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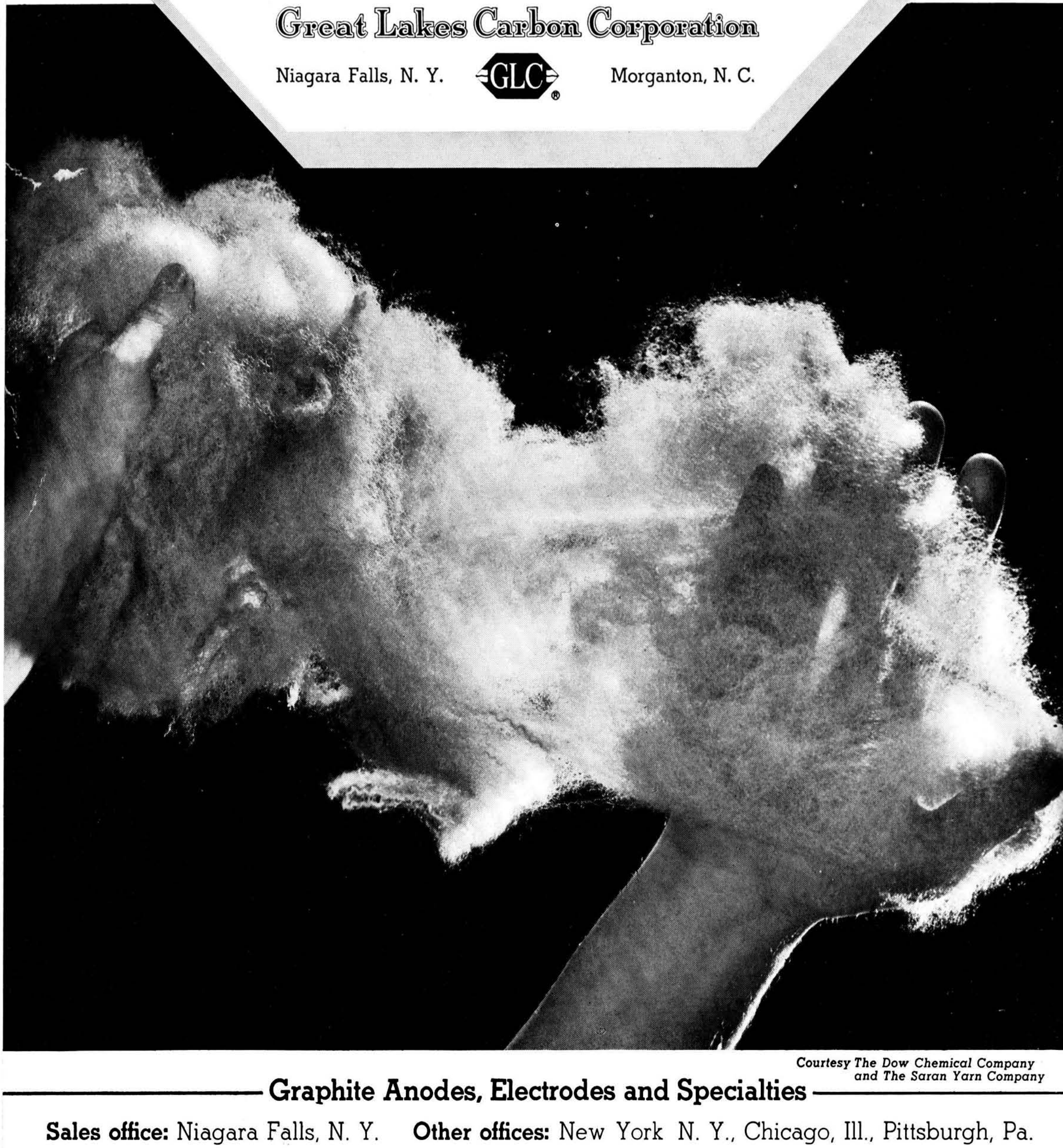
ELECTROCHEMICAL INDUSTRY

The Golden Gulf Coast



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CONTENTS

Editorial

Regional Feature

Technical Papers

Feature Section

Current Affairs

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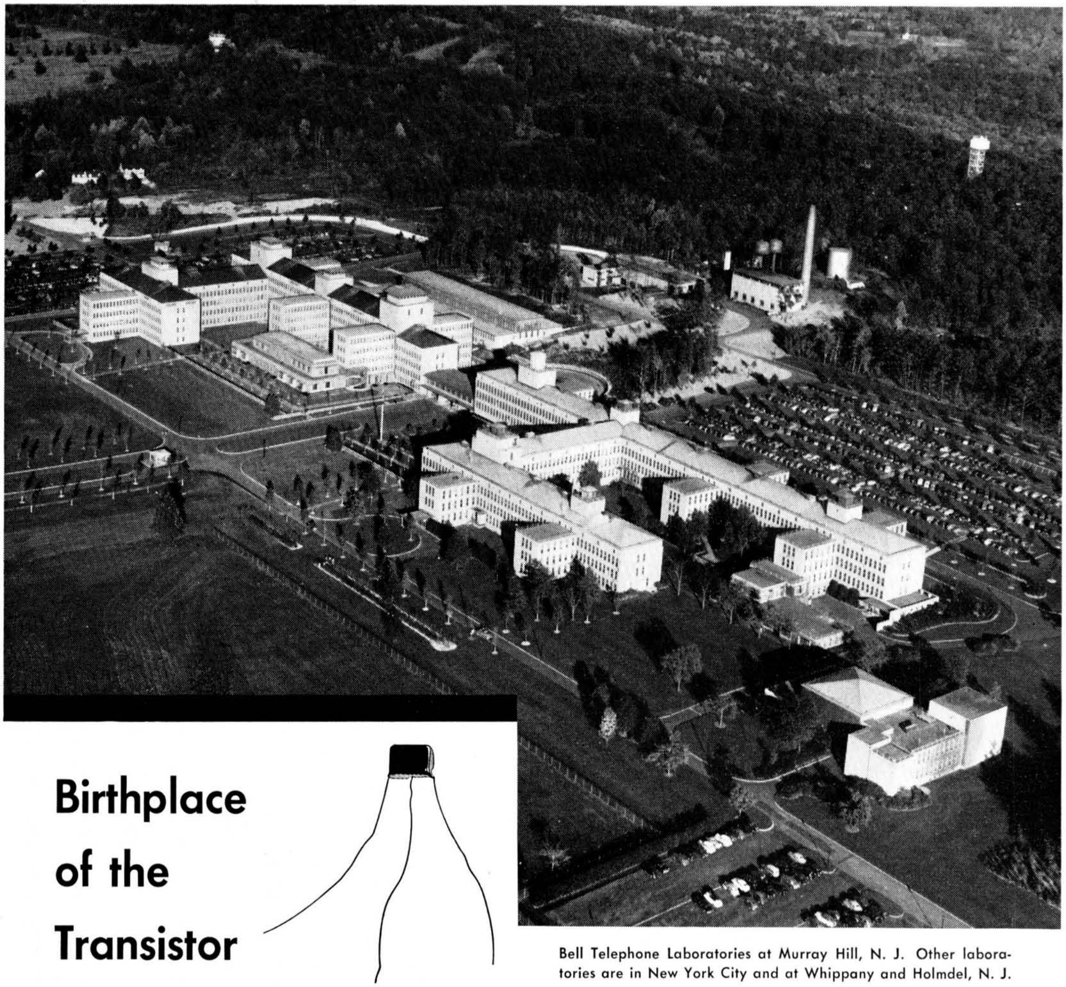


Birthplace of the Transistor

Bell Telephone Laboratories at Murray Hill, N. J. Other laboratories are in New York City and at Whippany and Holmdel, N. J.

The ***Transistor,*** that revolutionary new electronics device, is a product of *telephone* research. It was conceived, invented and developed at Bell Telephone Laboratories by men in search of ways to improve telephone service. It was announced just five years ago.

The ***Transistor*** can do most of the things that vacuum tubes can do—and others, too—but it is not a vacuum tube. It works on entirely new physical principles. Rugged, simple and tiny, the Transistor uses incredibly small amounts of power—and then only when actually operating.

Transistors promise smaller and cheaper electronic equipment and the spread of electronics where other equipment has not been able to do the job as economically. They are already at work in the Bell System, generating the signals that carry dialed numbers between cities, and selecting the best route for calls through complex switching systems. Engineers see many other possibilities: for example, as voice amplifiers in telephone sets to aid the hard of hearing, and as switches.

Recognizing the tremendous possibilities of the ***Transistor*** in every phase of the electronics industry, the Bell System has made the invention available to 40 other companies. Thus, again, basic research to improve telephony contributes importantly to many other fields of technology as well.

TRANSISTOR SUMMARY

Basically, a ***Transistor*** is a tiny wafer of germanium with three electrodes, over-all about the size of a coffee bean.

It can amplify signals 100,000 times on much less power than a pocket flashlight requires. This opens the door to its use in smaller telephone exchanges where vacuum tube equipment would be too costly to operate.

Unlike a vacuum tube, the ***Transistor*** has no vacuum and no filament to keep hot. It operates instantly, without "warm-up" delay. The Transistor can also be used as an electric eye and to count electrical pulses.

BELL TELEPHONE LABORATORIES

Improving telephone service for America provides careers for creative men in scientific and technical fields.

Editorial

Consumer Contribution to Chemical Industry

THE intelligent consumer is making increasingly important contributions to the growth and progress of the chemical industry. As his needs have become more complex and his requirements more specific, the consumer has found that he can no longer, and that he should no longer, rely upon the manufacturer to anticipate his wants or solve his problems. Knowing best his own purposes, he has found that he must carry on research in his own interest, if he is to protect his future. The intelligent consumer must understand why compositions of matter behave as they do, if he is to feel assured of obtaining the fullest satisfaction of his needs in terms of quality of performance and cost. There should be nothing antipathetic in the user's ideal of perfect service and the producer's goal of reasonable profit; their interests are mutual. The results of consumer research benefit both the consumer himself and the chemical industry by developing new needs for chemical products and by extending the uses of chemical products through improvement of their quality. A few examples will illustrate this reaction of research of the user on the progress of the manufacturing industry.

Fundamental studies had indicated that silicon approaching intrinsic purity would have scientifically interesting and possibly useful electronic properties. This led a prospective user to persuade a chemical company to undertake a collaborative effort toward the development of a process for the commercial production of the highly pure product. With the success of this project, the user who sponsored and financed it got what he wanted—a source of super-purity silicon—and the chemical manufacturer got a new product he could sell profitably to the electronic industry.

A prospective large use of polyethylene was jeopardized by the discovery that some lots of the early production cracked when subjected to polyaxial stress. The problem was solved only by the research of the consumer which showed that the tendency to crack was related to the low molecular weight component of the polymer. The manufacturers were persuaded to modify their processes so as to shift the molecular weight range upward with the result that they now sell more than ten million pounds of polyethylene a year for an application that otherwise would now be using a product from outside of the chemical industry. Moreover certain other users of regular grade polyethylene have lately discovered that they too are having cracking troubles. Thus, it is evident that one element promoting the present prospective fourfold expansion of polyethylene production was consumer research.

Large containers molded from polystyrene had not been feasible owing to a tendency to crack. A study of the surface crazing of this material led a potential user of these moldings to propose temperature annealing for the elimination of the strains responsible for both crazing and cracking. The success of such heat treatment—a common practice in metallurgy—has led to large volume manufacture of large polystyrene moldings to the satisfaction of both consumer and producer.

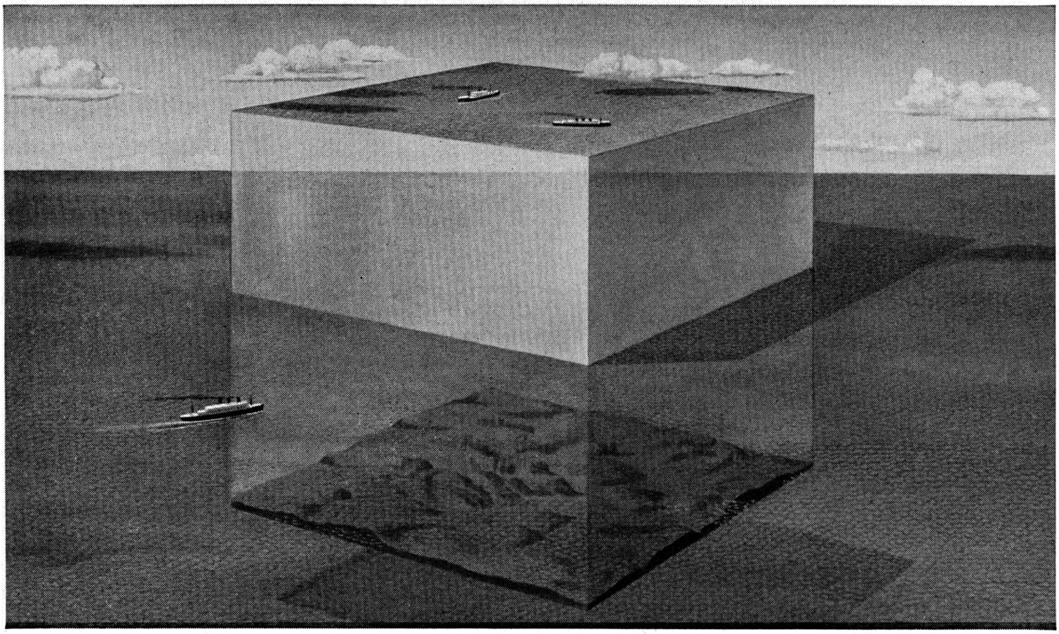
It was the need of the user of organic finishes to control quality that led to his development of modern methods for the measurement of finish quality. In turn, the paint manufacturer was able to use these methods to gauge the improvement in finishes he has been able to make with the newer resins. The result has been a twofold increase in durability and service life in organic finishes!

The foregoing description of the impact of consumer research on the development of the chemical industry should suggest the importance of intimate research level contact between the two groups. The consumer should have the opportunity to guide the manufacturer toward the production of the new products that will best serve user needs. The highly competitive nature of chemical industry should not prevent confidential collaboration toward the achievement of mutually desirable goals. Spared the expense and manpower previously necessary for the solution of customer problems, chemical industry can devote more effort to research basic to future progress.

—RMB

THE SEA IS AN INEXHAUSTIBLE SOURCE OF AN IMPORTANT METAL

Each cubic mile of sea water contains six million tons of MAGNESIUM, the lightweight metal of so many uses



Today, when this nation is confronted with a crisis in our supply of many raw materials, it is of immense significance that the sea around us contains an almost unlimited supply of Magnesium. For Magnesium is light, strong, practical and versatile—the answer to many manufacturers' needs. Also, Magnesium is highly important in many electrochemical processes including cathodic protection.

Dow began research on the extraction of Magnesium from brine over forty years ago. In 1941, at Dow's Freeport, Texas Plant, *the first commercial extraction from sea water was begun.* Dow pioneered in the production and development of Magnesium and its alloys and remains the leading producer and fabricator today.

Magnesium is only one of more than 600 chemicals produced by Dow. From Dow's many rapidly expanding plants throughout the nation flows an increasing abundance of chemicals and chemical products every year for both military and for civilian use. Besides Magnesium, these include Industrial, Agricultural, and Fine Chemicals as well as Plastics. THE DOW CHEMICAL COMPANY, Midland, Michigan.

you can depend on DOW CHEMICALS

THE GOLDEN GULF COAST

General Introduction

Oliver Osborn[1]

The Gulf Coast today is moving through what may well be the greatest industrial expansion of all times. Under the continuing impetus applied by the chemical industry, this region has become the setting for a mammoth demonstration of American ingenuity and creative ability. Little more than a decade ago, the coastal prairies of the Gulf were all but empty of industry. Those prairies have been transformed into industrial sites on which, it has been estimated, three out of every four chemical plants built in the United States since 1940 have been located.

What are these plants that, in little more than a decade, have come to represent an investment of some four billions of dollars of capital? *Chemical Engineering*, in November, 1951, stated that "at least 106 organic chemicals, 28 inorganic chemicals, four elemental gases, five industrial fertilizer chemicals, plus carbon black, sulfur, aluminum, iron, tin, zinc, cadmium, salt, and other items are now produced by industries in the Southwest." In the petrochemicals alone, there are now more than 50 producing plants on the Gulf Coast vs. the three established prior to 1940.

Significant, although less phenomenal than the mark made in the petrochemical field, has been the growth of the electrochemical industry along the Gulf Coast. In 1940, this phase of chemical activity was virtually nil. Today, electrochemical or electrothermic principles are being applied in the basic production patterns of a zinc plant, two magnesium plants, two sodium plants, four aluminum plants, eleven chlorine-caustic plants, eight electric steel plants, and four tungsten powder plants.

This blossoming of the Gulf Coast was neither accidental nor automatic. Industry has its reasons for choices of locations for expansion. Something made the Gulf Coast truly "golden" as an area for industrial activity, particularly for chemical production. The factors are not difficult to perceive.

Certainly an ever-increasing supply of oil and natural gas has been a major factor. Besides providing comparatively cheap sources for fuel and power, these are also the basic raw materials for an almost infinite number of products. Moreover, increased consumption of these resources has been parallelled by new discoveries so that proven reserves remain more than adequate. And in addition to the nearly 100 trillion cubic feet of natural gas reserves now existing in Texas alone, the Gulf Coast has a host of other raw materials in a fabulous storehouse.

Natural resources of the Gulf Coast include such basic materials as sulfur, salt, lime, and seawater. Sulfur has been or is being mined at some two dozen different locations; known salt domes number close to 150. Lime is available as oyster shell in reefs and beds liberally dotting the miles of coastline. As for seawater, it is estimated that there are some 320 million cubic miles available and, furthermore, that a single cubic mile contains 100 times more magnesium than is necessary to satisfy the present annual national consumption.

The chemical industry looking at the Gulf Coast has also been attracted by the ready availability of large blocks of relatively cheap land. Selection of plant sites has been greatly simplified by the "wide open spaces." In addition, a mild climate has made possible the adoption of a new and cheaper construction pattern—that for "open air" plants. Finally, the Gulf Coast has been endowed with at least a dozen deep water seaports which, for added convenience and attractiveness, are cross-connected by the Intracoastal Canal extending from Brownsville, Texas, to Carrabelle, Florida.

Thus, when referring to this land of chemical bonanza, it is quite proper to speak of it not only as the Great Gulf Coast but also as the Golden Gulf Coast.

The papers which follow deal with processes of interest to the electrochemical industry. Based on Gulf Coast experiences, they describe some of the more important electrochemical industries and power generating methods of the region.

F. L. Kaestle, of the General Electric Company, covers the aluminum industry; W. J. Rave, of the Dow Chemical Company, Texas Division, tells of the sea water magnesium process; Frank Chrencik, of the Diamond Alkali Company, summarizes chlorine-caustic production; and H. L. Norris, Jr., of the Fish Engineering Corporation, describes some of the privately operated power plants of the area.

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[1] Journal Regional Editor, Houston. The Dow Chemical Company, Texas Division, Freeport, Texas.

THE ALUMINUM INDUSTRY OF THE GULF COAST AREA

F. L. Kaestle[1]

Foreword

Of all of the vast industrial expansion in the Gulf Coast area during and since World War II, no other major industry is comparable to the aluminum industry in the high percentage of total national production which has shifted to a new area in so short a time.

Considering basic reduction facilities alone, the Gulf Coast annual production capacity by the end of next year will be 920 million lb, or 31 per cent of the national total of 2900 million lb. And all of this has come to the area within the past four years.

Availability of low cost power or fuel is the primary factor in the location of aluminum reduction plants. For this reason, all earlier plants were located where abundant hydroelectro power was available. But not enough additional hydro power could be produced to support the additional aluminum production authorized in the past six years. It was natural that the industry should turn to the abundant fuels of the Gulf Coast for a large share of the recent expansion.

Until recently, natural gas alone has been the basic fuel for Gulf Coast industrial power. But with the advent of the new lignite-burning plant of the Aluminum Company at Rockdale, Texas, a second abundant source with a promising future has emerged.

Aluminum Production of the Area

When facilities now under construction are completed next year, the annual production of the four primary reduction plants of the Gulf Coast area will be approximately as follows:

Aluminum Company of America:	
Point Comfort, Texas	185 million lb
Rockdale, Texas	175 million lb
Reynolds Metals Company:	
Corpus Christi, Texas	160 million lb
Kaiser Aluminum Corporation:	
Chalmette, Louisiana	400 million lb
Total	920 million lb

In addition to the aluminum reduction plants, three of the nation's six large alumina plants located in the Gulf Coast area will process enough bauxite to supply alumina to all of the area's reduction plants and a substantial amount to reduction plants in other areas of the country.

The production of aluminum from the ore, bauxite, involves first, the processing of bauxite by the Bayer process to alumina, pure aluminum oxide; and then, the electrolytic reduction of alumina to the metal, aluminum.

Bauxite for United States aluminum production comes principally from Arkansas, Dutch Guiana, British Guiana, and more recently, from Jamaica. Other sources in Haiti and Brazil are being developed. Bauxite is usually found near the surface and mining is an open-pit operation. Arkansas ore is either processed nearby or shipped by rail to other alumina plants. However, by far the greatest amount of ore used in the United States comes by sea-going ore boats from the Guianas and Jamaica by way of the Caribbean Sea.

Hence, one of the most important factors in the economic location of an alumina plant for foreign ores is that it be on a harbor to the sea. The alumina plants of the Aluminum Company at Mobile, of Kaiser at Baton Rouge, and of Reynolds at Corpus Christi emphasize this point.

It is the Gulf Coast's fortunate circumstance that economic power for aluminum reduction is also near these alumina plants.

The Alumina Process

In the Bayer-process alumina plant, bauxite, which has been finely crushed and washed, is treated with a solution of hot caustic soda in which sodium-aluminate forms and goes into the solution leaving the impurities in suspension. After filtration, the solution is cooled in high-tower precipitation tanks. Under supercooled conditions, aluminum hydroxide crystallizes out of solution when "seeded" with like crystals from a former batch. The solid hydroxide is then washed free of caustic and kiln-dried to produce aluminum oxide, or alumina, in a fine white powder form ready for the reduction plant.

Under typical conditions, for each 100 lb of bauxite processed, approximately 40 lb of alumina is produced from which 20 lb of aluminum will be reduced. In the process, 5 lb of caustic are used and the equivalent of about 250 ft^3 of gas are required for heat for the kilns and for process steam. Thirty kwhr of electrical energy are used to drive the grinders, pumps, fans, conveyors, mixers, and other machines of the process.

Since the alumina process is a batch process and a reasonable amount of alumina storage is feasible, the high degree of continuity of service required in the reduction plants is not as essential for alumina plants. Over the past years, however, the demand for increasing aluminum production has resulted in virtually around-the-clock capacity operation of all the major alumina plants. All of the Gulf Coast plants have already expanded since initial building or planning and all are capable of further expansion when needed.

The Aluminum Reduction Process

In the aluminum reduction plant, alumina is reduced to aluminum in electrolytic furnaces which, in the trade, are called "pots." A large number of pots are bus connected electrically in series, to form a "potline." The voltage per pot is approximately five volts. A typical 750-volt line would have about 160 pots of which 140 would be in service at one time.

Each pot consists of a large rectangular, rather shallow, iron shell, carbon lined, and having a movable carbon anode structure suspended in it. Alumina is dissolved in a bath of molten cryolite between electrodes. Direct current separates the aluminum oxide into aluminum which forms a molten layer on the bottom of the pot thereby forming the cathode, and oxygen which, on contact with the hot anode carbon, forms carbon dioxide which is drawn away by the ventilating fans.

Alumina is fed into the pot periodically at a rate of two pounds for each pound of aluminum produced. Molten aluminum is siphoned periodically into ladels, and thence transferred to holding furnaces from which it is cast into pigs for shipment. In the process, about one-half pound of anode carbon is consumed for each pound of aluminum produced.

For this reason, the anode carbon must be replaced continually. Two general types of pots are in common use having anode structures which make this carbon replacement feasible.

The first, and older in use, is the prebaked anode pot. In it the anode assembly has a movable steel structure with large

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[1] Industrial Engineering Section, General Electric Company, Schenectady, New York.

anode busbar headers, to which a large number of individual anode studs are bolted. The individual anodes are precast around the stud assemblies and baked out in a separate carbon plant near the potroom. These anodes are replaced continually as needed. The replaced studs and their remaining carbon are reclaimed in the preparation of the next batch of anodes in the carbon plant.

The other type, the Sodeberg pot, has a movable structure which supports a single large rectangular carbon anode, contained by several rows of removable horizontal channels on both sides and ends. Electrical contact is made by iron slugs driven horizontally into the carbon through holes in each row of channels on the two sides. The anode flexibles connect these slugs to the anode assembly busbar headers.

As the anode is consumed and lowered, the lower channels are removed, the lower slugs are pulled, and both are replaced at a higher level. A finely ground carbon and pitch mixture is periodically added at the top of the anode. The carbon bakes out and graphitizes before reaching contact with the electrolyte. The Sodeberg pot must have its anode formed and baked out before starting initially, and the pot is more complex and expensive than the prebaked anode type, but the carbon plant operation is a simpler process.

Some of the Gulf Coast plants have one type of pot and some the other. Neither is being superseded by the other. The choice is one of over-all plant economy and of desirable operating characteristics as judged by the user for each plant.

Both pots use petroleum coke as a source of carbon, and refinery pitch as a mixer, since with these the desired purity can be controlled and obtained. These materials also are readily available from the refineries of the Gulf Coast.

Power Requirements for Aluminum Reduction

In the aluminum reduction process alone, the d-c energy required is from 8½ to 9½ kwhr/lb. As an easy estimating figure, this means that for each 100 million lb of annual capacity, there must be 100 thousand kw of d-c generating or a-c generating and conversion electric equipment, operated on a virtually 100 per cent load factor.

For the Gulf Coast's 900 million lb of aluminum, the 900 thousand-kw power plant represents an investment of $180 million if estimated at $200 per kilowatt, and if all gas fired, would consume over 200 million cubic feet of gas per day. This is the key to the basic aluminum industry. With little influence by other factors, it goes almost anywhere that the most economical electric power can be had or produced.

Lignite as a New Fuel Source

As the use of natural gas rose sharply, it was natural that other fuel sources of the area should be sought from which low cost power could be produced. Lignite now gives that promise. Extensive pilot plant work had been done by the Bureau of Mines, and that work has now been projected into a large scale power plant. To be operated by Texas Power and Light Company for Alcoa's new Rockdale reduction plant, it will give lignite its first job in the heavy industrial field. The operating results will be of great national interest.

In the processing of lignite for industrial use by the Parry process, a dry fuel, "char," which is analagous to coke from the coke oven, is produced along with relatively large quantities of coal tar. It is by reclamation of the valuable byproduct tar, and its derivatives, that low net cost fuel is made possible.

Except for the adaptation of boilers to burn this specific fuel, char, the production of electric power is the same as that of any other modern coal-burning, steam-electric station of which the new Rockdale plant is a good example.

Alternate Power Systems from Natural Gas

Power production from gas-fired steam-electric stations is common utility practice on the Gulf Coast, and the Kaiser Aluminum plant at Chalmette, Louisiana, which will be the largest single aluminum plant of the area, produces 75 per cent of its power this way.

When natural gas is the fuel, the two common, and widely used power generating systems for large blocks of d-c power are: (*a*) steam-electric a-c generation with mercury arc rectifiers for conversion to d.c.; and (*b*) gas engines driving d-c generators, operating in parallel, and serving the potline directly.

Gas engines are used for all of the power at Alcoa's Point Comfort plant and Reynolds' Corpus Christi plant, and for 25 per cent of that at Kaiser's Chalmette plant. In approximate per cent of the total, the electric power for the Gulf Coast's aluminum reduction is produced as follows: 48 per cent by gas engines; 33 per cent by gas-fired boilers and steam turbines; 19 per cent by lignite-fired boilers and steam turbines.

There is no intent to make any economic comparison of the power systems themselves in this discussion. But each of the Gulf Coast's plants, the power systems it uses, and the plant's principal features are of interest.

KAISER ALUMINUM AND CHEMICAL COMPANY, CHALMETTE, LOUISIANA

The Kaiser Aluminum Company's reduction plant at Chalmette, Louisiana, near New Orleans, will have an annual capacity of 400 million lb for eight similar potlines, each of approximately 50,000-kw capacity.

Each of the first two potlines is served by a power plant having gas engines driving d-c generators. The other six potlines are served by mercury arc rectifiers, receiving power from Kaiser's new gas-fired steam-electric station.

Each of the two engine power plants contains 40 Nordberg vertical, radial, gas engines, each driving a 1290-kw, 750-volt G-E d-c generator. All generators are operated in parallel, each being connected to the potline bus by two circuit breakers.

The 250-volt shunt fields of all generators are served from a common station field bus, to which either of two alternate synchronous motor-driven main exciters may be switched. Each main exciter is controlled by an amplidyne exciter, used in this case as a high-gain amplifier, thereby permitting full voltage range control of the entire potline by means of a single low-power automatically controlled potentiometer for the amplidyne control field.

An engine-generator control cubicle mounted near its engine permits the floor operator to start each engine and parallel the generator on the potline bus. The master operator's panel provides load indication and control for each generator for proper division of load between units, and the over-all potline load control and metering equipment.

Since full range voltage control is available, each generator can be paralleled on the bus at no load, at the existing potline voltage at any time. Therefore, no main potline breaker is required.

All of the engines' auxiliaries (except the ignition system) such as, lube oil and water pumps, cooling fans, etc., are driven by standard 480-volt, 60-cycle induction motors, all served from a multiplicity of load center substations which, in turn, receive power at 13,800 volts from several alternate feeders from the plant power services of the steam station.

Each engine is cranked by using its connected d-c generator as a starting motor. When the potline is at or near normal operating voltage, any individual unit is started from a station starting bus which is then fed through a resistor from the potline bus. For start-up on a "dead" potline, the starting bus then is served by one of the normal exciter generators. Each engine is then brought to firing speed by means of variable voltage control of this exciter generator.

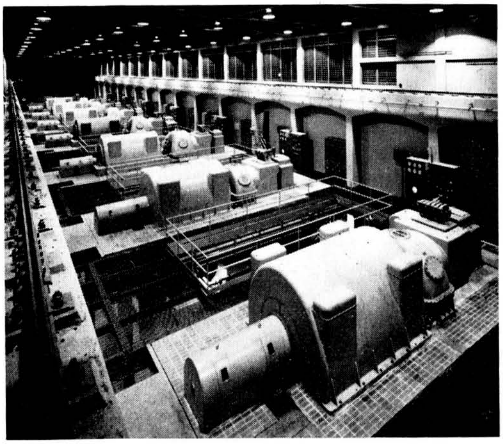

FIG. 1. Turbine-generator floor at Kaiser Aluminum Company's new Chalmette steam-electric station.

Except for its dependence on the steam plant for auxiliaries, each engine plant is independent, and includes sufficient spare capacity to maintain a high order of reliability.

The other six lines are served by ignitron rectifier equipment, two of General Electric and four of Westinghouse manufacture.

For each potline, the six or seven rectifier transformers are fed from a 13.8-kv bus, which is connected through a regulating autotransformer, to a main 13.8-kv feeder from the steam power station. The autotransformer provides voltage control of plus and minus 10 per cent, under load.

