; 20 ml/l XXXD[3]; *p*H 4.0; 140°F (60°C); 40 amp/ft$^2$; 1 mil per 30 minutes.

*Silver.*—Silver can be plated directly on beryllium using a strike bath as for plating silver on copper.

I. Silver-strike bath: 4.5 g/l AgCN; 70.0 g/l NaCN; 80 ± 10°F (25°C); 7.5 amp/ft$^2$; 5 minutes.

Thicker silver deposits are built up in a silver-plating bath.

II. Silver-plating bath: 75 g/l AgCN; 112 g/l KCN; 22.5 g/l $K_2CO_3$; *p*H 13.0 with KOH; 120°F (49°C); 25 amp/ft$^2$; 1 mil per 15 minutes.

*Tin.*—Tin can be plated directly on beryllium: 150 g/l $Na_2SnO_3 \cdot 3H_2O$; 15 g/l NaOH; 22.5 g/l $NaC_2H_3O_2$; 150°F (66°C); 25 amp/ft$^2$.

*Zinc.*—Zinc can be plated on beryllium directly or after immersion-zinc coating: 240 g/l $ZnSO_4 \cdot 7H_2O$; 15 g/l $NH_4Cl$; 30 g/l $Al_2(SO_4)_3 \cdot H_2O$; 70 g/l $MgSO_4 \cdot 7H_2O$; 1 g/l licorice; *p*H 4.0; 80±°F (25°C); 25 amp/ft$^2$.

Alkaline zinc baths could also be used with the advantage of better covering power.

*Other metals.*—Other electroplated metals can be applied directly on beryllium or over another metal that can be electrodeposited directly. Direct plating requires a bath that does not chemically attack beryllium. Modification of certain baths might be necessary.

### *Outgassing*

Hydrogen absorbed during pickling, chemical polishing, and/or plating, if not removed, can destroy a good as-plated bond. Atomic hydrogen enters the beryllium and can be outgassed through thin electrodeposited metals. If the atomic hydrogen combines to form molecular hydrogen under the electroplate, it is trapped and exerts high stress at the interface.

Periodic outgassing eliminated blistering in this work. The method of outgassing depended on the amount of hydrogen entering, the permeability of the electrocladding to hydrogen, and the subsequent operations.

Heat treating at 932°F (500°C) was used to outgas iron-plated beryllium prior to nickel plating. Outgassing occurred at room temperature in three to five weeks. When outgassing of the iron was omitted, the composite iron-nickel electroplate blistered at the iron-beryllium interface.

Chemically polished beryllium was outgassed by heating in boiling water for 30 minutes. After zinc-immersion coating and copper plating, the beryllium was again outgassed similarly. Omitting either outgassing step generally resulted in blistering of the copper plate within twenty-four hours.

## DIFFUSION AND ALLOYING

Diffusion at elevated temperatures complicated the protection of beryllium by electrodeposited metals. If little or no diffusion occurred, use at

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[3] Proprietary addition agent, Harshaw Chemical Company.

elevated temperatures would be mainly a problem of corrosion protection. However, when diffusion occurs, it introduces a continually changing electroplate-beryllium interface.

Solid-solution alloying could probably maintain a satisfactory bond between the electrocladding and the beryllium, but the rate of diffusion would tend to dictate the usability of such an electrocladding. If intermetallic compounds (generally weak and brittle) were formed, a good as-plated bond would probably be destroyed. When compounds are formed, apparently the crystal lattice is expanded, accompanied by a volume change, forcing a separation of the electrocladding on beryllium.

Nickel and beryllium start to diffuse at a temperature between 662°F (350°C) and 752°F (400°C) in 18 hours. After 666 hours at 600°F (316°C), no alloying was apparent.

Iron and beryllium start to diffuse at a temperature between 932°F (500°C) and 1022°F (550°C) in 18 hours. After 720 hours at 932°F (500°C), slight alloying was apparent.

These observations suggest that electrodeposited nickel on beryllium should be considered for extended use only at temperatures below 662°F (350°C). Similarly, iron on beryllium should be considered for extended use only at temperatures below 932°F (500°C). Chromium over electrodeposited copper on immersion-zinc-coated beryllium retained a good bond at elevated temperatures. The immersion zinc and thin copper (0.2 mil) formed a solid-solution alloy with the beryllium. Diffusion of the chromium plate with a copper-zinc-beryllium, diffusion-alloy surface was not observed. Heavy copper plate formed a brittle alloy with the zinc and beryllium, resulting in spalling of the chromium plate at elevated temperatures.

## Adhesion Testing and Inspection Methods

Adhesion tests are generally qualitative and destructive. However, the adhesion of electroplated metals on beryllium was estimated using the following tests:

(*a*) Filing or grinding an edge of the plated sample so that the stress is across the electroplate-beryllium interface. This stress will be influenced by the strength and thickness of the electrodeposited metal.

(*b*) Fracturing the electroplated beryllium sample.

(*c*) Chiseling or prying with a knife at the electroplate-beryllium interface.

(*d*) Heat and quench.

Nondestructive test methods for adhesion and other defects in electroclad samples were considered:

(*a*) Chemical polishing was used to reveal machining damage in the beryllium, presumably by removing a worked skin.

(*b*) "Zyglo" and "Dycheck" examinations were used to reveal pits and cracks by use of a fluorescent oil or dye penetrant. These inspection methods are said to reveal defects, open to the surface, of less than 0.000005 in. However, subsurface defects are masked.

(*c*) Magnetic-induction (Du Mont Cyclograph) testing, Magnaglo (magnetic-particle inspection), Reflectoscope, and Reflectogage (ultrasonic test methods) were considered. Evaluation beyond the scope of this investigation would be needed to apply these methods to electroclad metals on beryllium.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the JOURNAL.

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# Copper-Activated Zinc Sulfide Phosphors with Yellow and Red Emission[1]

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## ABSTRACT

Hexagonal, $H_2S$-fired ZnS:Cu phosphors prepared with 0.05 to 1 per cent Cu are characterized by a yellow-red luminescent emission obtained with ultraviolet, cathode ray, x-ray, and electroluminescent excitation as well as with infrared stimulation. Peaked at 6500 Å, the emission is shown to consist of two bands, a strong red band at 6700 Å and a weaker yellow band at 5800 Å. The intensity of the yellow band declines toward zero at −196°C, while the red band increases in intensity and moves toward longer wave lengths. With electroluminescent excitation, the yellow-red emission persists without changing to blue over the frequency range of 60 to 15000 cps.

Washed with NaCN solution to remove excess free copper sulfide, the phosphors retain only a certain percentage of the amount of Cu originally added. The amount of retained Cu is one or two orders of magnitude larger than in conventional phosphors, indicating a limit of solubility near 0.3 per cent Cu. The incorporation of Cu into the ZnS lattice must be explained without benefit of charge compensating ions. To account for the double band emission and the infrared stimulability, the presence of two species of Cu atoms may be assumed.

## INTRODUCTION

Copper-activated zinc sulfide phosphors have probably been studied more extensively than any other single phosphor system. However, all investigations have been concerned almost exclusively with the blue and green emission bands of these materials. It is surprising, therefore, that there has not been a more intensive exploration of some long wave length emission bands in ZnS:Cu phosphors, such as appear to have been first mentioned by Tomaschek (1). Further, no attempts seem to have been made to obtain these emissions at higher intensities. The existence of these bands should be of considerable interest even though it complicates, and to some extent perhaps obviates, some current attempts to find one single correlation between the emission bands of the phosphors on the one hand, and the valence of the activator atoms and their position in the host lattice on the other.

Tomaschek's phosphors were fluxed with NaCl and gave, in addition to strong blue and green bands, some weak, long wave length bands with reported peaks at 5700 and 6000 Å. They were fired under conditions which, in the light of the present work and additional evidence to be reported in a following paper, do not provide either a completely simple or a fully defined atmosphere. The importance of this latter point has already been stressed to a considerable extent by Kroeger and Hellingman (2). It has been reaffirmed in recent work on both simple and complex phosphors with a zinc sulfide base. It is revealed partly in the nature of the optical response of these phosphors, and to an even greater extent in the nature of their response to electroluminescent excitation.

Kroeger and coauthors (3) have given emission data on $H_2S$-fired ZnS:Cu phosphors with copper contents from zero up to about 0.0065 per cent added Cu ($10^{-4}$ gram atoms Cu per mole ZnS). These materials are reported as giving blue and green emissions whose intensity approaches zero at the higher concentrations of Cu investigated. There is also one very brief mention made of a weak red emission observed in products fired without halides. According to the present work, already summarized briefly (4), phosphors prepared with much higher copper concentrations can be made to emit long wave length radiation of appreciably higher intensity.

## EXPERIMENTAL

The phosphors were prepared from pure precipitated ZnS which was wetted down with solutions of copper salts, dried, sieved, and then fired in bottle shaped silica vessels in a current of $H_2S$. After cooling in $H_2S$ the phosphors were sieved, washed with a lukewarm solution of dilute NaCN and with water, and again sieved after drying.

The firing vessel was provided with an extended neck through which was inserted a long and narrow silica tube which reached the closed end of the vessel and served as inlet for the $H_2S$ gas. The emerging

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gas was disposed of by burning it, the gas stream having been adjusted to maintain a small flame. The whole assembly of firing vessel and inlet tube was placed in a tube furnace such that the entire firing tube was in the hot zone. Ventilation removed $SO_2$ with a minimum of annoyance.

Thus the firing vessel and the charge were continuously being swept by fresh $H_2S$, and gaseous products other than $H_2S$, if any, were quickly removed from the firing zone. Comparable results were obtained with pure $H_2S$ gas directly from a cylinder and with gas that was first washed with $Ba(OH)_2$ solution and then freed from water vapor.

The firing conditions were designed to preclude the formation or retention of oxide or halide contamination. The latter changed the phosphor characteristics when present in amounts even smaller than the activator equivalents. For this reason prolonged firing became necessary when the copper activator was introduced as the chloride. However, if the firing of copper chloride-activated phosphors was carried out long enough, their brightness and spectral emission eventually compared fully with that of shorter fired phosphors activated with an oxide or sulfide donor compound. Apparently, residual chloride was slowly expelled from the phosphors in firing, and activator oxide was converted into sulfide. On the other hand, longer firing was not desirable as the particle size of excessively long fired samples was found to increase considerably. Longer firing times were also necessary if the zinc sulfide raw material contained some zinc oxide, especially when the oxide was already incorporated in the sulfide in form of a solid solution.

In order to study the effect of some oxide additions smaller than the activator equivalent, weighed samples of ZnS:Cu, prefired for several hours in $H_2S$ at 800°C, were sealed into silica tubes of known volume and with air or oxygen admitted at calculated low pressures. The same technique could be used to study the effect of small amounts of halides.

For the development of the long wave length bands it was necessary to fire the phosphors at temperatures in excess of 1020°C. When the phosphors were fired at 1000°C or lower, only the normal blue and green bands were observed at low intensities. This was also true if the firing was carried out at 1100°C *in vacuo* (where a deficiency of sulfur is likely to result), or in atmospheres of sulfur vapor (where an excess of sulfur may be incorporated in the phosphor). Likewise, when the $H_2S$ firing atmosphere contained small amounts of air, water vapor, etc., the red emission did not develop. Suitable firing temperatures were about 1100°, 1200°C, or higher, depending upon the characteristics desired. Thus the red emission appears to be confined to phosphors of hexagonal structure which contain copper in a well defined (although not accurately known) state of valency, and which contain sulfur in presumably exactly stoichiometric amount. In line with this premise, the red emission was expected as well as found in phosphors which were fired in an atmosphere of $N_2$ plus $CS_2$. However, these materials were of somewhat lower brightness due, so it seemed, to superficial contamination by elemental carbon.

The fired products did not contain all added Cu actively incorporated in the ZnS base material. In fact, most of the added Cu survived the firing in the form of free copper sulfide, presumably $Cu_2S$, which imparted to the fired products a dark gray color. This excess copper sulfide was removed readily by treating the phosphors with a dilute solution of cyanide as already indicated. The washed phosphors still had a tan to gray body color, depending upon the Cu content and the firing temperature, which did not disappear when cyanide solutions of higher concentration or higher temperature were used. Thus there was a definite division between free and bound copper sulfide in the fired products. Once in solid solution in ZnS, copper sulfide was not extracted from it by the cyanide wash.

The amounts of Cu that were retained by the washed phosphors were determined colorimetrically, following conversion of the sulfide into oxide to facilitate solution in acid. Optical density measurements were made of colloidal CuS precipitated in stable form from an acid solution containing gelatin (for the range of relatively high Cu contents), and of copper diethyldithiocarbamate extracted with $CCl_4$ (for the range of low Cu contents). Calibration curves confirmed the reliability of the methods.

The amounts of retained Cu depended upon the concentration of Cu that was initially added and the firing time and temperature. They increased with an increase in any of these factors. With normal phosphor firing conditions, they were nearly linearly proportional to the amounts of Cu added. Most of the bright phosphors retained of the order of 0.05 to 0.15 per cent Cu. For example, phosphors that were prepared with 0.5 per cent Cu and fired at 1100°C for ½ to 1 hour retained, on the average, about 0.12 per cent Cu after the cyanide wash; when fired at 1250°C they retained about 0.16 per cent Cu. The highest amount determined was 0.25 per cent Cu. A plot of the data indicated that a limit of solubility of copper sulfide in ZnS may be reached near 0.3 per cent Cu, which appears to be higher than had previously been assumed. At any rate, it is evident that the solubility of copper sulfide is about one or two orders of magnitude larger than the amount which is necessary to produce the conventional, bright green fluorescing ZnS:Cu phosphors.

The above data are presented as typical values obtained on typical phosphors with red emission. They are not true equilibrium or true solubility figures, as the solubility of copper sulfide in ZnS was also dependent upon other factors. As already mentioned, it increased slightly with much prolonged firing times and it also varied with the particle size of the materials, the coarser particles retaining more Cu than the fines.

While the amounts of retained Cu are thus known, it is not certain whether they are incorporated in the ZnS base in the form of a true solid solution, or in some other as yet unidentified association with the host lattice. An x-ray diffraction study of these phosphors is in progress to clear up this question. It has been ascertained, however, that the red emitting phosphors have preponderantly the hexagonal wurtzite structure of ZnS as would be expected from the preparative conditions.

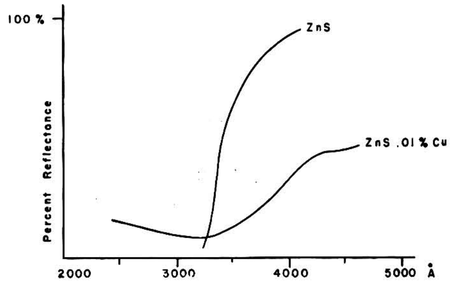

FIG. 1. Reflectance of ZnS phosphors fired at 1100°C in $H_2S$.

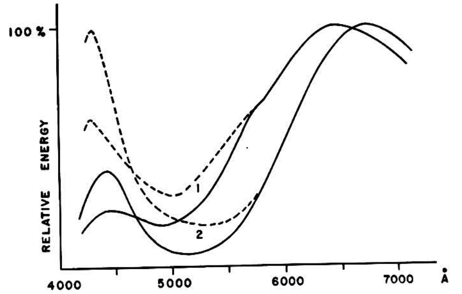

FIG. 2. Emission of ZnS:(0.1% Cu) fired at 1100°C in $H_2S$. Curves 1 at room temperature; curves 2 at −196°C. Dashed lines, 3300 Å; solid lines, 3650 Å excitation.

The emission curves shown in this paper were all taken on NaCN-washed phosphor samples. Except for intensity, there was no significant difference between the emission of washed and unwashed phosphors. All activator concentrations in the figures refer to the amounts of Cu in per cent by weight of ZnS which were added to the raw batch mixture. The emission curves were obtained with a recording spectroradiometer which was calibrated with Illuminant A. Proper corrections have been applied to the curves which have been normalized at the red peak positions in order to demonstrate relative changes more clearly.

The exact location and nature of the extreme emission bands have presented some difficulties. These were due to the low intensities encountered with many of the phosphors, and to the decline of the phototube sensitivity at the ends of the visible spectrum. Some attempts have been made to increase the sensitivity of the phototube through reduction of the background noise. The tube was housed in a Styrofoam adaptor (5) which permitted it to be cooled with liquid nitrogen. While the construction of a simple cooling adaptor is not completed, indications are that the equipment will perform as expected.

### *Excitation by Ultraviolet Radiation*

The optical fluorescence of the phosphors is due to an absorption band in the near ultraviolet, which is adjacent to the fundamental absorption of pure ZnS. The band is shown in Fig. 1 for a phosphor with 0.01 per cent added Cu (approximately 0.005 per cent retained Cu), fired in $H_2S$ for ½ hour at 1100°C. The band becomes stronger with increasing Cu concentration. It is unresolved and broader than the excitation band, as shorter UV radiation such as 2537 Å did not lead to appreciable fluorescence even though this radiation was absorbed strongly as in the case of pure ZnS; visible blue light was likewise absorbed to the extent of about 55 per cent but did not lead to fluorescence.

The excitation spectrum as such and the detailed dependency of the emission spectrum upon it have not been determined as yet. It was apparent, however, that at least two rather narrow excitation bands within the range of about 3000 to 4000 Å are involved. This was concluded from the changes in fluorescent color and intensity observed when the phosphors were excited by radiation of predominantly 3300 and 3650 Å, respectively. The phosphors looked red when excited by 3650 Å line radiation, but more orange when excited with (continuous) radiation near 3300 Å (6). This change in observed color is reflected in the emission curves of Fig. 2 for a phosphor with 0.1 per cent added Cu, at room temperature and at −196°C. The change of color was observed with phosphors fired at either 1100° or 1250°C. In addition, the intensity of the blue band was increased with the shorter wave length excitation, while its peak was shifted slightly toward shorter wave lengths. However, it did not increase to an extent which would account for the increased intensity in the yellow range. This rise is attributed to a separate band as discussed below.