Each 5000- or 6000-amp ignitron rectifier is provided with a 6-pole high speed anode circuit breaker, a cathode circuit breaker, ignition and auxiliary equipment, and a water-to-water heat exchanger with automatic temperature control.

The master operator's panel contains control and metering for each rectifier, as well as over-all control and metering for the potline.

To provide the nearly 350,000 kva of a-c power required, and well-integrated standby services for it, the Chalmette steam station includes: twelve 25,000-kw turbine generators for the six potlines; one 25,000-kw and two 10,000-kw turbine generators for auxiliary and plant services; one 25,000-kw spare turbine generator; two 40,000-kva transformer banks for interconnecting ties to the Louisiana Power and Light's 110-kv system.

The two 10,000-kw turbine generators are assigned to one of the two plant service buses, and one of the 25,000-kw units to the other. To these two plant service buses, each of which has two symmetrical sections, there are connected several pairs of feeder circuits. These logically arranged pairs each provide alternate service to important parts of the steam plant auxiliary loads, the engine plant auxiliary loads, and the general plant services.

The twelve 25,000-kw turbine generators normally assigned to the six potline loads are connected in pairs to six "stub" buses, each of which feeds a rectifier station. The spare 25,000-kw unit's stub bus feeds the rectifier station transfer bus which is common for all six potlines.

All of the six main generator stub buses, the spare unit stub bus, the two transformer tie lines, and both of the plant service buses are connected through synchronizing reactors to the station synchronizing bus. Normally the entire station will be operated as a single completely synchronized system. The synchronizing reactors limit the fault current under this condition to less than that of the 1000-mva station switchgear. The normal load division is such that a very small transfer of power through the reactors will occur.

With this very flexible system, a maximum utility of all generating units is assured for any desired division of loading between potlines or auxiliary services, and a very high order of reliability is provided under both normal and emergency conditions. Power may be taken from or delivered to the utility system as conditions warrant.

All 14 of the 25,000-kw units are duplicate G-E turbine generators having a nominal rating of 20,000 kw, 0.85 pf, 13,800 volts, 3 phase, 60 cycles, for steam conditions of 850 psig, 900 FTT. Each turbine has a maximum capability rating of 25,000 kw; the hydrogen-cooled generators have a maximum rating of 27,000 kva, and plant capacity has been assigned on this basis. The two plant service units are G-E turbine-generators rated 10,000 kw, 0.8 pf for the same steam conditions as the main units. Fig. 1 shows a view of the turbine floor.

There are 15 Foster Wheeler gas-fired boilers with Bailey control, 14 normally serving one 25,000-kw turbine each, and one serving the two 10,000-kw turbines. A steam header system transfers steam as needed. Each turbine has a full condensing capacity Foster Wheeler surface condenser, all receiving cooling water from the river water pump house on the Mississippi River adjacent to the plant.

Facilities are provided to deliver alumina to the storage silos either from rail cars or from river barges. Alumina is delivered from Kaiser's Baton Rouge alumina plant.

When under full production, this plant will have a greater output than any other single U. S. aluminum reduction plant. It will produce all its own power, and have operating, side-by-side under duplicate conditions, the two principal d-c power supply systems in current use: steam turbine generators with rectifiers, and gas engine-driven d-c generators.

ALUMINUM COMPANY OF AMERICA, POINT COMFORT, TEXAS

The Aluminum Company of America's reduction plant at Point Comfort, near Port La Vaca, Texas, when first installed, marked the beginning of the shift of aluminum reduction to the Gulf Coast. It now has a capacity of 185 million lb per year. This plant also marked the first postwar application of gas engines to power production in this industry.

For the new Point Comfort plant, the newly developed Nordberg radial, vertical gas engine was chosen, and a carefully coordinated engine plant design was developed to make effective and economical use of the new engine's features.

Originally, three potlines were installed, and two more were added later, all of approximately 37,500-kw capacity. Each of the five engine plants has 38 or 40 Norberg engines, each driving a 1100-kw, 667-volt d-c generator.

In the design of this plant, emphasis was placed on unitizing each engine-generator unit to an extent that, under normal operating conditions, a minimum of dependence on any common plant facilities other than the fuel gas supply and the potline bus itself, was involved. To accomplish this, several unusual features were employed.

All engine auxiliaries, except the ignition system, are separately induction-motor driven. The 400-volt, 24-cycle power for those of each engine is obtained from slip rings, mounted below the commutator on each d-c generator. All the 440-volt, 25-cycle auxiliary motors are connected directly to the slip ring supply and automatically start and stop as the engine starts and stops.

The shunt field of each generator is wound for approximately 550 volts and is self-excited from its own generator through a motor-operated rheostat. Since the generators are self-excited, the operating voltage range is limited to approximately 550 to 650 volts d-c. When the potline is in operation within this normal voltage range, any generator may readily be paralleled on the bus. For "dead line" starts, however, a 60,000-amp potline circuit breaker is used to disconnect the potline, and all generators are paralleled on the station bus at full voltage and no load. Load is applied by closing the potline breaker.

For the common station services and aluminum plant power, a number of 650 volt d-c to 4160 volt a-c motor-generator sets are operated in parallel to feed a 4160-volt distribution system from which load center substations provide 480-volt, 60-cycle plant services. This system permits all engine generators to be duplicate d-c units and makes the plant entirely self-supporting with a minimum of spare d-c units for both a-c and d-c power requirements.

Each engine is "cranked" by using its connected d-c generator as a starting motor. The field circuit is transferred to the station d-c bus for starting, and the armature is fed from the bus through a starting resistor, under normal conditions. A small gasoline engine-generator set provides starting power in emergency. Fig. 2 is a view of the engine room.

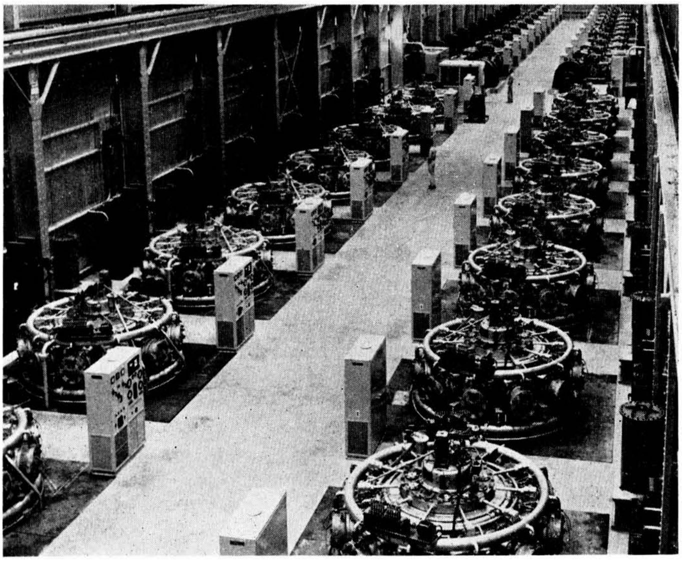

FIG. 2. Engine room at Aluminum Company of America's Point Comfort reduction plant.

The Point Comfort plant is on the coast and receives its alumina by boat from Alcoa's alumina plant at Mobile. The use of gas engines for all power sets a new pattern in the aluminum industry. This plant's output is greater than any other of Alcoa's reduction plants except that at Alcoa, Tennessee.

ALUMINUM COMPANY OF AMERICA, ROCKDALE, TEXAS

The newest of the aluminum plants in the Gulf Coast area is that of the Aluminum Company of America at Rockdale, Texas. The output here will be approximately 170 million lb per year from four potlines each rated approximately 45,000 kw.

The potlines themselves and the rectifier station equipment serving them are very much the same as those of other aluminum reduction plants which use standard a-c power from whatever source.

Each rectifier station is served by a 13.8-kw, 3-phase, 60-cycle feeder from the power station, through a regulating autotransformer, to the normal 13.8-kv bus. This bus serves six rectifier transformers, each of which serves two ignitron rectifiers each rated 6000 amp at 750 volts d-c, providing an installed capacity of 72,000 amp and 54,000 kw per line. Two of the four rectifier station equipments are Westinghouse and two are General Electric. Each rectifier is provided with an ITE Company anode breaker and cathode breaker. Water-to-air heat exchangers, one for each rectifier, are mounted on the roof of the rectifier station.

Phase-shifting autotransformers, connected ahead of each rectifier transformer, are arranged so that each line operates 36 phase a.c., and so that associated pairs of lines operate 72 phase. From wide experience in the trade, such a multiphased system is known to be adequate and desired, to avoid communication interferences for a rectifier system of this magnitude.

Unlike the other aluminum plants of the Gulf Coast area, the Rockdale plant is not on the coast, and alumina will be delivered by rail car. This is the typical case of the reduction plant going to the power source, in this case, the abundant lignite of the Rockdale area.

The new steam-electric power plant was planned to include substantial interconnecting ties with the Texas Power and Light system. These facilities were installed early in the program, and available power from this system has permitted the first two potlines to go into production while installation of the new plant with its lignite fuel processing facilities is being completed.

The new station will include three G-E turbine generators each having a nominal rating of 90,000 kw, 0.85 pf, and a maximum capability of 100,000 kw, 14,400 volts, 3 phase, 60 cycles for steam conditions of 1450 psig, 1000/1000 FTT, on a reheat cycle basis. Normally, all three units will operate to serve the aluminum plant and deliver additional power to the interconnected system. When a unit is out of service, the system will supply enough additional power to support full aluminum plant operation.

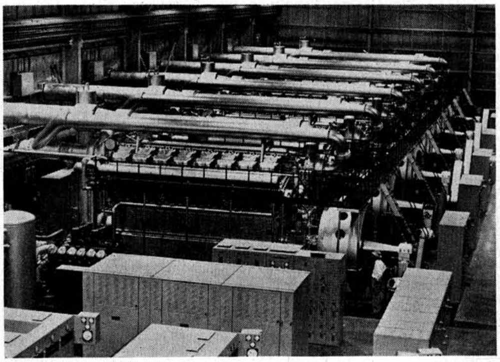

FIG. 3. A-c engine generator plant at the San Patricio plant of the Reynolds Metals Company.

The Westinghouse station switchgear, having 2500-mva air blast circuit breakers, provides a reliable station double-bus scheme, carefully integrated with current-limiting reactors, so that all three generators, the two tie transformer banks, and all feeders to the aluminum plant can be operated in parallel in any combinations desired to meet normal or emergency conditions.

It is early yet to describe or predict the performance of the lignite plant. But with large sources of lignite available in the area, this practical industrial use of it is a highly important power development, even in an area rich in gas resources.

REYNOLDS METALS COMPANY, CORPUS CHRISTI, TEXAS

The Reynolds Metals Company's San Patricio reduction plant and its adjacent La Quinta alumina plant at Gregory, Texas, near Corpus Christi, represent the area's first integrated bauxite to pig aluminum operation. The alumina plant is located on the bay where harbor facilities have been developed to receive ore boats from Reynolds' bauxite mines in Jamaica. The reduction plant will obtain its alumina directly, and more alumina will be shipped by rail to other Reynolds' reduction plants.

Each of the two potlines at San Patricio has a nominal rating of 100,000 amp at 725 volts or 72,500 kw. The ratings of all pots in the industry are steadily being increased, and these represent the furthest advance in this trend. The pots are of the Sodeberg type, and except for their size, are similar to others of the trade.

One of the potlines is powered by 33 Cooper Bessemer V-16, horizontal, four-cycle, supercharged, 327-rpm gas engines, each driving a G-E 2500-kw 725-volt d-c generator.

The other is powered by 41 General Motors 16-cylinder, vertical, two-cycle, 600-rpm gas engines each driving a G-E 2000 kw, 725-volt d-c generator.

The basic connections and entire electrical system operation of the two plants are the same. All engine and station auxiliaries are standard 60-cycle induction motor driven, served by load center unit substations, receiving power from the a-c generating station. Each generator has two d-c circuit breakers, and all 250-volt shunt fields of each line are served from either of two alternate field buses. Two alternate exciters, each with amplidyne control, are provided, either of which gives full range voltage control of the potline at any time, and permits paralleling any generator on the potline bus at no load, whatever its voltage at the time. Hence, no potroom breaker is required. The master operator has choice of: manual, automatic constant current, or automatic constant voltage control at will.

The auxiliaries for both d-c engine generator stations and approximately 6000 kva of aluminum plant power are served by a separate a-c engine-generator plant. This includes nine Cooper-Bessemer engines, essentially duplicate of those of the d-c station, except that here each drives a G-E a-c generator rated 2500 kw, 0.8 pf, 3175 kva, 4160 volts, 3 phase, 60 cycles, with a V-belt driven exciter.

The generators, in groups of three, serve three 4160-volt station bus sections, which, in turn, are normally paralleled through reactors to the station synchronizing bus. Interconnecting tie circuits are provided to the La Quinta alumina plant and to the utility system. The 4160-volt feeders are logically distributed on the three station bus sections to serve load center substations throughout the plant areas. Fig. 3 is a view of the a-c engine plant.

What Does the Future Hold?

The U. S. aluminum use for peace-time purposes is now about 2000 million lb per year, which is near the World War II peak production, and about five times that of the last prewar year. It is forecast, with good background evidence, that U. S. power production will double in the next ten years, and many sound-thinking groups feel that aluminum production also may well do this or more. The present use of aluminum is now increasing at a rate greater than this.

It is clear that, to even a greater extent than in the past, aluminum reduction plants will seek the most economical power locations, and since much further hydro development is unlikely, this means available and economical fuel sources. So it will be with all major basic industries in the years to come.

Therefore, the future of the aluminum industry on the Gulf Coast would seem to depend upon the availability and favorable cost of increasing quantities of natural gas, and the economic success of the new lignite fuel sources, as compared with the "at-the-mine" cost of coal in other areas where it is abundant.

Aluminum production doubtlessly will expand greatly. Any area will attract it, in proportion to the answer it gives to the electrical energy cost question.

The aluminum plants of the Gulf Coast already present an imposing industrial picture, and promise one even more imposing within the next decade.

MAGNESIUM PRODUCTION IN THE SOUTHWEST

W. J. Rave[1]

During 1953 the magnesium industry in the Southwest will consume approximately 1.4 billion kwhr of electrical energy to turn out the estimated 140 million lb of magnesium which will be produced this year. With a load of 160,000 kw, magnesium production in the Southwest is an important factor in the electrolytic industries of this part of the country.

Output of magnesium during 1953 will be the highest ever attained for the Southwest, with the exception of 1943 when four plants were in operation under the stimulus of war-time demand. In the past 12 years approximately 690 million lb of magnesium have been produced in Texas and Louisiana, the majority having been extracted from sea water.

This production has occurred in four plants, two operated by The Dow Chemical Company in the Freeport-Velasco area on the Gulf Coast 60 miles south of Houston, one by International Minerals and Chemicals Corporation at Austin, Texas, and one by the Mathieson Alkali Works at Lake Charles, Louisiana. The last two of these plants were operated only during the war-time period from 1942 through 1945, and have since been abandoned.

The first production of magnesium in the Southwest occurred in January 1941, when the plant of The Dow Chemical Company at Freeport, Texas, was first placed into operation. Establishment of this new plant site and the use of an entirely new process, developed by Dow for the recovery of magnesium from sea water, typifies the confidence that The Dow Chemical Company has always had in the growth of the magnesium industry. This first plant was planned in 1938 and 1939 before the expansion accompanying World War II had started.

The availability of raw materials such as salt for the production of chlorine, oyster shell for the production of lime, and natural gas as a source of power are among the factors which prompted the establishment of the first Dow plant on the Texas Coast. This plant, originally designed for an annual capacity of 14 million lb, was promptly expanded with the assistance of the British Government to a rated capacity of 18 million lb. Within less than a year following the initial operation of Dow's original plant, capacity was expanded by the U. S. Government to a total of 36 million lb per year. This plant operated at more than 120 per cent of rated capacity during the war years.

With the outbreak of World War II and its emphasis on air warfare, it was apparent that a considerable quantity of magnesium would be required. This led to the construction of three other Government-financed plants in the Southwest. The second magnesium plant, and the largest one in the area, was built in 1942 at Velasco, Texas, seven miles from the site of the original Dow plant, with a rated capacity of 72 million lb per year. The Velasco plant, built at a cost of $56,000,000, gained considerable publicity by the fact that construction from first piling to first production took a little less than six months. This plant, operated by The Dow Chemical Company for the Government, produced magnesium successfully until its shutdown in 1945, reaching an output of over 80 million lb in 1943.

Both of these plants, one at the original Dow plant site, and the Government plant at Velasco, use the Dow process for extraction of magnesium from sea water and use the Dow Type E cell (Fig. 1) for the electrolysis of the magnesium chloride. Both the Dow process and the Dow cell have been described in the literature (1–3). The flowsheet of the Dow process is shown in Fig. 2.

The third magnesium project in the Southwest, also Government-built, was a plant located at Austin, Texas, with some of the magnesium chloride facilities being at Carlsbad, New Mexico. This plant used a part of the Dow process under license, particularly the Dow electrolytic cells. Although a chloride electrolysis plant, it was designed to use dolomitic limestone as its chief source of magnesium. It was planned that a part of the magnesium chloride, at least that equivalent to the make-up chlorine requirements, would be recovered as a by-product of the manufacture of potash by International Minerals at Carlsbad. The Carlsbad operation was only partially successful and a substantial amount of the raw material, both in the form of a chloride and a hydroxide, was supplied by the Government's Velasco plant. The Austin plant, with a rated capacity of 24 million lb per year, operated successfully during 1942, 1943, and 1944, producing a total of a little more than 45 million lb, but was abandoned and scrapped following the end of the war. This process has also been

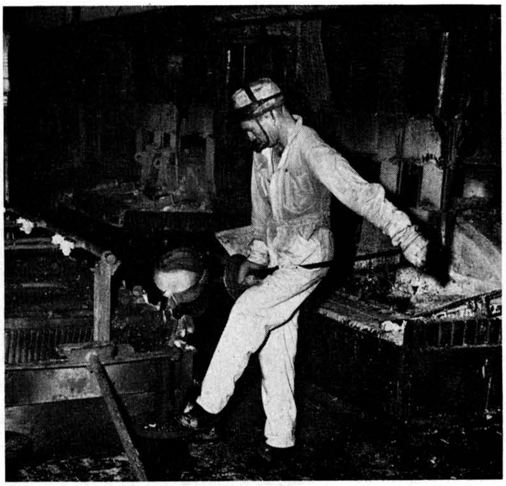

FIG. 1. Dow Type E cell used at Freeport, Velasco, and Austin plants.

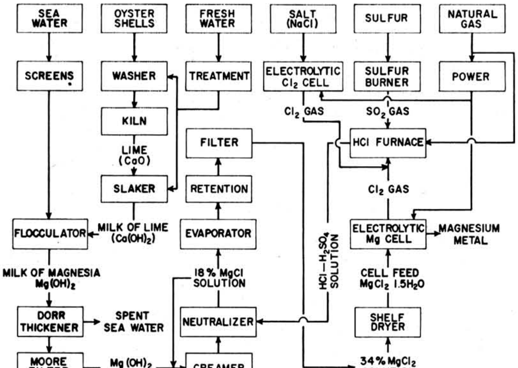

FIG. 2. Dow sea water magnesium process flowsheet

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[1] Texas Division, The Dow Chemical Company, Freeport, Texas.

described in the literature (5, 6). Its flowsheet is given in Fig. 3.

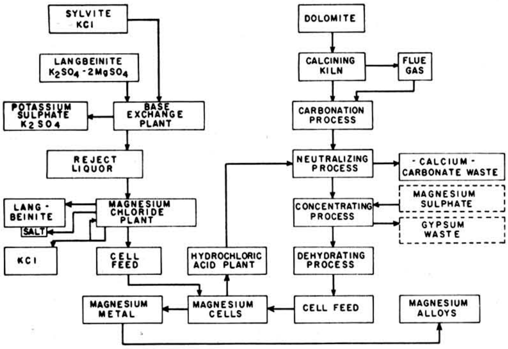

FIG. 3. International Minerals magnesium process flowsheet

TABLE I. *Magnesium production in the Southwest* (1000's of pounds)

Calendar years	Dow Freeport, Tex.	Dow Velasco, Tex.	International Austin, Tex.	Mathieson Lake Charles, La.	Total
1941	14,269				14,269
1942	42,315	20,948	2,158		65,421
1943	43,191	80,253	25,539	2,384	151,367
1944	41,160	60,741	17,936	2,985	122,822
1945	33,653	5,262			38,915
1946	10,066				10,066
1947	24,688				24,688
1948	20,006				20,006
1949	23,195				23,195
1950	31,453				31,453
1951	42,651	18,768			61,419
1952	49,866	76,057			125,923
Total	376,513	262,029	45,633	5,369	689,544

FIG. 4. Dow Chemical Company magnesium chloride plant at Freeport, Texas

The Government plant designed and operated by the Mathieson Alkali Works at Lake Charles, Louisiana, was the fourth magnesium production installation built during the period. It had a designed capacity of 54 million lb per year, but a total production of a little more than 5 million lb was obtained and the plant was shut down and abandoned as a magnesium plant in 1944. The principal raw material for the process was dolomite stone, calcined with locally produced natural gas. The resulting oxides of calcium and magnesium were treated with calcium chloride, a product of the parent Mathieson plant in Louisiana. The mass was then treated with carbon dioxide obtained from the calcination of the dolomite, which converted the calcium into insoluble carbonate, leaving magnesium chloride. Much of the magnesium chloride feed preparation was in standard design equipment, while the electrolytic cell was one developed by Mathieson. The process and cell held some promise. Had its development been at a normal pace, it might have been ultimately successful; but under the pressure of war-time magnesium demands, an untried process was used as the basis of a full plant design. Operations were not successful and time did not permit normal growth.

A summary of the production in these four plants from 1941 through 1952 is given in Table I.

The loss of war-time demand for magnesium in 1945, and the general slump of the reconversion period, together with the magnesium scrap that had accumulated during and immediately following the war, caused the complete shutdown of all magnesium plants, including Dow's privately owned plant, in 1945. However, this complete shutdown proved

TABLE II. *Magnesium consumption, by industry uses in 1952* (Magnesium Association)

	%
Aircraft: engines, wheels, air-frames, etc.	29.3
Aluminum industry	20.4
Electrochemical uses: underground anodes, fresh water anodes, sea water anodes, etc.	8.5
Ground transportation: trucks and trailers, automotive, etc.	7.6
Machinery and tools: portable tools, business machines	6.2
Chemical and metallurgical uses	6.0
Materials handling: dockboards and skids, foundry equipment, concrete industry, etc.	4.7
Electrical equipment: radar, radio, TV, etc.	3.5
Magnesium powder	2.4
Consumer products: ladders and hand tools, furniture, sporting goods, etc.	1.6
Textile industry	0.8
Printing and engraving	0.4
Unclassified and miscellaneous	8.6

premature and Dow's own facilities were started at a reduced rate after a six-month shutdown. Production at Dow's plant has, in general, continued to increase since that date, and will probably exceed 55 million lb in 1953.

That part of the plant at Dow's original plant site at Freeport constructed by the British Government was purchased by Dow in 1946, and the facilities constructed by the U.S. Government were purchased, in part, in 1947; the balance was purchased in 1949. A further expansion to this plant was added by Dow in 1952, giving a total capacity of approximately 59 million lb in Dow's privately owned plant at Freeport.

The Velasco plant, built by the Government, was shut down with the rest of the plants in the area in 1945, but on the recommendation of the Symington Committee, this plant, together with six other Government-owned magnesium plants (not including the Austin and Lake Charles plants), was retained by the Government as a part of the National Industrial Reserve. The Velasco plant was maintained in a stand-by condition by the Government from 1945 through 1950 and was returned to operation in 1951. The plant is now being operated for the Government by The Dow Chemical Company under a lease agreement to supply magnesium for the national stock pile and for the current armament program. Although originally rated at 72 million lb, the Velasco plant has consistently operated above rated capacity and is generally listed as having a capacity of 80 million lb per year at the present time, giving the combined Freeport and Velasco plants a rated capacity of 140 million lb.

In at least two aspects, magnesium production in the Southwest is unique among the primary metals. First, magnesium is one of the few primary metals produced on a closely integrated basis with the chemical industry. Chemicals have been produced as by-products in the production of aluminum, steel, and other metals, but because of the chemistry involved in the chloride process, magnesium production and production of chemicals strengthen each other on raw materials, by-products, etc.

Second, magnesium is the only primary metal being economically produced from an unlimited ore supply available domestically. Other metals are now being produced from ore bodies which may be exhausted in the foreseeable future. This exhaustion of the higher yield domestic ores will require that many of our primary metals be derived from lower grade or overseas deposits. The magnesium content of the ocean waters of the world has been estimated to be 2×10^{15} tons, which, for all practical purposes, is an inexhaustible supply. This abundance of raw materials led the Paley Commission to the conclusion that magnesium production might increase from 20,000 tons in 1950 to a possible high of 1,000,000 tons in 1975 (7).

It has frequently been pointed out that these two unique factors in magnesium production both favor long range stability in magnesium costs. Emphasis on probable price stability has at times neglected the fact that the costs of many materials and services such as power, graphite, plant construction, and labor involved in the production of magnesium, have risen more rapidly over the past ten years than has the price of magnesium. This is particularly true of the power costs in the Southwest which have risen sharply as natural gas has been piped in increasing quantities to other parts of the United States. The net result appears to be that, while abundant raw materials will act as a long range stabilizing influence on the magnesium cost, the market price of magnesium should be expected to adjust to its proper relationship to the general commodity index.

The recent Government order shutting down five of the six Government plants which were placed in operation in 1951 leaves all of the magnesium production in the United States concentrated in the Southwest, with the exception of a small amount of magnesium produced on a captive basis for use in titanium production. Not only is all the nation's commercial magnesium production concentrated in the Southwest, but a preponderance of the world production as well. Although the American Southwest should continue to be a major factor in the magnesium industry, we cannot expect to maintain our exclusive position. Electrical power and natural gas are neither as cheap nor as readily available as was the case 15 years ago, and the combination of power and sea water or other raw materials, such as underground brines, are available elsewhere. Strategic considerations also indicate that the production of primary magnesium should not be too highly concentrated in one locality. Although the Southwest may not maintain its exclusive position in the magnesium production, it will be a dominating factor for many years to come.

On a national scale, magnesium consumption promises to grow and expand. Consumption of primary magnesium, which amounted to 40 million lb in 1950, is projected at approximately 90 million lb for 1953 and 160 million lb for 1959.

New applications for magnesium, both in the structural and in the chemical and metallurgical fields, are being found, and those connected with magnesium are optimistic that its growth, both nationally and in the Southwest, will continue.

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ELECTROCHEMICAL CHLORINE-CAUSTIC SODA PRODUCTION IN THE GULF COAST AREA

Frank Chrencik[1]

Well in step with the vast, rapid growing, chemical industries of the Gulf Coast area is basic and essential chlorine, with its co-products of caustic soda and hydrogen, or elemental sodium in lieu thereof. Abundance of salt in many scattered and practically inexhaustible salt domes is attractive to chlorine producers in itself, but when enhanced with abundance of natural gas, sulfur, petroleum, sea water, iron, coal, lime, and agricultural products, a sound, diversified, chemical industry is readily visualized. All salt sources for the 11 chlorine manufacturers in the Gulf Coast area are from domes formed through a prehistoric, geological phenomenon so that deeply underlying salt strata have been forced sufficiently close to the surface to permit access by drilling and dissolving. All chlorine producers in the Gulf Coast area, with the exception of the Ethyl Corporation, have captive salt deposits from which brine requirements are obtained. Current rate of salt usage from the widely scattered salt domes is estimated at present at 6100 tons per day.

The Gulf Coast area, which affords the American dreamer of a chemical empire his best opportunity to succeed today, is along the Texas, Louisiana, and Alabama coast line, at an inland distance of usually less than 50 miles. While producers of chlorine find the majority of their chlorine consumed within a comparatively small radius of their works, over 95 per cent of the chlorine produced within the area is consumed therein. Railroads, inland waterways, and the Gulf provide a strategic point of origin for export as well as domestic shipping. Not to be ignored is also the ever increasing pipeline method of transporting, not only chlorine but numerous basic chemicals, petroleum, and gas products. Perhaps the oil industry deserves credit for pointing the way. The Diamond Alkali Company, for example, ships substantial quantities of chlorine, caustic soda, and hydrogen by this method. The newness of the area presents the advantage of having plenty of space for industrial expansion and pipeline easements, which might not be the case in the saturated Northern industrial developments.

Growth of the Chlorine Industry

Prior to World War II, the Gulf Coast area requirements for chlorine and caustic soda were satisfied with a few hundred tons per day, with approximately 100 tons being shipped to consumers and the balance used captively by The Dow Chemical Company and Ethyl Corporation as the primary, captive chlorine users at that time. Solvay and Southern Alkali (now Columbia Southern Chemical Corporation) produced most of the chlorine sold as such. The Gulf Coast area now lists the following producers of significance at the indicated locations. It will be noted that all of these manufacturers, with the exception of Frontier Chemical, located in the northwestern part of Texas, are in close proximity of the Gulf Coast.

Dow Chemical Company, Freeport, Texas
Ethyl Corporation, Baton Rouge, Louisiana
Ethyl Corporation, Pasadena, Texas
Solvay Process Company, Baton Rouge, Louisiana
Diamond Alkali Company, Pasadena, Texas
Columbia Southern Chemical Corporation, Lake Charles, Louisiana
Columbia Southern Chemical Corporation, Corpus Christi, Texas
Champion Paper & Fibre, Pasadena, Texas
Mathieson Chemical Corporation, McIntosh, Alabama
Frontier Chemical Company, Denver City, Texas
Gulf Oil Corporation, Port Arthur, Texas

These producers represent a presently combined, daily chlorine production capacity of 3210 tons of chlorine, which also reflects a total electrolytic, caustic soda capacity of 3260 tons, plus 220 tons of elemental sodium (Ethyl Corporation), and 29 million cubic feet per day of hydrogen. Fig. 2 shows the chlorine producing plants in the Gulf Coast area. Thus the production of chlorine has increased from about 520 tons per day in 1943 to 3210 tons in the current year, 1953. The indicated, better than sixfold increase over the past decade has placed these chlorine plants in the position of producing about 30 per cent of the nation's entire production, with Texas alone producing about 22 per cent of the nation's supply. The Dow Chemical Company contributes a large portion to both of these percentages.

Upgrading of Products

The upgrading of basic and intermediate chemicals captively has been a foremost subject in chemical manufacturing circles throughout the nation. Foremost in this trend is The Dow Chemical Company, with Diamond Alkali Company moving strongly in this direction. Ethyl Corporation has always maintained captive chlorine and sodium capacity as a prerequisite to tetraethyllead manufacturing, but also has in recent years expanded to other products involving chlorine. For those producers who sell chlorine as such, more than likely this chlorine is being shipped a comparatively short distance to a purchasing plant which furnishes other captive materials such as hydrocarbons. It seems that the petroleum industry favors the term "petrochemicals" when they are the users of purchased chlorine and caustic soda for captive upgrading of their hydrocarbons. The captive chlorine users, on the other hand, seem to favor terms such as "organic chemicals," "chlorinated hydrocarbons," etc. To date, there seems to be no definite indication as to which of these two basic types of industry can claim a closer position to the end-item consumer market and the stages of profit taking involved. Perhaps the third basic type of industry, such as Union Carbide and Celanese, who purchase most of their basic chemicals, enjoy this distinction, at least for the present. Captive users of chlorine and caustic soda are now producing such products as plastic monomers and polymers, solvents, pharmaceutical intermediates, detergents, organic insecticides and herbicides, fuel additives, refrigerants, etc. Dow, Diamond, and Ethyl are particularly active in these fields. Each of these basic categories of products includes many types which are continually increasing in variety and application. This type of demand for chlorine clearly indicates the trend toward increased usage of chlorine for chemicals in relation to the older applications such as pulp and paper, sanitation, and textiles. The past ten years have seen chlorine demand for chemicals produced in the Gulf Coast area rise from about 70 per cent of total chlorine production in 1943 to over 90 per cent of current chlorine production, this notwithstanding the fact that there has been over a sixfold increase in capacity during the past ten years.

The Problem of Co-product Disposal

While chlorine capacity expansion has in most cases caused a corresponding increase in caustic and hydrogen, the demand

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[1] Diamond Alkali Company, Pasadena, Texas.

for these co-products has not increased as well; however, local demand and export facilities to South American markets, in particular, have maintained a more balanced picture as compared to other areas. The petroleum industry in itself is a very substantial consumer of caustic soda, in that caustic is involved in many phases of petroleum processing, beginning with caustic required for the mud used in oil drilling operations and, finally, in the sweetening process in finished gasoline treatment. Caustic soda is produced in a number of forms such as standard, 50 per cent, commerical, 70 per cent, and in a number of anhydrous forms, such as solid, flake, and powder. A notable advancement in the fusion of caustic to anhydrous form is illustrated by the dowtherm-heated, evaporative type of process used for this purpose by the Diamond Alkali Company and Columbia Southern. Very substantial advantages have been realized by this revolutionary change from the conventional, cast-iron, fusion pots to the dowtherm-heated evaporative arrangement.

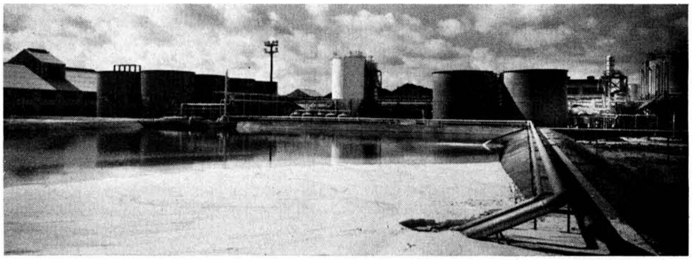


FIG. 1. View of surplus salt storage and brine treating facilities of the Diamond Company. Brine treatment for removal of impurities is an important prerequisite prior to the electrolysis of brine.

Hydrogen markets have had very little influence on the economic justification for a chlorine plant, but it is worthy of mention in that hydrogen is becoming recognized as a co-product of value. It is enjoying increasing demand to the extent that the electrolytic process of decomposing salt is pointing to a three-component output of salable products, in lieu of two customarily recognized as chlorine and caustic soda. Ammonia, anhydrous hydrochloric acid, and hydrogenation of unsaturated hydrocarbons are examples of present day hydrogen usage.

Electrolytic Cells

Electrolytic cells used among the Gulf Coast chlorine manufacturers are as varied as in any other part of the nation, perhaps even more so in view of the fact that many plants have adopted a design-and-build-your-own policy. Capacity trends in the cell designs have also increased very substantially in the past ten years, in that a 10,000-amp cell in 1943 was considered very substantial indeed. Present day cell capacities of 20,000–30,000 amp are not uncommon. Cell designations used among the local chlorine manufacturers are such as Hooker S-3, the Dow Cell, the Diamond Cell, Allen Moore, and the Downs Cell in case of chlorine-sodium production at Ethyl. The area, at present, claims only one mercury cell installation, and that is the Mathieson Cell being used in the Mathieson Chemical Corporation's new chlorine plant at McIntosh, Alabama. Enthusiasm for the mercury cell, following access to European technology of this type, has not been appreciably felt in the Gulf Coast area. There are many factors to consider in choosing between the two basic types of electrolytic cells, namely, diaphragm and mercury. It is known that the mercury cell produces a more pure grade of caustic than electrolytic cells do; however, the type of caustic usage involved in the Gulf Coast area has been satisfied with electrolytic quality. In such cases where quality demands must be met for specialized application, it appears that the electrolytic caustic can be purified satisfactorily. Another consideration is the captive power generation that exists among the chlorine producers. This arrangement provides manufacturers with a cheap source of process steam for evaporation of cell liquor from electrolytic cells, whereas mercury cell users usually purchase power from outside sources and make commercial caustic strength directly off the cell without the necessity of subsequent concentration in steam heated evaporators. What the ultimate size and capacity of the various electrolytic cells employed will be eventually is difficult to forecast, as fairly intensive research and development work is directed toward increased capacity per unit cell and thereby reducing building and other facility requirements to house the increasingly concentrated output of such electrolytic equipment.

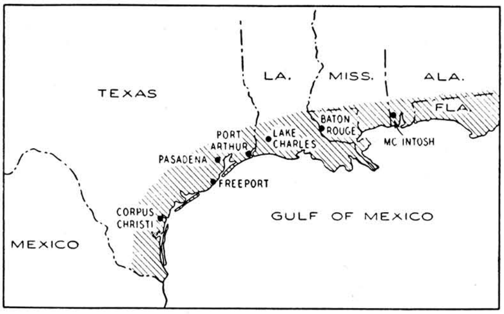


FIG. 2. Chlorine producing plants in the Gulf Coast area. Columbia Southern Chemical Corp., Corpus Christi, Texas, and Lake Charles, La.; Dow Chemical Co., Freeport, Texas; Diamond Alkali Co., Pasadena, Texas; Champion Paper & Fiber Co., Pasadena, Texas; Ethyl Corp., Pasadena, Texas, and Baton Rouge, La.; Solvay Process Co., Baton Rouge, La.; Gulf Oil Corp., Port Arthur, Texas; Mathieson Chemical Corp., McIntosh, Ala.

Power Supply

The chlorine industry in this area generates approximately 70 per cent of its power requirements, or approximately 7,200,000 kw per day. Many factors enter into a decision as to whether captive power generation is justified as compared to purchase from a public utility. Perhaps one of the most determinant factors is the requirements for steam which can be extracted from power-generating turbines. In the case of a public utility, the latent heat from steam must be condensed after the turbine and discarded with the condensing water without further benefit. This same heat, representing over 60 per cent of energy iuput to the turbine, can be utilized to material advantage in a chemical processing arrangement, particularly one that utilizes diaphragm cells where 10-12 per cent caustic soda liquor must be concentrated to 50 and 70 per cent strength. With the huge influx of electrochemical industries to the Gulf Coast area, the public utility system could not originally meet these sudden demands and public utility power has been in quite critical shortage until recent months when very substantial expansion on the part of public utilities has accorded appreciable relief to the general Southwest area power shortage and left an improved outlook for future supply for those who contemplate additional power requirements in the future.

Outlook for the Future

There are still substantial quantities of undeveloped resources in Texas. This, combined with climate, geography, and the anticpated influx of population, contributes to a picture of future growth. Manufacturers of consumer end-items have very little direct dependency on natural resources and consequently they are somewhat slower in realizing the benefits of this new industrial area. Many well-established Northern industries will pay the penalty of high transportation costs for materials from the South and maintain the advantage of operating with previously established facilities, or even expanding them, and being located closer to the center of the United States population. A favorable tax situation for Gulf Coast industries has been preserved to date; however, state legislatures are continuously scrutinizing the conspicuously new industrial activity as a potential source of increased revenue. Potential plants have this economic discouragement to be concerned with. State, county, and school districts tax revenue has been materially enhanced by industries through normal taxation already and an added tax burden against the basic industries specifically may well be the cause of the death of the goose that is laying the golden egg.

POWER FOR GULF COAST ELECTROCHEMICAL PLANTS

H. Lee Norris, Jr.[1]

The history of the electrochemical industry along the arc of the Gulf Coast extending roughly from Corpus Christi, Texas, to New Orleans, Louisiana, is a brief one in regard to years. The development of the power plants which, of course, has paralleled the electrochemical industry, has been marked by mammoth-sized installations. As the growth of the electrochemical industry along the Gulf Coast has been unparalleled, so also has the growth of the power-producing facilities.

The two chief features that the power plants serving electrochemical installations have in common are, with one notable exception, that they all burn gas and, in design, they are generally unconventional.

The reserves of natural gas available in this area have been unprecedented both in size and in number of fields, and, until only a few years ago, they had no sizeable market. Growing general industrial activity, the tremendous growth of the electrochemical industry, and the development of the network of large-diameter, interstate pipelines have given this gas a market and have occasioned a rapid rise in market price, which leads some people to predict a gas shortage in the Gulf Coast area. Whether or not a shortage develops will depend primarily on the rate of discovery of new gas reserves and upon the price of natural gas relative to other fuels. Some authorities predict that in the not too distant future, the price of gas on a heat-content basis will approximate the cost of petroleum residium or other petroleum fuels on a heat-content basis. The reflection of this thinking may be seen in the Rockdale works of the Aluminum Company of America which has been designed around lignite fuel.

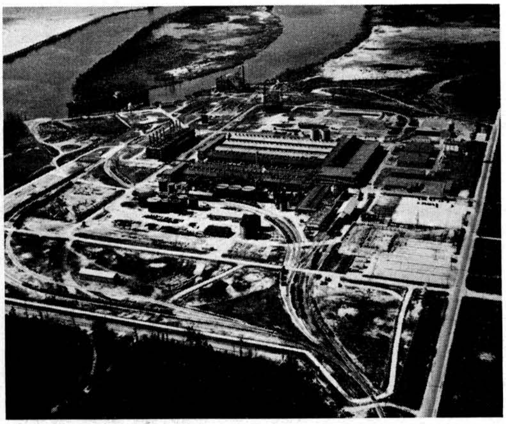
There follows in this article the principal data of the power plants for the electrochemical industry. For various reasons it is not feasible to estimate the cost of generating power for individual plants.

Brief descriptions of an engine plant and steam plants are included to show the contrast between the types of construction. None of these plants can be considered conventional, as in some respects they have all deviated, some slightly and others greatly, from the usual means of generating power. In all cases, the load factor is as nearly unity as the operating and maintenance skills of the various companies can make it approach unity. In fact, it is something of a salient industrial achievement for these plants to come as close to unity load factor as they do.

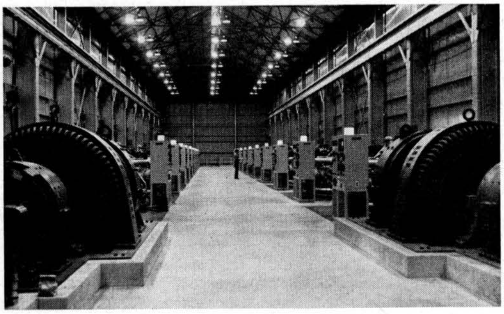
Climate, also, has influenced the design of the plants almost as much as the type of fuel and of load, because in no case is a power installation completely enclosed in a conventional building. In all cases, the engine plants have the engines and generators located inside buildings, but the buildings themselves, instead of being the massive masonry structures usually associated with power production, are of light-weight, steel frame sheet-aluminum construction. All of the steam plants have either one boiler, all the boilers, or all the boilers and turbines located outdoors.

In the Gulf Coast area, where temperatures below freezing normally exist less than fifty hours per year and where rain is likely to come in tropical downpours followed by extended periods of dry weather, outdoor construction has been thoroughly proved. Weather interferes very little with heavy maintenance in outdoor installations because the extreme reliability of modern steam generators and steam turbines makes major overhaul an infrequent operation.

Summarized in Table I are pertinent data relative to Gulf Coast electrochemical power-generating facilities; it does not take into account energy purchased from the local utility networks. Many of the Gulf Coast electrochemical plants have substantial utility interconnections and these are called upon to furnish sizeable blocks of power depending upon availability of such power from the network, outages of the electrochemical industries' own generation equipment, and the urgency of demand for the products.



Aerial view of Columbia-Southern Chemical Corporation's plant at Lake Charles, Louisiana.



Individual engine control panels and motor-generator sets shown here are in one of the five engine rooms of the Aluminum Company of America plant at Point Comfort, Texas.

There is some hydroelectric generation of power in Texas, although its total is small in comparison with the generating capacity by thermal-power plants. Some of this hydroelectric energy finds its way into electrochemical production through utility interconnections.

THE DOW CHEMICAL COMPANY, FREEPORT, TEXAS

The first electrochemical plant of magnitude on the Gulf Coast was that of The Dow Chemical Company at Freeport, Texas, and reference to Table I shows it to have the largest generating capacity of any of the companies described. Proper description of the various installations for producing power at The Dow Chemical Company plant should be the subject

---

[1] The Fish Engineering Corporation, Houston, Texas.

TABLE I. *Summary of Gulf Coast electrochemical power generating facilities*

Names Locations	Alcoa Rockdale	Am. Smelt. & Ref. Corpus Christi	Columbia-So. Corpus Christi	Columbia-So. Lake Charles	Diamond Alkali Houston	Dow Chem. Plant 1 Freeport	Dow Chem. Plant 2 Freeport	Dow Chem. Plant 3 Freeport	Alcoa Point Comfort	Reynolds Metals San Patricio
Number of units	3	3 a.c. 5 d.c.	5	8	3	7	5	3	194	9 a.c. 74 d.c.
Kw rating of units	100,000	2000 & 5000 a.c. 2500 d.c.		7500 to 15,000	10,000	3–10,000 3–20,000 1–30,000	1–35,000 2–40,000 1–45,000 1–60,000	3–40,000	1100/1200	2500 a.c. & d.c. 2000 d.c.
Total kw rating	300,000	21,500	37,500	70,000	30,000	120,000	220,000	120,000	228,000	187,000
Turbine steam pressure psig	1,450	400	850 & 400	400	850	400	1250 & 235	1250	Gas engine	Gas engine
Turbine steam temperature	1005°F	750°F	825°F & 700°F	750°F	900°F	750°F	900/575°F	950°F	Gas engine	Gas engine
Generated voltage	14,400	2300 a.c. 500 d.c.	13,800 & 2,300	13,800	13,800	13,800	14,400	13,800	667 d.c.	4160 a.c. 725 d.c.
Rectified voltage	750	500	600/700	650	645	800 max.	800 max.	800 max.	None	None
Type rectifiers	Hg arc	Hg arc	Hg arc		Hg arc	Hg arc	Hg arc	Hg arc	None	None
Process steam pressure	None	75 psig	400; 140 & 15 psig		150 & 18 psig	400; 150 & 30 psig	450; 235 & 30 psig	400; 150 & 30 psig	None	None
Turbines (location)	Outdoor	Indoor	Indoor		Indoor	Indoor	Indoor	Indoor	None	None
Boilers (location)	Outdoor	3 Indoor 1 Outdoor	2 Outdoor 3 Indoor		Outdoor	Indoor	Indoor	Outdoor	None	None
Fuel	Lignite	Nat. gas	Nat. gas	Nat. gas	Nat. gas	Nat. gas	Nat. gas	Nat. gas	Nat. gas	Nat. gas
No. kw installed by years from 1940	Being installed at present	1942—16,500 1951— 5,000	1941— 7,500 1952—30,000		1948—30,000	1941—70,000 1942—20,000 1951—30,000	1942—120,000 1951— 40,000 1953— 60,000	1952—80,000* 1953—40,000	1949—132,000 1951— 96,000	1952—187,000
Total generation 1952 mwh		164,955	942	565,000	288,000	1,095,000	1,377,000	67,000	1,230,814	Partial year
End use of power	Al	Zn, Cd, & H_2SO_4	Cl_2		Cl_2 & caustic	Cl_2 & Mg & plant utility	Cl_2 & Mg & plant utility	Cl_2 & Mg & plant utility *No. 1 Nov. 1 No. 2 Dec. 12	Al	Al

of an entire list of papers describing this installation which has many unique features. The original installation, made in 1939, was built around generating steam at 400 psig, 750°F total temperature, and used extracted steam in order to achieve the best practicable heat balance. In all plants the minimum amount of steam is condensed and sea water from the Gulf of Mexico is used for cooling water.

The evaporation of caustic soda is the largest use of process steam and its use, up to moderately high pressures in the synthesis and processing of organic chemicals, is very extensive. Most of the electric energy is used for chlorine-caustic and magnesium production, with a relatively small amount required for lighting, pumping, etc.

The Dow power production takes place in three separate plants, electrically interconnected, each of which is designed to meet a definite need with available equipment at the time of design. This accounts for the wide difference in their design features. In fact, Plant B is probably the only power plant ever built with a "topping" turbine being installed during the original construction.

AMERICAN SMELTING AND REFINING COMPANY, CORPUS CHRISTI, TEXAS

The Corpus Christi plant of the American Smelting and Refining Company produces zinc and cadmium by the electrolytic process and generates the necessary power in a steam power plant producing both direct and alternating current. The a-c generators are of the conventional type and were manufactured by Westinghouse Electric Corporation. D-c generating sets, also of Westinghouse manufacture, consist of a turbine, reduction gear, and a double armature d-c generator, the armatures being placed back to back which places the commutators on each end of the rotor. A part of the direct current is generated and load balance is achieved by the use of one 2500-kw Allis Chalmers mercury arc rectifier.

Steam is produced at 400 psig and 750°FIT. Three of the boilers are located inside the brick power-plant structure and the new boiler presently being installed is a semi-outdoor installation. The firing aisle is enclosed as an extension of the building. Circulating water is provided by conventional mechanical draft cooling towers located adjacent to the building. The plant is entirely functional in its design, there being no fuss or frills. To provide power for an expansion program now underway at Corpus Christi, the American Smelting and Refining Company has arranged to purchase up to 10,000 kw from Central Power and Light Company and rectify it at 600 volts with mercury arc rectifiers for additional zinc production.

REYNOLDS METALS COMPANY, SAN PATRICIO WORKS

The San Patricio Works is located near Corpus Christi, Texas, and all direct current for the reduction of aluminum is generated at the works by spark-ignited gas engines driving d-c generators.

Two types of engines are used: Cooper-Bessemer LSV-16 cylinder horizontal exhaust-gas, turbo-charged engines and General Motors 16-358X vertical engines. Each engine has 60-cycle a-c motors driving its lubricating pump, jacket water pump, fan, and scavenging blower in the case of the General Motors engine. The jacket water and lubricating oil are cooled by fan-blown, extended-surface heat exchangers just outside the building. Two speed motors are used for temperature regulation of jacket water and lubricating oil running at either high or low speed according to the weather.

The a-c power to drive auxiliaries as well as for general use is generated by nine Cooper-Bessemer LSV-16 engines driving 2500-kw a-c generators.

There are three power houses: one, housing 33 Cooper-Bessemer LSV-16 engines for d-c production; one, housing 41 General Motors 16-358X engines for d-c production; and one, housing 9 Cooper-Bessemer LSV-16 engines for a-c production. In addition to generating facilities, the a-c power house contains distribution load centers and an 8-cylinder LeRoi engine driving a small alternator for dead starting purposes. After starting, each a-c unit's auxiliaries are driven by the a-c power generated by that unit which requires an auxiliary transformer for each a-c unit. This gives the maximum of reliability.

The Cooper-Bessemer engines are air-started in the conventional manner and the General Motors engines are started by motoring the generator on the bus.

The buildings are steel frame with corrugated aluminum siding and each has an overhead crane. In the case of the horizontal engines, the buildings are of one-story construction and for the vertical engines, they are of two-story construction. The vertical generators are on the first floor and the engines are on the second. The generators are surrounded by a steel plate cylinder which supports the engine.

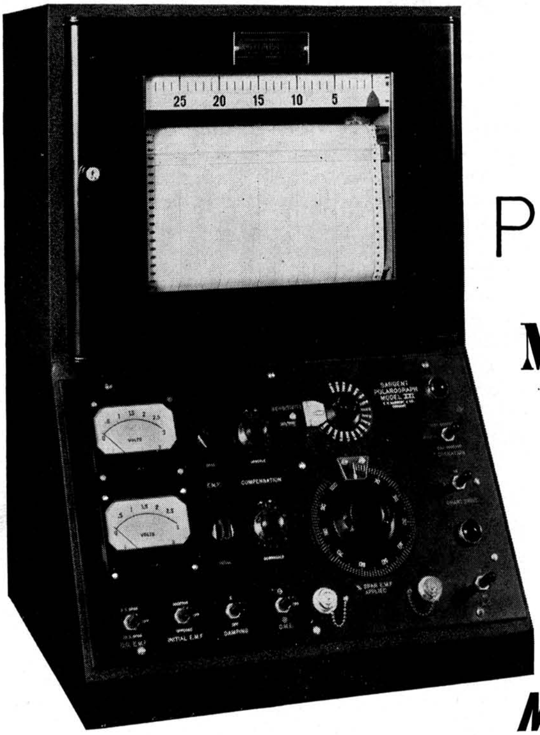
A large amount of ventilating air is required for the buildings, as all generators are self-ventilated. Each engine has as one of its auxiliaries a ventilating fan to supply and distribute its proportional amount of ventilating air.

All generators, switch gear, and load centers are of General Electric Company manufacture, and the d-c buses are aluminum bars.

Almost 1,800,000 kw of installed generating capacity are devoted to the electrochemical industry on the Gulf Coast area. This is an impressive total and is almost certain to become much greater within the next few years.

Acknowledgment

The author appreciates information in this article that was made available to him by the Aluminum Company of America, American Smelting and Refining Company, Columbia-Southern Chemical Corporation, Diamond Alkali Company, The Dow Chemical Company, and the Reynolds Metals Company.



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Structural Properties of Some Synthetically Prepared Manganese Dioxides[1]

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ABSTRACT

Various forms of manganese dioxide have been made by methods described in the literature and examined by chemical analysis, x-ray and electron diffraction, and electron microscopy. Conclusions reached by previous workers mainly from x-ray analysis have, in general, been confirmed, but some new facts emerge, the most important being evidence of slightly differing forms of α-MnO_2 dependent in part on crystal size, and of the presence of layers of MnO and γ-Mn_2O_3 or Mn_3O_4 on the surface of certain of the preparations.

INTRODUCTION

Elucidation of the structure of naturally occurring manganese dioxides has proved to be a topic of very great difficulty. Owing to the importance of this material in electrochemical applications, a good deal of attention has recently been paid to the nature of materials prepared synthetically under controlled conditions. Out of many references to work of this nature we quote three of a general character; a paper on the solid oxides and hydroxides of manganese by Moore, Ellis, and Selwood (1), a review of certain better characterized manganese oxides by Cole, Wadsley, and Walkley (2), and a study of manganese dioxides by Delano (3) based on several thousand x-ray diffraction photographs.

From a consideration of these and other papers, the following general conclusions on the state of knowledge of the manganese oxides may be made. Three forms of manganese dioxide exist, α-MnO_2 or cryptomelane, β-MnO_2 or pyrolusite, and γ-MnO_2 or ramsdellite. The designation γ has also been used for certain dispersed forms of manganese dioxide, but since opinion seems to be in favor of these being poorly crystalline ramsdellite no confusion exists in giving this name to both. A further modification, manganous manganite, is known which changes to α-MnO_2 on heating. Of the lower oxides, two varieties of Mn_2O_3 are known to exist, α and γ, the x-ray diffraction pattern from the form being almost identical to that given by Mn_3O_4. The monoxide, MnO, completes the series.

Recently we have had occasion to prepare a large number of samples of manganese dioxide for electrochemical examination and this has given us an opportunity of carrying out chemical analyses and structural examinations, the latter by electron microscopy, and x-ray and electron diffraction. Some interesting points have emerged from this study and are described below.

EXPERIMENTAL

X-Ray, Electron Microscope, and Electron Diffraction Techniques

Photographs of the manganese oxides, prepared as rod-shaped specimens about 0.3 mm in diameter with water and gum tragacanth, were taken on a Metropolitan-Vickers demountable x-ray set using a 9 cm powder camera. Unfiltered iron radiation was used, the manganese dioxide specimen acting as its own β filter. The wave length of the α radiation was taken to be 1.9373 Å (4).

The electron micrographs were obtained, using standard techniques, by means of a Metropolitan-Vickers E.M.3 instrument, and most of the electron diffraction was also carried out on the same instrument. This enabled a direct comparison to be made between the appearance of the specimen and a diffraction pattern from a related portion of the observed image. Some use was also made of an electron diffraction instrument of the type described by Finch (5).

For an accurate determination of the interplanar spacings by electron diffraction we used thallous chloride as a codeposited standard, as suggested recently by Boswell (6). $a_o = 3.834$ Å was taken as the length of the edge of the cubic cell (7).

Preparative and Analytical Techniques

All materials used were of Analar purity and solutions were made up with distilled water.

The samples obtained were analyzed for available oxygen, that is oxygen in excess of the formula MnO, total water, and, in some cases, potassium. Available oxygen was determined by the method of Eberius and Le Blanc (8) in which the oxide is

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[1] Manuscript received March 5, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

TABLE I. *Preparative methods and analytical data*

Preparative method	Comments on preparation	Analysis
1. β-MnO_2 from manganese nitrate	Modified Bhatnagar procedure [see (1) p. 863]	$MnO_{1.98} \cdot 0.2H_2O$
2. $MnSO_4 + (NH_4)_2S_2O_8$	[See (10) p. 3040 and (1) p. 865]. Washed by decantation with hot water and filtered through a No. 4 sintered glass filter 2*a*. Dried over concentrated H_2SO_4 for several days, and finally over phosphoric acid 2*b*. Dried at 60°C for several days 2*c*. Dried at 100° C for several days	2*c*. $MnO_{1.95} \cdot 0.25 H_2O$ agreeing exactly with Selwood, *et al.*, (10). No potassium found but there seemed to be some ammonia present which was not removed by heating for 24 hr at 200°C in oxygen
3. $K \cdot MnO_4 + MnSO_4 + KNO_3$	Same as for the method given in (1) p. 3040, for the preparation of the γ II oxide except the preparation was separated through a No. 4 sintered glass filter. The sulfate-nitrate solutions were divided into portions (*a*), (*b*) and (*c*) and treated separately, in the case of (*c*) with a considerable excess of permanganate. These preparations were dried at 100°C	Not so reproducible as for 2, e.g., 3*a*. $MnO_{1.93} \cdot 0.17 H_2O$ 3*b*. $MnO_{1.90} \cdot 0.20 H_2O$ 3*c*. $MnO_{1.88} \cdot 0.41 H_2O$
4. 100 g $KMnO_4$ in 600 ml distilled water. 50 ml concentrated HCl added drop wise	Washed by decantation and finally separated through a No. 4 sintered glass filter 4*a*. Dried at 100°C 4*b*. Used directly for diffraction and microscopy	(*a*) Analyzed as $MnO_2 \cdot 0.82 H_2O$ and (*b*) as $MnO_{1.928}$ but both were associated in addition with $(K_2O)_{0.139}$
5. Commercial B.D.H. sample of manganese	Some of this sample was heated at 530°C for 100 hr	Composition as received $(K_2O)_{0.106}$ $MnO_{1.92}$ $(H_2O)_{1.09}$

TABLE II. *Structural details*

	Results from x-ray and electron diffraction and electron microscopy
Prep. 1.	Well crystallized. Indexed on a b.c. tetragonal unit cell with a_o = 4.404 ± 0.001 Å; c_o = 2.873 ± 0.001 Å. E.D.: superimposed patterns from relatively few single crystals of β-MnO_2. Electron microscopy showed massive aggregates of relatively small surface area.
Prep. 2.	Very diffuse x-ray diffraction lines with spacings 4.03, 2.42, 2.12, 1.63, 1.39, 1.06 Å agreeing almost exactly with Selwood, *et al.* (1). Electron microscopy of 2*a*, *b*, and *c* showed remarkable agglomerates and straw shaped particles as shown in Fig. 1 and 2. Fig. 2 closely resembles an electron micrograph taken from α-MnO_2 by McMurdie and Golavato (11). Electron diffraction showed three different patterns either singly or together corresponding to: (*a*) A face-centered cubic structure, Fig. 3, identified as MnO (rock salt structure) a_o =4.43 Å. (*b*) Sharp diffractions of either Mn_3O_4 or γ-Mn_2O_3 as described in (1). (*c*) A highly resolved pattern of a type described by Butler and Thirsk (12) from α-MnO_2 with a body-centered tetragonal unit cell calculated as: a_o = 9.88 ± 0.03 Å, c_o = 2.845 ± 0.005 Å, a_o/c_o = 3.47. The c_o axes of small crystallites in parallel array lying along the long axis of the needles of Fig. 2 which thus are composite.
Prep. 3.	X-ray analysis for these comparable preparations showed them to be very different in structure. All the lines were rather diffuse. 3*a*. Mixture of the γ form with some α-MnO_2. 3*b*. α-MnO_2 predominated over the γ form. 3*c*. Only α-MnO_2 observed. Electron micrographs similar to Fig. 2; aggregates similar to Fig. 1 not observed. Electron diffraction gave the three patterns as described above but the α-MnO_2 was more finely crystalline. In this case the pattern corresponded to a body-centered tetragonal lattice with a_o = 9.81 ± 0.003 Å, c_o = 2.86 ± 0.01 Å, a_o/c_o = 3.43. By x-rays the dimensions for the α-MnO_2 were: a_o = 9.85 ± 0.02 Å; c_o = 2.852 ± 0.006 Å; a_o/c_o = 3.45.
Prep. 4 and 5.	X-ray photographs of preparations 4 and 5 were identical and corresponded to manganous manganite. The *d* spacings for preparation 4 are listed in Table III together with those for the corresponding oxide prepared by Copeland, Griffiths, and Schertzinger (13). They are to be compared in the same table with the two preparations of α-MnO_2 referred to above and with the pattern from preparation 5 after sintering, showing this preparation after heat-treatment also to have become a well crystallized α-MnO_2.

heated with hydrochloric acid, the chlorine evolved being forwarded by carbon dioxide and adsorbed in potassium iodide solution. The iodine liberated, estimated by titration with a sodium thiosulfate solution, standardized against potassium iodate.

Water was estimated by Penfield's method (9) and potassium by a flame photometer.

The various oxides were prepared as shown in Table I, most of the methods being quite standard. Table II includes x-ray and electron diffraction data and comments on the electron microscopy. Table III is concerned particularly with the effect of sintering on the oxides.