Some typical emission curves for phosphors with increasing Cu concentrations are shown in Fig. 3 and Fig. 4 for 1100° and 1250°C firing temperatures, respectively. The phosphors were excited with 3650 Å radiation. With room temperature excitation of the 1100°C phosphors, there are principally two emission bands, one in the blue at about 4500 Å, the other in the red with a peak at 6500 Å (Fig. 3). The position of the blue band did not change when the firing temperature was increased to 1250°C, but the peak of the red band moved to 6600 Å for room temperature excitation (Fig. 4). This, however, does not reflect a true shift of the band, as will be discussed below. The emissions of phosphors prepared with 1 per cent Cu or more did not further change in characteristic manner, but their intensity was much lower.

Despite the peak location at 6500 Å, the phosphors do not look as red as (Zn, Cd)S:Cu phosphors with the same peak emission. This must be attributed to the extraordinary broadness of the red band which extends from the infrared into the green and has an estimated half width of 1500 Å or more. This compares with 500 and 650 Å for the half widths of the normal blue and green bands in ZnS:Cu. The red band reaches 50 per cent of peak intensity at about 5600 Å, whereas the red band of a (Zn, Cd)S:Cu phosphor with 6500 Å peak emission reaches 50 per cent at about 6000 Å; hence the more orange appearance of the $H_2S$-fired ZnS:Cu phosphors.

The position of the blue and red bands was found to be invariant with activator concentration. The relative intensity of the bands, however, varied strongly with activator concentration in the phosphors fired at 1100°C, while it did not vary appreciably in the phosphors with 0.05 to 0.5 per cent added Cu that were fired at 1250°C. Thus curve 1 in Fig. 4 represents materials with a tenfold increase of activator content, while curves 1 to 3 in Fig. 3 cover the same range for phosphors fired for ½ hour at 1100°C. The absolute intensity of the bands also varied considerably with the Cu content at both firing temperatures. As the concentration of Cu was increased, the intensity of the blue band declined rapidly, while the intensity of the red band built up, reaching an optimum for optical excitation near about 0.1 per cent added Cu, and declining again strongly from 0.5 to 1 per cent Cu. The brightest phosphors with yellow and red emission were about one-fourth as bright as (Zn, Cd)S:Cu phosphors of similar color. Nevertheless, the appearance of a resolved red band could be observed in $H_2S$-fired samples of ZnS prepared with as little as 0.01 per cent Cu or less—this despite the fact that the phosphor's normal emission was predominantly blue with UV excitation.

The intensity of the blue and red bands and the position of the red band at room temperature were also a function of the firing time when the phosphors were prepared at 1100°C; they were much less time-dependent when the materials were fired at 1250°C or higher. In the latter cases, the particle size increased appreciably and the phosphors were of darker body colors even if there existed no differential in retained Cu content compared with the 1100°C materials. Prolonged firing at 1100°C led to a reduction in intensity of the blue band, to an increase in intensity of the red emission, and to a shift of its peak position from 6500 to 6600 Å. This is shown in Fig. 5 for phosphors prepared with 0.5 per cent Cu, and with excitation at room temperature. The red band of the sample fired at 1100°C for 3 hours was nearly identical with that of samples fired at 1250°C for ½ to 2 hours. The emission of the long-fired 1100°C sample is still slightly higher in in-

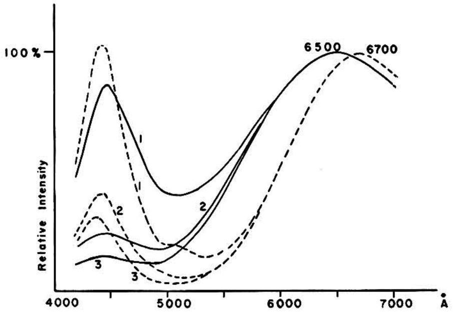

FIG. 3. Emission of ZnS:Cu phosphors fired at 1100°C in $H_2S$, with 3650 Å excitation. Solid lines, excitation at room temperature; dashed lines, excitation at −196°C. Curves 1, 0.05% Cu; curves 2, 0.1% Cu; curves 3, 0.5% Cu.

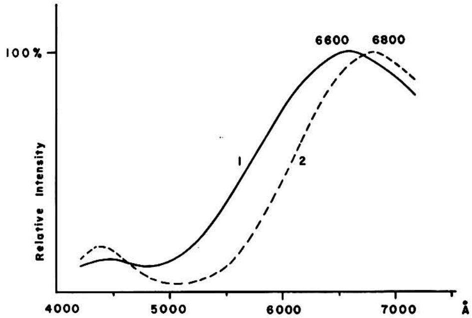

FIG. 4. Emission of ZnS:Cu phosphors fired at 1250°C in $H_2S$, with 3650 Å excitation. Solid line, excitation at room temperature; dashed line, excitation at −196°C. Concentrations of 0.05 to 0.5% Cu.

tensity in the blue and yellow ranges than the 1250°C samples, for reasons given below.

When the phosphors were excited at −196°C, several changes in emission were observed as shown in Fig. 2 to 4. In all cases, the blue band increased in relative intensity and moved slightly toward shorter wave lengths. The red band increased considerably in absolute intensity and moved about 200 Å toward longer wave lengths. Thus the peaks of emission of the phosphors fired at 1100°C for ½ hour moved from 6500 to 6700 Å, and the peaks of the 1250°C phosphors moved from 6600 to 6800 Å. While the shift of peak amounted to 200 Å, the contraction at the half width level amounted to 300 to 350 Å. This resulted in the visual change of color from orange-red to a brighter crimson red to which the now sharper blue band at the shorter wave length position contributed significantly.

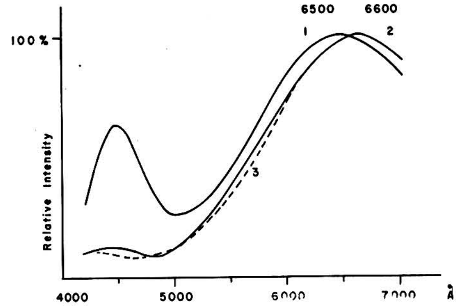

Fig. 5. Room temperature emission of ZnS:(0.5% Cu) phosphors with 3650 Å excitation. Curve 1, ½-hr firing at 1100°C; curve 2, 3-hr firing at 1100°C; curve 3, ½- to 2-hr firing at 1250°C.

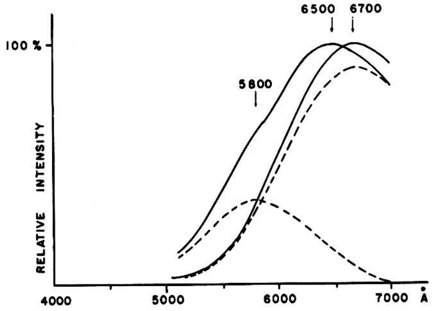

Fig. 6. Resolution of observed emission at room temperature into two subbands at 5800 and 6700 Å.

As mentioned before, the measurements in the deep red were not fully reliable. For this reason, there is somewhat more uncertainty associated with the measured 6800 Å peak than with the 6500 Å peak, and the position of this peak cannot be considered as having been as reliably established as the 6500 Å peak.

The recorded emission curves of all phosphors were actually not quite as smooth as drawn in the graphs of Fig. 3 to 5. They all showed a slight but definite hump in the yellow which was real and extended into the green. This hump has been reproduced in curves 1 of Fig. 2 and 6. It was always more pronounced with 3300 than with 3650 Å excitation and gave the impression of a separate, lower intensity emission band in the yellow. The hump was also much stronger at room temperature than at −196°C where only some of the phosphors showed it at all.

From these findings it is concluded that the 6500 Å emission of the phosphors is a complex band as observed at room temperature and possibly, although to a much lesser extent, at −196°C. The emission is considered to be the resultant of two bands, namely, a strong red band with a room temperature peak at 6700 Å or slightly beyond, and a weaker yellow band with a peak at about 5800 Å. At the 6500 Å position, about 85 per cent of the total emission intensity is furnished by the 6700 Å band and about 15 per cent by the 5800 Å band; at the position of the hump in the yellow, about 60 per cent of the total intensity is contributed by the 5800 Å band, the balance chiefly by the 6700 Å band. Thus the room temperature emission of the 1100°C phosphors can be synthesized from the two contributing bands as shown in Fig. 6. It must be regarded as a transitional emission which develops between the initial blue and the terminal red emissions.

The yellow 5800 Å band thus emerges as a transient emission which is possibly due to a transient crystal structure or to a different and transient arrangement of some of the activator atoms in the host lattice. It is the first of the two bands to develop in phosphor preparation and, for this reason, is stronger in the phosphors that were fired at the lower temperature for a shorter time. The red 6700 Å band is the slower of the two to develop, such that either longer firing times or higher firing temperatures are necessary for its more complete isolation. However, 3-hour firing at 1100°C is not quite equivalent to ½ hour firing at 1250°C. This will explain why the long-fired 1100°C sample in Fig. 5 has still slightly more yellow emission than the same composition fired at 1250°C or higher. The changes of structure involved would have to be of rather subtle nature, as the x-ray patterns have so far shown only extremely slight changes of spacings in the normal hexagonal pattern.

The 5800 Å band loses intensity at low temperatures and it approaches zero or very low intensities when the phosphors are excited at −196°C. It is this declining contribution of the yellow band which causes the peak emission to shift toward longer wave lengths when excited at −196°C—this in addition to the gain in absolute intensity of the red band which thus has a temperature coefficient of opposite sign. The question whether the 5800 Å band has a finite intensity in the 1250°C phosphors, and in materials excited at −196°C, cannot be answered conclusively at this time. More precise measurements are necessary which have to extend farther into the infrared, and decay constants for the emissions at the shorter and longer wave length positions, respectively, will have to be determined. The extension of this work will then permit the final location of peak positions for the red band, i.e., whether it is located at 6700 Å or beyond.

In addition to the main blue and red bands, some phosphors also showed the presence of the normal green band at 5200 Å. This band was more strongly excited by 3300 than by 3650 Å radiation, and it began to show evidence of resolution with low-temperature excitation. This is shown, for example, by phosphor 1 in Fig. 3. The contribution of this green band is not considered to be significant or important. It may merely be the result of a slight inhomogeneity of the phosphor.

When the $H_2S$-fired ZnS:Cu phosphors were excited at elevated temperatures, the yellow and red emissions became very weak, approaching extinction already at temperatures not much higher than 100°C.

### *Excitation by Cathode Rays, Infrared, and Electroluminescence*

With excitation by 5000-volt cathode rays and moderate beam currents, the phosphors fired at 1100°C gave only blue and green emissions with peaks at 4500 and 5200 Å. The bands, although of low intensity, were well resolved, the green band becoming stronger with increasing Cu concentration up to about 0.3 per cent added Cu or higher. The phosphors fired at 1250°C or higher, however, also showed predominantly yellow and red emission. The emission curves had the same shape as the curves of the phosphors excited with 3300 Å UV radiation, with a relatively stronger contribution of the 5800 Å band to the total emission, and with the characteristic hump of the curve in the yellow range. The yellow and red emission was also observed with x-ray excitation of the phosphors.

The $H_2S$-fired ZnS:Cu phosphors with higher activator contents were of even greater interest because of two other properties. They responded to infrared stimulation and to electroluminescent excitation. Following excitation by either 3300 or 3650 Å radiation, the color of the stimulated light was orange in all cases. The brightest stimulation was obtained with phosphors prepared with 0.01 to 0.1 per cent added Cu. The stimulated light of phosphors fired at 1250°C was slightly brighter than that of the 1100°C materials, but of the same color. The samples with 0.01 per cent added Cu were especially interesting as they gave a weak blue fluorescence and a fairly long lasting blue phosphorescence with 3650 Å excitation, but a rather strong orange emission when stimulated with infrared. The phosphors with higher Cu contents had a much shorter (orange) phosphorescent decay and gave the same emission in stimulation. The number of traps in these phosphors did not appear to be very large, as all trapped energy was released in form of a fairly short-lasting single glow. However, their storage ability was quite good at room temperature. The intensity of the stimulated light was almost as high after many hours of storage in the dark as it was immediately following excitation.

A rough stimulation spectrum has been obtained for samples with 0.01, 0.05, and 0.1 per cent added Cu and fired at 1100°C, using a number of suitable filter combinations over the source of infrared. The stimulation spectrum was found to be substantially independent of the Cu concentration over the range listed. Radiation of wave length longer than 1.25 $\mu$ was rather ineffective for stimulation. Optimum stimulability was found to lie within the range of 0.8 to 1.1 $\mu$.

With electroluminescent excitation in either oil or solid dielectric suspension, the phosphors produced the same emission bands which were found for optical excitation, but in somewhat different relative and absolute intensities. The blue band again predominated at low concentrations of Cu and at lower firing temperatures. The red band was the strongest in phosphors made with 0.5 per cent Cu at 1100°C, and with less Cu (about 0.2%) in phosphors fired at 1250°C. The visual color appearance of the luminescence changed from lavender to rose to orange with increasing firing temperature and activator concentration. The absolute intensity with 60 cps excitation was rather low. There was no characteristic effect of the Cu concentration upon the shape and position of the red band. It was chiefly the total brightness which varied, except at very low concentrations of Cu where the blue band predominated. Nevertheless, the orange emission under a-c field excitation was observed with as little as 0.0005 per cent added Cu, although extremely faint, while it was absent in a phosphor made with 0.00005 per cent added Cu. The red emission could be conveniently isolated and utilized by means of red filters such as Tenite Red or Wratten #29.

The emission of Destriau-type, green emitting electroluminescent ZnS-ZnO:Cu phosphors shifts toward blue with higher frequency excitation. This is also true of ZnS phosphors activated with Cu and Pb (7), for which preparative details have not been published. In contrast to this effect, the $H_2S$-fired ZnS:Cu phosphors either retained the relative intensity of their red emission, or they showed a gain, as the frequency was raised from 60 to 15,000 cps. Thus the phosphors did not change in color, unless it was to brighter orange-reds, as the frequency was raised over a rather wide range. This relative gain in red emission was in addition to the normal absolute gain in brightness resulting from the higher frequency excitation *per se.* The emission curves of several phosphors fired at 1100° and at 1250°C and excited with 5000 cps current in oil or solid dielectric cells are shown in Fig. 7. The red band as such can be considered to be identical for all phosphors regardless of firing temperature and activator concentration. It is concluded that the 5800 Å band in the 1250°C phosphors is more strongly excited by electroluminescence than by UV radiation.

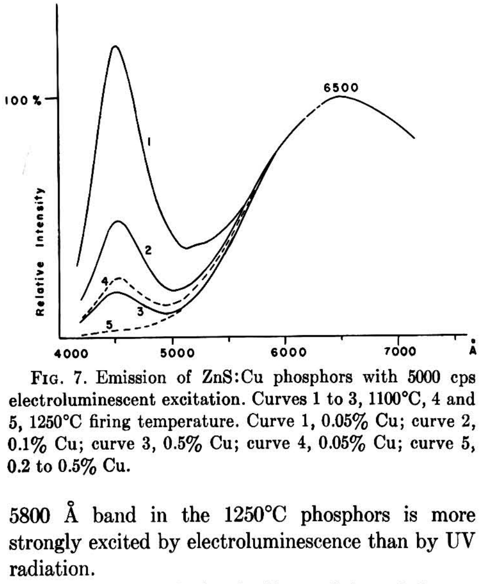

FIG. 7. Emission of ZnS:Cu phosphors with 5000 cps electroluminescent excitation. Curves 1 to 3, 1100°C, 4 and 5, 1250°C firing temperature. Curve 1, 0.05% Cu; curve 2, 0.1% Cu; curve 3, 0.5% Cu; curve 4, 0.05% Cu; curve 5, 0.2 to 0.5% Cu.

Both the infrared stimulability and the red electroluminescent response were destroyed when the phosphors were prepared with NaCl flux or in atmospheres of $H_2S$ with small amounts of oxide additives. In the latter case, the response was only a weak blue of very low intensity.

## DISCUSSION

It has been shown that the combination of $H_2S$-firing with high activator concentrations in ZnS:Cu phosphors resulted in the development of a fairly bright orange-red emission. This emission was observed with optical and with electronic excitations as well as with infrared stimulation. It is a complex emission which consists of at least two bands, a strong red band with a peak at 6700 Å or beyond, and a weaker and poorly resolved yellow band with a peak at 5800 Å. While low temperature excitation allows the isolation of the pure red band, it has not been possible so far to isolate and investigate the yellow band by itself. There are, however, a number of reasons why the independent existence of this band is believed to have been established. These are:

1. The emission curves taken at room temperature with UV excitation show a slight but definite hump in the yellow which continues into the green; this hump is somewhat stronger in phosphors with lower Cu concentration (0.1%) and those fired at lower temperatures (1100°C).
2. The intensity of emission in the yellow range is appreciably greater with 3300 than with 3650 Å excitation.
3. The hump in the curve is observed with all forms of excitation.
4. With electroluminescent excitation of the 1250°C phosphors, the emission in the yellow range is of greater intensity than the emission of the same phosphors excited by UV radiation.
5. The intensity of the yellow band is a function of both the firing time and the firing temperature; an increase of either leads to a reduction of the 5800 Å band intensity.
6. The observed shift and change of shape of the red band with excitation at −196°C are readily explained with the existence of a separate band in the yellow whose intensity decreases on cooling and may reach zero at −196°C. The emission as observed at room temperature can be synthesized from two bands of normal shape and peaks at 5800 and 6700 Å or beyond.

The yellow band at 5800 Å is presumably identical with the 5700 Å band reported by Tomaschek for NaCl-fluxed phosphors. A counterpart for Tomaschek's 6000 Å band has not been found.