TABLE III. *Comparison of the reflections of manganous manganite and* α-MnO_2

Prep. 4a		Prep. 5		Manganous manganite prepared by Copeland, Griffiths, and Schertzinger (13)		Prep. 3c		Prep. 5 heated at 530°C for 100 hr		
I	d	I	d	I	d	I	d	I	d	hkl
S	7.39	S	7.25	MS	7.13	S	7.03	S	7.00	110
						M	4.94	S	7.92	200
VW	3.64	VW	3.63	W	3.53	VW d	3.49	W	3.48	220
						MS vd	3.12	VS	3.12	130
								VW	2.452	400
W	2.43	W	2.44	M	2.41	S vd	2.401	S	2.396	121
								VW	2.195	240
				VW d	2.14	M d	2.150	S	2.151	301
								VW	1.926	150
						W d	1.826	MS	1.832	141
								VW d	1.637	600
						W d	1.539	MS	1.540	251
W	1.415	W	1.414	VW	1.418	W	1.424	M	1.430	002
						VW d	1.355	M d	1.354	451
								VW	1.298	312
a_o = 10.4 c_o = 2.84 a/c = 3.65		a_o = 10.3 c_o = 2.84 a/c = 3.63		a_o = 10.0 c_o = 2.84 a/c = 3.52		a_o = 9.85 ± 0.02 c_o = 2.852 ± 0.006 a/c = 3.454		a_o = 9.83 ± 0.01 c_o = 2.862 ± 0.003 a/c = 3.434		

All reflections from preparation 4*a* and preparation 5 as received were diffuse, from preparation 5 sintered, sharp. VS, very strong; S, strong; MS, medium strong; M, medium; W, weak; VW, very weak; d, diffuse; vd, very diffuse. All cell dimensions in A.

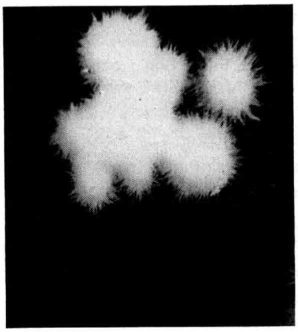

FIG. 1. Electron micrograph of MnO_2 prepared from ammonium persulfate and manganous sulfate. Gold shadowed 45°. × 5300.

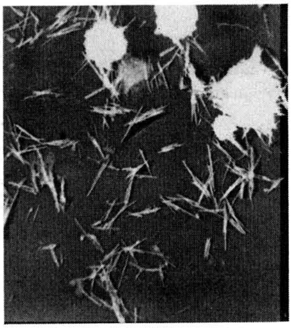

FIG. 2. Electron micrograph of α-MnO_2 formed in preparation 2. Gold shadowed 45°. × 5300.

DISCUSSION

Table I is self-explanatory except in the case of preparation 2. Glemser (14) gives the formula of the oxide prepared in this way as $MnO_{1.93}$. Glemser's results, however, require further examination since his figures for the oxygen/manganese ratio do not seem to do justice to the analyses. He determined available oxygen, total manganese, and water. From each of the first two, the percentage manganese dioxide was calculated and the composition given as a mean of the two different determinations. We prefer to express the manganese in terms of manganese oxide. A general formula for a manganese oxide may then be written as $x\mathrm{MnO}\cdot y\mathrm{O}^*\ z\mathrm{H_2O}$ (where O* is the available oxygen) which may be rearranged as $\mathrm{MnO}_{1+y/x}\cdot\frac{z}{x}\ \mathrm{H_2O}$. When Glemser's results are recalculated in this way, the values for the oxygen/manganese atomic ratio are in better agreement with the values of other workers. In the present case, the formula of Glemser's oxide becomes $MnO_{1.96}\cdot 0.30\ H_2O$. It appears, therefore, that this method of preparation gives an oxide of reproducible composition.

The electron micrographs given by preparation 4 resembled those of Fig. 1, but the oxide was apparently in a more finely dispersed state. This was confirmed by the electron diffraction patterns. The latter only showed MnO with certainty and more diffuse patterns which corresponded with the presence of Mn_3O_4 or γ-Mn_2O_3.

The electron diffraction patterns from preparation 5 before heat-treatment corresponded to those previously described as due to MnO and Mn_3O_4. No other characteristic pattern was observed.

Attempts were made to remove the surface oxide layers from these preparations by prolonged refluxing with nitric acid followed by washing and drying at room temperature, but we were unable to make any alteration detectable by electron diffraction; the conclusion is reached that, in the cases described, definite lower oxides of manganese are present on the surfaces of the aggregates and fine particles may consist almost entirely of the lower oxides. In view of the very large surface of some of the specimens, the presence of lower oxides must contribute significantly to the departure from stoichiometry of the mass of material if, as is customary, one regards the dioxide as a homogeneous material.

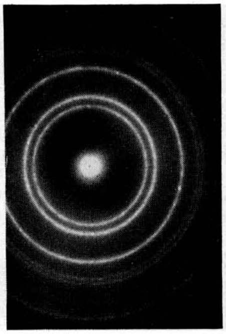

FIG. 3. Electron diffraction picture from surface oxide (MnO).

A criticism of this work may be levelled at the possibilities of decomposition taking place during the photographing of the specimens by the combined action of the electron beam and the high vacuum.

It was suggested to the authors[2] that there might be some possibility of reduction by traces of vacuum oil in the system. The phenomena of carbon deposition on specimens by the action of the electron beam is well known and may be demonstrated very clearly by glancing incidence electron microscopy. There is little doubt that the process must occur during the examination of our oxides, although no evidence was found of the characteristic pattern from cracked carbon films.

Glemser and Einerhand (15), studying the higher nickel oxides, reported the presence of nickelous oxide by electron diffraction, but associated in this case with apparent decomposition of the specimen.

We have noted the presence of NiO in higher nickel oxides when using electron diffraction, but unfortunately our specimens are of such a form that electron microscopy is incapable of showing any change in the appearance of the specimen. It should be added that the Finch instrument with silicone-filled diffusion pumps yields results with both the manganese and nickel oxides similar to those with the E.M.3 instrument.

Some of the above experimental observations would indicate that reduction in the beam is quite a possibility. Nevertheless the authors do not consider them to be conclusive. The lower oxides are not observed in all the specimens and when they are seen, not necessarily on the most reactive dioxides; preparation 5, for example, was very unreactive but shows strong MnO diffractions.

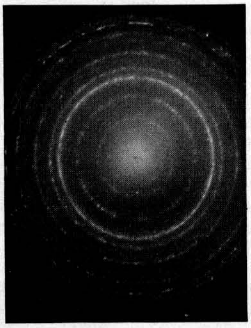

FIG. 4. Electron diffraction pattern from α-MnO_2 prepared from ammonium persulfate and manganous sulfate.

The whole phenomenon seems to be one requiring the most careful examination, particularly from workers dealing with reducible systems and using electron diffraction and microscopy. The point is of importance since electron diffraction is by far the most powerful technique for surface studies of this type and a knowledge of these effects, whether artifacts or not, is most essential.

Several interesting points emerge from an examination of the data in Table III. First, the process of increasing crystallinity is accompanied by a large decrease in the a_o parameter, the c_o parameter changing but slightly. This is best shown by the variation in a_o/c_o. This would infer that the Copeland, Griffiths, and Schertzinger preparation is more highly crystalline than either of our own, a fact which is borne out by the appearance of an extra

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[2] By private communication from N. C. Cahoon.

reflection (301) in the diffraction photograph from their oxide. Second, preparation 3*c*, which from the diffuseness of the diffraction lines is not as crystalline as the heated preparation 5, is shown to have a slightly larger unit cell. What the actual rearrangement within the unit cell corresponding to these changes in cell dimensions is we can only surmise, but this may be solved by closer attention to and measurement of the actual intensities during recrystallization. Here we seem to have good evidence that manganous manganite is a poorly crystalline form of α-MnO_2.

ACKNOWLEDGMENTS

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Oxidation of Metals at High Temperatures[1]

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ABSTRACT

The available data on the oxidation rates of pure metals from 300° to 1000°C have been analyzed in terms of concentrations of defects in the oxide structures and defect diffusion coefficients. Quantitative agreement with the diffusion theory is obtained in the cases of p-type oxides such as cuprous oxide and nickel oxide, in which cationic vacancies arise by solution of oxygen at the oxide-oxygen interface. The parabolic oxidation rates in the cases of some n-type oxides, such as zinc oxide and zirconium oxide, are characterized by low activation heats and large negative activation entropies. In some of these cases anionic diffusion seems likely. In the case of zinc oxide, the diffusion of radiozinc during oxidation supports the cationic diffusion mechanism. The data on linear oxidation rates fall into two classes; evidence is presented to show that one class represents reaction at the oxide-oxygen interface, and the other, reaction at a metal-oxygen interface.

INTRODUCTION

Considerable new data have been obtained in recent years on the oxidation rates of pure metals from 300° to 1000°C. It is the purpose of this paper to analyze the factors that control the absolute values of these rates. Our understanding of these reactions is based on the pioneer experimental and theoretical work of Wagner (1) and on the Wagner-Schottky analysis of defects in ionic crystals (2).

The present treatment is divided into six sections: (*a*) the empirically observed rate laws are set forth; (*b*) the laws of diffusion of reactants through a growing oxide film are described; (*c*) the defects in oxide structures, which provide diffusion mechanisms, are discussed in terms of statistical thermodynamics; (*d*) cationic diffusion coefficients in metal oxides are analyzed in terms of defect concentration and defect mobility; (*e* and *f*) the observed oxidation rate constants are related to the results of the preceding sections.

EMPIRICAL RATE LAWS

If a coherent, nonscaling oxide film is formed, most of the measurements of metal oxidation above 300°C can be fitted to the *parabolic law*,

$$dy/dt = k_1/y \qquad \text{(I)}$$

where k_1 is the *parabolic rate constant.* On integration with the initial conditions, $y = y_0$ at $t = 0$, equation (I) becomes

$$y - y_0 = \Delta y = 2k_1(t/\Delta y) - 2y_0 . \qquad \text{(II)}$$

This is probably the best form in which to apply the law, since it allows one to discard the initial oxygen uptake, and to set the origin of time, $t = 0$, at any desired film thickness y_0. If the law is followed, a plot of y against $(t/\Delta y)$ gives a straight line, the slope of which is $2k_1$, and the intercept, $-2y_0$. The calculated y_0, however, will usually have little quantitative significance, in view of the uncertain initial surface area, nonisothermal initial conditions, and possible departures from the parabolic growth law in the first stages of oxidation. The advantage of the use of equation (II) is that it provides a method for discarding all these initial uncertainties.

In some cases a linear growth law has been observed, $dy/dt = k_0$. The transition from a parabolic to a linear rate is usually associated with a breakdown of the film, as, for example, in the oxidation of magnesium above 500°C (3). In some cases, however, a linear law has been observed even with a coherent film, for example, in the oxidation of titanium above 800°C (4), or in the oxidation of molybdenum with nitric oxide (5). In such instances, it has been concluded that the diffusion of reactants through the film is rapid compared to the actual interface reaction rate.

An intermediate type of rate law has also been considered,

$$dy/dt = k_1/(k_2 + y). \qquad \text{(III)}$$

This represents a case in which diffusion and interface reactions have comparable specific rates. On integration with $y = 0$ at $t = 0$, equation (III) yields

$$y = 2k_1(t/y) - 2k_2 . \qquad \text{(IV)}$$

This expression is identical in form with equation (II), and in no experiments so far reported have the effects of an initial surface film and of a possible

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[1] Manuscript received March 24, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

departure from the parabolic law been adequately separated. Instead of trying to make this separation by an analysis of initial rates, it would appear to be more useful to study systems to which equation (III) might apply even over extended periods of reaction. Such systems might be expected at high temperatures and low oxygen pressures when the oxide film is an oxidation semiconductor like cuprous oxide. For example, it has been reported (6) that the oxidation of pure iron in carbon dioxide-carbon monoxide mixtures follows a parabolic law below 900°C and a linear law at 1000°C, so that the intermediate region might provide a suitable experimental illustration of equation (IV).

THE DIFFUSION PROBLEM

The typical situation that arises during the growth of an oxide film on a metal is shown in Fig. 1. To focus attention on a concrete example, let us suppose that the metal ions diffuse through the oxide, by way of interstitial positions, and react at the oxide-oxygen interface. The diffusion of oxygen in the opposite direction is assumed to be negligible. If the concentration of interstitial ions at any point x in the oxide is c_i, and the diffusion coefficient for the interstitial ions is D_i, the diffusion is governed by the equation

$$D_i \delta^2 c_i/\delta x^2 = \delta c_i/\delta t. \qquad \text{(V)}$$

The problem is complicated by the motion of the outer boundary, at $x = y(t)$. If we introduce $r = x/y$, equation (V) becomes

$$D_i y^{-2} \delta^2 c_i/\delta r^2 = \delta c_i/\delta t - r y^{-1} y' \delta c_i/\delta r \qquad \text{(VI)}$$

where $y' = dy/dt$. It is evident that the equation is separable only if $yy' = k_1$, i.e., the parabolic rate law. In this case,

$$(D_i/k_1)\delta^2 c_i/\delta r^2 + r\delta c_i/\delta r = 2t\delta c_i/\delta t. \qquad \text{(VII)}$$

With the boundary conditions $c_i = c_0$ at $r = 0$; and $c_i = c_1$ at $r = 1$, the solution of equation (VII) is

$$c = c_0 + \frac{c_1 - c_0}{\text{erf } (k_1/2D_i)^{\frac{1}{2}}} \text{erf } [(k_1/2D_i)^{\frac{1}{2}} r]. \qquad \text{(VIII)}$$

This represents a steady-state solution of the diffusion equation, so that $c = c(r)$ for all t, but c is not a linear function of r, as c would be of x in the case of a stationary outer boundary.

The growth rate of the film is

$$dy/dt = k_1/y = -D_i(\delta c_i/\delta x)_{x=y}(n_i + c_1)^{-1} \qquad \text{(IX)}$$

where n_i is the number of metal ions per unit volume in a stoichiometric oxide structure. Hence,

$$k_1 = -D_i(n_i + c_1)^{-1}(\delta c_i/\delta r)_{r=1}. \qquad \text{(X)}$$

Writing $(k_1/2D_i)^{1/2} = z$, we obtain the solution as given by Booth (7),

$$\pi^{1/2} z \exp(z^2) \text{ erf}(z) = (c_0 - c_1)(n_i + c_1)^{-1}. \qquad \text{(XI)}$$

The relation between k_1 and the diffusion coefficient D_i is obtained by solving this equation. A simple result is found when $z << 1$, i.e., when $(k_1/2D_i)$ is a small fraction. It will be shown in equation (XII) that $k_1/D_i \sim f_i$, the fraction of defects in the oxide, interstitial ions in this example. Since f_i is usually below 10^{-3}, it is possible to apply the solution of equation (XI) valid for small z to most practical cases. Since c_1 is much less than n_i, equation (XI) thus becomes

$$2z^2 = (c_0 - c_1)\, n_i^{-1} = f_0 - f_1 \qquad \text{(XII)}$$

and

$$k_1 = D_i\,(f_0 - f_1).$$

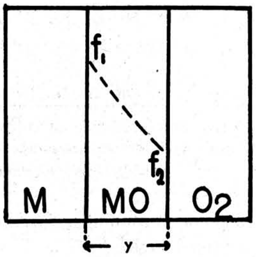

FIG. 1. A growing oxide film on a metal. The mole fractions of interstitial metal ions at the interfaces are f_1 and f_2.

This is exactly the expression obtained for steady diffusion through a slab of constant thickness.

The general solution of equation (VII) is

$$c = \exp\,(z^2 r^2/2) \sum_A t^{-A/2} \cdot [\alpha_A F_{1+A}(\sqrt{2}zr) + \beta_A F_{1+A}(\sqrt{2}izr)]. \qquad \text{(XIII)}$$

The $F(\sqrt{2}zr)$ are the parabolic cylinder functions. It is necessary to consider whether any solutions of this form can be found for physically reasonable boundary conditions. The requirement that the film growth proceeds through the diffusion of metal imposes in itself a boundary condition, operative at $r = 1$,

$$(-D_i/y)\ (\delta c_1/\delta r)_{r=1} = (n_i + c_i)^{-1}_{r=1}(dy/dt).$$

If we try to fit this condition with conditions representing reaction rate expressions at either boundary, we are led back to the time-independent solution with constant concentrations at each boundary as the only possible answer. Thus a necessary condition for the parabolic growth law of an oxide film, if the growth rate is controlled by diffusion, is that the concentrations of the diffusing species be constant at the boundaries.

The problem of the growth law with a rate-determining reaction at the outer boundary has not yet been solved for the case of a moving boundary. By analogy with the above discussion, however, it may be expected that the corresponding solution for a stationary boundary is a good approximation if the defect concentration in the oxide is small. Let us consider, therefore, a layer of oxide extending from $x = 0$ to $x = y$, with a constant concentration of interstitial ions at the metal-oxide interface, and a first-order surface reaction with rate constant k_2 cm sec^{-1} at the oxide-oxygen interface. By analogy with the solution of the exactly corresponding problem in heat conduction (8), we obtain for the steady-state concentration,

FIG. 2. Schematic representation of cationic vacancies in Ni:O (*a*) ■ undissociated vacancy, (*b*) ◪ singly dissociated vacancy, (*c*) □ doubly dissociated vacancy.

$$c/c_0 = 1 + (k_2/D_i)\,(y - x)/1 + (k_2/D_i)y.$$

Hence the rate of growth of the film,

$$\begin{aligned} dy/dt &= -(n_i + c_y)^{-1}D_i(\delta c/\delta x) \\ &= (n_i + c_y)^{-1}(k_2/D_i)c_0/1 + (k_2/D_i)y. \end{aligned}$$

Since $n_i >> c_y$,

$$dy/dt = (k_2c_0/n_iD_i)/\ 1 + (k_2/D_i)y. \quad \text{(XIV)}$$

This has the form of equation (III), and on integration with the initial condition $y = 0$ at $t = 0$,

$$y = (2c_0/n_i)\ t/y - 2D_i/k_2. \quad \text{(XV)}$$

The above expressions are all based on the diffusion of uncharged particles, whereas in a growing oxide film the diffusing species is more likely to be an ion. This problem has been discussed by Mott and Gurney (9). The results for low temperatures and thin films show many interesting special features (10), but the only result we require is that applicable to thick films and high temperatures, where the net effect of the space charge is to introduce a factor of 2 (for completely dissociated defects and electrons) into the relation between parabolic rate constant and diffusion coefficient. Thus, instead of equation (XII), we have

$$k_1 = 2D_i\,(f_0 - f_1). \quad \text{(XVI)}$$

DEFECTS IN OXIDES

The diffusion of ions through the oxide films is greatly facilitated by the occurrence of defects in the oxide structures, such as interstitial ions and vacancies. In most cases, the mobility of the defects is so much higher than that of ions in normal lattice positions that the entire observed diffusion can be ascribed to the defects.

The defects can be divided into two classes, stoichiometric and nonstoichiometric. The former are those described by Frenkel and Schottky. The nonstoichiometric defects are the results of solution of an excess of metal or of oxygen in the oxide. An excess of metal can occur through an interstitial solution of metal atoms (which may be dissociated to ions and electrons), or through vacancies at some of the normal oxide-ion sites with electrons attached to the positive hole (and these complexes may be entirely or partially dissociated). An excess of oxygen can dissolve in the oxide either in the form of interstitial oxygen atoms (possibly dissociated) or in the form of vacant cation sites with a corresponding number of electrons removed from neighboring ions. In Fig. 2, these cation vacancies are shown for the case of nickel oxide.

We shall consider a few examples that are of special importance in the study of high temperature oxidation rates.

Zinc Oxide

If zinc oxide is prepared by the thermal decomposition of zinc oxalate, or by the complete oxidation of zinc in oxygen, it has an extremely low electrical conductivity, of the order of 10^{-7} ohm^{-1}cm^{-1} at 25°C. If this material is heated in air at 1000°C and then cooled, its conductivity is greatly enhanced to about 10^{-2} (11).

It has usually been assumed that the increased conductivity is caused by the formation of interstitial zinc atoms (Zn_i) according to the following reactions (12):

$$\begin{aligned} &ZnO\ (c) = Zn\ (g) + \tfrac{1}{2}\,O_2 && (A) \\ &Zn\ (g) \ \ = Zn_i && (B) \\ \hline &ZnO\ (c) = Zn_i \quad + \tfrac{1}{2}\,O_2. && (C) \end{aligned}$$

The standard free energy of reaction (A), ΔF^0_1, can be obtained from the measured equilibria in the reduction of ZnO by CO or H_2 (13). The ΔF^0_2 of reaction (B) can be calculated from the partition function of zinc vapor as an ideal monatomic gas, and that of the interstitial zinc as an ideal solute in the zinc oxide crystal. The result obtained for the mole fraction f of interstitial zinc atoms in equilibrium with zinc vapor at 1 atm is

$$-\ln f = (U/RT) + \ln (2\pi m\nu^2)^{3/2} (kT)^{-1/2} A. \qquad \text{(XVII)}$$

Here U is the energy necessary to transfer a zinc atom from the vapor to an interstitial position; ν is the vibration frequency of the interstitial zinc atom; m is the mass of a zinc atom; and A is a conversion factor from cc atm to ergs. A convenient notation for small fractions of defects is to write $pf = -\log f$, so that equation (XVII) becomes

$$pf = U/4.57T + \log (2\pi m\nu^2)^{3/2} (kT)^{-1/2} A. \qquad \text{(XVIII)}$$

In order to calculate the concentration of interstitial zinc from the over-all reaction (C), it is necessary to add $\Delta F_1^0/4.57T$ to the pf in equation (XVIII).

An estimate of U can be obtained as follows. The structure of zinc oxide is based on a hexagonal closest packed array of oxide ions, with zinc ions occupying half the tetrahedral holes. Let us assume that interstitial zinc atoms enter the octahedral holes. These have a radius of 0.67 Å, whereas the radius of the zinc atom in metallic zinc is 1.39 Å. The energy U_0 to introduce a sphere of radius a_1 into a smaller spherical hole of radius a_2 in an isotropic elastic medium (14) can be calculated from the formula,

$$U_0 = \frac{6\pi a_2^3}{(\alpha + 1)\beta_1} (\Delta/a_1)^2 \qquad \text{(XIX)}$$

with

$$\alpha = (1 + \gamma_2)/2(1 - 2\gamma_2)\, a_2\beta_2/a_1\beta_1 .$$

Here β_1 is the compressibility of zinc, 1.7×10^{-6} cm²kg⁻¹; β_2 is the compressibility of zinc oxide, 0.75×10^{-6}; $\Delta = a_2 - a_1$; γ is Poisson's ratio for ZnO, taken to be 0.25. The estimated contribution to U is then 10 kcal/mole. This figure will be lowered by the Van der Waals attraction between the zinc atom and the surrounding oxide ions, which can be estimated from the London equation,

$$E_0 = -(3/2)\, I_a I_b/(I_a + I_b)\, d_A d_B/r^6.$$

The I's are the ionization potentials, the d's the polarizabilities, and r is the internuclear separation. In this case, $I_{\mathrm{Zn}} = 9.4$ ev, $I_{\mathrm{O}^-} = 54.8$ ev, $d_{\mathrm{Zn}} = 2.00$, and $d_{\mathrm{O}^-} = 2.75 \times 10^{-24}$ cc; $r = 2.80$ Å. Thus $E_0 = 0.125$ ev/pair, or 17 kcal for the six oxide ions surrounding an octahedral hole.

From the elastic distortion and the Van der Waals terms, therefore, $U = -7$ kcal, an estimate subject to uncertainty but probably of the right order. It is unlikely that ν is less than 10^{12}, and this figure will be used in the calculation of pf. The results are shown in Fig. 3. Curve A is the equilibrium value of Zn_i from the reaction $\mathrm{ZnO} = \mathrm{Zn}_i + \frac{1}{2}\mathrm{O}_2$, with an oxygen pressure of 0.2 atm. Curve B gives the concentrations of Zn_i in equilibrium with zinc vapor at 1 atm, and curves C and D, the concentrations in equilibrium with liquid zinc and solid zinc, respectively.

The extent of dissociation of interstitial zinc atoms into ions and electrons is indicated by the electrical conductivity σ of zinc oxide. There seems to be general agreement that plots of log σ vs. T^{-1} can be represented by two straight lines (15). The temperature coefficient of σ in the low temperature region (about 25°C) may be ascribed to the thermal excitation of an electron from the interstitial zinc atom into a "conduction band," $\mathrm{Zn}_i = \mathrm{Zn}_i^+ + \mathrm{e}$. The concentration of electrons from such a dissociation can be calculated (16) from the equation,

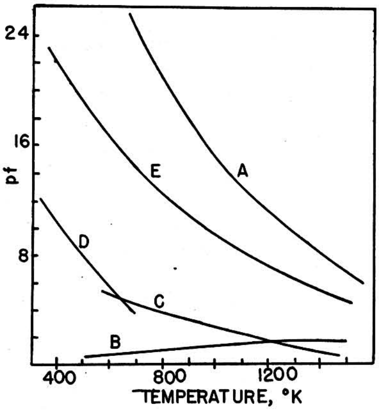

FIG. 3. Calculated fractions of interstitial atoms or ions in zinc oxide. (A) Interstitial Zn in ZnO in equilibrium with air; (B) in equilibrium with zinc vapor at 1 atm; (C) in equilibrium with liquid zinc; (D) in equilibrium with solid zinc; (E) interstitial Zn⁺ ions in ZnO in equilibrium with air.

$$\begin{aligned} n(N - n)^{-1/2} &= 2V^{1/2} (2\pi\, mkT/h^2)^{3/4} \exp(-E_1/2kT) \\ &= 4.55 \times 10^8\, T^{3/4} \exp(-E_1/2kT). \qquad \text{(XX)} \end{aligned}$$

Here n is the number of electrons, N is the number of donor atoms, V is the volume of the crystal, m is the electronic mass, and E_1 is the energy difference between the donor level and the conduction band. For $\frac{1}{2} E_1$ we may take the activation energy of the low temperature conductivity, about 5.5 kcal (11).

It is worthwhile to notice the structural factors that determine the value of E_1. We may write $E_1 = e_1 + e_2 + e_3 + e_4$. The e_1 is the Madelung energy of the Zn_i^+ ion, which can be calculated readily by the method of Frank (17). The e_2 is a distortion energy provided by the fact that the ion occupies less volume than the atom. The e_3 is the energy to remove the electron from the atom, which may be set equal to I_1/κ^2, with κ the dielectric constant of ZnO, and I_1 the first ionization potential of Zn. The e_4 is the polarization energy e_p. Introducing the values for these quantities, we obtain $E_1 = 11 = 25 - 9 + 2 - e_p$, so that the polarization energy can be estimated as 7 kcal.

Combining equations (XVIII) and (XX), we obtain

$$pf^+ = \tfrac{1}{2}pf + 3.23 - \tfrac{3}{4}\log T + E_1/9.14T \quad \text{(XXI)}$$

where f^+ is the equilibrium mole fraction of Zn_i^+. The values of pf^+ from this equation are shown in curve E of Fig. 3.

The observed activation energy for the high temperature conductivity varies from 16 to 28 kcal, apparently depending on the concentration of donors. It is likely that at temperatures up to 1000°K the production of new donors does not appreciably affect the observed conductivity, which is probably determined by the second ionization of "frozen" interstitial atoms.

The response of the conductivity to changes in oxygen pressure is almost instantaneous above 770°K (18). It is evident that adsorption of oxygen on the oxide surface can provide effective traps for the conduction electrons, with a consequent fall in the conductivity (19).

It is of interest to consider why dissociation of ZnO does not give anion vacancies $\square_a$, according to

$$2ZnO = 2Zn^+ + \square_a + \tfrac{1}{2}O_2 .$$

The ΔH for this reaction can be estimated from the following steps:

$$\begin{array}{ll}
O^=(c) = O^=(g) + \square_a & e_m - e_p \\
O^=(g) = O + 2e & A_1 + A_2 \\
O = \tfrac{1}{2}O_2 & D/2 \\
2e(g) + 2Zn^{+2}(c) = 2Zn^+(c) & e_m - 2e_p' - 2I_2.
\end{array}$$

$$\text{Thus} \quad \Delta H = 2e_m - (e_p + 2e_p') - \frac{D}{2} - (A_1 + A_2) - 2I_2 = 963 - (e_p + 2e_p').$$

With the reasonable estimates (20, 21), $e_p' = 160$, $e_p = 450$, $\Delta H = 193$ kcal, which is considerably larger than the ΔH for forming interstitial zinc atoms. If the $\square_a$ were formed by solution of Zn(c) in ZnO, the ΔH would be lowered, by the heat of formation of ZnO, to $193 - 83 = 110$ kcal.

In crystals such UO_2, however, there is evidence that anion vacancies do occur, with U^{+3} ions to preserve electrical neutrality (22). The transition $U^{+4} \rightarrow U^{+3}$ releases more energy than $Zn^{+2} \rightarrow Zn^{+1}$. One may, in general, expect to find anion vacancies in oxides in which the metal ion bears a charge of +4 or more.

We have not considered stoichiometric defects in this discussion. They will, of course, occur to some extent, but their formation requires much more energy than that of interstitial excess ions. Consider, for example, the energy E_3 required to move a zinc ion from a normal lattice site to an interstitial position, leaving a vacant cation site. $E_3 = e_m - e_p + e_i$. The e_m is the Madelung energy of ZnO; e_p is the polarization energy of the positive vacancy; and e_i is the energy of the interstitial Zn_i^{+2} relative to that of the gaseous ion. For ZnO, e_m is 970 kcal; and e_i is about 50. From the calculations on CaO and MgO (20) it is unlikely that e_p is more than 450 kcal. Thus E_3 is about 570 kcal. This energy is so much higher than the energy of formation of excess Zn_i^{+2}, that we can ignore such stoichiometric defects. A similar conclusion will probably be valid for all stoichiometric defects in oxides that involve the removal of a multiply charged ion from a normal to an interstitial position.

Another possibility is that defects in ZnO might occur through the formation of vacant anion sites with a pair of singly charged Zn_i^+ ions to preserve electrical neutrality. Such a defect would appear to be most unlikely from an energetic standpoint since it would involve the loss of the large Madelung energy with the recovery of even less polarization energy than in the Frenkel type with cation vacancies.

Beryllium Oxide

Few data are available on defects in BeO, which has the same structure as ZnO. It is interesting, however, to predict from the thermodynamic data the relative concentrations of Be_i^{+2} ions and Zn_i^{+2} ions. The heat of sublimation of Be at its melting point is 78 kcal, compared to 31 kcal for Zn. Considering this predominant factor alone, we should expect the concentration of Be_i^{+2} to be less than that of Zn_i^{+2}, for the oxides in equilibrium with the solid metals, by a factor of $\exp(78\text{-}31)/3RT$, or about 6×10^3 at 1000°K. For interstitial ions arising from the dissociation reaction, the difference in ΔF_1^0 between ZnO and BeO would introduce a factor of $\exp(102/3RT)$ at 1000°K, or about 6×10^7.

Cuprous Oxide

The discussion of the formation of interstitial atoms and ions given for ZnO can be applied also to Cu_2O. The reaction $Cu_2O = \tfrac{1}{2}O_2 + 2Cu_i^+ + 2e$ would in fact have a lower ΔF^0 than the corresponding ZnO reaction, so that one might at first expect a considerable concentration of interstitial Cu_i^+ in the oxide in equilibrium with air. On the other hand, the vapor pressures of solid and liquid copper are much lower than those of zinc, so that the concentration of interstitial copper in the oxide in equilibrium with the metal would be much lower than in the case of Zn-ZnO.