The red emitting ZnS:Cu phosphors continue the pattern set by a number of different phosphors, in which an increase of the activator concentration led to the development of new emission bands at much longer wave lengths (8). In the case of ZnS:Cu, bright blue and green emission bands are obtained with low concentrations of Cu up to about 0.01 per cent added Cu as an upper limit; the yellow and red emission bands are most prominent in the range of 0.1 to 0.5 per cent added Cu. While not all of the added activator is retained by the fired and NaCN-washed phosphors, the amount of Cu actually incorporated in the red fluorescing materials is by one or two orders of magnitude larger than it is in the blue and green emitting phosphors. It had previously been assumed that the limit of solubility of copper sulfide in zinc sulfide was lower, and that complete quenching of the fluorescent response occurs even below such lower limits. This is approximately correct with respect to the blue and green emissions, but it does not hold for the red emission.

The incorporation of relatively large amounts of copper sulfide in zinc sulfide and the red fluorescence of the resulting materials are obtained without benefit of negative or positive ions which would facilitate substitutional replacement of zinc ions in the host lattice. The presence of coactivators such as $Cl^-$ or $Al^{3+}$ may be necessary for the development of the intense blue and green emissions of Cu in ZnS; it is not necessary—actually detrimental—for the development of the red emission in the same type of phosphors with higher Cu contents.

The exact manner in which the copper activator is incorporated in the red emitting phosphors remains to be determined. A solid solution of copper sulfide in form of (normally hexagonal) CuS in hexagonal ZnS would seem to offer no problem as the $Cu^{2+}$ and $Zn^{2+}$ ions are not too different in size. However, as pointed out by Kroeger, the thermodynamic stability of CuS at the firing temperatures of 1100°–1300°C is so low that copper, in all likelihood, is present in form of $Cu_2S$ with monovalent Cu. Thus a true solid solution of (normally cubic) $Cu_2S$ in hexagonal ZnS would be possible only with the formation of a large number of lattice defects. The reluctance of copper sulfide to form solid solutions with ZnS, as shown by the low solubility of approximately 0.3 per cent Cu, speaks both for the monovalent state of Cu and for a strong defect structure of the phosphors. The existence of such structures in mixed sulfides of different valences has already been demonstrated in the case of SrS-$Ce_2S^3$ (9) where several mole per cent of $Ce_2S_3$ were found to enter the SrS lattice substitutionally. While this system involved di- and trivalent sulfides, solid solutions of mono- and divalent sulfides should be similarly possible.

When higher activator concentrations caused the appearance of new, long wave length emission bands in other phosphor systems, it was proposed that these emissions may be due to "pairs" or multiples of activator atoms or ions. The formation of such "pairs" would be plausible in the cases of phosphors in which the effective activator concentration is so near the limit of solubility as in the case of the $H_2S$-fired ZnS:Cu phosphors. This is especially so if the restrictions applying to strongly ionic crystals are relaxed or altered in the case of crystals with substantial homopolar binding such as ZnS. Whether these pairs constitute associations of like ions such as $2Cu^+$ or of unlike pairs such as $Cu^+$ and $Cu^{2+}$ or $Cu^+$ and $Cu^0$, etc., is largely a matter of speculation with the knowledge presently available.

The partial reduction of copper ions to neutral copper atoms in atomic subdivision in the phosphors should receive more serious consideration.[2] The preparative conditions would make the formation of neutral copper atoms more plausible than in the phosphors containing additional elements such as $Cl^-$ or $Al^{3+}$ which Kroeger has appropriately termed "stabilizers." It is in these materials, however, that Kroeger and Hellingman (10) associate the shorter wave length blue emission with pairs of $Cu^+$ and $Cu^0$. It would seem more likely that such pairs should be responsible for a longer wave length red emission. This would also be in accord with the rapid loss of fluorescent intensity at but slightly elevated temperatures which was observed for the red band and which is considerably stronger than that for the blue band.

The infrared stimulability of the red emitting ZnS:Cu phosphors is puzzling because stimulability of sulfide phosphors is generally associated with materials having two different activators incorporated in them. (There are exceptions in nonsulfide systems.) Since pure zinc sulfide without any copper addition, carried through all stages of phosphor preparation save for the addition of Cu, was devoid of any response to fluorescent excitation, the stimulability as well as the normal fluorescence of the ZnS:Cu phosphors must be attributed to the copper activator. One may thus have to assume that copper is present in the form of at least two species of copper atoms or ions, one of which assumes the role of the dominant or emission activator, the other that of the auxiliary or trapping activator which determines the stimulation sensitivity. Possibly one of these species is responsible for the yellow, the other for the red fluorescent emission during excitation. As an alternative, sulfur atoms may be considered to play a more important role in the mechanism of phosphor emission, by assuming one or more of the functions usually associated only with metal activators. It is not likely, however, that this would involve any appreciable stoichiometric excess of sulfur, as the phosphors fired in sulfur vapor did not show the red luminescence.

The experimental evidence thus favors the view that the $H_2S$-fired ZnS:Cu phosphors contain two or more species of activator atoms or their associa-

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[2] When the phosphors were fired for longer times at temperatures of about 1300°C, a fairly copious deposit of small, well formed crystals was found at the cooler portions of the firing vessel. Identified by their sharp x-ray pattern as pure silicon, the crystals must have formed from vaporized Si formed by reduction of the silica firing vessel. If a reduction of $SiO_2$ by $H_2S$ is thus possible, the reduction of copper sulfide to elemental Cu should be equally possible, as an appreciable amount of $H_2S$ is dissociated at the high firing temperatures.

tions, which are different from the activator centers in phosphors prepared with lower concentrations of activator. Without much further work it is not possible to arrive at any definite conclusion about their true nature. The existence of the yellow and red emissions points out that the situation in ZnS:Cu phosphors is actually much more complicated than it was when only the blue and green emissions were considered, and that any future models developed will have to be consistent with the new observations.

Even less can be offered to explain the electroluminescent response of the phosphors, and its independence of the frequency of the exciting current. The green emission of the Destriau-type phosphors has been attributed to a slight oxide (or $Cu^{2+}$ ?) content of the materials. However, the response to a-c field excitation is not limited to sulfide materials which contain oxides. Thus the absence of oxides or halides is neither a condition for, nor one against, the electroluminescent response of the red emitting ZnS:Cu phosphors.

## ACKNOWLEDGMENT

Acknowledgment is due to Mr. F. W. Pikus who carried out most of the analytic copper determinations. Also, the author's thanks are due to Dr. F. J. Studer and Dr. P. D. Johnson of the General Electric Research Laboratory in Schenectady for a number of the optical measurements.

Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the JOURNAL.

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# Electroplating on Zirconium[1,2]

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## ABSTRACT

**Methods are described for producing adherent electroplates on zirconium. As-plated adhesion (about 6000 psi) is obtained by prescribed etching of the zirconium surface prior to plating. Prebaking and heat treatment of nickel- or iron-plated zirconium produces alloy bonds of about 50,000 psi (as indicated by modulus of rupture). Other metals are electroplated over diffusion-bonded nickel or iron plate.**

## INTRODUCTION

Methods for plating on metals such as chromium, stainless steels, aluminum, or magnesium are not applicable for plating on zirconium. Zirconium is resistant to acids and alkaline solutions, except hydrofluoric acid.

## METHODS FOR PRODUCING ADHERENT ELECTROPLATES ON ZIRCONIUM

### *General Comments*

Electroplated metals on zirconium prepared by conventional procedures for plating on other metals are electroformed shells and can be separated or peeled easily. Heat treatment of these electroplate-zirconium composites resulted in localized blistering or over-all separation at the electroplate-zirconium interface.

Adherent electroplates on zirconium (50,000 psi, as indicated by modulus of rupture) are produced by a prescribed etching of the zirconium surface, nickel or iron plating, prebaking, and heat treating to alloy bond the interfaced layers of the two metals. Other metals may be electroplated over the nickel-plated or iron-plated zirconium as desired.

The following general procedure (discussed later in greater detail) is recommended for producing adherent nickel electroplates on zirconium:

1. Descale. (*a*) Sandblast, (*b*) vapor blast, or (*c*) surface grind
2. Alkaline clean
3. Rinse
4. Chemical etch. Solution: $NH_4F$—18–52 g/l, HF—3–16 g/l; molar ratio: $NH_4F/HF$, 1.2–4.1; temperature: 100°F (38°C); time: ¾ to 3 min; metal removed: 0.6 mil; container: polyethylene.
5. Rinse
6. Nickel plate. Solution: $NiSO_4 \cdot 7H_2O$—330 g/l, $NiCl_2 \cdot 6H_2O$—46 g/l, $H_3BO_4$—37 g/l, $H_2O_2$—added periodically to prevent pitting, *p*H 2.0; temperature: 140°F (60°C); current density: 40 amp/ft$^2$; plate thickness 1–2 mils.
7. Rinse and dry
8. Prebake. temperature: 400°F (204°C)—air is o.k.; time: 2–4 hours.
9. Heat treat. Temperature: 1300°F (704°C)—air is o.k.; time: 10–45 min; quench: air or water.

### *Preliminary Surface Preparation*

*Descaling.*—After fabrication at elevated temperatures, zirconium retains an adherent, chemically resistant skin. No aqueous chemical method was found to remove this skin without pitting the underlying zirconium. Mechanical removal of this skin by sandblasting, vapor blasting, or surface grinding is satisfactory.

*Chemical polishing.*—Chemical polishing of the zirconium was considered for improving the zirconium surface for plating. Bright smoothened surfaces were produced by immersion in dilute solutions of hydrofluoric acid (4% HF). However, chemical polishing had little or no effect on the as-plated adhesion or on the diffusion bonds.

Since chemical dissolution in solutions of hydrofluoric acid alone is rapid, a more easily controlled chemical polishing solution was investigated. The following solution chemically polishes zirconium, and the rate of metal removal can be controlled by the temperature of the solution: $NH_4FHF$—100 g/l; $HNO_3$—400 ml/l; $H_2SiF_6$—200 ml/l; $H_2O$—to 1 liter.

The approximate rate of metal removal vs. temperature is as follows:

| | |
|---|---|
| 70 to 80°F (24°C) | 0.0006 in. removed/min |
| 80 to 85°F (28°C) | 0.0008 in. removed/min |
| 90 to 95°F (33°C) | 0.0018 in. removed/min |
| 100 to 110°F (40°C) | 0.0025 in. removed/min |
| 110 to 120°F (46°C) | 0.0040 in. removed/min |

*Cleaning.*—Electrolytic or soak alkaline cleaning is used to remove surface dirt.

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[1] Manuscript received September 15, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

[2] Based on work performed under AEC Contract No. 7405-eng-92.

### *Etching of Zirconium Prior to Plating*

Good as-plated adhesion and the best diffusion bonding depends on proper etching of the zirconium surface prior to electroplating. Etching in solutions of ammonium fluoride and hydrofluoric acid is satisfactory. However, the molar ratio of $NH_4F$:HF is important. Molar ratios of 1.2 to 4.1 are recommended. The effects of concentration and molar ratio of ammonium fluoride and hydrofluoric acid on the as-plated adhesion are as follows:

| $NH_4F$, Mole/l | HF, Mole/l | $NH_4F$/HF, Molar ratio | As-plated adhesion, psi |
|---|---|---|---|
| 0.00 | 0.50 | 0 | <1000 |
| 0.44–0.88 | 0.44–0.88 | 1.0 | <1000 |
| 0.49–0.98 | 0.40–0.80 | 1.2 | >6000 |
| 0.66–1.32 | 0.25–0.44 | 3.0 | >6000 |
| 0.83 | 0.05 | 16.6 | <1000 |
| 1.67 | 0.09 | 18.8 | <1000 |

Etching for ¾ to 3 min at 100°F to remove about 0.6 mil of the surface is recommended. The time of etching is dependent on the amount of free HF in the solution. About 0.6 mil is removed in ¾ min in the solution containing 36 g/l $NH_4F$ (0.98 *M*) and 15.5 g/l HF (0.78 *M*), whereas 3 min are required in the solution containing 52 g/l $NH_4F$ (1.4 *M*) and 7 g/l HF (0.35 *M*).

### *Electroplating*

*Nickel.*—Electroplating on zirconium from wetting-agent-free baths is recommended. Although wetting agents (and probably other organic additions) in the plating bath do not appear to affect the as-plated adhesion, their inclusion in the diffusion alloy results in a 20 per cent weaker bond.

The recommended electroplate thickness is 1 to 2 mils. About 0.5 mil of the electroplated metal is alloyed with the zirconium in a subsequent heat treatment. Heavy electroplates tend to separate from the zirconium during heat treatment because of the difference in thermal expansions of the two metals.

*Iron and other metals.* — Since nickel, diffusion bonded to zirconium, is a satisfactory basis for subsequent plating with more nickel or with other metals, the emphasis in this work was with nickel. However, iron can be successfully electroplated on and diffusion bonded to zirconium.

Copper and silver directly on zirconium were also investigated. Copper electroplated on zirconium appeared well bonded after hot rolling. Silver and zirconium did not show any alloying until about 1850°F (1010°C), at which temperature a low-melting, eutectic alloy formed. Simple heat-treatment diffusion bonding of electroplated copper or silver to zirconium is prevented by the low solubility of hydrogen in copper and silver resulting in blistering.

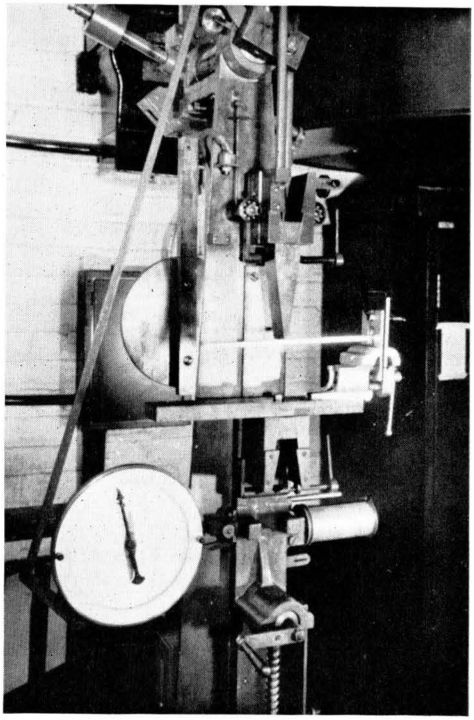

FIG. 1. Silver-solder-test setup with a specimen clamped in the Amsler testing machine and ready for breaking.

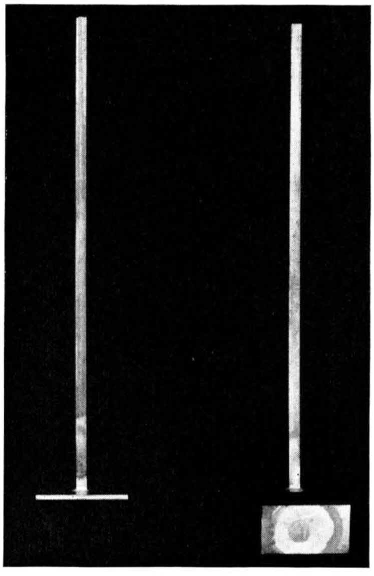

FIG. 2. Silver-solder-test assemblies before and after testing.

### *Prebaking*

To prevent blistering of nickel and iron electroplates on zirconium caused by rapid evolution of hydrogen during diffusion heat treatment, prebaking at 400°F (204°C) is recommended. Specimens diffusion bonded within a day or two after plating and without prebaking generally blistered. Others held at room temperature for three weeks or more before diffusion bonding showed only limited blistering. Prebaking at 400°F (204°C) for 2 to 4 hours eliminated blistering. A one-hour prebake was insufficient.

Three hydrides of zirconium have been identified by electron diffraction of zirconium cathodically pickled in dilute sulfuric acid. The surface showed $Zr \cdot H_2$ over layers of ZrH and $Zr_4H$. Probably, hydrides are formed during etching of and plating on zirconium. This hydride formation is reversible and explains the necessity of prebaking. In addition, it partially explains why electroplated copper and silver on zirconium were not satisfactorily diffusion bonded. The low solubility of hydrogen in copper and silver prevents outgassing through the electroplate and allows concentration of the hydrogen and separation at the copper- or silver-zirconium interface.

### *Diffusion Heat Treating*

The strength of the alloy bond is related to the amount of diffusion. The effects of heat treatment on the diffusion-alloy bond are as follows:

| | | |
|---|---|---|
| 1100°F | 240 min | No bond |
| 1200°F | 240 min | Good bond |
| 1300°F | 45 min | Good bond |
| 1500°F | <5 min | Good bond |
| 1300°F | 240 min | Fair bond |
| 1500°F | 45 min | Fair bond |
| 1500°F | 240 min | Poor bond |

Good bonds are about 50,000 psi (modulus of rupture), fair bonds are 35,000 psi, and poor bonds are 5,000 psi.

The best diffusion bonding of electroplated iron on zirconium occurs at 1500°F (816°C) in 10–45 min.

## EXPERIMENTAL METHODS

### *Design of Experiments*

The development of a reproducible process for diffusion bonding electroplated nickel to zirconium required the selection of proper conditions. Since many ramifications are involved, most of the experiments were of the factorial type (1) and were subjected to analysis of variance.

### *Test of Adhesion*

Qualitative adhesion tests such as filing or grinding the edge of a sample, bending a sample to fracture, sawing, and wire-brush burnishing were initially used. However, the results depended upon the thickness of the electroplate and upon its physical properties. Several quantitative tests were considered, but generally were not adaptable to rapid testing.

Numerical results were needed for an analysis of variance. Therefore, soft- and silver-solder tests were used to estimate the comparative strengths of the electroplate-zirconium bonds. For the silver-solder tests, the end of an alloy-steel bar (¼-in. square by 10 in. long) was silver soldered (mp 1070°F) so as to be perpendicular to the sample being tested. In a 1000-lb Amsler testing machine, the bond was broken by applying a known force perpendicular to the steel bar at a distance of six inches from the silver-solder joint. The test setup is shown in Fig. 1. Samples before and after testing are shown in Fig. 2.

For the soft-solder tests, 3/16-in. brass rod was soft soldered to the sample being tested. The electroplate-zirconium bond was tested by hanging known weights on the brass rod 6 inches from the solder joint.

The soft-solder test was used to evaluate as-plated adhesion. Since the soft-solder test was not severe enough, the silver-solder test was used for diffusion-bonded samples. The short-time heating during soldering did not appear to influence comparative evaluation.

To obtain data for calculating a modulus of rupture, a series of samples were prepared with the plated area being tested isolated by bandsaw cuts through the silver solder and the electroplate into the zirconium. So, in effect, the area being tested became an integral part of the steel test bar.

For calculating the modulus of rupture, the flexure formula, $S = MC/I$, was used. $S$ is the modulus; $M$ is the bending moment; $C$ is the distance from the neutral axis to the outermost fiber of the test area; and $I$ is the moment of inertia of the test area.

**Any discussion of this paper will appear in a Discussion Section, to be published in the December 1953 issue of the JOURNAL.**

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# Discussion Section

## ROLE OF CRYSTAL ORIENTATION IN THE OXIDATION OF IRON

**Earl A. Gulbransen and Roswell Ruka** (pp. 360–368)

M. E. STRAUMANIS[1]: What was the technique in preparation of the samples for obtaining the electron diffraction patterns?

What was the thickness of the iron samples, and how were they prepared?

EARL A. GULBRANSEN: I believe we have described under the section Samples and Apparatus the preparation procedures.

## CORROSION OF ALUMINUM BY CARBON TETRACHLORIDE

**Milton Stern and Herbert H. Uhlig** (pp. 381–388)

M. E. STRAUMANIS[2]: What is the rate of corrosion at room temperature?

Are there no indications for the action of local elements?

Is $C_2Cl_6$ the only corrosion product, or are there also other products?

Is hydrogen evolved when hydrogen chloride is in the carbon tetrachloride?

MILTON STERN: We have conducted no tests at room temperature. However, the literature indicates that at this temperature there is little or no attack of aluminum by dry carbon tetrachloride for a period of six months[3]. In wet carbon tetrachloride, however, the reported rate is about 8 mdd for the same period of exposure.

In answer to the question concerned with reaction mechanism, it is difficult to visualize the operation of local elements in producing the high reaction rate observed (about 40,000 mdd) in an environment of such low conductivity. Additional work, soon to be published, has been conducted on this system. A mechanism which entails a free-radical chain reaction adequately explains the experimental facts.

A free-radical process would be expected to produce many side reaction products. Hexachlorethane is one of the major reaction products, but is by no means the only product. No measurable quantities of gas are liberated when pure aluminum reacts in dry carbon tetrachloride. However, no experiments were conducted to determine whether hydrogen is evolved when the system contains hydrogen chloride.

## ELECTRON DIFFRACTION STUDIES ON THE OXIDATION OF PURE COPPER AND PURE ZINC BETWEEN 200° AND 500°C

**E. A. Gulbransen and W. R. McMillan** (pp. 393–401)

F. R. MORRAL[4]: It may be of interest to call attention to a study of the films formed on zinc, coated on steel[5]. It was found that the thickness and the surface orientation appeared to be affected by the environment under which the ZnO film formed.

J. T. WABER[6]: In connection with experiments on epitaxis, it has been found that a 6 per cent error in lattice constants of the substrate and deposit can be tolerated without the formation of pseudomorphic structure of exactly the type that Finck and Quarrel suggested. Recent work indicates that the differences in the lattice constants can be accommodated by a reasonably high concentration of dislocations on the composition plane. Several translation distances away from composition plane, there need be very few dislocations and the original lattice dimensions are to be observed. Hence, this is a modern interpretation of what Finck and Quarrel claimed to have seen. Their ability to determine lattice constants of one or two monolayers is open to question.

A slightly different type of pseudomorphism has been observed. Dr. Schulz of the Institute for the Study of Metals has been able to force substances normally crystallizing in the sodium chloride lattice to adopt the cesium chloride structure by choice of the substrate. Pauling in his "Nature of the Chemical Bond" indicates that there is only 3.6 per cent difference in the lattice parameters of NaCl and CsCl modifications of a given crystal. Van Der Merwe[7] discusses these ideas more fully.

W. H. J. VERNON[8]: In their valuable paper the authors kindly refer to the electron diffraction work carried out by the late Dr. G. Shearer in conjunction with the oxidation experiments of Vernon, Akeroyd, and Stroud. Their brief comment, however, is likely to be somewhat misunderstood since it makes no reference to the critical temperature (ca. 225°C) found in the course of these experiments. It was concluded that the film on the abraded zinc surface was amorphous; but it was further stated (from the examination of films covering a wide range of temperatures and times of oxidation) that: "*on prolonged heating below*, and *very rapidly above*, the critical temperature, the film

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THIS Discussion Section includes discussion of papers appearing in the JOURNAL of The Electrochemical Society, **99**, No. 7–12 (July–December 1952).

[1] University of Missouri, School of Mines, Department of Metallurgy, Rolla, Mo.

[2] University of Missouri, School of Mines, Department of Metallurgy, Rolla, Mo.

[3] F. H. RHODES AND J. T. CARTY, *Ind. Eng. Chem.*, **17**, 909 (1925).

[4] Kaiser Aluminum & Chemical Corporation, Division of Metallurgical Research, Spokane, Wash.

[5] H. J. YEARIAN AND F. R. MORRAL, "Electron Diffraction Study on Hot Galvanized Sheets," *Metals and Alloys*, **12**, 54 (1940).

[6] Los Alamos Scientific Laboratory, Los Alamos, N. Mex.

[7] *Disc. Faraday Soc.*, on "Crystal Growth," No. 1, 201 (1949).

[8] Chemical Research Laboratory (D.S.I.R.), Teddington, England.

showed the normal pattern of zinc oxide, but at no stage could the extra lines required for the pseudomorphic film be detected." The reference in the present paper ("after heating, the oxide film gave the pattern of normal zinc oxide") should be read in the light of the words italicized above.

## ELECTROLYTIC REDUCTION OF ORGANIC COMPOUNDS AT CARBON CATHODES

**Sherlock Swann, Jr., C.-Y. Chen, and H. D. Kerfman**
(pp. 460-466)

Harold J. Read[9]: I should like to inquire about two points relating to the electrodes:

(*a*) Will you provide additional details on the way in which the electrodes were manufactured, particularly with respect to binder materials and porosity?

(*b*) Was a new electrode used for each run and, if not, what precautions were taken to clean the electrodes between runs?

Sherlock Swann, Jr.: I am going to ask Dr. Winslow to answer the first question (referring to the manufacture of carbon).

(*b*) A new electrode was used for each run in the studies on the behavior of different types of cathodes.

N. M. Winslow[10]: (*a*) All types of agglomerated carbon are made from granular or powdered carbon and a liquid binder capable of conversion to carbon when heated at elevated temperature. Mixtures of suitable proportions of particles and binder are formed into desired shapes by well-known processes such as extrusion or molding. The formed shapes then are baked to convert the binder to carbon. In the finished product the particles are coated with, and held together by, carbon derived from the binder. While any of a large number of materials can be used as binder, practically all commercially available carbons, including those varieties used by Dr. Swann, are made with coal tar pitch.

The carbon obtained from all coal tar pitches is quite similar in nature, and it would follow that the surface of all types of agglomerated carbon is similar except for the following consideration: the proportion of carbon particles and binder, and the yield of carbon from the binder, are such that if a piece of carbon is cut to desired shape, as in making the electrodes used by Dr. Swann, most of the external surface of such electrodes will consist of cross sections of particles. Particles differ markedly in nature, and it follows that the electrode surface on which electroreaction takes place must differ greatly unless a large proportion of the internal surface, i.e., surface consisting of binder carbon, is effective. I believe that electrode reactions seldom penetrate the electrode very far; however, it seems likely that the depth of penetration of a reaction which involves diffusion of ions in solution must be determined by the number and size of pores, to which Dr. Read has made reference, and it is unfortunate that carbons have not been made to order for studies such as that presented by Dr. Swann.

In answer to the question on porosity, I would like to offer the opinion that this is one of the two fundamental properties of carbon which are pre-eminent in determining its electrochemical behavior. Porosities of all three of the carbons used by Dr. Swann almost always fall in the range of 20 per cent to 25 per cent, and diameters of practically all the pores in the range of one to 10 microns. It is very probable that, given a pore size permitting penetration of the electrode reaction to an appreciable depth, the difference between 20 per cent and 25 per cent porosity might mean the shifting of a very significant proportion of the total reaction from the external face of the electrode, where the surface is characteristic of the particles, to the internal surface which probably is characteristic of the binder. It is even more probable that a tenfold variation in pore size might, on the one hand, permit quite extensive reaction within the pores, and, on the other, almost totally restrict reaction to the external surface. It is unfortunate that the state of our knowledge is such that the pore size and volume have never been correlated precisely with the results of an investigation such as that of Dr. Swann. Both volume and size of pores are properties which could be controllably made to order, within fairly wide latitude, to suit the requirements of an electrochemical application.

The other fundamental property of carbon which I believe largely determines electrochemical behavior is crystallinity, i.e., size, perfection, and orientation of the carbon or graphite crystals. With metals it is quite generally accepted, as a result of work by several investigators, including Dr. Swann and some of his coworkers, that it makes considerable difference in both ease and direction of reaction whether the reaction takes place on the sides or the ends of a crystal. The same conclusion seems justified for carbon, particularly since carbon is perhaps unique among conductors with respect to the very wide range of crystal sizes in which it occurs.

The graphite, coke, and lampblack electrodes of Dr. Swann's paper, thus designated in recognition of the type of particles used in manufacture, represent recognized levels of crystal size. In the graphite, the crystals have dimensions of the order of many thousands of Angstroms up to perhaps several microns. (In high quality artificial graphite or natural graphite, crystal size may be many microns or even millimeters.) In the coke, the crystals are intermediate in size, of the order of a few thousand Angstroms. The lampblack is microcrystalline, crystal size ranging from about one hundred up to perhaps several hundred Angstroms.

In addition to any direct bearing crystal size may have on electrode reaction, it probably is of indirect importance in two ways: first, because large crystals of graphite are leaf- or needle-shaped, they are oriented in the processes used in forming. Thus, for electrochemical applications, the use of graphite increases the probability that all of the surface of an electrode consists of crystal faces, or sides, depending on how the electrode is cut from the original piece of agglomerated carbon. Second, crystal perfection quite generally decreases with crystal size. Hence if points of disorder in the crystals are an influence in directing or promoting an electrode reaction, the probability of having such disorder would be greater with lampblack than with graphite.

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[9] Division of Metallurgy, Pennsylvania State College, State College, Pa.

[10] National Carbon Company, Cleveland, Ohio.

To sum up what has turned out to be a very long and involved answer to a very short question, I would say that the three forms of carbon used by Dr. Swann can be briefly characterized as follows: porosity of all three probably lies in the range of 20 per cent to 25 per cent, and characteristic pore size in the range of one to 10 microns, these properties being not more precisely known. The three forms differ primarily, and in a fairly well-known way, in the crystalline characteristics of the particles used in manufacture. Such characteristics vary from the large, fairly well oriented and reasonably perfect crystals of macrocrystalline graphite, through the intermediate coke type, to the small, unoriented and imperfect crystals of lampblack.

## EFFECT OF CORROSION AND GROWTH ON THE LIFE OF POSITIVE GRIDS IN THE LEAD-ACID CELL

**J. J. Lander** (pp. 467–473)

L. H. CALLENDAR[11]: Having been connected for some 20 years with the battery industry on the technical side, I found this paper very interesting, and there are one or two points I should like to take up.

(1) It is stated on page 473, second paragraph, that failure in the particular cells investigated corresponds to about 1 per cent of growth. This is an extraordinarily low amount of growth to produce grid failure. We find in standard batteries, of somewhat heavier construction, probably, than the particular American Navy portable battery, that the plates may hold together and give satisfactory capacity up to 5 per cent growth either horizontally or vertically or both, though this, of course, depends on the design of the grid.

(2) On the same page it is stated that grid structure with frames heavier than crossed members delays the start of growth. This is probably the case, but what is much more important in practice is that provided the frame is stronger than the inner members, it will not be broken by them. But in some 'drawing board' design of grids which have been put on the market, both the frame and the major internal members are of approximately the same cross section and strength. The result of this is that, under growth, the frame is broken, the plate disintegrates, and capacity collapses rapidly.

I am doubtful, however, whether the strength of the grid frame or otherwise affects the growth as such. What happens with a strong grid frame is that the inner members, since they cannot push outward, tend to bend upward or downward, this as a rule doing no harm to the capacity of the battery.

(3) Page 472, bottom. With the growth and distortion of the plate, the protective oxide film cracks or opens out at bends, thus giving opportunity for further and deeper penetration of the metal by corrosion. There is a curious effect also noticed that although at least 50 per cent of metal may remain below the corrosion film, the metal itself becomes brittle. I am not sure what the explanation of this is, but it may be due to gaseous absorption, as is commonly known with hydrogen in steel.

(4) Page 473, third paragraph. It is certainly true that the start of growth, which seems to be determined by the relative amount of peroxide and metal left in the thinner members of the grid, disturbs the contact between the grid and the active material, and makes the latter more easily carried out of the plate by gassing.

## ELECTRICAL CONDUCTIVITY OF MOLTEN CRYOLITE AND POTASSIUM, SODIUM, AND LITHIUM CHLORIDES

**Junius D. Edwards, Cyril S. Taylor, Allen S. Russell, and L. Frank Maranville** (pp. 527–535)

RICHARD B. ELLIS[12]: (1) How was cryolite cleaned from the cell? (2) How much clearance was there between the outer electrode and the container?

ALLEN S. RUSSELL: (1) Cryolite was cleaned from the cell by sodium carbonate fusion.

(2) The clearance between the outer electrode and the container was about 1 cm.

E. M. WISE[13]: (1) What was the range of frequencies used?

(2) Could lower frequencies be used at a low C.D.?

(3) Have inductive methods been considered?

ALLEN S. RUSSELL: The first question has been answered in the published version of the paper, which appeared in the December 1952 JOURNAL.

(2) The lower limit of frequency could not be extended appreciably with our bridge by the use of lower current density alone.

(3) Inductive methods have been considered for measuring the electrical conductivity of reactive fused salts. However, these require an inert insulating container and no such material has yet been found for cryolite.

A. FLEISCHER[14]: The purity of cryolite should be mentioned. The low values reported by Arndt and Kalass apply to a cryolite having a high silica content according to the figures given in their paper.

ALLEN S. RUSSELL: This information has been given in the published version of the paper, which appeared in the December 1952 JOURNAL.

MORRIS FEINLEIB[15]: The reason for using platinized platinum electrodes in conductivity cells for aqueous media is that these electrodes are nearly reversible with respect to the main electrode reactions, i.e., the oxidation of hydrogen and reduction of hydrogen ions on one hand, and the oxidation of hydroxyls or reduction of oxygen on the other hand. In cryolite or other fused electrolytes, this situation no longer exists: the electrode reactions during the anodic and cathodic cycle of the applied AC are not the same, i.e., there is irreversibility, and therefore polarization. Such a polarization (activation polarization) may not be removable even by the use of a high-frequency AC. The error due to this polarization is especially serious in a low-constant cell. However, practical considerations will limit the choice of possible electrode materials. Thus, from

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[12] Southern Research Institute, Birmingham, Ala.

[13] The International Nickel Company, Inc., New York, N. Y.

[14] Box 349, Easthampton, Mass.

[15] Kaiser Aluminum & Chemical Corporation, Division of Metallurgical Research, Spokane, Wash.

a reversibility standpoint, molten aluminum electrodes might be ideal in cryolite, if a practical cell could be built with such electrodes. Here, again, it is seen that we have to build our cells and equipment around the available materials of construction, rather than the other way around.

J. F. GALL[16]: The author described difficulty because of slowly changing composition of fused cryolite through loss of fluorine content. Our experience with fluorides at high temperatures shows that they are sensitive to water vapor in the contacting atmosphere, so that hydrolysis occurs and fluorine is lost as hydrogen fluoride. Perhaps, then, the composition change could be avoided by surrounding the conductance cell with a dry and inert atmosphere such as carefully dried nitrogen. The cryolite charge should also be dried before it is melted.

## THE NATURE OF THE FILMS FORMED BY PASSIVATION OF IRON WITH SOLUTIONS OF SODIUM PHOSPHATE

**M. J. Pryor, M. Cohen, and F. Brown** (pp. 542–545)

H. J. WRIGHT[17]: What electrochemical method was used in determining the thickness of the phosphate film?

How did it vary with pH?

We are interested in this for studies of corrosion-resistant film forming.

M. COHEN: The oxide film on the iron was reduced electrochemically by cathodic reduction. The weight of the iron in the film, which was dissolved by this cathodic reduction, was determined calorimetrically. The thickness was calculated assuming a density of iron oxide of approximately 5. The conditions for cathodic reduction and a method for determining film thicknesses amperometrically have been outlined by Miley and Evans[18] and Pryor and Evans[19].

## PRIMARY CURRENT DISTRIBUTION AROUND CAPILLARY TIPS USED IN THE MEASUREMENT OF ELECTROLYTIC POLARIZATION

**Sidney Barnartt** (pp. 549–553)

ROBERTO PIONTELLI AND GIUSEPPE BIANCHI[20]: In his paper published in this JOURNAL[21] S. Barnartt applies the method of Piontelli and Bianchi (the mapping of equipotential surfaces)[22] for the study of the problem of polarization measurements by means of the Luggin-Haber capillary. Barnartt says: "Piontelli and Bianchi have obtained such maps but used an incorrect model." Barnartt had evidently no opportunity of considering our subsequent papers on this subject[23, 24, 25]. In these papers also the obvious advisability of working with true "geometric models" was observed, although the results so obtained are not essentially different from those obtained with the simple apparatus originally employed, with the main purpose of giving evidence on the disputed nature of the errors involved in the measurements of polarization voltages. The hope of attaining any quantitative solution of the whole problem in this way is in fact rather illusory. Let us note incidentally that, according to our experience, an apparatus such as that designed by Barnartt involes in particular an error due to the formation of a "meniscus" at the liquid surface. At the beginning of our work we also employed alternating currents[26], but finally we found the continuous current method preferable (lead anodes in lead sulfamate baths, a type of system characterized by very low polarization). This led to greater simplicity, to elimination of interference by parasitic capacities, and to a more direct comparison of the primary current distribution with the distribution established in conditions where the effects of polarization not only are not negligible but where they are the main object of study.