Interstitial copper is not actually found in Cu_2O in equilibrium with air, because the solution of excess oxygen in the oxide is a more favorable reaction:

$$\tfrac{1}{2}O_2 + Cu_2O = 2Cu^{+2} + 2\Box_c + 2O^{=} \qquad (D)$$

where $\Box_c$ denotes a vacant cation site. If the vacancies produced by this reaction are more numerous than the interstitial ions, the latter at equilibrium will be virtually annihilated by the reaction $Cu_i^+ + \Box_c = Cu^+$. This is simply the reverse of the reaction leading to stoichiometric Frenkel defects, which has a low equilibrium constant. One factor that favors a reaction like (*D*) for Cu_2O as compared to ZnO is the relative ease of formation of the Cu^{+2} ion: $Cu^+ = Cu^{+2} + e - 20.3$ ev; $Zn^{+2} = Zn^{+3} + e - 40$ ev. It is necessary, however, to divide these ionization potentials by κ^2, about 40, so that this contribution to the energy difference would appear to be only about 0.5 ev or 12 kcal. Thus the energetic factors for excess metal and for excess oxygen are often closely balanced. The entropy factor favors loss of oxygen from the oxide rather than solution of oxygen in the oxide, and at 1000°K this difference in $T\Delta S$ may amount to 20 to 40 kcal. It has been found that Cu_2O heated in O_2 contains excess oxygen, whereas Cu_2O heated in vacuum may contain excess copper (23). Although ZnO heated in air contains excess zinc, it is likely that in oxygen at high pressure, or in equilibrium with energetic oxygen species such as O_3 or O_2^+, ZnO would dissolve excess oxygen, with a formation of Zn^{+3} or O^- ions to preserve electrical neutrality.

The most accurate measurements of the oxygen excess in Cu_2O appear to be those of Wagner and Hammen (24). The pressure dependence of the solubility from their data is as $P_{O_2}^{1/5}$, whereas from equation (*D*), with practically complete association of vacancies and positive holes, we should expect a $P_{O_2}^{1/4}$ dependence. From their data one obtains $\Delta H^0 = 7.4$ kcal for the heat of formation of one *associated* cation vacancy. The concentration of associated vacancies in equilibrium with air is given by the empirical equation,

$$pf = (7400/4.57T) + 1.82. \qquad \text{(XXII)}$$

The activation energy E for the high temperature conductivity of Cu_2O is from 8 to 18 kcal. The E may be set equal to $\tfrac{1}{2}\Delta H^0 + \tfrac{1}{2}U$, where U is the energy required to free the trapped positive hole. Thus U is about 20 kcal.

The experimental ΔH for vacancy formation can be used to obtain an estimate of the polarization energy at the vacancy and the Cu^{+2} site, by means of the following cycle:

$$\begin{array}{lll}
Cu^+(c) & = Cu^+(g) + \Box_c & e_m - e_p \\
Cu^+(c) & = Cu^{+2}(c) + e & I_2 - e_m - e_p' \\
Cu^+(g) + e & = Cu\ (g) & I_1 \\
Cu(g) + \tfrac{1}{4}O_2 & = \tfrac{1}{2}Cu_2O & e_f \\
\tfrac{1}{2}Cu_2O + \tfrac{1}{4}O_2 & = Cu^{+2} + \Box_c + O^{=} & \\
 & \multicolumn{2}{l}{\Delta H = I_2 - I_1 - e_p - e_p' - e_f.}
\end{array}$$

Introducing the experimental quantities, we obtain $27 = 470 - 179 - 102 - (e_p + e_p')$, or $e_p + e_p' = 162$ kcal. Calculations for NaCl (20, 21) indicate that the e_p at a vacant Na^+ site is 56 kcal if the ions are held rigidly in place, or 110 kcal if the ions are free to move to new equilibrium positions. It is reasonable that e_p should be lower in the Cu_2O structure, for a Cu^+ site has two $O^{=}$ neighbors at 3.01 Å, compared with the six Cl^- neighbors at 2.31 Å of Na^+ in NaCl.

Manganous, Ferrous, Cobaltous, and Nickelous Oxides

These oxides behave as typical *p*-type semiconductors, with an excess of oxygen and vacant cation sites. Ferrous oxide is not stable below 560°C, decomposing into Fe and Fe_3O_4; and the FeO structure may contain a large excess of oxygen, up to 1.3 atom per cent in equilibrium with iron, or from 1.9 (700°C) to 3.5 (1300°C) atom per cent in equilibrium with magnetite (25, 26). The solution of oxygen can be represented by

$$2M^{+2} + \tfrac{1}{2}O_2 = O^{=} + \Box_c + 2M^{+3}\ (O^-). \qquad (E)$$

The question of whether the positive hole resides on metal ions, on oxide ions, or on both, must in this case be considered in some detail, since removal of an electron from an M^{+2} ion is related to the third ionization potential, as compared to the considerably easier process in cuprous oxide, which is related to the second ionization potential of copper.

The energies required to abstract an electron from M^{+2} and $O^{=}$ can be estimated on the basis of an ionic model for the oxide structures by consideration of the following two cycles: (*a*) removal of M^{+2}; $M^{+2} = M^{+3} + e$; replacement of M^{+3} in solid. The net result is the removal of an electron from an M^{+2} ion in the crystal, and the required energy is $W_m = I_3 - e_m - e_p'$, the e_p' being the polarization energy resulting from replacement of an M^{+2} by an M^{+3} in the crystal. (*b*) Removal of $O^{=}$; $O^{=} = O^- + e$; replacement of O^- in solid. The net result is the removal of an electron from an $O^{=}$ in the crystal, and the required energy is $W_o = e_m - A_2 - e_p''$, the e_p'' being the polarization energy resulting from replacement of an $O^{=}$ by an O^-, and A_2 the electron affinity of O^-. The numerical values in ev are summarized in Table I, the polarization energies being estimated from the rigid structure calculations on oxides having the same crystal structure (20). These estimates indicate that it is somewhat easier to remove an electron from an M^{+2} than from an $O^{=}$, thus supporting the usual picture (27) that the positive hole is an M^{+3} ion. It must be remembered, however, that the K series of x-ray emission spectra from such oxides (28) displays a broad band, about 10 to 15 ev wide, which has usually been attributed (29) to transitions from what is called the "$2p$ band of the oxide ions" to the vacant K level in the oxide ions. The band width is much larger than the probable energy differences between W_m and W_o, and it seems likely that the band contains electrons from both the metal and the oxygen. One might call the positive hole a hybrid of $Ni^{+3}O^{=}$ and $Ni^{+2}O^{-}$ structures. The trapping of the positive hole at the site of the cation vacancy would not significantly alter this picture, since the activation energy required to release the trapped hole is less than 2 ev [NiO(30)]. There is an experimental value of the thermionic work function of NiO of about 4.5 ev (31), a figure consistent with the removal of an electron from the top of a band 10 ev wide, whose center lies at about −10 ev, as in Table I.

TABLE I

	MnO	FeO	CoO	NiO
I_3	33.7	30.6	33.5	35.4
e_m	20.5	20.7	20.9	21.1
e'_p	4.2	4.3	4.4	4.5
A_2	6.5	6.5	6.5	6.5
e''_p	2.9	2.8	2.7	2.6
W_m	9.0	5.6	8.2	9.8
W_o	11.1	11.4	11.7	12.0

We may now consider the energies ΔH to form cation vacancies in FeO, CoO, and NiO. In the case of FeO, the experimental value (26) of ΔH for the solution of one atom of oxygen from O_2 into the FeO phase is −56 kcal at 25°C. If the figure is compared with a ΔH calculated from the usual cycle, the polarization energy $e_p + e'_p$ can be estimated as 437 kcal, which is about half the Madelung energy. The estimated heats of formation of vacancies in CoO and NiO by solution of oxygen from O_2 would be −23 and −14 kcal, respectively. These figures refer to undissociated vacancies.

CATIONIC DIFFUSION COEFFICIENTS IN THE OXIDES

The diffusion of cations in oxides like those under consideration proceeds almost entirely by way of the defects. Thus the cationic diffusion coefficient D can be written (32) to a very good approximation as the diffusion coefficient for a defect D_i times the probability of finding a defect, i.e., the defect fraction f_i,

$$D = D_i f_i . \qquad \text{(XXIII)}$$

If the solid is in equilibrium with its environment, the defect fraction is an equilibrium quantity, which can be related to the standard free energy of formation of defects, or calculated by statistical thermodynamics. In some cases, however, the f_i may have a nonequilibrium value as the result of "freezing" of defects produced at higher temperatures.

The defect diffusion coefficient D_i can be related to the difference in free energy between an initial configuration and one at the saddle point between two free energy minima a distance d apart. Thus Eyring (33) has obtained

$$D_i = (RTd^2/Nh) \exp (\Delta S_i^*/R) \exp (-\Delta H_i^*/RT). \qquad \text{(XXIV)}$$

A typical equation for the formation of defects in a p-type oxide was equation (E), for which the equilibrium constant can be written as

$$K = (+)^2(\square_c)P_{O_2}^{-1/2},$$

so that for completely dissociated vacancies and positive holes, $(\square_c) = K^{1/3}P_{O_2}^{1/6}$. In this case, therefore,

$$f_i = \exp (\Delta S^0/3R) \exp (-\Delta H^0/3RT)P_{O_2}^{1/6} .$$

The general form of equation (XXIII) for D therefore becomes:

$$D = (RTd^2/Nh) \exp [(n^{-1}\Delta S^0 + \Delta S_i^*)/R] \exp [(n^{-1}\Delta H^0 + \Delta H_i^*)/RT]P_{O_2}^{\frac{1}{2}n} . \qquad \text{(XXV)}$$

The n is an integer equal to the number of particles formed by dissociation of the defect. A similar expression is found for an n-type oxide, except that the ΔS^0 and ΔH^0 refer to the formation of an interstitial metal ion.

In order to separate the two factors in D, an independent determination of the variation of defect concentration with temperature is necessary. Then one can evaluate ΔS^0 and ΔH^0, and hence the ΔS_i^* and ΔH_i^* for the defect mobility.

The D_i for defects is expected to have a small ΔS_i^*, probably slightly positive (34, 35). A large negative ΔS_i^* for defect mobility strongly indicates short-circuiting diffusion paths, such as those provided by grain boundaries. The effective diffusion coefficient in a polycrystalline material will then depend on the fraction of the cross-sectional area that is occupied by the grain boundaries. For example, with a grain diameter r, and an effective grain-boundary diameter δ (36), the fraction of open area would be $2\delta/r$. With $\delta = 5$ Å and $r = 100$ Å, the factor is 10^{-1}; with $r = 1000$ Å, 10^{-2}, etc. Thus, in grain-boundary diffusion the effective activation entropy is lowered by $-R \ln (2\delta/r)$.

In metal-oxide systems, we must consider the possibility that both the metal and the oxygen may diffuse along the grain boundaries. In contrast with the situation in metals, however, the ΔH^0 term in equation (XXV) is probably about the same for the grain boundary and the volume formation of defects, so that a major energetic factor in favor of the boundary process does not occur in oxides, so far as metal diffusion is concerned. In oxides without anion vacancies, oxygen diffusion would seem certainly to occur preferentially along the boundaries, perhaps as atomic oxygen. This process will be important in metal oxidation, however, only if it has a rate comparable to or greater than that of the metal diffusion.

Diffusion measurements have been made with radioactive copper in cuprous oxide (37) and radioactive zinc in zinc oxide (38). The copper diffusion was followed in strips of oxide made by the oxidation of spectroscopically pure copper. The surface of the Cu_2O strip was coated with an extremely thin layer of active copper, and the diffusion proceeded at 800° to 1000°C and 10^{-2} cm oxygen pressure. The self-diffusion coefficients could be represented by $D = 0.044 \exp (-36 \text{ kcal}/RT) \text{ cm}^2 \text{ sec}^{-1}$. The D at 1000°C is in excellent agreement with a value calculated from the conductivity data of Wagner (1) by means of the Einstein relation $D = kT\theta\sigma/e^2n$, where θ is the transference number of the Cu^+ ions, e is the electronic charge, and n is the number of Cu^+ ions in a cc of Cu_2O. This agreement indicates that there is no diffusion of copper via uncharged species, such as trapped vacancies.

It is desirable to tabulate diffusion results in oxides under standard conditions, and for a p-type oxide like Cu_2O the best choice for a standard state would appear to be at one atmosphere oxygen pressure. The D's recorded in Table II have been reduced to the standard state under the assumption that they depend on the seventh root of the oxygen pressure, as the conductivities do. The average vacancy concentrations from equation (XXII) are also included in the table. Since $D = D_i f_i$, it is possible to separate the vacancy diffusion coefficients D_i. In the last column of the table is listed the time τ for the vacancy concentration at the center of a 0.02-cm thick slab of oxide to fall to one-tenth of its initial value, after the concentration at the surface is reduced to zero (for example, by exposure of the oxide strip to vacuum). These figures are of interest in connection with the frequently used concept of "frozen defects." In this case, which is probably typical of many p-type oxides, the freezing of vacancies would not be expected until quite a low temperature is reached. It should be noted that τ depends on the square of the thickness of the slab.

If the over-all diffusion coefficients are fitted to equation (XXV), with the use of equation (XXII) to give ΔH^0 and ΔS^0, and $d = 3.05$ Å, $n = 2$, one obtains: $\Delta H^0 = 7.4$ kcal; $\Delta S^0 = -8.0$ cal deg^{-1}; $\Delta H_i^* = 30.1$ kcal; $\Delta S_i^* = 4.6$ cal deg^{-1}. The ΔH^0 and ΔS^0 refer to the formation of undissociated vacancies; the negative ΔS^0 represents the loss of entropy when gaseous oxygen dissolves in the oxide. The ΔH_i^* and ΔS_i^* are in a sense still composite terms, since the vacancy must dissociate before it becomes mobile. The observed ΔH_i^* is made up of about 12 kcal for the dissociation energy and 18 kcal for the activation energy of mobility of the free vacancy.

Disks of ZnO were prepared by sintering the compressed powder. The radioactive zinc was deposited in thin layers, and the decline in surface activity was measured as a function of time and temperature. The measurements were made in air from 1100° to 1600°K, and the results can be summarized in the equation $D = 1.5 \exp (-74 \text{ kcal}/RT) \text{ cm}^2\text{sec}^{-1}$. Thus $\Delta H^* = 72$ kcal.

TABLE II. *Diffusion of copper and cation vacancies in cuprous oxide*

(Standard pressure = 1 atm O_2)

Temp, °C	f_i	D, cm²sec⁻¹	D_i, cm²sec⁻¹	τ, sec
1000	1.0×10^{-3}	9.7×10^{-8}	9.7×10^{-5}	1.1
900	7.9×10^{-4}	2.8×10^{-8}	3.5×10^{-5}	3.0
800	5.9×10^{-4}	7.2×10^{-9}	1.2×10^{-5}	8.6
600	2.6×10^{-4}	1.5×10^{-10}	5.8×10^{-7}	181
400	7.4×10^{-5}	3.9×10^{-13}	5.3×10^{-9}	2.0×10^{4}
200	6.7×10^{-6}	3.5×10^{-18}	5.2×10^{-13}	2.0×10^{8}

The ΔH^0 for the formation of interstitial Zn_i^{+2} has been estimated for reactions (A), (B), and (C) above. $\Delta H^0 = 110 - 7 + 11 + 40$. The first term is the heat of the dissociation of $ZnO = Zn(g) + \frac{1}{2}O_2$; the second term is the heat of solution of zinc atoms in interstitial positions in the oxide; the last two terms are the heats of the first and second ionizations of interstitial zinc atoms. Since $\Delta H^* = \Delta H_i^* + (\Delta H^0/3)$, we obtain the activation heat for the mobility of interstitial Zn_i^{+2} as $\Delta H_i^* = 21$ kcal. The rather low ΔH_i^* appears reasonable when it is recalled that the zinc oxide structure contains a series of channels parallel to the hexagonal axis and joining successive octahedral holes.

If the diffusion of zinc was studied in zinc oxide in equilibrium with solid or liquid zinc, the activation energy would be considerably lower, since the interstitial zinc would then be formed, not by the highly endothermic dissociation of the oxide, but by solution of zinc from the solid or liquid. The expected heat of activation would be $\Delta H^* = \Delta H_i^* + (\Delta H^{0\prime}/3)$, where $\Delta H^{0\prime}$ is the heat of vaporization of zinc plus the heat of solution of the zinc vapor in the oxide to yield interstitial ions. Thus $\Delta H^{0\prime} = 30 + 44 = 74$, and $\Delta H^* = 46$ kcal.

PARABOLIC RATE CONSTANTS

The numerical values of the parabolic rate constants may now be analyzed in terms of the preceding discussion of defect concentrations and diffusion coefficients. The most reliable data are summarized in Table III.

TABLE III. *Parabolic rate constants for metal oxidation*

Temp range, °C	Metal	Oxide	ΔH*	ΔS*	Reference
p-type oxides with cation vacancies					
800–1000	Cu	Cu_2O	33.8	0.5	(37)
			35.5	−0.3	(39)
500–1000	Ni	NiO	34.7	−17.0	(40)
700–1000			35.0	−10.5	(41)
700–1000	Co	CoO	36.3	−10.0	(42)
700–950	Fe	FeO*	22.4	8.6	(43)
400–600	V	V_2O_3	30.7	−7.2	(45)
350–450	Mo	MoO_2	36.5	0.5	(44)
n-type oxides with interstitial metal					
360–400	Zn	ZnO	28.5	−22.6	(46)
350–450	Al	Al_2O_3	21.4	−28.6	(47)
750–950	Be	BeO	50.3	−7.5	(50)
			59.5	−3.4	(51)
700–900	Cr	Cr_2O_3	66.3	+12.0	(52)
500–900	Zr	ZrO_2	32.0	−7.1	(50)
400–500	W	WO_3	45.7	11.0	(44)
250–450	Ta	Ta_2O_5	27.4	−10.0	(53)
n-type oxides with anion vacancies					
200–425	Zr	ZrO_2	16.8	−27.3	(49)
350–600	Ti	TiO_2	24.3	−22.8	(48)

* Outer layer Fe_3O_4.

P-Type Oxides

In these cases, which include copper, iron, cobalt, and nickel, the oxide contains an excess of oxygen with associated cationic vacancies. Diffusion coefficients measured in the oxides exposed to air or reduced oxygen pressures should be directly comparable with parabolic constants measured under the same conditions, since in both the diffusion and the metal oxidation the cation vacancies are formed by the same process, the solution of oxygen at the oxide-oxygen interface.

From equation (XVI), since $f_0 \gg f_1$, $k_1 = 2D_i f_0$. If f_0 is the equilibrium defect concentration, one obtains from equation (XXIII)

$$k_1 = 2D. \qquad \text{(XXVI)}$$

This relation applies when the rate constant and the diffusion coefficient refer to the same oxygen pressure. This relation is closely followed by the experimental data on copper oxidation and diffusion of radiocopper in cuprous oxide (37).

Consider next the growth of FeO on Fe. In all the work so far reported, the oxygen pressure has been such that the oxide film was composed of at least two layers. In the case cited in Table III, the inner layer was FeO and the outer one Fe_3O_4. The microscopically measured thickness of the FeO layer yielded the parabolic rate constants given in the table. From the iron-oxygen phase diagram (25, 26) it is known that the ΔH to transfer an oxygen atom from Fe_3O_4 to FeO is close to zero. Hence, the observed $\Delta H^* = 22$ kcal must be simply the mobility of a cation vacancy in FeO. Since the ΔS for the formation of the vacancy in FeO by solution of oxygen from Fe_3O_4 is, of course, also about zero, the observed positive ΔS^* for the oxidation rate also represents the mobility term alone. This is the normal positive entropy of activation that would be expected owing to the increased randomness attendant on the passage of a cation from a normal site to the saddle point. It may also include a contribution from the dissociation of the vacancy.

In the case of NiO, there is no outer layer of higher oxide, and the equilibrium vacancy concentration at the NiO-O_2 interface is maintained by solution of oxygen from the gas. In Cu_2O the solution of $\frac{1}{4}O_2$ is required for each vacancy, whereas in NiO, $\frac{1}{2}O_2$ is required. Since the entropy of gaseous oxygen is about 48 cal deg^{-1} per mole, a considerable contribution to the negative ΔS^* for nickel oxidation is due to this factor. We do not yet know, however, whether cationic diffusion in nickel oxide proceeds through singly dissociated or doubly dissociated vacancies.

N-Type Oxides

In the cases of zinc, aluminum, beryllium, and chromium, the excess of metal most probably occurs in interstitial positions. Diffusion coefficients measured in the oxides exposed to oxygen cannot be directly compared with the parabolic rate constants, since the excess metal in the oxide, in the one case, comes from a dissociation of the oxide, and, in the other case, from solution from the underlying solid metal. In absence of underlying metal Cr_2O_3 is a *p*-type oxide.

In the case of zinc oxide, it was shown how the ΔH^* for diffusion in air, 72 kcal, would be reduced to 46 kcal for diffusion in ZnO in equilibrium with solid Zn. Even this figure, however, is markedly higher than the observed $\Delta H^* = 29$ kcal for the parabolic rate constant. This ΔH^* is coupled with a large negative ΔS^*, and in fact the parabolic rate constants for Zn, Al, Ti, and Zr all share this peculiarity of a low ΔS^*. It may be noted also that in all these cases the oxidation rate has been measured at a comparatively low temperature and with thin oxide films.

The parabolic rate constants for Be and Cr have normal ΔS^* and rather large ΔH^*. The ΔH^* of 55 for BeO should be predictable from the observed diffusion data on ZnO, since ZnO and BeO have the same crystal structures. The heat of sublimation of Zn is 30 kcal, and that of Be is 78 kcal. This difference would lead to an increase in ΔH^* for the Be diffusion of $48/3 = 16$, so that if this were the only factor involved, the ΔH^* for Be oxidation would be $45 + 16 = 61$ kcal, instead of the observed 55. The 6 kcal difference may be ascribed to the larger polarization energy of the Be^{+2} ion as compared to Zn^{+2}, as well as to a slightly lower activation energy for mobility, due to the smaller size of the Be^{+2}.

No data are available on the Cr-Cr_2O_3 system that would permit an analysis of the observed ΔH^*. If the diffusing species is an interstitial Cr^{+3} ion, one would expect it to be highly mobile. The large ΔH^* would then be due to the heat of sublimation of chromium, a contribution of $84/4 = 21$ kcal from this source; and the energy required to strip three electrons from the interstitial Cr, about 31 kcal from this source; and about 15 kcal for the mobility activation energy. There is as yet no way of deciding, however, whether diffusion of Cr^{+2} ions, or even Cr^+, might not be a more favorable process.

When one returns to Zn, Ti, Al, and Zr, the most puzzling problems in all the oxidation kinetics are encountered. Al follows an exponential type of law below 300°C as does Zn below 350°C. The range of validity of the parabolic law is limited at higher temperatures, for zinc by the melting point at 420°C, for aluminum and titanium by transitions to a linear law at 500° and 750°C, respectively. Titanium oxidation is further complicated by solution of oxygen in the metal. The zirconium case is particularly instructive, since it exhibits a normal diffusion behavior at high temperatures and an extremely low ΔS^* at low temperatures.

The apparently attractive hypothesis that the low ΔH^* and large negative ΔS^* for these reactions indicate grain-boundary diffusion of metal does not withstand closer analysis. The crystallite size in the Al_2O_3 film on Al is so small that no electron diffraction pattern is observed (44), and in the case of ZrO_2 on Zr the crystallite size is probably about 100 Å (50). Thus it is difficult to see how the effective ΔS^* could be lowered by a grain-boundary diffusion by more than about 8 cal deg^{-1}. Diffusion of oxygen ions via anion vacancies, or of oxygen atoms via grain boundaries would provide a mechanism of large negative ΔS^*. In ZrO_2 and TiO_2 anion vacancies would be energetically likely. The adsorption of oxygen from the gas is associated with an entropy loss of about 20 cal deg^{-1} per anion vacancy in these cases. Further experimental work on the diffusion coefficients of anions and cations in these oxides is required to prove this mechanism.

In the case of zinc oxidation, at least five different mechanisms have been suggested: (*a*) diffusion of oxygen inward along grain boundaries (54); (*b*) diffusion of oxygen via anion vacancies; (*c*) diffusion outward of interstitial zinc (55); (*d*) outward migration of interstitial zinc caused by the electric field of surface oxide ions (56); (*e*) a rate-controlling reaction at the oxide-oxygen interface (57). A possible reason for the diverse interpretations might be that not all observers were studying the same process, since the oxidation rate of zinc is very sensitive to the pretreatment of the surface. Thus, 40-hr exposure to oxygen at 400°C can produce about 100 Å of ZnO if the zinc is first "passivated" by dipping in concentrated nitric acid, or about 1000 Å of ZnO if the zinc is first oxidized for 10 hr at 300°C, or about 5000 Å of ZnO if electropolished zinc is exposed directly to oxygen at 400°C.

Measurement of diffusion of radioactive zinc during oxidation should allow one to decide between mechanisms (*a* or *b*), (*c* or *d*), and (*e*). It is unlikely that a distinction could be made between (*c*) and (*d*).

The test cannot be made by the technique used for copper oxidation (58, 59), because the self-diffusion coefficient of zinc at 400°C is much larger than the diffusion coefficient of zinc in ZnO. The procedure used, therefore, was first to oxidize the zinc foil to about 1000 Å of ZnO. It was then rinsed in water, wiped free of excess water, suspended briefly in ammonia vapor, dipped into a solution of radioactive zinc acetate, rinsed in water, and dried. This treatment produced a thin layer of radioactive $Zn(OH)_2$ on the surface, which is converted to ZnO in the subsequent heat treatment. The tracer used was Zn-65. After 50 hr at 400°C, the oxide was removed in 4 to 5 layers by etching in dilute acetic acid. Uniformity of removal was checked by reversal of the interference colors of the oxide. Nevertheless, the etching procedure is a source of major error in the experiments, which, therefore, have only a semiquantitative value.

In Fig. 4 is a plot of the activity of Zn as a function of distance in the oxide layer. From this curve the diffusion coefficient of Zn in the ZnO film can be estimated to be $D = 10^{-16}$ cm^{2}sec^{-1}. The parabolic rate constant at 400°C is $k = 1.8 \times 10^{-16}$ cm^{2}sec^{-1}. This result is good evidence against the mechanisms of oxygen diffusion (*a*, *b*) which would predict virtually no diffusion of the Zn through the oxide. It also tends to disprove the surface reaction mechanism (*e*), which would predict extremely rapid diffusion of zinc, and an almost uniform distribution of Zn* through the oxide layer.

The large negative ΔS^* for the oxidations of zinc and aluminum remains difficult to explain, and further experimental work on these reactions is obviously required.

LINEAR RATE CONSTANTS

Relatively few measurements of the linear rate constants are available, but this subject should be one of increasing interest in view of the fundamental importance of the elementary reactions involved. The available data are summarized in Table IV. The rate constants k_0 are expressed in the form $k_0 = A \exp(-E/RT)$, with A in gram atoms of oxygen per cm² sec. The constants appear to fall into two groups, those with small A and large E, and those with large A and small E.

TABLE IV. *Linear rate constants* $k_0 = A\ e^{-E/RT}$ *for metal oxidation*

Metal	Temp range	A	E	Reference
	°C	*eq cm⁻²sec⁻¹*	*kcal*	
Ca	300-500	6.6×10^{-6}	8.1	(60)
Th	350-500	5.2×10^{-2}	22.0	(61)
Ta	300-500	1.0×10^{-5}	20.8	(5)
Ti	650-930	2.8	43.8	(4)
Al	400-550	6.5×10^{4}	47.7	(47)
Mg	410-575	1.1×10^{5}	50.5	(3)

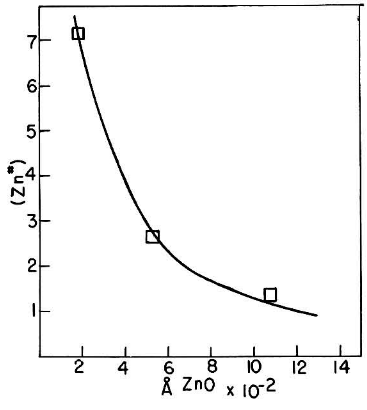

FIG. 4. Diffusion of radioactive Zn in ZnO film on zinc foil. Distribution of Zn after 40 hr at 400°C.

If an over-all reaction proceeds through two consecutive steps, e.g., metal oxidation proceeding through diffusion followed by interface reaction, the step with the smaller activation energy will tend to become rate-determining at the higher temperatures. The linear rate constants for titanium, aluminum, and magnesium, as given in Table IV, have higher activation energies than the parabolic constants for the same metals. It may be concluded that these linear rates are not steps in the low temperature, diffusion controlled oxidation. They probably represent reactions at a metal to oxygen interface, and not at an oxide-oxygen or oxide-metal interface.

In the cases of calcium, thorium, and tantalum, on the other hand, the linear rates may well be reactions at the oxide-oxygen interface, i.e., steps in a sequence of diffusion and interface reaction. It would probably be premature to attempt any more detailed analysis of the linear rates at this time.

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Surface Reactions of Steel in Dilute $Cr^{51}O_4^{=}$ Solutions: Applications to Passivity[1]

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ABSTRACT

Interactions between a steel surface and anions containing chromium-VI were studied by radiotracer methods supplemented by contact potential measurements. In chromate solutions of high enough concentration, the behavior of steel is analogous to that of chromium, i.e., it is passive and is found to remove a definite number of chromate ions from solution. The relationships among solution composition, radioactivity retained on the passive surface, and contact potential indicate that at least a portion of the activity is present as adsorbed chromate ion. In dilute solutions, where corrosion occurs, radioactive chromium in excess of that associated with a passive surface appears on both anodic and cathodic areas.

Deductions relative to the structure of a passive surface are made from these and other data from the chromium-chromate system.

Introduction

An earlier paper (1) gives the results of an investigation of the type and extent of interaction between a chromium surface and chromate ion in solution. In order to have the comparison between a naturally passive and a naturally active metal, many of the experiments performed with the chromium-chromate system were repeated using steel surfaces. The object of this paper is to present these data together with some deductions relative to the structure of passive surfaces.

Other work with radioactive chromate and steel surfaces has been reported (2, 3), but these have been of a preliminary nature with few or no experimental details.

Experimental

The general experimental approach was similar to that described for the chromium-chromate system (1), and consisted of counting the radioactivity retained on a steel surface after contact with an aqueous solution of radioactive chromium-VI anions of given concentration and *p*H. Supplementary data were obtained from changes in contact potential of coupons immersed in inactive solutions of identical concentration and *p*H. Contact potentials were measured vs. abraded and aged platinum by the method of Zisman (4).

Reacting surfaces were prepared from S.A.E. 1020 steel. Disks 2.8 cm in diameter by 0.8 mm thick were used for contact potential measurements, and 3 cm x 6 cm sheets of the same thickness were formed into hemicylinders for immersion in most of the radioactive solutions. This shape was used in order to obtain optimum geometric relationship between counter tube and sample. In the initial experiments where autoradiographs were taken, flat samples were used. Coupon surfaces were abraded just before use with No. 2 emery, scrubbed with thiophene-free benzene and allowed to air dry. This treatment produced a surface (at least partially oxidized) giving satisfactorily reproducible results (±10%).

The roughness factor of the steel surfaces used was not known with the same accuracy as were the counting and contact potential data. Use of a modification (5) of the polarization capacity method of Wagner (6) gave an average value of 20 for the coupons themselves. The roughness factor for Armco iron abraded with No. 2 emery was found by krypton adsorption at liquid nitrogen temperatures to be 3.8. In view of the meager data in the literature for the roughness factor of analogous surfaces, it is at present impossible to assign a very definite value to the roughness factor.

Radioactive solutions were prepared by dilution of a stock sodium chromate solution made with double distilled water. The sodium chromate was obtained by oxidation of spectroscopically pure chromium which had been partially converted to Cr^{51} (1). The systems were open to air.

Results

Effect of Concentration; Passivating vs. Corrosive Solutions

Initial experiments consisted in immersing flat abraded steel plates (2.5 cm x 7.5 cm x 1.55 mm) in

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active chromate solutions in the range of 10^{-4} to $10^{-3}M$ and at *p*H 7.5. This range was dictated by the amount of active chromate available and by the fact that $10^{-3}M$ chromate passivates steel while $10^{-4}M$ does not. The coupons were exposed to 200 ml of solution for 48 hours, at the end of which time three distinct and reproducible behavior patterns appeared:

1. Coupon 1 ($10^{-4}M$ solution), active corrosion with large anodic and cathodic areas. The corrosion products were easily removed by simple wiping and showed a high concentration of radioactive chromium. There was no radioactivity on the anodic areas after removal of the loose corrosion products, but the bright cathodic areas were highly active (see Table I and Fig. 1a). The radioactivity from the cathodic areas could not be removed either by wiping or by scrubbing with filter paper or cloth.

2. Coupon 2 (3 x $10^{-4}M$ solution), most of the coupon remained bright and uncorroded but a few small anodic areas appeared bearing an adherent corrosion product which could not be removed by washing or wiping. The data of Table I and Fig. 1b show that the areas of corrosion product bear some excess radioactivity, but that most of that on the coupon as a whole is distributed over the uncorroded surfaces.

3. Coupons 3 and 4 (7 x 10^{-4} and $10^{-3}M$ solution), remained perfectly bright and free of any visible corrosion product, i.e., were passivated by the chromate solutions. The counting data and autoradiographs (Table I and Fig. 1c) show that within the resolving power of the radiographs in each case a definite and uniformly distributed amount of radioactive chromium was retained on the steel surfaces. This activity could not be removed by any nondestructive physical treatment of the surface such as rubbing, washing, or boiling in distilled water.

Additional information was obtained by returning coupons 3 and 4 to their respective solutions for an additional period of 72 hours. In all instances, coupon 4 remained passive, showing no change either in appearance or in acquired radioactivity. However, coupon 3 in 7 x $10^{-4}M$ solution tended to become badly corroded and picked up additional activity both in the corrosion product and on the cathodic (uncorroded) areas.

The inferences from these data are quite plain. In the case of complete passivation (coupon 4 in 1 x $10^{-3}M$ chromate), a definite amount of uniformly distributed radioactivity appears on the passive steel surface, and is indeed a discrete portion of that surface since it cannot be removed by simple physical means. Where slight attack occurs in the presence of chromate ion (coupon 2 in 3 x $10^{-4}M$ solution), the pickup of radioactivity increases some-

TABLE I. *Radioactivity picked up by steel surfaces*

Chromate conc.	Coupon	c/m	Remarks
1 × $10^{-4}M$	1	377	Extensive corrosion after 24 hours. Distinct anodic and cathodic areas. Corrosion products nonadherent and removed before counting. (Fig. 1a).
3 × $10^{-4}M$	2	175	Few small areas of corrosion. Corrosion product very adherent and not removed. (Fig. 1b).
7 × $10^{-4}M$	3	153	No visible corrosion.
1 × $10^{-3}M$	4	151	No visible corrosion. (Fig. 1c).

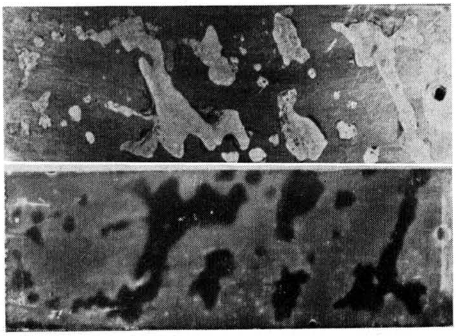

FIG. 1a. A corroded steel coupon after exposure to 1 × $10^{-4}M$ chromate (upper) and its radioautograph. Dark portions of latter are anodic areas on which no Cr^{51} was retained. (Corrosion products removed from anodic areas before radioautographs prepared.)

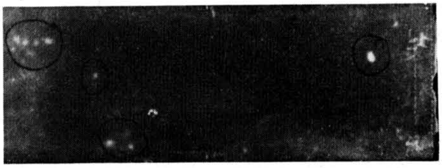

FIG. 1b. Radioautograph of steel coupon showing high concentration of radioactivity at circled spots. These spots are caused by adherent corrosion products. Exposure was to 3 × $10^{-4}M$ chromate.

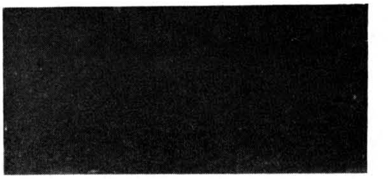

FIG. 1c. Radioautograph of passive steel coupon showing apparent uniform distribution of Cr^{51}. Exposure was to 1 × $10^{-3}M$ chromate.

what and at least a portion of the extra chromium is associated with the points of corrosion, almost certainly with the adhering corrosion product. In the case of intense corrosion resulting in a voluminous, loose corrosion product, the activity picked up by the steel rises sharply, and the increase is found to be associated not only with the corrosion products but also with the cathodic portions of the surface.

Considering now only the case of a steel surface passivated in 1 x $10^{-3}M$ chromate solution of pH 7.5, it was shown that a fixed and reproducible amount of Cr^{51} activity was associated with the passive surface. In terms of chromate ion this radioactivity represents 5.2 x 10^{15} ions per cm² of projected area, or 48 x 10^{-8} grams of chromium per cm². Hoar and Evans (7) have reported 3.4 x 10^{-8} g/cm² of chromium in films stripped from steel passivated in $0.67M$ chromate. Brasher and Stove (2) report 5.5 x 10^{15} chromate ions per cm² are taken up from 0.1 per cent radioactive potassium chromate solution of unspecified pH.

TABLE II. *pH changes produced by steel in chromate solution*

Initial pH	ΔpH
4.2	+0.1
6.0	+0.1
7.8	−0.2
9.25	−1.2
10.3	−0.4
11.15	±0.0

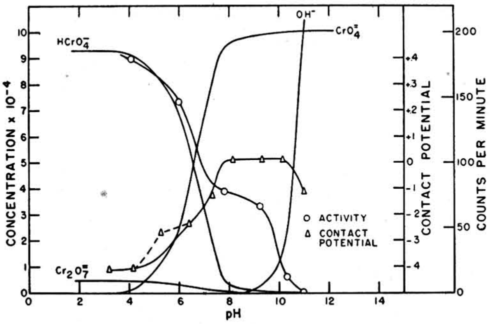

FIG. 2. Relationships among ionic species in solution, pH, activity pickup, and contact potential for steel-chromate system.

Effect of pH *on the Activity Retained by Passive Surfaces*

The data presented in the foregoing section established the fact that at pH 7.5 a steel surface passivated by chromate solution retains a fixed and reproducible amount of chromium in one form or another. In the previous work (1) with passive chromium surfaces in radioactive chromate solutions, a quantitative relationship was found between solution pH and the amount of activity retained by the chromium surface. It was of interest, therefore, to determine if passive steel surfaces exhibited an analogous behavior.

It must be emphasized that, in all experimental procedures which follow, passive, or at least visibly uncorroded, surfaces were dealt with and that at no time was it possible to detect differences among the exposed coupons other than by differences in radioactivity and contact potential.

Solutions originally 1 x $10^{-3}M$ in chromate ion and covering the pH range of 11.1 to 4.2 were prepared as described elsewhere (1). Two sets of initial determinations were made. In the first, the coupons were exposed to the active solutions for 72 hours; in the second, for 120 hours. At the end of these periods coupons were removed, rinsed in distilled water to remove physically adhering solution, blotted dry with filter paper, and counted. Later experimentation showed that the same results could be obtained with one-hour exposures, i.e., the equilibration period of the system did not exceed one hour.

The 72-hour counting data as a function of initial solution pH are plotted as circles in Fig. 2. The overall relationship between activity retained by the passive steel surface and solution pH is identical to that found for chromium in more dilute solutions. Moreover, there was a marked change in pH of the solutions during equilibration just as there was with the chromium-chromate system. These changes are given in Table II and are similar to those for the chromium-chromate system (1).

A point of particular interest is that coupons in the active solutions of pH 11.0 acquired absolutely no radioactivity from solution although they were no different in appearance from the rest.

In an effort to identify the form in which chromium was retained on or by the steel surface, exchange experiments were tried using inactive solutions of sodium chromate and chromium-III nitrate. In neither case was exchange of the surface radioactivity observed in either hot or cold solutions.

Contact Potentials of Passive Steel Surfaces; Effect of pH

Contact potential data were obtained by exposing steel disks to 1 x $10^{-3}M$ nonradioactive chromate solutions covering the pH range of 3.3 to 11.0. All potentials reported are vs. abraded and aged platinum as reference. Positive values indicate a decreasing electronic work function relative to platinum, and negative values an increasing work function. The contact potential of any given steel coupon was found to rise slowly upon removal from chromate solution and exposure to the air, and data were obtained by removing only one coupon at a time from solution and measuring its potential within 30 seconds after washing in distilled water and blotting dry.

The contact potential of the original abraded disks was found to be uniformly +0.4 volt in agreement with the value reported by Uhlig (8). Immersion of these disks in inactive solutions of chromium-VI anions over the *p*H range of 3.3 to 11.0 produced changes from the initial +0.4 volt to the values shown in Fig. 2. The particular data shown are for 24-hour exposure to the solutions. Shorter periods of contact (such as one hour) resulted in curves of identical form but displaced to somewhat lower values (0.05 to 0.1 volt). Coupons exposed to sodium hydroxide of *p*H 11.0 exhibited essentially the same final potential as those in chromate solution of the same *p*H. For example, Fig. 2 shows steel exposed to $1 \times 10^{-3}M$ chromate solution of *p*H 11.0 to have a contact potential of −0.12 volt and to have picked up no radioactivity from solution. The contact potential of a similar coupon in $1 \times 10^{-3}M$ sodium hydroxide (*p*H 11.0) was found to be −0.15 volt.

It should be noted that the entire contact potential curve of Fig. 2 lies at least 0.4 volt below the potential of the original abraded surface. At each point the contact potential (ΔV) of a surface is given by:

$$\Delta V = 4\pi\mu\eta$$

where μ is the dipole moment per unit area, and η is the number of molecules per unit area. Thus, one important consequence of the contact potential data is that the passivation of a steel surface by chromate or dichromate of any *p*H results in a considerable change in its net dipole moment. The direction of change is such that it represents a dipole oriented with its negative end toward the solution side of the interface and its positive end toward the metal. The second consequence is that the net change observed is a sensitive function of solution *p*H just as was the amount of radioactivity retained on the surface.

DISCUSSION

Interpretation of Results

Fig. 2 as a whole represents the effect of solution *p*H as the independent variable on three separate dependent quantities: the radioactivity retained on a steel surface in equilibrium with an active solution of chromium-VI anions, of given *p*H; the contact potential of that surface; and the concentration of the various anionic species present. Inspection of this figure shows that there is almost certainly a relationship between the composition of the solution, the radioactivity acquired, and contact potential. In fact, solution composition rather than *p*H may be regarded as the true independent variable. For example, at *p*H 8.0 and below, the solution changes composition from essentially pure chromate to a mixture of hydrogen chromate and dichromate, and at exactly the same *p*H the activity and contact potential curves undergo a rapid change in slope. In a like manner those portions of the curves between *p*H 11.0 and 8.0 represent a region of constant chromate concentration but an exponentially decreasing hydroxyl ion concentration. Thus, one must conclude that the observed properties of passive steel surfaces given in Fig. 2 are a function of the environment to which they were exposed, i.e., the type and number of anions in solution. In this respect there is complete agreement with the analogous passive chromium-chromate system for which similar contact potential, radiotracer, and *p*H data have been found (1).

In a previous section it was shown that one of the steel surfaces passivated at *p*H 7.5 in $1 \times 10^{-3}M$ chromate solution retained 48×10^{-8} grams of chromium/cm^2, or the equivalent of 5.2×10^{15} chromate ions. Considering this number of ions close packed on the surface with a roughness factor of either 20 or 4, one calculates the equivalent of 0.65 or 3.25 monolayers of chromate ion.

The question naturally arises as to the chemical and physical form of the chromium which has been shown to be firmly fixed in or on a steel surface passivated in chromate solution. In forming conclusions, the following experimental and derived facts were considered:

1. The amount of radioactive chromium retained by a passive steel surface in the solutions employed is a definite and reproducible function of the type and concentration of the anionic species in solution, and through this mechanism a function of solution *p*H.
2. The contact potentials of passivated steels are related to solution *p*H and composition and/or the amount of chromate ion removed from solution. In other words, the average dipole moment of a passive steel surface is a function of the type and relative numbers of anions in the solution producing it.
3. A steel coupon passivated in $1 \times 10^{-3}M$ chromate solution of *p*H 11.0 acquires no radioactivity and exhibits the same contact potential as if in sodium hydroxide alone of the same *p*H. This permits the conclusion that hydroxyl ion rather than chromate ion has determined the passive character of the surface in this instance.

4. Over the *p*H range of 11.0 to 8.0 there exists an inverse relationship between the number of chromate ions removed from solution by steel and the change in hydroxyl ion concentration as indicated by *p*H. In addition it may be shown from Fig. 2 that the activity vs. *p*H curve above *p*H 8.0 is a function of the chromate to hydroxyl ratio.

5. The radioactivity on a passive steel surface is firmly fixed, and does not exchange with either chromium-III or chromium-VI in solution.

6. Roughness factor and counting data indicate a maximum of 3.25 equivalent monolayers of chromate ion removed from solution of *p*H 8.0 and 1 x $10^{-3}M$ in concentration. This may be less if the total area seen by the ions in solution is more closely given by the polarization capacity, a solution method, than by gas adsorption. This is clearly a debatable point which can be settled only by much more extensive work on available 'real' area.

7. The data of Fig. 2 and the facts outlined above are analogous to those of the passive chromium-chromate system where anion exchange properties have been demonstrated (1).

It is concluded that the best interpretation of all of these facts is that these passive steel surfaces must have as their outermost component an equivalent monolayer of irreversibly adsorbed anions. Without this concept it is not possible to explain the dependence of both counting and contact potential data on solution composition, or the relationship between chromate or dichromate ion removed from solution and contact potential. If only the counting and roughness factor data are considered, a decision as to the nature of the surface is more difficult. For example, the activity vs. *p*H curve of Fig. 2 could be interpreted as representing reduction to chromium-III which was then retained on the surface. However, the contact potential data represent changes in dipole moment which cannot be related to a change in extent of a single reaction such as chromium-VI reduction. If such were the case, then the contact potential vs. *p*H curve should bear a constant relationship to the activity vs. *p*H data, which it does not. At *p*H 7.5 and below, for example, the activity and contact potential curves diverge sharply.

The data of Fig. 2 represent, therefore, an indication of the type and relative numbers of the various anions held by the passive steel surface. Between *p*H 11.0 and 8.0 the data represent simply the ratio of chromate ion to hydroxyl ion in the adsorbed layer and this in turn is a reflection of their ratio in solution. At *p*H 11.0, where both ions are of equal concentration in solution, only hydroxyl is adsorbed. At *p*H 8.0 chromate ion is essentially the only anion present, and hence makes up the monolayer. Below *p*H 8.0 the solutions become increasingly poorer in chromate ion and more concentrated in dichromate and hydrogen chromate. Since the activity retained continues to increase over this region, the indication is that chromate ion is continually displaced by dichromate (or polylayer hydrogen chromate) as the concentration ratio changes. In this connection it is of interest to note that the count at *p*H 3.3 is twice that at *p*H 8.0.

In the absence of more conclusive surface area data, it is not possible to say that adsorption is the only process whereby chromate or other anions may become a firm portion of a passive steel surface. For example, work with chromium (1) suggests that an oxide layer rather than the metal itself is the adsorbent for chromate and other anions. In the case of the steel surfaces used, we know them to bear some abrasion-produced oxide layer. It may be that some of the chromate removed from solution goes into the completion of this layer and explains the greater than monolayer coverage. This, however, does not detract from the main argument that at least one equivalent chemisorbed monolayer of chromate or other anion must constitute the outermost surface of passive steel.

Applications to Passivity; Passive vs. Active Metals

Where conditions were such as to induce passivity, the behavior of steel in chromate solutions was analogous to that of chromium. A definite and reproducible amount of radioactivity on the surface was found to be associated with the passive state. The effect of *p*H on activity picked up and on contact potential was found to be the same as that observed for chromium and is explainable on the same basis, i.e., preferential adsorption of a given anion.

The principal difference between the two metals is that chromium was passive in all solutions employed, while steel required a definite and fairly high chromate concentration for passivity. Chromium exhibited a greater affinity for chromate than did steel, since it acquired maximum activity from 5 x $10^{-6}M$ solutions, while steel required a concentration of 1 x $10^{-3}M$ or higher. However, the equilibrium period for steel was only one hour compared to 14 days for chromium.

These data suggest that chromium has a surface with a high tendency to chemically adsorb environmental constituents. This tendency is so great that chromium seldom exists without such a layer, so that replacement of one species by another is a lengthy process. Steel, on the other hand, adsorbs a more select group of species under more stringent conditions, but since abraded steel does not have associated with it any firmly sorbed species, pickup of chromate or other ion should be rapid. In other words, the behavior of chromium is indicative of exchange adsorption, whereas that of abraded steel represents primary adsorption. In either case the end point is the same.

The principal argument up to this point has been that there is associated with a passive steel or chromium surface a definite number of adsorbed anions. The fundamental differences in behavior between steel and chromium which have been outlined above further suggest that this adsorbed layer is an integral part of the passive state rather than a reproducible coincidence. As supporting evidence, consider the instance of chromium in mixed solution of chromate and sulfate or chloride ions (1), where, under adverse ionic ratios, chromate ion is adsorbed as strongly as if present alone, i.e., there is a greater tendency for a passivating anion to appear in the adsorbed layer than a neutral or nonpassivating one. One may, therefore, conclude that the adsorbed layer is itself partially responsible for passivity.

Data from the steel-chromate system add weight to the belief, advanced earlier (1), that a passive surface consists of an oxide layer bearing adsorbed anions of a specific type. In addition to the fact that the postulate of competitive adsorption best explains the experimental data, it is known that the steel surfaces used bore an abrasion-produced oxide which was nonprotective in the absence of specific anions.

The behavior of steel surfaces in chromate solutions of *p*H 11 and above is of particular interest. These surfaces were passive, yet picked up no radioactivity from solution. Passivity under these conditions must be attributed to the presence of hydroxyl ions, and is offered as additional evidence that passivity may be induced by nonoxidizing anions. Robertson (9) has shown that molybdate and tungstate ions in concentrations above $10^{-3}M$ passivate iron, and are comparable to chromate in their action. However, these ions are poorer oxidizing agents than chromate, so that their action may be attributed to adsorption.

The interpretation of a passive surface based on the evidence given here is somewhat similar to that of Hoar and Evans (10) in their revised theory of passivity and inhibition. These authors postulate that the protective value of an oxide is related to the ability of metal ions to migrate through it. A nonprotective oxide is one which is deficient in cations so that ions from the basis metal may migrate from defect to defect until they reach the surface. A corrosion inhibitor or passivator then becomes any environmental constituent which reacts with metal ions at the interface to produce an insoluble product. An accelerator is any ionic or molecular species which forms a soluble product or complex with the metal ions and leaves the way open for further migration. The data presented here, however, indicate that adsorbed anions at the oxide-solution interface rather than reaction products can be responsible for passivity.

ACKNOWLEDGMENT

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Quinones as Ion Source in Hydrocarbons[1]

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ABSTRACT

When orthodihydric phenol solutions in hydrocarbons or dioxane are subjected to oxidation, marked increase in electric conductivity takes place. Various aspects of this observation were studied experimentally, such as: the effect of the time of oxidation; effect of dilution; decay with time of the conductivity; d-c polarization; role of quinone concentration; effect of temperature of oxidation. The experimental results are tentatively explained by a generation during oxidation of intermediate ionic stages of relatively high stability. These oxidative ions, both positive and negative, might be semiquinones having completed electronic shells. Ions of this type appear to be representative of ions formed during oxidation of dielectric liquids.

INTRODUCTION

The purpose of this study was to obtain information on the chemical nature of ions present in oxidized hydrocarbons. In a previous paper (1) the author reported on studies of oxidized aldehyde solutions in hydrocarbons. Those results indicated that, on oxidation, orthodihydric phenols produced conductivities in some ways similar to those found in oxidized oils. It was concluded that ions derivable from such compounds are, to a certain degree, representative of ions in oxidized hydrocarbons. In the present paper a description of experimental results with dihydric phenols, mentioned only briefly in the paper cited, is presented in greater detail. In addition, the possible mechanism of ion formation, as well as their possible chemical structure, is presented.

CONDUCTIVITY OF OXIDIZED CATECHOLS

It was found that, upon oxidation, a solution of a dihydric phenol in a hydrocarbon showed a marked increase in electrical conductivity. The phenols used in these experiments were pyrocatechol and *p*-tert-butylcatechol; the latter was purified by distillation of the Eastman product. The hydrocarbons used were benzene, xylene, 2-2-4 trimethylpentane, *n*-octane, *n*-heptane, a hydrocarbon oil (viscosity 0.14 poise at 25°C) and, in addition, *p*-dioxane. The following oxidizing agents were used: potassium permanganate, potassium dichromate, magnesium perchlorate, silver oxide, sodium perborate, barium peroxide, and ozone. In all hydrocarbons, butylcatechol was used because of its high solubility; pyrocatechol was used with dioxane as solvent. The various combinations of solvents and oxidizing agents gave conductivity effects greatly varying in magnitude; in certain cases there was no effect observable. The experiments were carried out in stoppered graduated cylinders containing the solution and the oxidizing solid, and shaken at intervals.

Typical results are presented in Fig. 1 for benzene as solvent. All conductivities were obtained from bridge measurements using 100 to 1000 cps. The graphs show conductivity as a function of oxidation time for four solid oxidants. The concentration of butylcatechol was 3 millimole per liter. The effect is rather pronounced, the increase apparently continuing beyond the duration of the experiment for $KMnO_4$ and Ag_2O, the two strongest oxidants. In the majority of the combinations a yellow coloration appeared, increasing in intensity with time, as a sign that part of the catechol was converted to *o*-quinone. This point is discussed in greater detail later. On repeating experiments of this kind, the qualitative effect always remains the same, but the magnitude of the conductivities attained may in some cases show appreciable variation.

Fig. 2 presents results on hydrocarbon oil. Curve 1 shows that the effect is again rather pronounced; so was the yellow coloration. The yellow-reddish color of oxidized oils may be due partly to the quinone type of compounds. A control test was carried out with an addition of anhydrous Na_2SO_4 to check whether water formed during oxidation played a role in the conductivity effect; it may be seen that this is not the case. Curve 3 refers to a control test with $KMnO_4$ but without butylcatechol; it may be seen that oxidation of the latter is, indeed, the cause of the effect.

Fig. 3 refers to similar tests on two octanes with a dichromate and a peroxide as oxidants. It may be added that with permanganate the increase in conductivity in octanes was markedly greater.

Fig. 4 presents results with pyrocatechol and dioxane as solvent. The effect is particularly pronounced with silver oxide as oxidant. It may be re-

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called that, according to Willstätter, silver oxide is the best agent for preparing *o*-quinone from catechol in ether solutions (2). Curve 3 refers to a control test with Ag_2O, but without catechol.

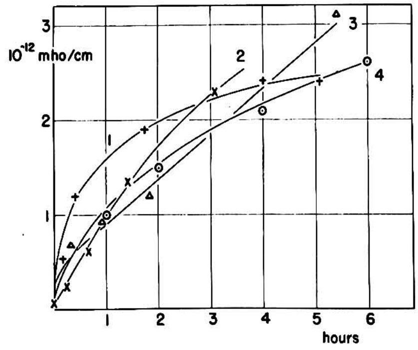


FIG. 1. Conductivity vs. oxidation time for 3 millimole/liter butylcatechol in benzene. Curve 1—$Mg(ClO_4)_2$; curve 2—$KMnO_4$; curve 3—Ag_2O; curve 4—$K_2Cr_2O_7$.

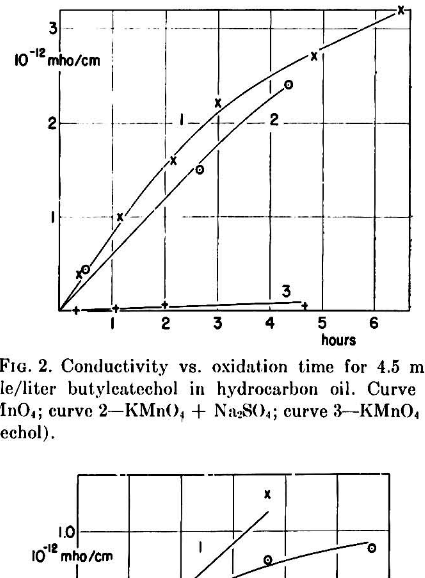


FIG. 2. Conductivity vs. oxidation time for 4.5 millimole/liter butylcatechol in hydrocarbon oil. Curve 1—$KMnO_4$; curve 2—$KMnO_4 + Na_2SO_4$; curve 3—$KMnO_4$ (no catechol).

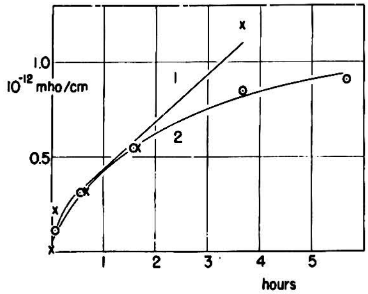


FIG. 3. Conductivity vs. oxidation time for octanes. Curve 1—butylcatechol 3 millimole/liter, trimethylpentane, $K_2Cr_2O_7$; curve 2—butylcatechol 4.5 millimole/liter, *n*-octane, BaO_2.

As mentioned in the author's previous publications, conductivity data are preferably reduced to the same dielectric constant if the variation of the latter in a series of measurements is pronounced. It was ascertained, however, that on oxidizing catechols, this variation is relatively small, and that the effect of the dielectric constant on the conductivity is moderate. The latter is shown for trimethylpentane and dioxane as solvents in Table I, the dielectric constant being increased in steps by additions of small amounts of chloroform. As an example, the total increase of dielectric constant for curve 1, Fig. 3, was 0.012, corresponding to an increase in conductivity of 4 per cent. Similarly, for curve 1, Fig. 4, there is a total increase of dielectric constant of 0.029, corresponding to an increase in conductivity of 16 per cent. These corrections being relatively small, they were not applied to the data covered by this paper.

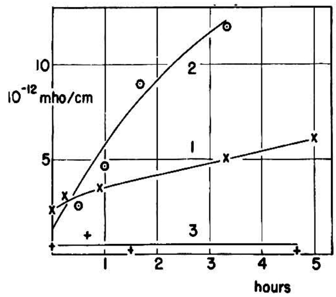


FIG. 4. Conductivity vs. oxidation time for 4 millimole/liter pyrocatechol in *p*-dioxane. Curve 1—$KMnO_4$; curve 2—Ag_2O; curve 3—Ag_2O (no catechol).

TABLE I. *Effect of dielectric constant on conductivity*

Trimethylpentane		*p*-Dioxane	
Dielectric constant	Conductivity	Dielectric constant	Conductivity
	× 10^{-12} *mho/cm*		× 10^{-12} *mho/cm*
1.929	13.7	2.370	4.0
1.933	13.8	2.393	4.6
1.942	14.2	2.415	4.9
1.950	14.7	2.435	5.6
1.974	15.9	2.461	6.4
1.999	17.1	2.493	7.4

A number of check tests were carried out in order to exclude the possibility of incidental causes for the increase in conductivity. In addition to those shown on the previous graphs, a check of *o*-cresol in benzene in contact with $KMnO_4$ may be mentioned. If salt formation were the cause of the effect, substitution of *o*-cresol for catechol should not make a difference since the acid strength of both is about the same. Yet the check test with cresol gave a conductivity of the order of 5×10^{-14}. Water formation also might be a possible cause. When a benzene solution of butylcatechol was kept in contact with water—a rather severe check—the original conductivity of 1×10^{-13} rose in four hours to about 4×10^{-13}, an order of magnitude about $\frac{1}{10}$ of that shown in Fig. 1. Hence, water formation is not a significant element.

In order to exclude the possibility of metals playing a role in cation formation, ozone was used as oxidizing agent. Ozone was generated in a high-voltage corona ozonizator through which oxygen was passed; this, in turn, was bubbled through the catechol solution in the presence of platinum black as catalyst. The order of magnitude of the flow rate was estimated to one microgram of ozone per second. The increase in conductivity for xylene is shown in Fig. 5. Since platinum black is known to act as a physical catalyst, the test excludes metals as possible cations.

Hydrogen ions are excluded since they exist in measurable amounts only in the presence of strong acids, sulfonic, picric, and the like (3), which are not formed when oxidizing catechols. This was substantiated by standard determination of the acid number of a 3.5 millimole per liter butylcatechol solution in benzene. The acid numbers before and after oxidation with permanganate were 0.015 and 0.020, both very low figures. It follows, therefore, that the cations must be organic ions.

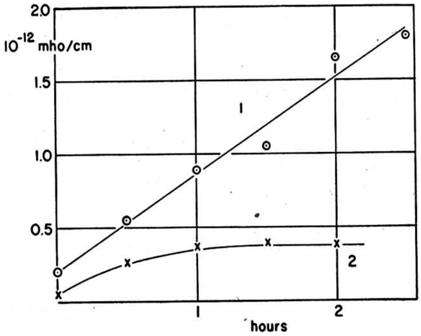


FIG. 5. Conductivity vs. oxidation time for ozone as oxidant in xylene. Curve 1—butylcatechol 6 millimole/liter; curve 2—no butylcatechol.

MECHANISM OF ION GENERATION

The question arises, by what mechanism are ions produced during oxidation of catechols? The question has a rather general importance if this type of ion formation is, as assumed, representative of oxidation processes in insulating liquids.

The chief source of ions is the catechol alone, in contrast to conductivities obtainable by the addition of an aliphatic acid, an amine, and a phenol (1), where three components are involved. Catechol is a weak acid (first dissociation constant in water: 3.3×10^{-10}) and is therefore a proton donor and the source of anions. The corresponding proton acceptor, the source of cations, is in all probability an oxidation product; this is the most likely assumption. There are two possibilities for those ions to be generated.