On the whole Barnartt's results provide another good confirmation of those results of our own which concern the "primary current distribution," and of the later results of Meunier[27]. The nature of this primary distribution was, however, rather obvious, and one could also predict it on the basis of well-known graphical methods for mapping electromagnetic fields, methods which we found satisfactory for a general control of our results.

The principal points of the problem of the methods for measuring polarization voltages are the following:

(*a*) Is it possible, and, in the affirmative in what practical conditions, to correct the results of the measurements obtainable by means of a Luggin-Haber capillary, in such a manner as to eliminate the ohmic drop contribution and any other source of systematic error?

(*b*) Can we attempt to eliminate this ohmic drop by pressing the capillary against the electrode surface?

(*c*) What is, on the whole, the best arrangement for polarization measurements?

As far as question (*a*) is concerned, in the case of the capillary placed through the back of the perforated elec-

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[16] Pennsylvania Salt Manufacturing Company, Philadelphia, Pa.

[17] Socony-Vacuum Oil Company, New York, N. Y.

[18] H. A. MILEY AND U. R. EVANS, *J. Chem. Soc.*, **1937**, 1295.

[19] M. J. PRYOR AND U. R. EVANS, *J. Chem. Soc.*, **1950**, 1259, 1266.

[20] Laboratorio di Elettrochimica, Politecnico di Milano, Milan, Italy.

[21] S. BARNARTT, *J. Electrochem. Soc.*, **99**, 549 (1952).

[22] R. PIONTELLI AND G. BIANCHI, *Gazz. chim. ital.*, **80**, 58 (1950).

[23] R. PIONTELLI AND G. BIANCHI, "Proceedings of 2nd Meeting of the International Committee of Electrochemical Thermodynamics and Kinetics" (CITCE), p. 379, Milan, 1950. Milan, Tamburini, 1951; R. PIONTELLI, G. BIANCHI, AND R. ALETTI, *Z. Elektrochem.*, **56**, 86 (1952).

[24] R. PIONTELLI, "Proceedings of 4th Meeting of CITCE," London-Cambridge, 1952, in print; R. PIONTELLI, G. BIANCHI, C. GUERCI, AND L. RIVOLTA, *ibid.*, in print; R. PIONTELLI, *Rend. ist. lombardo sci.*, in print.

[25] R. ALETTI, U. BERTOCCI, G. BIANCHI, C. GUERCI, R. PIONTELLI, G. POLI, AND G. SERRAVALLE, "Proceedings of 3rd Meeting of CITCE," p. 30, Bern, 1951. Milan, Manfredi, 1952. Also "Proceedings of 4th Meeting of CITCE," London-Cambridge, 1952, in print.

[26] R. PIONTELLI AND G. BIANCHI, *Gazz. chim. ital.*, **79**, 646, 863, 867 (1949).

[27] F. MEUNIER AND P. GERMAIN, "Proceedings of 3rd Meeting of CITCE," p. 263, Bern, 1951. Milan, Manfredi, 1952.

trode, the possibility exists for a reasonable evaluation of the error involved[24]. This is one of the advantages of this arrangement. Let us note incidentally that the explanation given by Barnartt of this error is based on oversimplifying the problem (see[24]). In the case of a "frontal" capillary, the possibility of correcting for the ohmic drop error depends in practice: (1) on the uniformity of the solution layer between capillary tip and electrode surface; (2) on the degree of disturbance in the current distribution introduced by the presence of the capillary.

If the capillary is distant enough from the electrode surface (as a security limit we suggest $d \geq 3$ capillary diameters; in practice $d \geq 1$ diameter may suffice), there is no disturbance of the current on the electrode surface. To the approximation of the implicit hypothesis of uniformity of the interposed solution* and if the distance of the capillary is exactly known, one may calculate the ohmic drop included in the measurements. It is, however, necessary to take account of the fact that current lines utilize in part also the solution at the entrance into the capillary. The potential surfaces are thus distorted†. The knowledge of the primary current distribution gives no definite answer to question (*b*), because the final current distribution, in the conditions of measurements, depends on the "throwing power" of the system in these conditions and thus depends also on the electrode "polarizability," which we try to eliminate in determining the primary distribution. On the other hand this polarizability must again be largely responsible for the eventual divergence between the measured polarization and that which would be measurable in the absence of shielding. The method of models, when applied in conditions for which the polarization phenomena cannot be neglected, is unable to give a quantitative answer to our problems. In fact a "geometric model" is then no more a "true model"[24, 29, *]. However, the qualitative evidence given by the experiments on models[22–25], the semiquantitative evidence attainable by successive approximations, and, moreover, a large series of results obtained with true polarization cells[25] are clearly supporting the opinion of the intervention, often in a decisive manner, of a true "shielding effect" in the polarization measurements when the capillary tip is near the electrode surface.

The results obtained with the capillary pressed against the electrode surface, or very near to it, may be affected by very large errors due to the "shielding effect," these errors being by defect for the absolute values of the polarization voltages.

To question (*b*) the answer must, therefore, necessarily be negative.

As far as question (*c*) is concerned, the method of mapping equipotential surfaces on models, in spite of its intrinsic limits (especially for the quantitative aspects of the problems), has led us to the realization of the entirely new arrangement[23–25] used for the last two years in this laboratory, and which, in our opinion, constitutes a great improvement, in spite of some complications of construction in comparison with the previous ones. Our new capillary, cylindrical in shape, with its terminal cross section closed by a very thin glass membrane, gives a full shielding of the covered surface, without any disturbance of the surrounding electrode surface. A bore, in the shape of a circular corona, establishes the contact between the internal solution of the capillary and the solution layer immediately near, i.e., at 10 to 40$\mu$ from the electrode surface. In this manner a very low ohmic drop is included, while no shielding effect intervenes. At least in the absence of obstructive layers on the electrode surfaces, the "direct method" of measurement of electrode polarizations has thus attained a very satisfactory form of realization. Another new satisfactory arrangement recently has been realized in this laboratory, and we shall give information on it in the near future.

H. J. WRIGHT[30]: What observations have been made of this in the study of cathodically protected systems?

SIDNEY BARNARTT: The answers to the question is: none.

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*To demonstrate that this hypothesis is by no means generally accepted, it is sufficient to remember the interpretation recently given by Bockris and Azzam[28] of their results concerning the dependence of the measured hydrogen overvoltages on the capillary distance. According to these authors, the change of this dependence law, when the distance is below a critical value, is due to the fact that the greater part of the ohmic drop is localized in the Prandtl layer at the electrode surface. Although this hypothesis is unable to explain the similar results one obtains in the case of metal polarizations (explained on the contrary by the consideration of the shielding effect) one cannot exclude, and in many conditions one must admit, the lack of uniformity of the solution layers at the electrodes.

† The possibility of taking account of this circumstance is discussed in footnote[24]. When the capillary is near the electrode surface one may foresee a certain disturbance of the distribution of current on this surface, but it should be difficult to foresee, on the basis of the primary distribution, the effective distribution in the various particular cases.

[28] J. O'M. BOCKRIS AND A. M. AZZAM, *Trans. Faraday Soc.*, **48**, 145 (1952).

* We consider here as a "true model" any one corresponding to the requirement that choosing suitably different units for measuring, in the real system and in the model, some quantities of the same class of physical dimensions, the figures expressive of the corresponding properties in the two systems may be made to coincide and therefore the unknown properties of the real system may be evaluated from measurements effected on the model.

[29] J. N. AGAR AND T. P. HOAR, *Disc. Faraday Soc.*, No. 1, 158 (1948).

[30] Socony-Vacuum Oil Company, New York, N. Y.

Technical Review

# Review of Articles on Luminescence for 1951-1952[1]

*Gorton R. Fonda*[2]

### New Phosphors

*Phosphates.*—Smith (1) found three crystalline forms of zinc orthophosphate and studied them under cathode-ray (CR) excitation. With low manganese, the normal form is stable at all firing temperatures and fluoresces at 5520 Å. Above 1 mole per cent Mn and above 800°C, another form of novel structure results which fluoresces at 6380 Å with 2½ times the luminescence energy. When prepared in the presence of magnesium or zinc orthophosphate, still another form results, with its emission at 6320 Å.

Froelich and Margolis (2) studied $Ca_3(PO_4)_2$:Ce:Mn, in which the cerium, whose emission peaks at 3600 Å, sensitizes the manganese emission at 6500 Å under excitation by 2537 Å. The crystalline form, stable above 1100°C, is brighter than the form found below 1100°C, but both have the same emission. In liquid air the manganese band decreases sharply and the cerium band increases two- to threefold, although a change in temperature has no effect with cerium alone. Under CR the phosphor emits red when prepared with excess base and yellow-orange with excess acid. Firing with sodium makes the phosphor sufficiently susceptible to 3650 Å at 300°–500°C that it acquires value as a color corrector for the high-pressure mercury lamp.

Additions have been made to the halophosphates. Ranby (3) describes activation of calcium fluophosphate by silver to give an emission band at 3200 Å to 4800 Å under 2537 Å, and to serve also to sensitize the manganese emission. Anderson and Wells (4) describe the halophosphates of magnesium and barium activated with uranium, silver, and thorium. With uranium, the barium compound gives a green emission. Under 3650 Å, it is comparable to ZnS:Cu; and under 2537 Å, to zinc silicate. Wollentin, Wei, and Nagy (5) modified McKeag's cadmium chlorphosphate by substituting chlorides of barium, strontium and magnesium plus zinc. The brightness and maintenance are inferior to the calcium halophosphates but their peak emission is extended to 5900 Å to 6080 Å.

*Silicates.*—Jenkins and McKeag (6) prepared silicates of the alkaline earths, activated with europium, whose emissive color varies with the mole ratio of metal oxide to silica. With a ratio of 2 to 3 the emission is green, and is shifted to the blue with decreasing ratio. They are most efficiently excited by 3650 Å to the brightness of zinc cadmium sulfides of the same emissive color. They describe also a calcium pyrophosphate activated with dysprosium, which is excited most strongly by CR and has brighter phosphorescence than zinc cadmium sulfide.

Double alumino-silicates of an alkaline metal combined with an alkaline earth and activated with copper have been studied by Claffy and Schulman (7). The brightest has the molar composition, $0.5Na_2O + 0.5CaO + 1.0Al_2O_3 + 6.0SiO_2 + 0.02Cu$; its emission has the same spectral distribution as unactivated calcium tungstate, with one half the brightness. Nagy, Wei, and Wollentin (8) synthesized a hardystonite, $Ca_2Zn(SiO_3)_3$, activated with lead. The introduction of zinc shifts the emission peak from 3350 Å to 3450 Å and yields a performance in lamps equal to Froelich's cerium-activated calcium phosphate.

*Sulfides.*—Prener (9) produced a zinc sulfide activated with arsenic which emits a red As band at 6200 Å in addition to the unactivated blue band. With high arsenic, a band appears at 5200 Å. The emission of the zinc oxide phosphor has been shifted to shorter wave lengths by solution in it of magnesium oxide, up to 25 mole per cent, as found by Smith (10). Magnesium has a similar effect in the zinc and zinc-cadmium sulfides activated with silver or copper. With copper there is a very long phosphorescence under CR.

Kroeger, Bril, and Dikhoff (11) found that a single component screen for TV can be prepared from the phosphor ZnCdS(Al):Ag:Au, which has the same ICI point as the usual mixture of two sulfides. In brightness, current saturation, and color change toward the yellow with increase in beam current, it is close to the usual mixture.

A zinc sulfide activated with 0.01–1.0 per cent Cu has been prepared by Froelich (12) in pure $H_2S$ without oxide or chloride addition. The normal blue and green bands appear under 3650 Å and also a yellow band and a strong red band at 6500 Å to 6700 Å. All four bands respond moderately to electroluminescence. Under CR only the blue and green bands appear. When prepared similarly with aluminum equal to the copper content, a green band and one at 5800 Å are emitted under 3650 Å; it is not excited by CR nor under electroluminescence.

*Miscellaneous.*—Schulman, Ginther, and Klick (13) studied a sodium chloride activated with lead. Under excitation by 2730 Å, it emits at 3200 Å with low lead and at both 3200 Å and 3850 Å with high lead. With increase in temperature, the 3850 Å band decreases much faster than the 3200 Å, showing a similarity in this respect also to the manganese-activated zinc and calcium silicates. The phosphors are unstable. Phosphors of lead and manganese chlorides with potassium chloride have been prepared by Ginther (14), and their emission and complex excitation bands were measured. $K_4MnCl_6$:Pb emits at 6100 Å under 2537 Å, 2700 Å to 3000 Å, or 3650 Å. The manganese band is sensitized by thallium as well as by lead. A much weaker emission at 6300 Å is given by KCl:Mn:Pb.

Kroeger, Ouweltjes, and others (15) developed a phosphor discovered by Travnicek for color correction in the high-pressure mercury lamp by application to the outer bulb. It is a basic magnesium arsenate with six moles MgO to one mole $As_2O_5$, activated with quadrivalent manganese. Its emission includes five bands in the range 6200 Å to 6580 Å. Its quantum efficiency is 75 per cent under 2537 Å and 3650 Å. Its brightness remains constant to 500°C and then decreases rapidly as the decay constant rises. For good maintenance it must be operated in an oxygen atmosphere.

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[1] This review covers the articles published since the last annual review, which appeared in the March 1951 JOURNAL, page 35C.

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Kroeger, Vink, and Van den Bomgaard (16) found that magnesium oxide with nickel emits green luminescence under CR at liquid air temperature. Larach (17) prepared a complex phosphor, $Zn_2Nb_2Ta_2O_{11}:Mn$, which shows green luminescence under CR at an intensity which is 10 per cent of zinc silicate.

### Phosphor Characteristics

*Oxygen-dominated.*—Several papers deal with zinc silicates. CR luminescence has been measured in a demountable tube for aluminized screens of different thickness by Larach and Shrader (18). The increase in brightness with applied voltage tends toward saturation at 2–6 mg/cm², but at 9 mg/cm² the results nearly fit the equation $L = KV^{0.8}$. Larach (19) repeated Anderson's and Wells' preparation of barium zinc silicate and confirmed its red emission under ultraviolet (UV). Under CR he finds its main band to be at 5300 Å, with a secondary at 6900 Å.

Vlam (20) measured the emission of zinc silicate with 0.1 per cent Mn at 15°K under 2537 Å. The photographed spectrum showed 19 lines, a few of which had been observed previously by Randall and by Shrader. Klick (21) repeated measurements on this phosphor and also on others, including $ZnWO_4$, KCl:Tl, ZnS:Cu, ZnS:Ag, CdS:Ag, and CdS at 77°K and at 4°K. Only those showing edge emission have a tendency to exhibit line emission. Those with activators showed no change below 100°K. Possible explanations involve interactions between excitons and the conduction level. The many lines found by Vlam were not confirmed.

The excitation spectra of various silicates, including both the green and yellow fluorescing zinc silicates, zinc beryllium silicate, calcium and barium silicates, and various tungstates, have been recorded by Oszy (22). The effect of change in temperature upon emission spectra and intensity has been determined by Jerome (23) for some of the current lamp phosphors, including calcium halophosphate, calcium silicate, zinc beryllium silicate, and magnesium tungstate. The CR luminescence of calcium sulfate activated by manganese has been studied by Watanabe (24).

*Sulfides.*—Bube (25) analyzed copper-activated zinc sulfides and confirmed Kroeger's conclusion that the chlorine content is a function of the copper concentration. He finds, however, that the mole ratio of chlorine to copper decreases with increase in copper content. He believes that the results are in accord with his previous conclusion that the green emission with low copper is due to interstitial ions of $Cu^+$ and that the blue emission with high copper is due to $Cu^{++}$ ions substituted for zinc.

That oxygen may also be a coactivator as a substitute for chlorine has been shown by Kroeger and Dikhoff (26) for solutions of zinc oxide in zinc sulfide. It introduces a new absorption band and shifts the emission bands of copper, silver, and gold by 150 Å toward longer wave lengths. It fails to give the brightness attained with chlorine. When both chlorine and oxygen are present, the emission bands of each appear in a composite band whose peak is shifted only 100 Å from the band with chlorine alone. Oxygen increases the phosphorescence and introduces additional glow peaks. It is believed to be associated with the activator ions.

Related to this is the description by Verwey and Kroeger (27) of the method of "controlled valency," exemplified in semiconductors by the decomposition product formed at 1200°C from a mixture of nickel carbonate with a small amount of lithium carbonate. In the resulting nickel oxide there is thought to be enough trivalent nickel ions to compensate for the monovalent lithium ions present. The same consideration applies to zinc sulfide phosphors in which the presence of a monovalent activator finds compensation in the presence of an equivalent amount of monovalent halogen or of a trivalent cation. They believe that this mechanism is applicable to other phosphors.

Unexpected emission bands have been observed by Fehr and coworkers (28) in silver-activated zinc cadmium sulfides high in cadmium. Under CR the emission band with high silver was shifted to shorter wave lengths by increase in current density. Under UV at 77°K the apparent shift was resolved into two bands, one of which corresponded to the new band found under CR. It proved to be the silver band which is suppressed at 25°C. The other band was that normally observed in the unactivated phosphor.