First, one can think of a thermodynamic equilibrium between the ions and the two parent compounds: the reduced and oxidized form. Let the concentrations of these two forms be c_r and c_o, that of the ions of either sign c_i, then in equilibrium

$$c_i^2 = K c_r c_o \qquad \text{(I)}$$

with K = equilibrium constant. If the solution is diluted with the pure solvent in a ratio $r:1$, both c_r and c_o are reduced by the same factor; hence the new ion concentration c_i' is given by

$$c_i'^2 = \frac{K}{r^2} c_r c_o$$

or

$$c_i'/c_i = 1/r. \qquad \text{(II)}$$

A thermodynamic equilibrium thus leads to a conductivity proportional to the dilution ratio $1/r$.

Second, it is possible that the above equilibrium constant K is so small that practically no ions are produced thermodynamically. This is another way of saying that the basic strength (ability of accepting a proton) of the oxidation product of catechol is too small. Practically nothing is known of the basic strength of *o*-quinones; Egerton and McLean (4), in agreement with others, found that *p*-quinones are very weak bases. Even in this case, ions may be generated kinetically in the process of oxidation. These ions are then not absolutely stable, but may be so relatively. This is possible if the path in reverting from the ion to the stable form leads through a potential hump that slows down the conversion rate to an appreciable degree. Ions of this type, clearly different from those resulting from an electrolytic dissociation, will be called oxidative ions in the present connection. Ions present in the solution by this mechanism are reduced proportionally to the factor $1:r$, if the solution is diluted in a ratio $r:1$. Hence the same conductivity-dilution relation must prevail as in the previous case. Discrimination between the two possibilities by means of dilution tests is not possible.

It can be shown that equation (II) holds in a first approximation for oxidized catechol solutions. Fig. 6 presents on a bilogarithmic scale conductivity σ as a function of dilution ratio r. A dotted line, curve 3, indicates the slope for $\sigma \sim 1/r$. The two experimental curves, for benzene and oil, are, with regard to their slope, close to the dotted line. Acid-amine-phenol solutions show quite differently shaped, downward convex dilution curves (1). Curves from strong acids in dielectric solvents (3) are also convex toward the abscissa, σ at low concentrations varying with the square root of the acid concentration.

While it is not possible on the above basis to differentiate between the two possible mechanisms of ion generation, there are a number of other observations which are in favor of the second mechanism producing oxidative type ions. These observations will be discussed later. It is understood, however, that a definite conclusion in this regard will need further experimental work.

INSTABILITY OF OXIDATIVE IONS

It was observed that in several combinations, although not in all, the solution decanted from the solid oxidant showed a conductivity decreasing with time. Fig. 7 presents two examples of this behavior. On several samples, tested after standing a number of days, the conductivity still showed a high level. Although such behavior is observed in other dielectric liquids also, it may be interpreted as indicating the presence of oxidative ions which, as explained, are not absolutely stable.

The instability is more striking if iodine is used as an oxidant, the iodine being, of course, in solution. As a result of oxidation, the iodine is reduced to hydriodic acid which is a strong acid and soluble in xylene in small concentrations; its effect on the conductivity must be taken into consideration.

From acid number measurements, the percentage of I_2 undergoing reduction was estimated. A 0.2 millimole per liter I_2 solution in xylene had an acidity of $0.06 \times 10^{-3}N$; a 3 millimole per liter butylcatechol solution, $0.23 \times 10^{-3}N$. A solution containing both had an acidity of $0.38 \times 10^{-3}N$, a net increase of $0.09 \times 10^{-3}N$, which corresponds to about 25 per cent of the iodine added.

Next, the conductivity due to HI in xylene was determined (Fig. 8). Although this is a flat S-shaped curve, the average slope corresponds closely to $\sigma \sim \sqrt{c_{\mathrm{HI}}}$, as mentioned before; strong acids behave as typical weak acids in hydrocarbons.

Fig. 9, curve 1, shows the time dependence of σ for a xylene solution of 0.16 millimole per liter I_2 and 3.2 millimole per liter butylcatechol. The amount of HI present is about $0.08 \times 10^{-3}N$, corresponding (Fig. 8) to $\sigma = 0.5 \times 10^{-12}$ mho/cm. The excess of σ for curve 1 above that level is then due to oxidative ions of the catechol. They can be seen to be relatively unstable, in contrast to the ions from HI, shown by curve 2, the concentration of which for the same time of 30 minutes decreases to a much lesser degree.

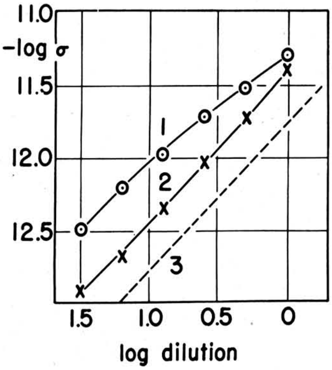


FIG. 6. Conductivity vs. dilution ratio. Curve 1—butylcatechol 3.5 millimole/liter, benzene; curve 2—butylcatechol 4.5 millimole/liter, hydrocarbon oil; curve 3—45-degree line.

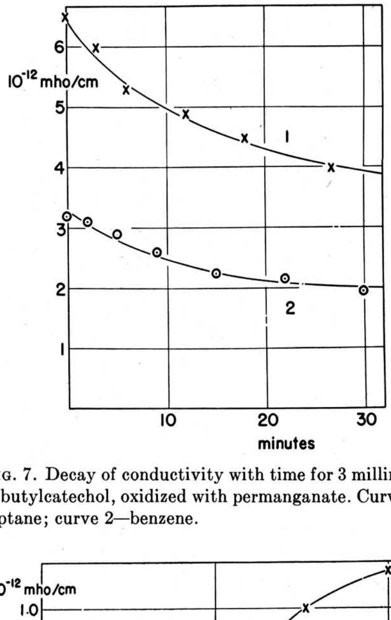


FIG. 7. Decay of conductivity with time for 3 millimole/liter butylcatechol, oxidized with permanganate. Curve 1—*n*-heptane; curve 2—benzene.

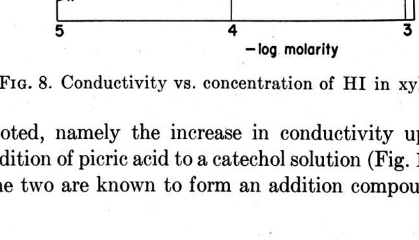


FIG. 8. Conductivity vs. concentration of HI in xylene

In this connection another observation may be quoted, namely the increase in conductivity upon addition of picric acid to a catechol solution (Fig. 10). The two are known to form an addition compound, and, in the course of this process, positive ions of the type postulated above might be formed in the presence of the strong picric acid. These ions are very unstable as curve 1 shows. Curve 2 refers to a control test containing picric acid only; σ is seen to be of a much lower level and stable.

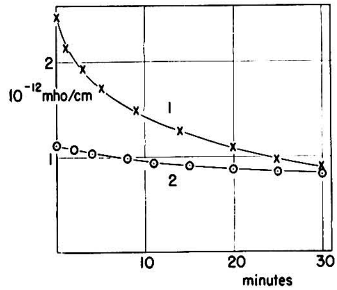


FIG. 9. Decay of conductivity with time in xylene solutions. Curve 1—iodine 0.16 millimole/liter, butylcatechol 3.2 millimole/liter; curve 2—HI 1.3 millimole/liter.

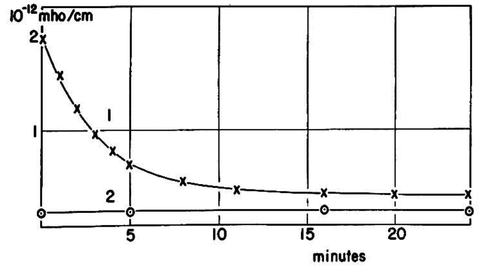


FIG. 10. Decay of conductivity with time in xylene solutions. Curve 1—butylcatechol 2.6 millimole/liter, picric acid 0.17 millimole/liter; curve 2—butylcatechol none, picric acid 0.17 millimole/liter.

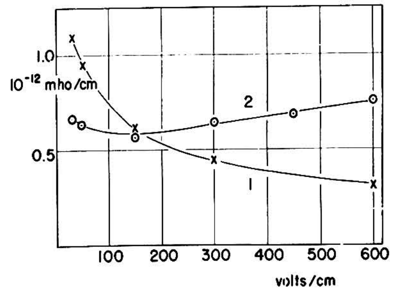


FIG. 11. D-C conductivity vs. field intensity. Curve 1—butylcatechol in xylene, oxidized by permanganate; curve 2—acid-amine-phenol solution in benzene.

D-C POLARIZATION

In measuring the conductivity with direct current instead of alternating current, as in all previous measurements, decreasing conductivity with increasing field intensity is observed, if the original level of conductivity is 10^{-12} or less (see curve 1 of Fig. 11). The initial value, corresponding to the lowest field of 30 volts/cm is some 20 per cent lower than the a-c value. From then on, σ decreases markedly in a range of moderate field intensities. Each value is fairly constant with regard to time. Such a decrease is due to polarization because of the limited number of ion pairs between the electrodes. Ions accumulate near the electrodes of opposite sign; an equilibrium is reached between ion migration in the electric field and diffusion in the opposite direction. Because of the resulting nonlinear potential drop there is an apparent increase of total resistance, more so the higher the current density. For conductivities of around 10^{-11} this polarization was not observed.

In case the ion concentration is immediately restored by electrolytic dissociation, such an effect does not take place. This is shown by curve 2 of Fig. 11, referring to an acid-amine solution. After a flat minimum there is a gradual increase of σ with increasing field, a behavior usually encountered in dielectrics (increase of ionic mobility).

TABLE II. *Effect of further addition of catechol on conductivity*

Concentration of butylcatechol in benzene, millimole/liter	Conductivity, 10^{-12} mho/cm
1.2	6.0
1.9	5.2
2.6	4.9
4.0	4.9
6.1	5.2
9.6	5.7

The d-c polarization as observed can be construed as due to a limited number of ion pairs, consistent with oxidative ion generation.

ROLE OF CATECHOL AND O-QUINONE CONCENTRATION

If all ions were in thermodynamic equilibrium with catechol and its chief oxidation product, *o*-quinone, the concentration of these two should determine the conductivity. Certain experiments were carried out in this respect, and they seem to indicate that this is either not the case or is to only a limited extent.

Table II shows results from a continued addition of butylcatechol to a permanganate-oxidized benzene solution. There is no significant change in σ, indicating that the ion concentration is determined rather by the previous oxidation process.

In another experiment the effect of *o*-quinone was checked. The latter was prepared from catechol according to Willstätter and Pfannenstiel (5), and its conductivity-concentration diagram in dioxane containing 3.6 millimole per liter catechol was established (Fig. 12). There is a pronounced increase of σ, indicating that there is a certain ion concentration determined by equilibrium. The next question was what part this effect played in the oxidation tests.

Fig. 13, curve 1, shows a σ vs. time relation for catechol in dioxane. Next, it was necessary to establish the quinone concentration for each point. This was done by means of a Klett photoelectric colorimeter, using a blue filter. In a separate test, a calibration curve (not shown) between quinone concentration and optical density was established. From the optical density of the solution (curve 1, Fig. 13) at the times shown, the quinone concentration was determined. Fig. 12 now was used; from that curve the conductivity at each quinone concentration was read. These conductivity data were plotted in curve 2, Fig. 13. This shows that the total change in σ due to *o*-quinone present is only about 12 per cent; the major part of the effect must be due to oxidative ions.

In certain combinations, for instance catechol in benzene, very pronounced oxidation takes place by silver oxide (2) so that the quinone concentration is high; yet the increase in conductivity is small. All these results show that the ion concentration is determined rather by the path that the oxidation process takes, depending on whether it leads through ionic stages that persist to a certain extent.

TEMPERATURE OF OXIDATION

It appeared to be of interest to conduct oxidation tests at different temperatures. Results of such a series are shown in Fig. 14 for butylcatechol in xylene. All conductivities were measured at 25°C, the oxidation being carried out at temperatures ranging from zero C to 75°C. The result seems to show that at zero C, as well as at 50° and 75°C, the conductivity levels reached are lower than at 25°C. This observation needs further experimental verification, but a tentative explanation may be given as follows. Oxidation rate increases with increasing temperature, hence the σ-levels should also increase with rising oxidation temperatures. It is possible, on the other hand, that the higher the temperature, the more direct the oxidation, without going through intermediate ionic stages. In this manner an optimum temperature for the σ-level might result, which may well be in the neighborhood of room temperature. This observation is, therefore, also in keeping with the concept of oxidative ions.

CHEMICAL STRUCTURE OF OXIDATIVE IONS

Up to this point nothing was said about the possible chemical structure of the cation, except that it

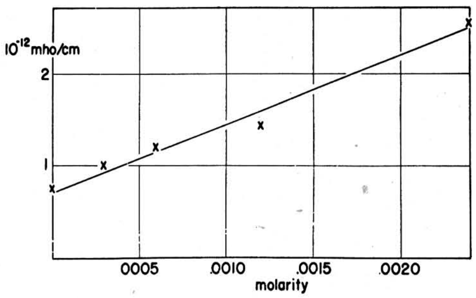


FIG. 12. Conductivity vs. concentration for *o*-quinone in dioxane, containing 3.6 millimole/liter catechol.

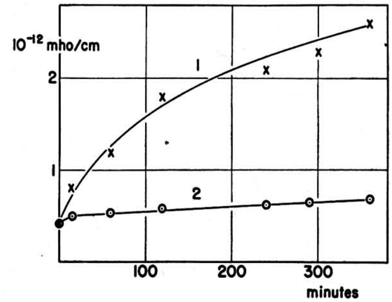


FIG. 13. Conductivity vs. oxidation time for 4.5 millimole/liter catechol in dioxane, oxidized by $KMnO_4$. Curve 1—observed data; curve 2—plotted after Fig. 12, from *o*-quinone produced.

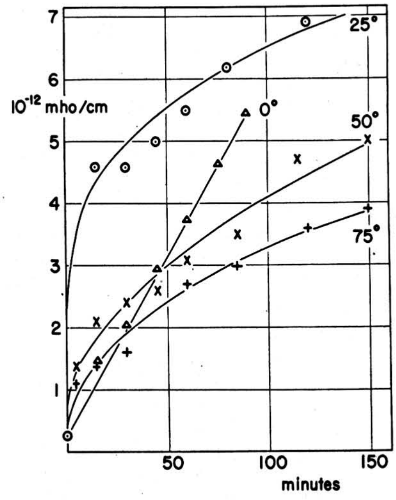


FIG. 14. Conductivity vs. oxidation time at different oxidation temperatures as shown. 3.5 millimole/liter butylcatechol in xylene, oxidized by $KMnO_4$. All conductivities measured at 25° C.

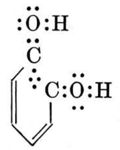
is an oxidation product of catechol. And, indeed, the experimental material does not permit a final conclusion in this respect. It is possible, however, to form a hypothesis which has a certain degree of probability.

Whereas the main oxidation product of catechol is *o*-quinone, an intermediate oxidation product, quinhydrone, was long ago established by Willstätter. The generally bimolecular structure of the latter for all quinones has been questioned by various authors, Weitz, for instance (6). Elema as well as Michaelis (7) proved experimentally for some quinones that the intermediate form, called semiquinone, is monomolecular. The existence of monomolecular intermediate forms can be considered as definitely established.

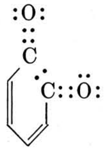
TABLE III. *Comparison between catechol and hydroquinone in dioxane*

Ag_2O			$KMnO_4$		
Time in min	σ, 10^{-12} mho/cm		Time in min	σ, 10^{-12} mho/cm	
	Catechol	Hydroquinone		Catechol	Hydroquinone
0	0.40	0.31	0	0.30	0.31
30	1.5	0.15	45	0.75	0.18
60	5.1	0.15	105	0.83	0.20
120	9.2	0.18	270	1.4	0.28

If one tries to use this concept for catechol, a difficulty arises. The pertinent electronic structure of catechol (I) and *o*-quinone (II) is shown below.

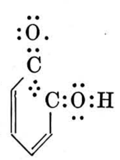


I

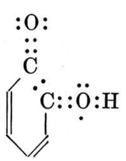


II

The structure of the semiquinone, containing only one hydrogen atom, may be derived from either of these two, thus:

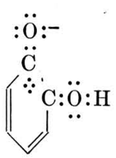


III

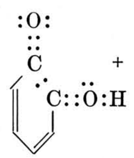


IV

Both structures contain an unpaired electron; hence both are free radicals and must be rather unstable. Both, however, must considerably increase in stability, if to III an electron is added and from IV an electron is removed, thus:



V



VI

In these two saturated structures possessing completed octet shells throughout, V is a negative, and VI a positive ion, the first having benzenoid, the second quinonoid structure; both are electrically charged semiquinones of appreciable stability. The first is the monovalent anion of catechol, which is a weak acid, while the second is the cation of an *o*-quinone, which has accepted a proton. One might picture also bivalent ions of this kind. These structures fit as a special case into the general mechanism of ion generation described previously.

As mentioned before, no noticeable ion formation can be expected from mixing the two compounds. They might form, however, as intermediate oxidation stages. The oxidation of catechol, which may be described by a reaction such as:

$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O,$$

then takes place to a certain fraction in two ionic stages, thus:

$$C_6H_4(OH)_2 + O = C_6H_4O(OH)^+ + (OH)^-$$

$$C_6H_4(OH)_2 + (OH)^- = C_6H_4(OH)O^- + H_2O,$$

resulting in a quinonoid cation and a benzenoid anion. The two ions may partly recombine, forming one molecule of quinone and one of catechol, but may partly persist for a long time as relatively stable oxidative ions.

These ionic formulas were derived from monomer molecules, but similar considerations would hold if the molecules were dimers, tetramers, or the like.

COMPARISON OF ORTHO- AND PARA-COMPOUNDS

One might ask whether the described conductivities are observable with para-compounds as well. Some experimentation along this line gave a negative answer to the above question, as Table III shows, referring to a comparison between catechol and hydroquinone, 4.5 millimole per liter in dioxane, using Ag_2O and $KMnO_4$ as oxidants.

The reason for this difference is probably the same that causes the oxidation rate of catechol to be altogether higher than that of hydroquinone. As may be seen from the structural formulas, a change from I to II involves only two carbon atoms, whereas a corresponding change in para-compounds involves the entire ring. It appears that not only the oxidation rates differ, but also the fraction that follows an oxidation path along ionic stages is larger for ortho- than para-compounds.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Formation of Immersion Zinc Coatings on Aluminum[1]

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ABSTRACT

It has been recognized for many years that aluminum and its alloys require specific surface preparation for successful electrodeposition of the various metals. Such special treatment is necessary because of the high position of aluminum in the electromotive force series and because of the relatively impervious and rapidly formed oxide film. Many procedures for plating on aluminum have been presented in the literature, most of them falling into one of the following categories: (*a*) surface roughening or roughening plus heavy metal deposition by immersion prior to electroplating; (*b*) anodic oxidation followed by electrodeposition in the pores of the coating; (*c*) direct zinc plating prior to plating with other metals; (*d*) immersion deposition of zinc prior to plating with other metals. The zinc immersion procedure is now considered the most practical and economical of the various processes and, accordingly, has the greatest commercial application. In general, this procedure requires less time and equipment, is less critical to control, and has wider applicability than other known methods.

GROWTH OF ZINC IMMERSION PROCESS

An alkaline zinc immersion bath was patented by Hewitson (1) in 1927, and zinc immersion procedures were employed by Altmannsberger (2) in 1931 and 1932, by Braund and Sutton (3) in 1935, by Elssner (4) also in 1935, and by Layner and Orlova (5) in 1936. Later patents were issued to Korpiun (6) in 1939 and Perner (7) in 1942. The zinc immersion process, however, was not widely applied until relatively recent years, during which significant work has been reported by Bengston (8), Meyer (9, 14), Ehrhardt and Guthrie (10), Bullough and Gardam (11), Heiman (12), Keller and Zelley (13, 15), and Bailey (16). While good commercial plating on aluminum is now entirely feasible, further study into the mechanism of the process may result in a still more improved plated surface, especially with regard to resistance to corrosion.

CORROSION OF PLATED ALUMINUM

The zinc immersion process, or any process involving a layer of zinc between the aluminum and the electrodeposit, introduces a specific corrosion problem. In many environments zinc is anodic to aluminum; consequently, it tends to protect both the aluminum and the electrodeposit. This results in undercutting at the interface, and subsequent blistering and flaking of the deposit. Thus, while plated steel, for example, may fail by rusting, the rust spots usually can be removed by polishing and the original appearance restored. However, a plated aluminum surface that has blistered is permanently defaced.

A suggested mechanism for this type of corrosion is diagramatically illustrated in Fig. 1. Item (a) shows the cross section of a plated aluminum surface that has been grooved to the base metal, thus exposing aluminum, zinc, and electrodeposit to the corrosive environment. In item (b) the zinc has protected the electrodeposit and the aluminum by self-sacrifice until the throwing power of the reaction has been exceeded. At this point, item (c), aluminum protects the electrodeposit by self-sacrifice until zinc is again exposed. Starting with item (d), the cycle repeats itself. Undercutting of the deposit in this manner becomes evident by the appearance of blistering and lifting. Fig. 2 is a photograph of the cross section of a corroded, grooved sample demonstrating this type of lifting.

Consideration of such mechanism results in the following conclusions on the performance of plated aluminum:

1. The thinnest practicable zinc film produces the best corrosion results, for it permits the least lateral penetration before the throwing power is exceeded.
2. Those aluminum alloys with the lowest solution potentials provide the most resistant plated products. Thus, 24S alloy should be better than 2S alloy because of a lower potential difference between base metal and electrodeposit.
3. Large breaks in the deposit are less harmful than small, because small breaks furnish a correspondingly small anode area to protect the electrodeposit. Therefore, attack is more rapid, and blistering and lifting occur earlier. For this reason stress cracks, such as might appear on bright nickel plate, are very harmful, and bright plating baths must be operated with caution.

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[1] Manuscript received November 10, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

4. Finally, any modification of the immersion deposit that decreases the rate of solution of zinc by the anodic reaction would be beneficial.

As early as 1927, Work (17) plated on a smooth aluminum surface by applying a thin electrodeposit of zinc prior to plating with other metals. Such plated aluminum had excellent appearance and good adhesion but failed rapidly in corrosion tests. Work could overcome this rapid corrosion only by employing a heat treatment, a step which is objectionable commercially. The zinc film was apparently the source of the difficulty, and although Work specified the thinnest zinc layer which he believed practicable, it still was considerably thicker than present immersion deposits. In like manner, poor results attributed to the zinc immersion process may often be traced to the properties of the immersion film.

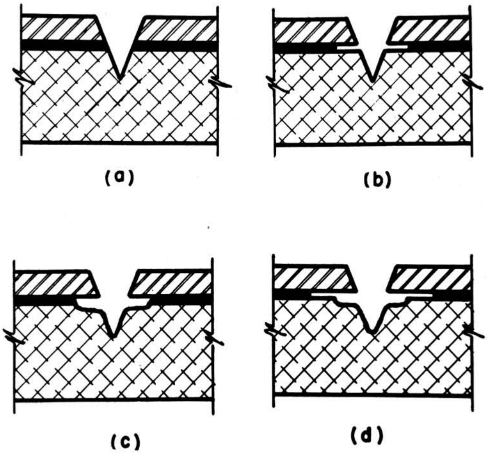

FIG. 1. Corrosion mechanism of aluminum plated by the zinc immersion process.

DEPOSITION OF THE ZINC FILM

One of the reasons that zinc has been so successful for immersion deposits on aluminum is its relative proximity to aluminum in the electromotive force series of metals. Indeed, the relative order of the two metals is interchangeable, depending on the environment. Metals further removed from aluminum in this series are more difficult to deposit by immersion, such deposits usually tending to be granular and nonadherent.

It is understandable then that the potential difference between zinc and aluminum, in a given immersion bath, would determine to a large extent the weight and character of the zinc deposited. Since the zinc film is so important in the resistance to corrosion of electroplated aluminum, this potential difference becomes a very significant property. In general, the zinc-aluminum potential difference, in a given immersion bath, depends on two factors: (*a*) the particular aluminum alloy in question; and (*b*) the surface conditioning treatment employed on that alloy.

Choice of alloy is important because of the inherent differences in solution potential among the various aluminum alloys. Thus, in alkaline immersion baths, 2S has a greater potential difference with respect to zinc than does 24S-T3. Consequently, the increased driving force of the immersion reaction results in a heavier film of zinc on the 2S. Fig. 3 is a graph of zinc-aluminum potential difference for various aluminum alloys. This graph does not purport to show absolute potential differences, but rather it indicates relative initial values and the intervals of time to reach a steady value, as determined with a recording potentiometer.

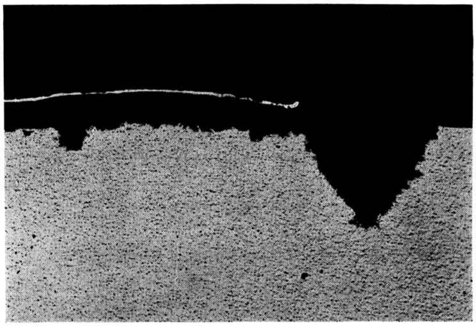

FIG. 2. Cross section through grooved plated panel after salt spray exposure. Shows undercutting and lifting of the deposit. 20×.

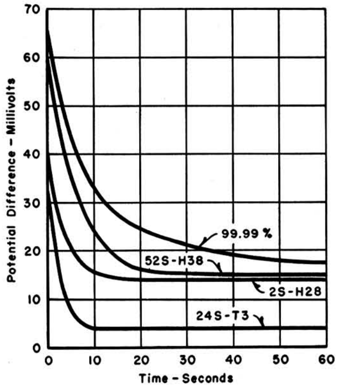

FIG. 3. Potential difference between various aluminum alloys and high purity zinc in a solution of 500 g NaOH per liter and 100 g ZnO per liter.

Usually, however, the alloy is specified according to other requirements, and it may be necessary to plate on one with adverse potential properties. It is then that surface conditioning becomes particularly important. By selecting the proper pretreatment it is frequently possible to decrease markedly the potential difference between zinc and the aluminum alloy. For example, a double immersion treatment on 2S provides a lower zinc-aluminum potential difference and a lower weight of zinc than does mild alkaline cleaning. In turn, mild alkaline cleaning results in a lower zinc-aluminum potential difference than does solvent degreasing. Fig. 4 shows qualitatively the zinc-2S aluminum potential difference for various conditioning treatments. The zinc-aluminum potential difference varies with the conditioning treatment apparently because of the nature of the film formed by the treatment, the effect of the treatment on constituents and surface irregularities, or a combination of these factors.

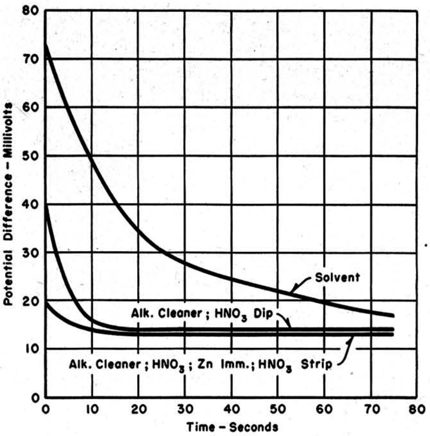

FIG. 4. Potential difference between 2S-H28 with various conditioning treatments and high purity zinc in a solution of 500 g NaOH per liter and 100 g ZnO per liter.

TABLE I. *Effect of the conditioning treatment on the zinc immersion film on 2S-H28*

Treatment	Coating wt.	Zinc content	Resistance*
	mg/dm²	*%*	*microhms*
Electrodeposited zinc			5
Solvent cleaned; 30 sec Zn imm.†	15.8	93.8	10
Alk. cleaner; HNO_3 dip; 30 sec Zn imm	5.3	83.0	15
Alk. cleaner; HNO_3 dip; double 30 sec Zn imm	2.5	72.5	70

* Surface resistance was measured by a Kelvin Bridge using 0.25 in.² contacts and 500 lb pressure.

† The zinc immersion solution had a composition of 500 g of NaOH per liter and 100 g of ZnO per liter.

Extremely thin zinc deposits, such as produced by a double immersion treatment, are not continuous films of pure zinc. This condition is not detrimental as long as there is sufficient zinc to provide satisfactory electrodeposition and is definitely beneficial from a corrosion point of view. Both chemical analysis and contact resistance measurements have been employed to indicate the nature of the zinc film. For an electroplated or heavy immersion zinc coating the resistance is low and the percentage of metallic zinc is high. As the film becomes thinner, however, the resistance increases and the percentage of zinc decreases. Table I summarizes contact resistance and zinc analysis data for various weights of coating.

Of course, time and temperature of immersion also affect the weight of zinc deposited, although their relative importance frequently depends on the conditioning treatment selected. It is a good policy, however, to maintain these variables as low as conveniently practicable. While the conditioning treatment has been considered with respect to its effect on the zinc coating weight, it has two other important functions which must be fulfilled first. One of these is the removal of all the grease, dirt, and disturbed metal resulting from the polishing and buffing operations. The second is to remove those constituents which are not covered in subsequent operations and thus result in blister formation. These factors are obviously very important for obtaining a sound electrodeposit of attractive appearance.

MODIFICATION OF THE IMMERSION SOLUTION

Although proper surface preparation and careful control of the operating conditions have improved markedly the results obtainable with the zinc immersion process, a modification of the zincate bath[2] appears desirable to utilize it to the fullest advantage.

For example, while the "double immersion" technique has been shown to produce a low weight of zinc, it does not always completely overcome the effect of constituents on magnesium and magnesium silicide type of alloys. Also, on 2S alloy it is sometimes possible to so reduce the weight of zinc by means of the double immersion that the surface resistance is too high for satisfactory coverage by the plating bath.

The addition of a small amount of ferric chloride, maintained in solution by the tartrate ion, has proved to be very beneficial to the zincate bath. Not only does it increase the effectiveness of the double immersion treatment on magnesium-containing alloys, but it also provides for more consistent electroplating coverage on all other alloys. Furthermore, double immersion from this modified solution has improved the plating of die castings to the extent that

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[2] The modified zinc immersion procedures are the subjects of pending patent applications.

items on which the standard techniques have failed are often successfully finished.

A small amount of iron can be detected in the immersion film deposited by the modified zincate bath. The resistance to corrosion of aluminum plated with this type of film is improved for most of the alloys, notable exceptions being 24S and 75S. Improvement in corrosion properties is possibly a function of the percentage of metallic zinc in the modified film and its consequent effect on the anodic solution of that film. Fig. 5 demonstrates the increased resistance to corrosion that can be obtained with a modified zinc immersion.

Usually, 1 to 2 g of ferric chloride crystals are employed per liter of immersion bath, and approximately 10 g of Rochelle salt per gram of ferric chloride crystals will maintain the iron in the highly alkaline solution. A large excess of ferric chloride is to be avoided, for it results in blistering of the electrodeposit. With alloys of high magnesium content it may also be of value to increase the Rochelle salt content to 100 g/l. The modified solution is prepared by dissolving the zinc oxide in concentrated sodium hydroxide in the usual manner, then adding the iron as a water solution of ferric chloride and Rochelle salt. Composition of the solution is shown in Table II.