Bube (29) measured the change in photoefficiency of copper-activated zinc sulfide as a function of temperature and copper content. He also determined the accompanying change in photoconductivity and concludes that its process is different from that of luminescence. Single crystals of zinc sulfide were grown by Piper (30) in evaporated quartz bulbs by vaporization at 1170°–1200°C, 5 mm long and 3 mm² in cross section. Johnson (31) gave a general survey of the preparation of phosphor single crystals.

Transparent screens of manganese-activated zinc sulfide have been prepared by Studer, Cusano, and Young (32) either (*a*) by passing a stream of zinc vapor containing a little manganese chloride vapor over a heated glass surface at a few mm pressure of $H_2S$, or (*b*) by first vaporizing a film of $ZnF_2:Mn$ and then converting to ZnS:Mn by heating in $H_2S$. Transparent screens have also been prepared of zinc and zinc-cadmium sulfides with various activators.

By radioactive tracer study, Dreeben and Ward (33) determined the distribution of calcium, europium, and samarium between phosphor and flux melt in the preparation of the *IR* sensitive phosphor, (Ca, Sr)S:Eu:Sm. Brauer (34) studied the emission spectra of the sulfides and oxides of magnesium, strontium, calcium, and barium activated with europium. The europium proved to be trivalent in the oxides and divalent in the sulfides. Gobrecht and Hahn (35) studied the phosphors prepared without activators by variable reduction of alkaline sulfates. Their emission, quantum yield, and decay were measured under 3660 Å and 2540 Å at various temperatures. Red emission under 3660 Å is ascribed to polysulfide formation, and blue emission under 2540 Å, to incorporation of alkali atoms.

### Phosphorescence and Thermoluminescence

A survey of the most important work of the past ten years was compiled by Stoeckmann and augmented by Przibram (36). It includes also *IR* stimulation. Of particular interest are: (*a*) the relations of doubly activated phosphors to photoelectric-conductivity and photography; (*b*) the application of reaction kinetics to electron exchanges in solid bodies; and (*c*) the investigations of traps and thermoluminescence.

Nelson and Berbert (37) and Bull and Garlick (38) recorded glow curves for $Zn_2SiO_4:Mn:As$. The arsenic serves only to produce exaggerated phosphorescence of the power law type. Their results are in essential agreement despite differences in composition and preparation of the phosphors. Bull and Garlick estimated that the number of traps introduced by arsenic was 50 times greater than in its absence and occurred when the manganese concentration was 100 times the arsenic. They measured the pronounced effect of arsenic in zinc beryllium silicate, zinc cadmium silicate, and cadmium silicate but found no effect in the silicates of calcium, strontium, barium, and magnesium activated with manganese.

Wallick (39) measured the thermoluminescence of 92ZnS·8CdS:Cu and ZnS:Ag and found that segregated crystals 14 microns in size respond the same as the original mixture from −160° to 0°C, whereas smaller crystals contain more shallow traps. There was no effect of size on phosphorescence. Bull and Mason (40) studied the electron trap distribution in the *IR* sensitive phosphors of zinc sulfide activated with Cu:Mn, Cu:Pb, and Mn:Pb, and conclude that long wave length radiation discloses classes of traps for which no evidence is given in glow curves. In an extended discussion of electron traps, Wise (41) considers their possible relation to the F and F′ color centers of alkali halides. Schoen (42) discussed the electron transitions in sulfides at different temperatures and the evaluation of glow curves, with many references to papers dealing with the subject.

Related to the *IR* sensitive sulfides are the calcium oxide phosphors of Janin, Crozet, and Clerc (43), activated with combinations of copper, lead, and manganese. Neither copper nor manganese alone showed *IR* sensitivity. Strong sensitivity was shown by combinations of manganese with copper or lead, especially the latter, in the range of 0.9–1.6 microns.

The stimulation and quenching of stored luminescence by ultrasonic radiation have been demonstrated by Schreiber and Degner, and by Eckardt and Lindig (44) for sulfide phosphors. The strongest effects appear to have been shown by ZnS:Cu and SrS:Bi.

### Theoretical Interpretations

Williams (45) evaluated quantitatively the absorption and emission spectra of KCl:Tl for various temperatures and calculated the electron transitions responsible for them. The dependence of spectral emission and intensity upon temperature and exciting wave length were correlated with the absorption data on this phosphor by Johnson and Williams (46) for the purpose of providing a detailed picture of the energy relationships. The energy levels obtained for two excitation states account for the occurrence of a three-band emission. A fourth band appears on the introduction of cadmium and its position is also accounted for. Klick (47) utilized an alternate procedure for arriving at these relationships. His results are in agreement with Williams for the same phosphor. They indicate that his method may be used for other simple phosphors to calculate configurational coordinates from experimental data. This method has been applied by Klick and Schulman (48) to determine the potential energy curves of the levels involved in optical transitions of divalent manganese ions in zinc silicate. These curves are in agreement with excitation and emission bands and with their optical characteristics. The curve for the first excited state is displaced so slightly, 0.06 Å, from that of the ground state as to indicate that therein lies the cause for the effectiveness of manganese in so many phosphors and also for the reported asymmetry of its low temperature emission.

Schoen (49) showed that the calculation of similar characteristics for sulfides must be corrected for changes in lattice orientation that result on excitation. He proposed also an energy diagram to account for the radiationless transitions and discussed his conception of losses in excitation energy to the lattice.

In samarium-activated tungstates and molybdates, the decrease in the bluish emission of the basic compound on increase in temperature is accompanied by an increase in the red samarium emission. To account for this, Botden (50) developed a theory of resonance transfer of excitation energy that may extend over many lattice sites. He extended the theory to account for the occurrence of sensitized luminescence which results from the transfer of the excitation energy of the sensitizer ions to activator ions. The latter are incapable of responding directly to photoexcitation. He based his conclusions on measurements for the change in quantum efficiency with temperature for the phosphors $Ca_3(PO_4)_2$:Ce:Mn and $Sr_3(PO_4)_2$:Sn:Mn. He considered other cases also, such as the halophosphates.

Leverenz and North (51) presented evidence that luminescence centers formed by manganese ions in zinc silicate interact over several interatomic spacings. Arpiarian and Curie (52) described two systems of electronic levels to account for the distinct behavior of iron and nickel, as compared with cobalt, in quenching luminescence. Pfeiffer and Fonda (53) ascribed the abnormal emission of the yellow fluorescing zinc silicate to distortions in structure extending over several unit cells.

The theories for the origin of multiple band emission in phosphors activated with divalent manganese have been reviewed and discussed by Kroeger and Zalm (54), on the basis of all accumulated evidence. Of the two theories already proposed, Weyl's coordination theory and Maurer's cluster theory, the latter is preferred because its insufficiencies seem less important than those in the coordination theory. Schulman (55) disagreed and discussed grounds for the existence of serious errors in the four assumptions made by Kroeger to support the cluster theory.

### Electroluminescence

D-c electroluminescence in silicon carbide, germanium, and silicon were studied by Lehovec and coworkers and by Haynes and Briggs (56). They attribute it to optical recombinations of electrons and holes at N-P junctions. The electroluminescence of single crystals of copper-activated zinc sulfide has been studied by Piper and Williams (57). The light increased exponentially with applied d-c voltage. With AC, the average light output varied linearly with the frequency. Below a critical voltage only light appeared which was out of phase with the voltage. Above this value, additional light appeared which was in phase with the voltage and increased rapidly with the voltage. Similar work has been reported by Böer and Kuemmel (58).

Roberts (59) made comparative tests on a copper-activated zinc sulfoselenide powder suspension in a variety of dielectric matrices. The only effect of the dielectric is apparently to modify the electric field in the phosphor. The brightness depends critically upon the field thus produced. Increasing the dielectric constant of the matrix augments the electric field in the phosphor, thereby enhancing the brightness. The brightness does not depend critically upon the temperature in the range −100° to 50°C.

### Radioluminescence

Morrish and Decker (60) determined the phosphorescence decay of pure potassium chloride emitting at 4550 Å and 5300 Å, and of lithium fluoride emitting in the UV after irradiating with x-rays at various temperatures. The initial decay was ascribed to F′ centers and the final, to F centers. Sodium chloride activated with 1 per cent AgCl has been found by Furst and Kallman (61) to be as efficient under gamma radiation as anthracine. There is no luminescence under UV or visible light until it has been exposed to high energy radiation. Excitation by gamma rays is presumed to liberate electrons which are trapped at the lattice vacancies of color centers. Stimulation by light elevates them to the conductivity band and further transitions give rise to phosphorescence. Jentschke and coworkers (62) measured the fluorescence efficiencies of sodium iodide activated with thallium under excitation by electrons and heavy particles and found it to be stronger than anthracine.

Schulman and coworkers (63) reviewed the subject of radiophotoluminescence and concluded that silver-activated glass furnishes the most satisfactory means for measuring doses of gamma rays from ten to a few thousand roentgens. Their dosimeter is reasonably independent of energy, it is stable with time, and is not seriously affected by exposure of the glass to UV or to temperatures from −70° to 100°C.

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# Current Affairs

## Electrochemical Society Condemns Astin Dismissal

When Secretary of Commerce Sinclair Weeks announced last March that he had asked for the resignation of Dr. Allen V. Astin, Director of the National Bureau of Standards, he brought down upon himself a storm of protest. The only specific reason given by the Secretary for his action was that in his opinion the Bureau had not been "objective" in its testing of a commercial mixture claimed to increase the life of lead-acid batteries.

The Board of Directors of The Electrochemical Society, meeting in New York on April 12, voted unanimously to make a formal protest, which was sent to President Eisenhower, Secretary Weeks, and the Small Business and Commerce Committees of the Senate. The statement was given to the press by Dr. J. C. Warner, President of the Society, on April 14 and to the members of the Society in the course of his Presidential Address. The text of the statement was as follows:

### Text of Protest

"The Electrochemical Society strongly condemns the dismissal of Director Astin of the National Bureau of Standards prior to a full and impartial investigation of charges which question the integrity of the Bureau. This arbitrary action of the Secretary of Commerce, casting doubt as it does upon the integrity and competence of government scientists and government laboratories, will seriously impair the operation of the Federal Trade Commission, the Food and Drug Administration, and other federal agencies established for the protection of the public. The Society takes a grave view of the challenge which this action implies to the promulgation of standards by government laboratories. The Society is alarmed about the devastating effect of the summary dismissal of Dr. Astin upon the morale of technical personnel in the government service and on the ability to recruit in the future such personnel. This unfortunate action is particularly lamentable in this period of international tension when the welfare of our citizens leans so heavily upon our ability to maintain superiority in science and technology.

"The Electrochemical Society urges that Congress authorize a thorough investigation of the scientific facts in the case and invite the leading technical societies to nominate a group of qualified scientists and engineers to undertake this task and make public its findings.

"Finally, the Society believes that nothing short of restoring Dr. Astin to his former position can begin to repair the damage and injustice done the National Bureau of Standards, its director, and technical employees."

### Weeks Reverses Stand

This and similar protests from technical societies and many individuals apparently helped persuade Secretary Weeks to reverse his position. On April 17, Mr. Weeks announced that he had asked Dr. Astin to remain as Director through the summer. A new committee, to be appointed by the National Academy of Sciences, is to appraise the quality of the Bureau's work on battery additives, and to make a definitive statement on the merits of the one in question. This belated acceptance by Mr. Weeks of the suggestion made by Dr. Astin on March 4 is in accord with the proposal of The Electrochemical Society as quoted above.

Two other groups of technical men are to advise Secretary Weeks concerning the Bureau. A special committee composed of members from seven scientific and engineering societies and headed by Dr. M. J. Kelly, president of Bell Telephone Laboratories, will evaluate the functions and operations of the Bureau as a guide to future policy. The National Bureau of Standards Visiting Committee, of which Dr. R. F. Mehl, Director of the Metals Research Laboratory of the Carnegie Institute of Technology, is chairman, has been asked to submit a panel of names from which Mr. Weeks can expect to select a successor to Dr. Astin.

## 5th Meeting of CITCE in Stockholm in July

The fifth annual meeting of the International Committee of Electrochemical Thermodynamics and Kinetics (CITCE) will take place in Stockholm, Sweden, on July 25 to 28, 1953, i.e., immediately before the International Congress of Pure and Applied Chemistry.

The program of the meeting will include papers under the following headings:

1. Fundamentals: Electrochemical Nomenclature and Definitions.
2. Experimental Methods in Electrochemistry.
3. Electrochemical Behavior of Metals and Non-Metals: 3.1 Potential—*p*H Diagrams (Equilibrium Diagrams and Practical Diagrams); 3.2 Polarization Curves; 3.3 Miscellaneous.
4. Applications to Corrosion.
5. Electrolytic Phenomena.
6. Applications to General and Analytical Chemistry.
7. Miscellaneous.

Information concerning the organization of the meeting can be obtained from the Secretary General of the Committee (CITCE), Dr. Marcel Pourbaix, University of Brussels, Brussels, Belgium; from the Secretary for Sweden, Dr. Uno Trägårdh, Royal Institute of Technology, Stockholm, Sweden; or from the President of CITCE, Dr. Pierre Van Rysselberghe, University of Oregon, Eugene, Oregon.

# High Registration, Varied Symposia Score Success at N. Y. Meeting

The largest registration in the history of the Society was recorded at the 103rd meeting in New York, on April 13–17. A total of 712 members and guests attended the technical sessions and social functions. Of this number, about 60 were women.

The technical program presented sessions sponsored by the Electric Insulation, Electronics, Electro-Organic, Electrothermic, and Theoretical Divisions and offered a total of 135 papers. The 3-day symposium on "Application of Electrochemistry to Biology and Medicine" drew a large and interested audience, and the Electronics sessions, including Round Tables on Luminescence and Phosphor Screen Application, also were well attended. Keen interest and a good attendance likewise characterized the sessions of the other Divisions participating. The sizable group present at the Richards Memorial Lecture on "Transistor Physics," by Dr. William Shockley, indicated the interest in this particular field.

Heading the social calendar, was the Reception for Dr. and Mrs. Warner on Tuesday evening, followed by the Annual Banquet. In his presidential address, Dr. Warner expressed the Society's appreciation to all of the committee chairmen and others who had contributed to the splendid success of the meeting.

President Warner also suggested an expression of appreciation to Dr. Colin G. Fink, Honorary Chairman of the New York Meeting, for his distinguished service to the Society over a period of many years. A resolution was offered to this effect, and seconded, by members on the floor.

Another feature of the banquet was the annual awards of the Young Author's Prize and the Francis Mills Turner Memorial Award.

### Young Author's Prize

The Young Author's Prize of $100 and a year's membership in the Society was presented to W. E. Kuhn of The Carborundum Company, Niagara Falls, New York (see group picture), for his two papers, "Production of Titanium Ingots by Melting Sponge Metal in Small Inert Atmosphere Furnaces" and "Development of Graphite Electrodes and Study of Heat Losses with Different Electrodes in the Single Electrode Inert Atmosphere Arc Furnace"; both of these appeared in the March 1952 issue of the JOURNAL.

Mr. Kuhn was born and educated in Toronto, Ontario, and graduated with honors in metallurgical engineering from the University of Toronto in 1934. He then joined the Ontario Research Foundation and, in December 1944, was appointed Research Fellow to work on a fellowship sponsored by Turbo Research Limited, and later by the National Research Council, Ottawa. This work was concerned with an investigation of properties of titanium made from powder, for possible use in gas turbines for jet aircraft. A paper covering certain phases of this work was published by Mr. Kuhn and two other authors, for which they were awarded the Leonard Medal in 1951 by the Engineering Institute of Canada.

Following three years with the Titanium Alloy Manufacturing Division of National Lead Company, Niagara Falls, Mr. Kuhn joined The Carborundum Company in 1952 as research engineer, to supervise research on zirconium and related metals.

*Top row, left.* Seen at the reception preceding the informal dinner on Monday evening are R. S. McKay, the Society's new President; Max A. Lauffer, of the University of Pittsburgh, speaker at the dinner; O. H. Bauer; Henry B. Linford; and Harry R. Copson, General Chairman for the New York Meeting. *Center:* Recent Past Presidents of the Society who attended the meeting—George W. Heise, R. M. Burns, W. C. Moore, R. M. Hunter, not-quite-Past President J. C. Warner, and C. L. Faust; seated are Mrs. Burns, Mrs. Moore, Mrs. Hunter, and Mrs. Warner. *Right:* Leading figures in the "Biology and Medicine Symposium" talking it over with Editorial Director R. M. Burns (*right*) at the reception Monday evening are (*left to right*) H. H. Jasper, L. R. Blinks, George Scatchard, and T. Shedlovsky.

*Bottom row, left.* John R. Musgrave and W. C. Lilliendahl relaxing during the Luminescence Section's social hour Monday afternoon. *Center, left:* A group at the reception preceding Monday night's dinner—Clifford A. Hampel, Mrs. A. S. White, O. W. Storey, and Mrs. E. F. Kiefer. *Center, right:* J. C. Warner, Society President, awarding the Young Author's Prize to W. E. Kuhn at the banquet Tuesday evening. *Right:* Incoming and outgoing "First Ladies," Mrs. R. J. McKay (*left*) and Mrs. J. C. Warner.

*Left:* John R. Dunning, Dean of Engineering at Columbia University, addressing the Society luncheon on Monday. Also visible in the picture are R. J. McKay, Marvin J. Udy, H. H. Uhlig, and Hans Thurnauer, newly elected 3rd Vice-President. *Center:* Group of ladies about to start the gay whirl of "ladies' activities" arranged for Tuesday by Mrs. A. C. Loonam, Chairman of the Ladies' Committee for the meeting. *Right:* William Shockley, of Bell Telephone Laboratories, delivering the Richards Memorial Lecture on Wednesday afternoon.

### Turner Memorial Award

P. T. Gilbert of The British Non-Ferrous Metals Research Association, London, was the winner of the Francis Mills Turner Memorial Award, Sponsored by the Reinhold Publishing Company, consisting of $100 worth of books and a year's Electrochemical Society membership. His paper, entitled "The Nature of Zinc Corrosion Products," appeared in the January 1952 issue of the JOURNAL.

P. T. GILBERT

Dr. Gilbert studied at the University College of the Southwest of England, Exeter, and was awarded the B.Sc. degree in chemistry by London University in 1943. He then joined the Corrosion Section of British Non-Ferrous Metals and carried out research on the corrosion of zinc and galvanized steel in supply waters. He received the Ph.D. degree from London University in 1950 for a thesis based on this work, and for work included in the prize-winning paper mentioned above.

He was appointed head of the Cor[illegible]sion Section of the B.N.F.M.R.A. in 1948. He has published a number of other papers, mainly on various phases of work in the corrosion field.

## Candidates Nominated for Society Offices, 1954

The Nominating Committee, appointed at the April 12 Board of Directors' meeting in New York, reported at an adjourned session on April 14 that the following candidates were proferred for offices in the National Society for the coming year:

*For President—*

Marvin J. Udy

*For Third Vice-President—*

Norman Hackerman
Fred W. Lowenheim
John R. Musgrave

The two other Vice-Presidents, H. H. Uhlig and Hans Thurnauer, since they were elected for a three-year term, will automatically become first and second Vice-President, respectively.

The above slate will be voted on in the fall ballot-by-mail election—the successful candidates to assume office in the spring of 1954. This report was submitted by H. R. Copson, John F. Gall, R. M. Hunter, H. J. Read, and G. W. Heise, Chairman.

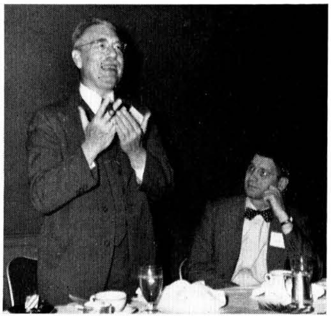
## Peter Debye Honored

Professor Peter J. W. Debye, Nobel Laureate and professor of chemistry, Cornell University, was honored at a formal luncheon on April 15, 1953 under the auspices of the Electric Insulation Division. Professor T. G. Bullen, Iona College, delivered the Invocation.

A scroll bearing the following inscription was presented to the guest of honor:

"The Electric Insulation Division of The Electrochemical Society acknowledges its indebtedness to P. Debye without whose imagination, vision, and inspiration many advances in dielectrics would not have been possible."

In his talk entitled "An Historical Interpretation of the Concept of Molecular Charge," Dr. Debye reviewed the provocative suggestions of Van der Waals and Condon on molecular attraction, emphasized the magnitudes of intermolecular forces predicted from their equations, and told of recent significant experimental work at Utrecht establishing the value of $x$ in the reduced equation of state $\left(\alpha + \frac{3}{\beta x}\right)(3\beta - 1) = 8\gamma$ as 2.3 − 3.3.



Peter J. Debye speaking at the luncheon meeting of the Electric Insulation Division on Wednesday. On the right is J. R. Bukey, Division member.

### ASTM Annual Meeting

The 1953 annual meeting of the American Society for Testing Materials will be held in Atlantic City from June 29 through July 3. Program will appear in the May ASTM Bulletin.

# Industrial Progress in Canada—1952*

*A. C. Holm*

Releases from the Dominion Bureau of Statistics covering the calendar year 1952 confirm earlier observations that Canada last year reached a new peak in its postwar prosperity, surpassing the previous record-breaking year, 1951, by a comfortable margin on almost all counts. The following are increases in 1952 as compared to 1951:

| | |
|---|---|
| Gross National Product— | up 6% |
| National Income— | up 6% |
| Wages, Salaries, Miscellaneous Income— | up 12% |
| Public and Private Capital Expenditure— | up 12% |

For the seventh consecutive year Canada's budget has produced a surplus, despite large expenditures on defense and steady reduction of the national debt; since 1946 the per capita debt has fallen about 31%. This happy state of affairs has brought about a long-awaited reduction of personal income taxes (about 11%) and of corporation taxes (6 – 10%), both to take effect in July 1953.

All major props of Canada's economy—agriculture, forestry, hydroelectric power, manufacturing, and mining—contributed to this peak prosperity. Canada's farmers garnered a record wheat crop. The pulp and paper mills achieved an output second only to their all-time record high of 1951; newsprint exports, dollar-wise the country's largest export commodity, surpassed 1951 levels by about 3%. Production of electric energy in Canada reached 61,786 million kilowatt hours, up 8% over 1951. The volume index of industrial production reached a peak of 248.0% in October 1952 (1935–1939 = 100), all but three months recording increases over the 1951 average of 226.5. Value of Canada's mineral output touched a new high of $1,278,000,000, up 4.1% over 1951.

Exports reached a new peak of $4,714 million, up 16% over 1951. In contrast to the two preceding years, international trade yielded a net surplus, estimated at about $250 million. As in previous years, the United States and Canada remained "best customers," each country doing more export and import business with the other than with any other country. Some 54% of Canada's exports went to the U. S. in 1952, and about 74% of its imports originated there.

**This report on the interesting industrial situation in Canada—with particular attention to the extensive electrochemical and metallurgical advances—was prepared by A. C. Holm, Regional Editor of the JOURNAL for Canada.**

### New Projects for 1953

All signs point to a continued high level of prosperity through 1953. Investment in new plants and exploration and exploitation of new mineral deposits is proceeding at a brisk pace. The most spectacular projects now underway are the development of the huge Ungava (Quebec) iron ore deposits, the drilling for oil and natural gas in Western Canada, and the creation of a new aluminum smelter and hydroelectric plant in British Columbia. But an unprecedented number of other new enterprises have been started or planned throughout the length and depth of Canada, based on petroleum, natural gas, refinery and smelter gases, forest products, hydroelectric power, salt, pyrites, asbestos, and ores of copper, lead, zinc, nickel, cobalt, iron, tungsten, titanium, and uranium.

The following projects of an electrochemical or electrometallurgical nature underway or announced in 1952 will be of special interest to readers of the JOURNAL:

#### *Chlorine and Caustic Soda*

BRITISH COLUMBIA—New company, Hooker Chemicals Ltd., Vancouver, formed by the Hooker Electrochemical Company to produce chlorine for pulp bleaching.

ALBERTA—A $3 million plant is scheduled for Duvernay by Western Chemicals Ltd., Calgary.

ONTARIO—The Dow Chemical Company of Canada will spend $2 million on expanded chlorine facilities at Sarnia.

Marathon Paper Mills is completing a new $3 million plant at Marathon for pulp bleaching.

QUEBEC—Dominion Tar and Chemicals completed a $1 million addition to its plant at Beauharnois.

#### *Aluminum*

BRITISH COLUMBIA—The Aluminum Company of Canada has started on what could become the largest aluminum producing center in the world at Kitimat, with an ultimate capacity of over 500,000 tons per year. Together with the necessary power developments this project will cost some $500,000,000. The immediate goal is 90,000 tons of aluminum in 1954.

QUEBEC—A 45,000-ton per year addition to the Isle Maligne smelter was completed in 1952.

#### *Magnesium*

QUEBEC—Completion of a fourfold expansion of electrolytic magnesium production is scheduled for 1953 by the Aluminum Company of Canada at Arvida; the capacity is thereby raised to 4000 tons a year.

#### *Phosphorus*

QUEBEC—The Electric Reduction Company of Canada will complete in 1953 a $5 million plant with two 18,000 KVA furnaces for elemental phosphorus at Varennes, thereby nearly tripling its productive capacity.

#### *Ferrosilicon*

QUEBEC—Electro Reagents (Quebec) Ltd., a wholly owned subsidiary of Dominion Magnesium Ltd., will complete in 1953 a new plant ($1 million) at Beauharnois to produce 6000 tons annually of 75% ferrosilicon for use in magnesium production.

#### *Calcium Carbide*

ONTARIO—North American Cyanamid Ltd., at Niagara Falls, completed in 1952 a new carbide furnace and expansion of calcium cyanamide facilities at a cost of about $4.5 million.

#### *Tungsten*

BRITISH COLUMBIA—Kennametal of Canada Ltd. has begun the production of tungsten carbide directly from tungsten ore at its new refinery at Port Coquitlam, B. C.

#### *Titanium Slag*

QUEBEC—The Quebec Iron and Titanium Corporation at Sorel is bringing, during 1952–1953, its remaining four electric smelting furnaces into production. The five installed furnaces are designed to treat 1500 tons of Quebec ilmenite ore daily, producing some 700 tons of 70% titanium oxide slag and 500 tons of medium carbon steel daily.

### *Dry Batteries*

Ontario—National Carbon Ltd., Toronto, expects to complete a $1 million dry battery plant at Walkerton in 1953.

Unconfirmed press reports suggest that serious consideration is presently being given to the possibility of establishing an electric zinc smelter and an additional calcium carbide plant in the Province of Quebec and a huge electrometallurgical enterprise in the Yukon.

### Production of Electric Energy

Keeping pace with Canada's burgeoning industries, the installation of new hydraulic turbine capacity reached a record high in 1952 of about 1 million horsepower, bringing Canada's total developed water power to 14,304,000 hp. During 1953 another 950,000 hp is scheduled to be completed, and during 1954–1956 firm plans have been announced to bring in another 2.4 million hp. In addition some 690,000 kw of thermal power is being installed during 1952–1953, with another 100,000 kw on order for completion by 1956. Thus, during the five years 1952–1956, Canada will have added over 5 million hp to her power-generating capacity, according to present published figures. In some quarters it is felt that this new supply will be insufficient to meet the demand and that still further additions will be required.

It is interesting to note that Canada produces yearly about 4220 kwhr per capita, over 96% hydroelectric. For comparison, the United States in 1950 produced only 2560 kwhr per capita, about 26% hydro energy. These figures illustrate the important role played by electric energy, and particularly low cost hydro power, in Canada's processing and manufacturing industries.

Despite her abundant supplies and untapped resources of hydro power, Canada exports to the power-hungry United States only about 4% of her output. One reason for this apparent parsimony is that hydrolectric resources adjacent to the U. S. border are generally in the areas of Canada's heaviest concentration of population and greatest domestic demand for power. But another reason is Canada's firm belief that she will need all her electric power to supply her own needs in the future for the refining and processing of indigenous raw materials.

That Canada is not being overcautious in this policy is to some extent confirmed by the report of the "President's Materials Policy Commission," which in June 1952 reported to the President of the United States that the U. S. would require by 1975 an output of electrical energy equivalent to about 7250 kwhr per capita per year. That this estimate may not be too far off the mark is indicated by the fact that the Province of Quebec, Canada's largest hydroelectric producer, is already consuming some 5600 kwhr per capita per year, compared to 3200 in 1939. Canada's policy in this matter was recently reaffirmed by her Minister of Resources, Honorable Robert Winters, in definitely rejecting a request by the Aluminum Company of America for use of the headwaters of the Yukon River to generate power for a proposed 200,000 ton per year aluminum smelter near Skagway, Alaska.

## Fall Meeting Papers

Manuscripts in triplicate or abstracts (not to exceed 75 words in length) of papers to be presented at the Wrightsville Beach Meeting, September 13 to 16, must be received at Society headquarters, 235 West 102nd Street, New York 25, N. Y., *not later than July 1, 1953.*

## Fall Meeting at Wrightsville Beach, N. C., Sept. 13–16

The Electrochemical Society will hold its 104th meeting at Wrightsville Beach, North Carolina, on September 13–16. This is the location of the Harbor Island Testing Station and the Kure Beach Project of the International Nickel Company. It is about ten miles from Wilmington, N. C.

The Ocean Terrace Hotel will be convention headquarters.

In addition to The Electrochemical Society meeting at Wrightsville Beach, the annual meeting of the Sea Horse Institute is scheduled for September 16–18 and, also, the annual meeting of the Marine Borer Conference during the latter part of the week.

Sessions will be held on Corrosion and Electrodeposition; the Electrothermic Division have tentative plans for arranging a Round-Table Discussion; and the Battery Division is planning two Round-Table Discussions but no formal presentation of papers. Corrosion sessions will be held on Wednesday, September 16, which will coincide with the first day of the meeting of the Sea Horse Institute, and will be attended by members of both societies.

Tours will be arranged for the inspection of some of the interesting corrosion projects that are being carried out here.

Frank L. LaQue, who is head of the Corrosion Engineering Section, International Nickel Company, and also has charge of the Harbor Island-Kure Beach operations, is General Chairman of the fall meeting. Fred W. Lowenheim, Metal & Thermit Corporation, is Financial Committee Chairman. Since there is no local section of the Society at Wrightsville Beach, details of the arrangements have been assigned to staff members of the Nickel Company's testing station.

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## Division Activities at the Spring Meeting

### Electric Insulation Division

As a result of the recent election, held by the Electric Insulation Division at its meeting on April 15 in New York, the following members have assumed the offices noted below:

*Chairman*—R. A. Ruscetta, General Electric Company, Schenectady, New York

*Vice-Chairman*—A. Gunzenhauser, Transisola, Inc., New York, N. Y.

*Secretary-Treasurer*—L. L. Deer, U. S. Naval Ordnance Plant, Indianapolis, Indiana

THOMAS D. CALLINAN, *Chairman* (1952)

### Electronics Division

The luncheon and business meeting of the Electronics Division, held during the New York meeting, took place on April 14.

After calling the meeting to order, Chairman J. R. Musgrave read the report on Division activities during the past year. The Secretary read the financial report and informed the meeting that this year's Enlarged Abstracts booklet had proved so popular that the entire issue of 300 copies was sold out by noon on April 15th.

Symposia planned for the 1954 spring meeting include Luminescence, Rare Metals, Screen Application, Instrumentation, and Semiconductors.

A motion was made and seconded that the proposed changes to the Division's bylaws as published in the March and April issues of the Journal be approved. The reasons for these changes were discussed and a vote being taken, the motion was carried.

Dr. Froelich, Chairman of the Nominating Committee, submitted the following nominees for the 1953–1954 year:

*Chairman*—R. H. Cherry
*Vice-Chairman (Luminescence)*—J. H. Schulman
*Vice-Chairman (Rare Metals)*—A. U. Seybolt
*Vice-Chairman (General Electronics)*—A. E. Hardy

The term of *Secretary-Treasurer* (C. W. Jerome) has two more years to run.

There were no further nominations. The Secretary was instructed to cast a ballot for the above slate and, after the election, the new officers were introduced and responded.

C. W. JEROME, *Secretary-Treasurer*

### Electro-Organic Division

Twenty-three members of the Electro-Organic Division attended the Divisional luncheon and business meeting at New York on April 15th.

Chairman C. L. Wilson presided at the brief business meeting and introduced Mr. Jack Bain, Advertising Manager of the JOURNAL, to the members of the Division. Dr. Sherlock Swann gave a brief discussion of the status of the literature in the electro-organic field.

STANLEY WAWZONEK, *Secretary-Treasurer*

### Electrodeposition Division

For the fall meeting of the Society, the Electrodeposition Division is now arranging several sessions dealing with general problems of electrodeposition. Papers for this program are invited.

Triplicate copies of manuscripts or abstracts (not over 75 words in length) must be received at Society headquarters, 235 West 102nd Street, New York 25, N. Y., *not later than July 1, 1953.*

M. L. HOLT, *Chairman*

## SECTION NEWS

### Cleveland Section

"Electrical Properties and Constitution of Salt Melts" was the technical subject discussed at the Cleveland Section's meeting on April 7, with Frank E. W. Wetmore as the guest speaker.

Dr. Wetmore pointed out that very little is known of the constitution of concentrated electrolytes, especially molten salts. The method of study he used was that of transference and conductance in uniary and binary salt melts. He pointed out that there is no good explanation of what happens in such concentrated systems.

The after-dinner speaker at the meeting was Dr. John L. Sloop, chief of the Rocket Branch of the Lewis Flight Propulsion Laboratory. Dr. Sloop explained and showed models of rocket engines for aircraft and for rockets.

* * *

On April 12 the Cleveland Section sponsored a TV show on "Primary Batteries" over station WNBK as part of the Cleveland Technical Societies' project. R. W. Erwin, National Carbon Company, is the Section's chairman of this committee. Dr. R. S. Johnson and Dr. C. L. Hildreth, both of National Carbon Company, took part in the broadcast.

### New York Metropolitan Section

At the April 1st meeting of the New York Metropolitan Section an enthusiastic audience heard a discussion on molybdenum by two speakers from the Westinghouse Electric Corporation.

W. C. Lilliendahl of the Research Department, Lamp Division, at Bloomfield, N. J., discussed the occurrence, preparation, production, and industrial importance of the metal.

The need for new metals or alloys that will withstand unusual stress at relatively high temperatures has become of paramount importance in heat engines of the present and future, he said. Materials with high melting points, good hot-creep resistance and strength, cold ductility, and some degree of impact strength are required. Molybdenum shows considerable promise in these applications.

The metal is produced by arc-casting or by powder metallurgy processes, although both make use of molybdenum powder as a starting material. Nonmetallic impurities have considerable effect on the properties of the metal. Metal as currently produced shows no ductility in the fully crystallized state except at very low strain rates, Mr. Lilliendahl said. However, very good ductility has been observed in the worked, stress-relieved or partially recrystallized state.

J. H. Bechtold of the Research Laboratories at East Pittsburgh described the physical, chemical, and mechanical properties of molybdenum.

Although the metal is quite resistant to most chemicals, he stated, it is readily attacked upon exposure to air at temperatures above approximately 300°C. Much emphasis is currently being placed on the improvement of the oxidation resistance of the metal by the application of coatings or by the formation of alloys.

The tensile properties of molybdenum fall into four ranges of temperature: a brittle zone up to −75°C, a transition zone from −75° to 100°C, a ductile zone from 100° to 900°C, and an unstable zone above 900°C. To improve mechanical properties, Mr. Bechtold said, it is desirable to shift simultaneously the unstable zone to a higher temperature, and the transition zone to a lower temperature. The unstable zone can be raised by solid solution alloying. The transition from ductile to brittle behavior is due to rapid increase in yield strength, or resistance to deformation, with decreasing testing temperature. The creep properties of molybdenum above about 900°C are determined by the recrystallization temperature.

An enjoyable dinner and social hour preceded the technical session.

M. F. Quaely

## Niagara Falls Section

The April 8 meeting was "Ladies' Night" for the Niagara Falls Section. Following the social activities, the guest speaker, James O'Malley of Bell Aircraft Corporation, spoke to the group on the subject "Modern Research Aircraft."

In addition to the above meeting, the Niagara Falls Section sponsored a two-hour panel discussion on the subject of "Non-Metallic Materials of Construction for Chemical Process Equipment" at an Industrial Conference held by the Technical Societies Council of the Niagara Frontier in Buffalo, New York, April 22. The Niagara Falls Section supplied a moderator and four speakers for this panel discussion.

Milton Janes, *Secretary-Treasurer*

## Pacific Northwest Section

The spring meeting of the Pacific Northwest Section was held on Friday March 20 at Rose's Highway Inn, near Tacoma, Washington. Prior to the meeting a field trip was conducted through the chlorine and caustic soda manufacturing facilities of the Pennsylvania Salt Manufacturing Company of Washington.

The speaker for the evening was Professor W. Rylan Hill, of University of Washington, who discussed "Electronic Instrumentation in the Chemical Industry."

At the annual business meeting which was held after Professor Hill's talk, the following officers were elected to serve for the 1953–1954 term:

*Chairman:* Glen C. Ware, U. S. Bureau of Mines, Albany, Oregon

*Vice-Chairman:* Joseph B. Heitman, Pennsylvania Salt Manufacturing Company of Washington, Tacoma, Washington

*Secretary-Treasurer:* G. H. Kissin, Division of Metallurgical Research, Kaiser Aluminum and Chemical Corportion, Spokane, Washington

G. H. Kissin, *Secretary-Treasurer*

## Washington-Baltimore Section

The Washington-Baltimore Section held its 18th technical meeting on March 19, 1953, at the National Bureau of Standards.

W. J. Schwerdtfeger of the Bureau of Standards spoke on "Potential Measurements in Cathodic Protection."

The speaker said that while the theory of cathodic protection is generally understood, present techniques for determining the amount of current required for protection are based chiefly on potential measurements. The proper interpretation of a potential measurement, made while the protective current is flowing to a structure, requires a consideration of the geometrical factors associated with a corrosion circuit and also the resistivity of the corrosive medium.

Following a presentation of the theoretical considerations, Mr. Schwerdtfeger's remarks were centered on experimental laboratory data. Emphasis was placed on the proper positioning of the potential reference electrode by data obtained on bimetallic models corroding in a solution which caused relatively little polarization but brought out the effect of solution resistance. Data were also presented as obtained on similar models corroding in a solution which caused polarization to be predominant.

Fielding Ogburn, *Secretary*

## India Section

### Symposium on Electrolytic Alkali-Chlorine

The India Section symposium on "Electrolytic Alkali-Chlorine" was held at the Indian Institute of Science, Bangalore, on February 26, 27, and 28, 1953. The papers presented were:

1. Handling and Processing Equipment from Impervious Carbon and Graphite for Electrolytic Chlorine Industry—S. K. Vohra and C. J. Dadachanji
2. Utilization of Chlorine in the Electrolytic Production of Metals—T. L. Rama Char
3. Properties and Uses of Chlorinated Rubber—P. A. Porecha
4. Satisfying the Demand for Chlorine—V. Aravamuthan
5. Properties and Uses of Calcium Chlorite—P. A. Porecha
6. Future of the Chlorine Treatment of Sulfide Ores—V. Aravamuthan
7. Some Aspects of the Economics of Alkali-Chlorine—N. B. Shivaraman
8. Utilization of Surplus Alkali-Chlorine in the Production of Carbon Tetrachloride at the Spot—V. Aravamuthan.

There was a good-sized gathering drawn from research laboratories, electrochemical and electrometallurgical industries, and Government establishments. The members of the Indian Institute of Metals were also invited. The discussions that followed the papers were extremely interesting and formed an important part of the proceedings. The program was rounded off with a dinner and visits to research institutions and factories in Mysore State.

### Symposium on Metallurgy in Electroprocess Industries

A symposium on "Metallurgy in Electroprocess Industries" was held at the Indian Institute of Science, Bangalore, on February 27, 1953, under the joint auspices of the India Section and the Indian Institute of Metals. Papers read were:

1. Some Developments in the Electrolytic Production of Aluminum—R. Thyagarajan, R. S. Ramachandran, and K. K. Cherian
2. Electrolytic Production of High Purity Manganese Metal and Manganese Dioxide—T. Banerjee
3. Materials of Construction in the Chlorine-Alkali Industry—S. Ramaswamy, R. V. Ramani, and N. Subramanyan
4. Amalgam - Metallurgy: Present Trends and Future Possibilities—J. Balachandra.

The presence of members of both the institutions greatly contributed toward a lively discussion. The members of the India Section were invited for the technical meetings and social functions arranged by the Indian Institute of Metals for their annual meeting.

T. L. Rama Char
*Regional Editor for India*

## 2nd Request for ABC Questionnaire!!

Society members and subscribers who have not as yet returned the first ABC questionnaire (mailed in March) have been sent a second request. Please supply the information regarding job categories, which is needed by the Audit Bureau of Circulations (ABC) for a classification of Journal readers, relative to advertising. *It is very important that everyone return this questionnaire promptly.*

Send to The Electrochemical Society, Inc., 235 West 102nd Street, New York 25, N. Y.

## PERSONALS

**Ivy M. Parker** of Plantation Pipe Line Company has moved from Bremen, Ga., to the company's offices in Atlanta.

**Charles P. Roberts, Jr.**, Westvaco Chemical Division, Food Machinery & Chemical Corporation, has transferred from the Pocatello, Idaho, office to the company's plant at South Charlestown, W. Va.

**Peter J. Librizzi**, formerly senior chemist and supervisor of the coating laboratory at CRT Division of Allen B. DuMont Laboratories, Clifton, N. J., is now associated with the development laboratories of CBS-Hytron at the Newburyport, Mass., plant, as development engineer and chemist.

**I. Milton Le Baron**, International Minerals and Chemicals Corporation, Chicago, Ill., has been named Director of Research Laboratories of the Company, located at Skogie, Ill.

**Raymond F. Ledford** has left Sunbeam Corporation, Chicago, to become Director of Sales and Research at Industrial Filter & Pump Manufacturing Company, also of Chicago.

**Robert R. Banks**, formerly of Armour Research Foundation, Chicago, has joined the Air Reduction Company, Murray Hill, N. J.

**R. E. Zimmerman** has retired as Consultant, United States Steel Corporation, Pittsburgh, and is now residing in Short Hills, N. J.

**A. B. Hoefer** is now connected with F. B. Stevens, Inc., Detroit, Mich. Mr. Hoefer was previously with Udylite Corporation, Long Island City, N. Y.

**V. Aravamuthan** has been appointed junior scientific officer, Central Electrochemical Research Institute, Karaikudi.

**B. A. Shenoi** has been appointed senior scientific assistant, Central Electrochemical Research Institute, Karaikudi.

**John D. Morron**, Development Manager, United States Rubber Company, has transferred from Detroit, Mich., to the company's plant at Fort Wayne, Ind.

## NEW MEMBERS

In April 1953 the following were elected to membership in The Electrochemical Society:

### Active Members

Robert R. Adams, Battelle Memorial Institut fur Deutschland, Rheingau-Allee, 25, Frankfurt/Main, Germany (Electrodeposition)

Irving Amron, Sylvania Electric Products Inc., 35-22 Linden Pl., Flushing, N. Y. (Electronics)

William W. Bradley, Bell Telephone Laboratories, Murray Hill, N. J. (Corrosion)

John F. Dittman, The Eagle-Picher Company, mailing add: 431 Park Ave., Joplin, Mo. (Battery)

Fred W. Duggan, National Carbon Company, mailing add: 1995 Hampton Rd., Rocky River, Ohio (Battery)

Philip J. Elving, Department of Chemistry, University of Michigan, Ann Arbor, Mich. (Electro-Organic and Theoretical Electrochemistry)

Roman Evdo, U. S. Radium Corporation, mailing add: 379 Parkview Dr., Scotch Plains, N. J. (Electronics)

Alfonso Gomez, Sonolux, mailing add: Apartado Nacional 440, Medellin, Colombia (Electrodeposition, Industrial Electrolytic, and Theoretical Electrochemistry)

Fred L. Granger, Jr., National Carbon Company, mailing add: 18120 Ponciana St., Cleveland, Ohio (Battery)

John B. Harrison, Delco Remy Division, General Motors Corporation, Muncie, Ind. (Battery)

Moses G. Jacobson, J. T. Ryan Memorial Laboratory, Mine Safety Appliances Company, 100 N. Braddock Ave., Pittsburgh, Pa. (Battery, Electronics, and Theoretical Electrochemistry)

George J. Kiedaisch, Midwest Carbide Corporation, Box 554, Keokuk, Iowa (Electrothermic)

Martin Kuna, Bristol-Myers Products Division, 225 Long Ave., Hillside, N. J. (Theoretical Electrochemistry)

John S. MacNairn, Massachusetts Institute of Technology, Rm. 8-206, Cambridge, Mass. (Corrosion)

Phillip J. Maddex, Titanium Metals Corporation, mailing add: P. O. Box 2128, Henderson, Nev. (Electrothermic)

Carlo Panseri, Istituto Sperimentale dei Metalli Leggeri, Via della Posta 8/10, Milano, Italy (Corrosion)

William A. Pavlo, % Price Battery Corporation, Hamburg, Pa. (Battery)

Edson H. Phelps, Box 7556, Area B., Wright Patterson Air Force Base, Ohio (Corrosion and Theoretical Electrochemistry)

Felix A. Reiss, Chemistry Department, University of Michigan, Ann Arbor, Mich. (Electronics and Theoretical Electrochemistry)

Kumazo Sasaki, Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chigusaku, Nagoya City, Japan (Battery)

Oliver A. Short, E. I. du Pont de Nemours & Company, Inc., mailing add: 200 Hillside Dr., Lewiston, N. Y. (Electrodeposition)

Kiichiro Sugino, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan (Electro-Organic and Industrial Electrolytic)

Francis H. Taylor, Midwest Carbide Corporation, mailing add: 1023 Orleans Ave., Keokuk, Iowa (Electrothermic)

Malcolm Thomson, Sheffield Smelting Company, Ltd., P. O. Box 28, Shef field, England (Industrial Electrolytic)

### Associate Members

Charles A. Preschel, Phelps-Dodge Copper Corporation, mailing add: 62 Westerly St., Yonkers, N. Y. (Electric Insulation)

Joseph Raimondo, D. E. Makepeace Company, mailing add: 95 Unit St., Providence 9, R. I. (Electrodeposition and Theoretical Electrochemistry)

### Student Associate Members

Raymond W. Buckman, Jr., University of Cincinnati, mailing add: 218 E. 13 St., Covington, Ky. (Electrodeposition)

Gajendra N. Mohanty, University of Missouri, mailing add: 705 W. 12 St., Rolla, Mo. (Electrothermic)

## NEW PRODUCTS

Microscope-Metallograph. Newly designed metallurgical microscope and metallograph by Officine Galileo, the CSF, has been announced by the importers. Compact inverted design provides handling ease, confines work area to 13 x 8 x 8 in. Also allows group observation through projection. Features sharp, brilliant visual observation at all magnifications up to 1000× and photographic and projection observation up to 1500×. Opplem Co., Inc. N-8

Small-Type Tilter designed to meet the needs for a smaller, more simplified, less expensive unit suitable for handling 5 and $6\frac{1}{2}$ gal containers. Prevents accidents caused by spilling or splashing; chain holds container in position when tilted. General Scientific Equipment Co. N-9

High-Purity Carbon Rods. A high-purity spectrographite rod for critical chemical and metallurgical analysis by the spectrographic process is available. Compared to normal graphite electrodes which contain impurities of .02 to .05%, the new rod has less than .001%. It is supplied in lengths up to 12 in. long and in diameters of $\frac{1}{8}$, $\frac{3}{16}$, $\frac{1}{4}$, and $\frac{5}{16}$ inches. Stackpole Carbon Co. N-10

Portable Cooling Unit known as the Junior CHIL-ER; has a recirculating capacity of 3 gal per hr. Cools liquids to −10°F under thermostatic control of plus or minus ½ degree. When equipped with a heating element, temperatures may be controlled up to 140°F. Indicating thermometer included. Useful in pilot manufacturing rooms and laboratories. Mayer Refrigeration Engineers. N-11

Laboratory Filter. Improved type of porous stainless steel filter sheet, designated Grade X, is distinguished from previous materials by an approximately doubled tensile strength, extremely smooth surface, and by a very close control of thickness. Now available in the form of finished line filters; available from stock in .040-in. thickness, with a mean pore opening of 10 microns. Other thicknesses supplied on short notice. Micro Metallic Corp. N-12

## LITERATURE FROM INDUSTRY

Industrial X-Rays. 44-page illustrated buying guide lists a complete and diversified line of accessories and supplies required for industrial x-ray installation. Divided into four basic categories: (1) films and chemicals; (2) radiographic accessories; (3) darkroom accessories; and (4) viewing and filing equipment. Westinghouse Electric Corp. P-135

Rectifier. Brochure explaining the application of rectifiers to various operations is now available. Designed to convert AC to DC at the flick of a switch, these rectifiers can produce anything a motor generator set can—and are known for their trouble-free operation and almost unlimited life. Made in sizes from 3 to 1000 kw from 50 to 10,000 volts d-c output and either fixed or variable voltage, to accommodate any a-c voltage or frequency input. American Rectifier Corp. P-136

Practical Nickel Plating. 44-page publication with over 40 illustrations‘ tables, and charts. Provides the designer, specifying engineer, and user with basic information on electroplating and detailed information on nickel plating and its practices. Keyed bibliography suggests 41 sources of additional reading. International Nickel Co., Inc. P-137

Pickling Acid Inhibitor. 4-page brochure on "Rodine" pickling acid inhibitors explains advantages and economies of this method. American Chemical Paint Co. P-138

**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, 235 West 102nd Street, New York 25, N. Y.**

***Please print your name and address plainly.***

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Great Lakes Carbon Corporation.................. Cover 2
Hartman-Leddon Company. 167C
Kanthal Corporation....... 165C
National Carbon Company.. 163C
Ronal Chemicals, Inc...... Cover 3
Stackpole Carbon Company. 142C
Weston Electrical Instrument Corporation........ 141C

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### Positions Available

Wanted, Electrochemist: Excellent opportunity in large Eastern research laboratories with ample facilities for chemist with background in physical chemistry. Experience desirable in primary or secondary batteries, but not necessary. Salary commensurate with experience. Please submit complete resume of experience and education along with references and salary requirements. *Reply to Box A-246.*


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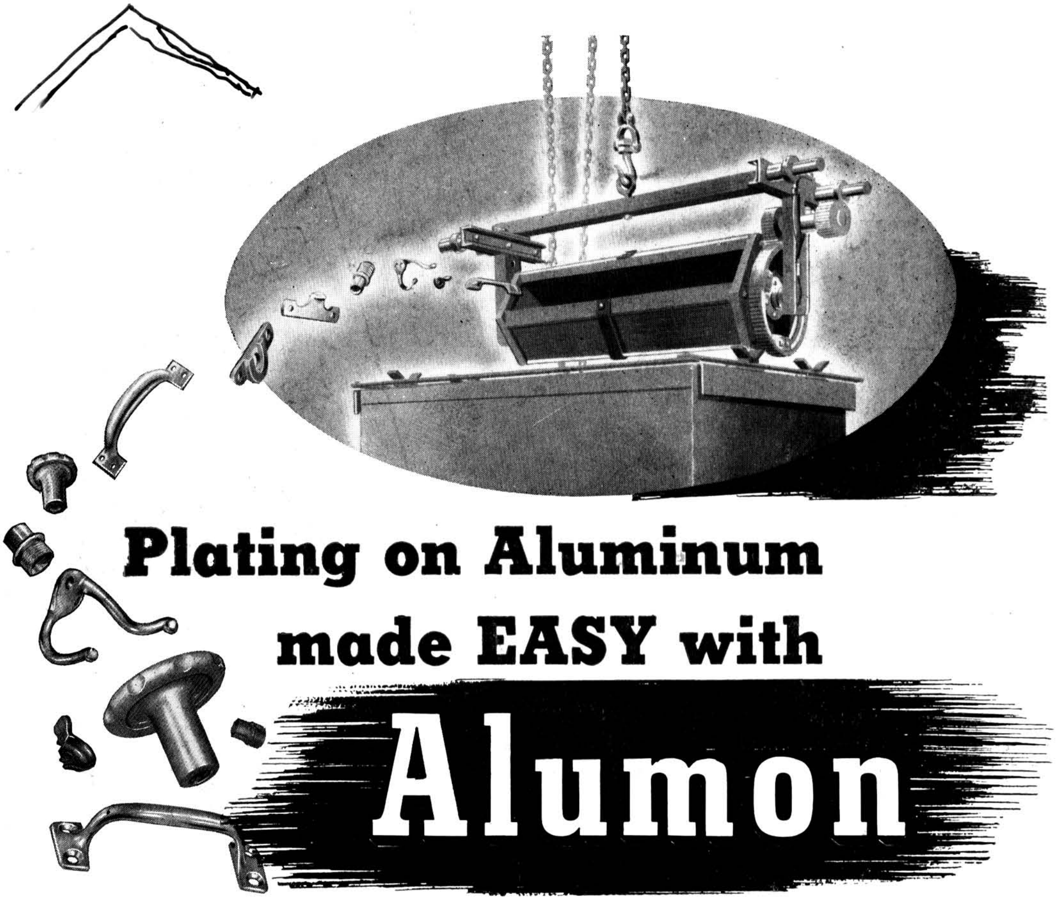

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