DILUTE IMMERSION SOLUTIONS

Most of the zincate baths in use today have basic compositions of 400–500 g of sodium hydroxide per liter and 80–100 g of zinc oxide per liter. Excellent results are obtained from this type of bath. It is extremely viscous, however, and has the inherent disadvantages of high drag-out and being difficult to remove by rinsing. Such characteristics become especially critical when it is desired to use automatic equipment. Various immersion solutions, less concentrated than the above described bath, have been reported in the literature, but, in general, the concentrated baths have been considered more reliable.

In any sodium zincate solution there is a minimum amount of sodium hydroxide necessary for the given quantity of zinc oxide. This sodium hydroxide content, which is in excess of the amount theoretically required to react with the zinc oxide, is necessary to prevent precipitation of zinc hydroxide. The more dilute the solution, the greater must be the ratio of sodium hydroxide to zinc oxide. For example, in a one liter solution the following ratios are commercially practical: 400 g NaOH for 100 g ZnO; 120 g NaOH for 20 g ZnO; 50 g NaOH for 5 g ZnO. The last two are possible dilute solutions.

Experimental work on the weight of the zinc film indicates that this value may be fundamental in the less satisfactory performance frequently encountered with dilute baths, for the weight of the zinc film tends to increase appreciably upon dilution of the immersion solution. The weight of zinc deposited from a dilute immersion would be expected to be a function of the potential difference between zinc and the aluminum surface in like manner to that previously described for concentrated immersions. Consequently, to decrease the coating weight it is necessary to adjust the solution or vary the conditioning treatment, thereby decreasing that potential difference.

Sodium nitrate and Rochelle salt are two important additions to dilute immersion solutions. Suitable sodium nitrate additions are on the order of 0.5 to 1.0 g/l, and in many cases reduce the coating weight by 30–50 per cent. An excess must be avoided, however, for as much as 2 g/l may result in a zinc film with a contact resistance too high for good coverage by subsequent plating baths. Rochelle salt aids in conditioning magnesium and magnesium silicide type alloys as well as in providing low coating weights. Likewise, dilute baths can be modified with the iron addition in the same manner as a concentrated solution. This markedly improves the resistance to corrosion of the electroplated aluminum and, except on 24S and 75S alloys, is undoubtedly the most important single additive.

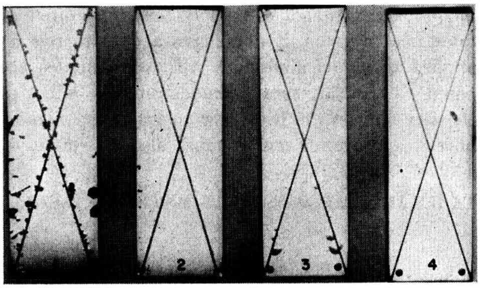

FIG. 5. Panels prepared with regular and modified zinc immersions after 300-hr exposure to the salt spray. Panel 1, 3S-H16 regular immersion bright nickel; panel 2, 3S-H16 modified immersion bright nickel; panel 3, 61S-T6 regular immersion Watts nickel; panel 4, 61S-T6 modified immersion Watts nickel.

TABLE II. *Composition of modified zinc immersion solution*

g/l	
500	Sodium hydroxide
100	Zinc oxide
1	Ferric chloride crystals
10	Rochelle salt

Surface preparation should be especially thorough when employing dilute immersion solutions. Most of the more effective conditioning treatments are applicable and the double immersion technique is of particular value. Also, time and temperature of immersion are more critical with dilute zincate solutions, and it is desirable to limit the immersion to a maximum of 30 seconds at a temperature of not over 75°F.

Probably the most practical dilute immersion bath for commercial operation would have a basic composition of 120 g/l NaOH and 20 g/l ZnO. This solution results in a relatively small increase in rinsing and drag-out properties over more dilute baths, yet at the same time it provides a greater reserve of zinc. Table III gives the complete composition of such a bath.

PERFORMANCE OF PLATED ALUMINUM

The two most widely used corrosion tests, namely salt spray and atmospheric exposures, have been employed in the evaluation of electrodeposits on aluminum. Although salt spray testing is often of questionable value, it does have a definite role as applied to plated aluminum. Grooved samples exposed to the salt spray demonstrate the effect of the zinc film on the resistance to corrosion. Atmospheric exposure, of course, must also be employed to obtain complete data on the outdoor life expectancy of plated parts.

TABLE III. *Composition of dilute modified zinc immersion solution*

g/l	
120	Sodium hydroxide
20	Zinc oxide
50	Rochelle salt
2	Ferric chloride crystals
1	Sodium nitrate

Interest in the performance of plated high strength aluminum alloy articles has resulted in the accumulation of considerable information on decorative chrome plated 24S-T4. Since 24S-T4 is a very favorable alloy on which to plate by the zinc immersion process, excellent resistance to corrosion can be obtained. Ordinarily, with 0.0015 in. nickel under the chromium, plated 24S-T4 would be expected to satisfactorily withstand at least three years' exposure in an industrial atmosphere.

The inherent properties of 24S-T4 alloy make it possible to obtain good results on this alloy without any special precautions in the zinc immersion bath. Other alloys are not so readily treated, but the application of the principles discussed above will produce good results on them as well. For example, 2S was included in another plating exposure program together with 24S-T4, brass, steel, and zinc. The 2S was plated using a double immersion from a modified solution, while the other metals were prepared according to best standard practices. It is significant that, after three years in the New Kensington, Pennsylvania, atmosphere, plated 2S is as good as the plated 24S-T4, and the plated aluminum compares favorably with the plated brass, steel, and zinc samples.

Recently there has been increased interest in plated aluminum die castings. As yet there is less background information on die castings, and unquestionably they are more difficult to plate satisfactorily than wrought alloys. One of the difficulties in the plating of die castings results from the greater percentages of copper, silicon, and magnesium usually found in casting alloys. However, the factors affecting the zinc immersion film appear to be more critical for castings than for wrought material. Use of the modified immersion solution seems to offer some advantage for castings. Casting alloys currently under consideration for plated finishes are No. 360, 380, and 218 alloys. While procedures have been developed for all three alloys, alloy 380 is probably the most suitable for electrodeposition. The plated finish on die castings of this alloy, when applied according to the best known methods, should withstand an industrial atmosphere for at least one year.

SUMMARY

To obtain corrosion resistant electrodeposits on aluminum, it is necessary to obtain good coverage on the thinnest possible zinc film. The surface conditioning treatment is important in this objective by removing dirt and grease, dissolving interfering constituents, and providing a surface with favorable potential properties. An addition of iron to the immersion bath itself aids materially in improving coverage and in decreasing the corrosion reaction in the zinc film. Dilution of the immersion bath introduces additional problems and, in general, necessitates closer control over surface preparation and operating conditions. Sodium nitrate and Rochelle salt, as well as the iron, have been employed as additions to dilute baths. By exercising a few precautions it is possible to obtain good service performance of plated finishes on wrought aluminum alloys. Casting alloys present a somewhat more difficult problem, but careful treatment should provide relatively good results in this field as well.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1954 issue of the JOURNAL.

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Polarography of Thioglycolic Acid[1]

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ABSTRACT

Thioglycolic acid exhibits polarographic behavior at the dropping mercury electrode similar to cysteine and glutathione. A reversible anodic wave is found, the characteristics of which correspond to the formation of a mercurous thioglycolate complex. This wave is suitable for the analysis of thioglycolic acid in solutions. A second irreversible anodic wave probably is due to the formation of an insoluble mercuric monothioglycolate. The standard potential of the electrode reaction has been calculated from the experimental results. Dithiodiglycolic acid is irreversibly reduced to thioglycolic acid at the dropping mercury electrode. Calculated diffusion coefficients of various species from polarographic data are given.

INTRODUCTION

Following a report from this laboratory[2] on the polarographic properties and determination of thioglycolic acid, a paper was published on the same subject by Liberti and Cervone (1). The results in the two papers differ in various minor respects and in a major respect regarding the interpretation of the reaction mechanism. The interpretation in the report is in agreement with that of Kolthoff and Barnum (2) for cysteine and with Stricks and Kolthoff (3) for reduced glutathione.

Larsson (4) reports values for the acid dissociation constants of thioglycolic acid to be 2.1×10^{-4} for K_1 and 2.1×10^{-11} for K_2 at 25°C. In this laboratory, Bush (5) titrated thioglycolic acid with sodium hydroxide using a glass electrode. From his data and using approximate ion activity coefficients as tabulated by Kielland (6), the values for the activity constants were calculated to be 2.5×10^{-4} and 2.8×10^{-11} at 25°C. These values are used in the calculations in this paper.

The polarography of dithiodiglycolic acid was briefly investigated.

EXPERIMENTAL

Purification of thioglycolic acid.—Thioglycolic acid of 99.8 per cent purity by an analysis to be described below was prepared by twice vacuum distilling Eimer and Amend "pure" thioglycolic acid. The fraction collected boiled at 95°–96°C at 8 mm pressure. A purity of about 99 per cent was obtained after one vacuum distillation. The distillation was carried out rapidly using an oil bath to prevent local overheating as thioglycolic acid loses water to polymerize under these conditions.[3]

Standard solutions of thioglycolic acid were prepared by direct weight in air-free water. These solutions did not change titer within one week.

Analysis.—Ten to 25 ml of approximately 0.1*M* solutions prepared by weight in air-free water was introduced into 20 ml of an air-free solution of 1.0*N* sulfuric acid containing starch indicator and a slight excess of potassium iodide over the number of moles of thioglycolic acid added. This solution was then titrated to the blue iodine end point with air-free 0.10*N* potassium iodate, a stream of nitrogen being passed over the solution during the titration.

Iodine, which is liberated upon the addition of iodate, oxidizes thioglycolic acid to dithiodiglycolic acid, $HOOCCH_2SSCH_2CO_2H$ (7). In the presence of air, a slight induced oxidation of the thioglycolic acid occurs.

Preparation of dithiodiglycolic acid.—Dithiodiglycolic acid was prepared from pure thioglycolic acid by oxidation with ferric alum in 0.1*N* sulfuric acid. The ferric solution was slowly added to the thioglycolic acid in 0.1*N* sulfuric acid until spot tests with potassium thiocyanate indicated an excess of ferric iron in the solution. The oxidized solution was extracted with ether, the ether layer separated, and evaporated to dryness. The white crystals remaining were twice recrystallized from ethyl alcohol.

Polarography of thioglycolic acid.—A Sargent Model XII photographic and a manual polarograph were used in the present work. The manual polarograph was of the type described by Kolthoff and

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[1] Manuscript received December 11, 1952. This paper was prepared for delivery before the New York Meeting, April 12 to 16, 1953.

[2] The experimental part of the present work was reported to the U. S. Public Health Service in November 1950.

[3] The distilled thioglycolic acid was stored at 0°C and the bottle in which it was kept was flushed with nitrogen during and after the removal of samples. Using this procedure, the extent of oxidation was less than 1 per cent in one and a half years. Thiolactides slowly formed, however, at the rate of about 0.5 per cent for each 3 months of storage.

Lingane (8) with a galvanometer having a 10-second period. All measurements were made at 25 ± 0.1°C with an external saturated calomel electrode, SCE. Two capillaries were used: capillary I—$m = 1.366$ mg/sec and $t = 4.53$ sec in 0.10N KCl with a closed circuit at a height of mercury of 80 cm; capillary II—$m = 1.005$ mg/sec and $t = 5.92$ sec with a closed circuit and a height of 70 cm.

All experiments were carried out at 25.0 ± 0.1°C.

Results and Discussion

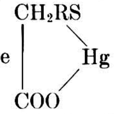
Polarograms were obtained for $10^{-3}M$ solutions of thioglycolic acid in buffers with paH between 1.0 and 12.45. In all of these solutions an anodic wave was observed (see Fig. 1). Throughout the pH range investigated, this wave is well shaped and clearly defined with no evidence of maxima or irregularities observed by Kolthoff and Barnum (2) for the anodic wave of cysteine. The height of the thioglycolic acid wave was found to be proportional to the concentration at least up to $3 \times 10^{-3}M$. The half wave potential was found to be independent of the concentration of the thioglycolate ion within the experimental error.

No specific buffer effect was observed in these solutions as sometimes occurs in the polarography of organic compounds. In regions where buffers overlap, the half wave potential is a function of only the paH (negative logarithm of the hydrogen-ion activity) and not of the buffer anions.

A small prewave appears at values of paH less than 4.6. This becomes more prominent as the paH decreases. This wave is not well developed and its height is difficult to measure. In 0.1M perchloric acid, 0.1M sodium perchlorate, its height appears to decrease slightly with increase in the concentration of thioglycolic acid. In several respects the prewave has the characteristics of an adsorption current (9).

A second anodic wave at more positive potentials than the wave described above is observed in acid buffers where the dropping electrode can be made sufficiently positive vs. SCE before the dissolution of mercury [see also (1)]. This second anodic wave is steep and on the limiting current region the galvanometer oscillations are erratic. In a solution of pH 1.0 this wave appears at about 0.23 volt vs. SCE. At this pH the height of the second wave (over the first wave) does not increase with the concentration of thioglycolic acid in solutions over $10^{-3}M$ while the height of the total first wave (prewave plus normal wave) is proportional to the concentration.

Stricks and Kolthoff (3) in the polarography of glutathione found two anodic waves similar in shape and behavior to those found for thioglycolic acid. They attribute the second wave to the formation of a Hg(II) compound of the type



Diffusion coefficients were calculated for the species, $HSCH_2CO_2H$, $HSCH_2CO_2^-$, and $^-SCH_2CO_2^-$ by means of the Ilkovic equation (10),

$$i_d = 607nD^{1/2}Cm^{2/3}t^{1/6}.$$

Assuming (v.i.) that n, the number of electrons involved in the oxidation per molecule of thioglycolate, is equal to one for the first anodic wave, the diffusion coefficients were calculated to be 9.2, 11.3, and 9.7×10^{-6} cm²/sec for RSH_2, RSH^-, and $RS^=$, respectively, at 25°C.

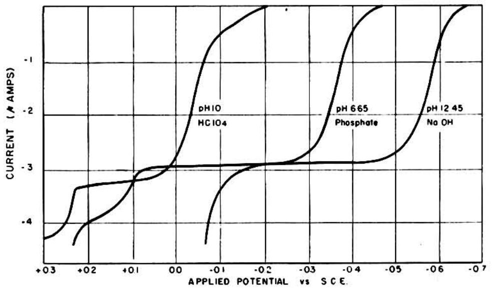


FIG. 1. Current-voltage curve of $1.10 \times 10^{-3}M$ thioglycolic acid in various buffers (not corrected for residual current).

Elving and Tang (11) report values of the diffusion coefficients of undissociated chloroacetic acids to be 10.0×10^{-6} cm²/sec and Kolthoff and Barnum (2) report a value for cysteine to be 7×10^{-6} cm²/sec. Thus, it may be safely concluded that the anodic wave of thioglycolic acid involves one electron.

Liberti and Cervone (1) report values from which the diffusion coefficient of thioglycolic acid is calculated to be 8.6×10^{-6}, but they do not mention any effect of pH.

Analysis of the Wave

The current-voltage curve of the first anodic wave of the monobasic thioglycolate ion in a buffer of 0.05M Na_2HPO_4, 0.05M NaH_2PO_4 at a paH of 6.65 was analyzed. A plot (Fig. 2) of the $\log i_d - i/i$ vs. the applied potential, $E_{app.}$, gave a straight line, while a plot of $\log (i_d - i)^2/i$ vs. $E_{app.}$ gave a curved line. During the anodic oxidation of thioglycolic acid at the dropping electrode a mercury compound is formed and not the disulfide. The primary electrode reactions may be given by equations (I) or (II).

$$HSCH_2CO_2^- \rightleftarrows \cdot SCH_2CO_2^- + H^+ + e^- \quad (I)$$

$$HSCH_2CO_2^- + Hg \rightleftarrows HgSCH_2CO_2^- + H^+ + e^- (II).$$

Both equations would give expression (III)

$$E_{\text{app.}} = E_{1/2} + 0.059 \log i/i_d - i. \qquad \text{(III)}$$

In Fig. 2 a slope of 0.050 volt of line I is found instead of the theoretical value of 0.0591. The authors' system behaves similar to cysteine (2) and glutathione (3) at the dropping electrode.

On the other hand, Liberti and Cervone (1) claim that thioglycolic acid and cysteine give waves that correspond to an equation of the form

$$E_{\text{app.}} = K + \frac{0.059}{2} \log \frac{i}{(i_d - i)^2} \qquad \text{(IV)}$$

They state that this behavior was observed after correcting their current-voltage curves for the *IR* drop in their polarographic circuit, but it is not clear how they calculated and applied the correction. The results shown here (corrected for *IR*) do not agree with their conclusion (see curve II, Fig. 2).

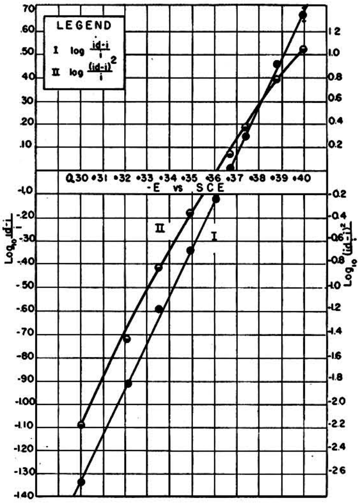


FIG. 2. Analysis of wave of $1.10 \times 10^{-3}M$ TGA in *p*H 6.65 phosphate buffer.

Moreover, measurements of the half wave potential of thioglycolate in *p*H 6.65 buffer made with the low resistance Sargent Model XII photographic polarograph gave values of −0.367 volt vs. SCE for a $6.6 \times 10^{-4}M$ solution of thioglycolate and −0.362 volt for a $3.3 \times 10^{-3}M$ solution. Assuming a total circuit resistance of 1,000 ohms, the corrected half wave potentials become −0.368 and −0.367 volt vs. SCE, respectively. Within the experimental error the half wave potential is, thus, seen to be independent of the concentration. This behavior is in accordance with equation (III). If equation (IV) were obeyed, a shift of about 20 millivolts in the half wave potential should have been observed for a five-fold change in thioglycolate.

Considering the variation of the half wave potential with *p*H, let RSH_2, RSH^- and $RS^=$ refer to the species formed in the various steps of ionization of thioglycolic acid.

The potential of the electrode at which reversible reaction (II) takes place is

$$E - E^0 + 0.059 \log \frac{a^0_{\text{HgRS}} - a^0_{\text{H}+}}{a^0_{\text{RSH}^-}} \qquad \text{(V)}$$

in which a^0 represents the activity at the electrode surface of the species denoted by the subscript. This equation can be written in terms of concentrations

$$E = E^0 + 0.059 \log a_{\text{H}^+} + 0.059 \log \frac{[\text{HgRS}^-]^0}{[\text{RSH}^-]^0} \qquad \text{(VI)}$$

assuming the activity coefficients of both univalent ions equal.

Except for slight changes in the diffusion coefficients, the height of the anodic wave is independent of the stage of ionization of thioglycolic acid. The diffusion current, i_d, of this wave is given by the equation:

$$i_d = k([\text{RSH}_2] + [\text{RSH}^-] + [\text{RS}^=]) \qquad \text{(VII)}$$

where the quantities in the brackets refer to the concentrations in the bulk of the solution and k is equal to $607\, nD^{1/2}m^{2/3}t^{1/6}$. D will be set equal to a mean value for all species of thioglycolic acid. This approximation is a minor one.

At any point on the current-voltage curve the current, i, is proportional to the difference of the concentrations of the diffusing species in the bulk of the solution and at the electrode surface, hence, the sum of the concentrations at the electrode surface

$$[\text{RSH}_2]^0 + [\text{RSH}^-]^0 + [\text{RS}^=]^0 = \frac{i_d - i}{k}. \qquad \text{(VIII)}$$

From the ionization constants of thioglycolic acid, K_1 and K_2, it can be shown that

$$[\text{RSH}^-]^0 = \frac{i_d - i}{k} \cdot \frac{1}{\frac{a_{\text{H}^+}}{K_1} \cdot \frac{\gamma_1}{\gamma_0} + 1 + \frac{K_2}{a_{\text{H}^+}} \cdot \frac{\gamma_1}{\gamma_2}} \qquad \text{(IX)}$$

where γ_0, γ_1, and γ_2 refer to the activity coefficients of uncharged, univalent, and divalent species.

The concentration of the oxidation product, $HgRS^-$, at the electrode surface can also be expressed in terms of the current, i, by the equation:

$$[\text{HgRS}^-]^0 = \frac{i}{k'}. \qquad \text{(X)}$$

Substituting equations (IX) and (X) into (VI) yields

$$E_{\text{app.}} = E^0 + 0.059 \log \frac{k}{k'} + 0.059 \log \left(\frac{a_{\text{H}^+}^2}{\text{K}_1} \cdot \frac{\gamma_1}{\gamma_0} + a_{\text{H}^+} + \text{K}_2 \frac{\gamma_1}{\gamma_2} \right) + 0.059 \log \frac{i}{i_d - i}. \quad \text{(XI)}$$

The ratio k/k' is equal to the square root of the ratios of the diffusion coefficients of the reduced to oxidized forms and is about equal to one.

TABLE I. *Half wave potential of $10^{-3}M$ thioglycolic acid solutions as a function of pa*H *at ionic strength of 0.2 capillary* I, *h_{Hg} = 80 cm*

*pa*H	Buffer	$E_{1/2}$ (obs.) vs. SCE	$E_{1/2}$ calc.
12.45	0.01*M* NaOH	−0.58	—
10.4	0.2*M* NH_4Cl, 1.0*M* NH_4OH	−0.56	−0.565
10.1	0.2*M* NH_4Cl, 0.5*M* NH_4OH	−0.55	−0.557
10.1	0.05*M* $NaHCO_3$, 0.05*M* Na_2CO_3	−0.55	−0.557
9.5	0.2*M* NH_4Cl, 0.1*M* NH_4OH	−0.52	−0.530
9.1	0.2*M* NH_4Cl, 0.05*M* NH_4OH	−0.50	−0.510
8.7	0.2*M* NH_4Cl, 0.02*M* NH_4OH	−0.47	−0.487
7.78	0.005*M* NaH_2PO_4, 0.05*M* Na_2HPO_4	−0.43	−0.434
6.75	0.05*M* NaH_2PO_4, 0.05*M* Na_2HPO_4	−0.38	−0.373
5.75	0.05*M* NaH_2PO_4, 0.005*M* Na_2HPO_4	−0.31	−0.313
5.62	0.20*M* NaOAc, 0.02*M* HOAc	−0.31	−0.306
4.60	0.20*M* NaOAc, 0.20*M* HOAc	−0.26	−0.245
(3.55	0.20*M* NaOAc, 2.0*M* HOAc	−0.20	−0.169)
(1.0	0.10*M* $HClO_4$, 0.10*M* $NaClO_4$	−0.044	+0.112)

The half wave potential, $E_{1/2}$, is then given by the equation:

$$E_{1/2} = E^0 + 0.059 \log \left(\frac{a_{\text{H}^+}^2}{\text{K}_1} \cdot \frac{\gamma_1}{\gamma_0} + a_{\text{H}^+} + \text{K}_2 \cdot \frac{\gamma_1}{\gamma_2} \right).$$

The values of $E_{1/2}$ observed as a function of *p*H are given in Table I and Fig. 3. The ionic strength of all the solutions was 0.2. Using values of $\gamma_0 = 1$, $\gamma_1 = 0.76$, and $\gamma_2 = 0.38$ as given by Kielland (6), and values of K_1 equal to 2.5×10^{-4} and K_2 equal to 2.8×10^{-11}, a value of E^0 equal to +0.025 volt vs. SCE was calculated from the observed $E_{1/2}$ at a *pa*H of 12.45. Values of $E_{1/2}$ were then calculated at other measured values of *pa*H and are also given in Table I.

The agreement of the observed values of $E_{1/2}$ with those calculated is good. At values of *pa*H of 4.60 and less, a deviation of the calculated values to more positive potentials than those observed is noticed. The prewave also appears in this region of *pa*H.

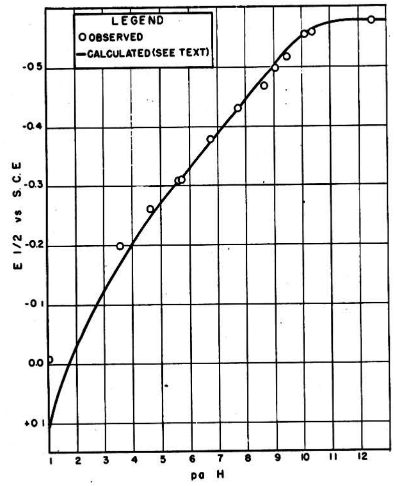


FIG. 3. Half wave potential of thioglycolic acid as a function of *pa*H.

Polarography of Dithiodiglycolic Acid

Fig. 4 gives polarograms obtained for $1.02 \times 10^{-3}M$ solutions of dithiodiglycolic acid in buffers of *p*H 3.00, 4.58, and 8.73. The cathodic waves were irregular and drawn out indicating irreversible electrode processes. The wave obtained in a phosphate buffer at *p*H 3.0 exhibits a flat maximum that extends over a range of about 0.6 volt. The maximum can be suppressed by 0.002 per cent gelatin, but in the range −0.25 to −0.95 volt vs. SCE the galvanometer oscillations remain erratic. The gelatin has no effect on the height of the normal diffusion current. In this buffer with 0.002 per cent gelatin the half wave potential was about −0.37 volt vs. SCE. The diffusion coefficient calculated in this solution is 6×10^{-6} cm²/sec assuming a two electron reduction. This value is close to the value of 5.3 ×

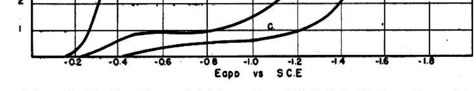


FIG. 4. Reduction of 1.02×10^{-3} *M* dithiodiglycolic acid. Capillary I, ht = 80 cm; A—phosphate buffer, *p*H 3.00; B—acetate buffer, *p*H 4.58; C—ammonia buffer, *p*H 8.73.

10^{-6} cm^2/sec calculated for cysteine by Kolthoff and Barnum (2).

ACKNOWLEDGMENT

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1954 issue of the JOURNAL.

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DECEMBER 1953 DISCUSSION SECTION

A Discussion Section, covering papers published in the January–June 1953 JOURNALS, is scheduled for publication in the December 1953 issue. Those who plan to contribute remarks for this Discussion Section should submit their comments or questions in triplicate to the managing editor of the JOURNAL, 235 West 102nd Street, New York 25, N. Y., not later than August 15, 1953. All discussions will be forwarded to the author, or authors, for reply before being printed in the JOURNAL.

The Mechanism of Electropolishing of Copper in Phosphoric Acid Solutions

I. Processes Preceding the Establisment of Polishing Conditions

J. Edwards[1]

ABSTRACT

An equation due to Elmore relating the time required to establish polishing conditions to the current applied has been tested with a copper anode in phosphoric acid. The dependence of a constant in Elmore's equation on anode area, phosphoric acid concentration, copper solubility, viscosity, and copper concentration has been investigated. The results show that the process is diffusion-controlled but that Elmore's hypothesis, that the onset of polishing coincides with the attainment of the solubility limit of copper in the electrolyte, is incorrect, since additions of copper to the electrolyte were found to have no effect on the constant, except insofar as they modified the viscosity. Two possible explanations of these results are advanced, based on the view that the controlling process is depletion of the anode layer with respect to either hydrogen ions or to those ions or molecules with which the copper ions are combined in the solution. It is shown how the latter interpretation can explain the principal features of electropolishing.

Introduction

The object of this investigation was to seek the mechanism of electropolishing of copper in phosphoric acid solutions by establishing, first, what conditions prevail at an anode undergoing polishing and, second, how such conditions produce (*a*) suppression of crystallographic etching and (*b*) smoothing.

The processes which occur in an electropolishing cell prior to the establishment of polishing conditions received quantitative treatment by Elmore (1).

On the assumption that the onset of electropolishing coincides with the attainment of the "solubility limit" of metal in solution at the anode surface, he derived from the simple diffusion equation the following relation between the applied current, i_o, and the transition time taken to establish polishing conditions, t_o: $i_o t_o^{\frac{1}{2}}$ $\frac{1}{2} c_m A \mathbf{F} (\pi D)^{\frac{1}{2}} =$ constant, where c_m is the solubility limit of the metal in the electrolyte, A is the area of the anode, D is the coefficient of diffusion of dissolved metal, assumed to be constant, and **F** is the faraday.

With a copper-orthophosphoric acid cell, Elmore showed $i_o t_o^{\frac{1}{2}}$ to be very nearly constant in each of six concentrations of orthophosphoric acid, the mean value falling from 2.72 at sp gr 1.200 to 0.7 at sp gr 1.600. No attempt was made, however, to relate the value of the constant to c_m, A, or D.

The present paper describes studies of the dependence of $i_o t_o^{\frac{1}{2}}$ on anode area, phosphoric acid concentration, copper solubility, viscosity, and copper concentration. Determinations have also been made of $i_o t_o^{\frac{1}{2}}$ for solutions having different phosphoric acid and copper concentrations but approximately the same viscosity. The results show that the process is diffusion-controlled. However, since the presence of large amounts of dissolved copper in the electrolyte was found not to modify $i_o t_o^{\frac{1}{2}}$, provided that allowance was made for viscosity changes, Elmore's view that the onset of polishing coincides with the attainment of the solubility limit of copper in the electrolyte cannot be true. Possible alternative mechanisms are discussed. The avoidance of etching under polishing conditions is explained as due to the suppression of the effect of slight potential differences on the anode surface. This was tested by experiments with a composite anode.

Experimental

Cell and Circuit

The cell used for the determination of $i_o t_o^{\frac{1}{2}}$ is shown in Fig. 1. The anode was the end face of a copper rod, covered at the sides with rubber tubing and fitted with a small glass shield to insure uniform current distribution and diffusion across a plane of known area, while reducing convection to a low value. In order to maintain a fairly constant resistance in experiments with different sizes of anode, the height of the shield (½ in. for the ¼-in. diameter anode) was made approximately proportional to the anode area. The cathode was a cylindrical piece of copper foil. The cell, containing 150 ml of electrolyte, was immersed in a thermostat at 25°C. Before any determinations were made a small amount of copper was always dissolved into the electrolyte by allowing the anode to electropolish for 15 min. Between each t_o determination, the solution was thoroughly stirred then allowed to settle.

Current was supplied to the cell from high tension batteries through a series resistance of about 3,600 Ω, different voltage tappings being used to provide different currents. During each t_o determination the current was kept steady by slight adjustment of the series resistance. The arrangement permits a considerable potential rise at t_o and consequently vigorous oxygen evolution which Elmore avoided. This, however, is no disadvantage in a study confined to processes occurring during the transition period.

Preparation of Solutions

The concentration of phosphoric acid is expressed as percentage by volume of concentrated acid (sp gr 1.71). Solutions containing dissolved copper were prepared in some cases by addition of copper phosphate, but more usually by dissolving copper anodically from a bar of pure metal con-

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[1] British Non-Ferrous Metals Research Association, London, England.

tained in a porous pot. Solutions of the desired viscosity were obtained by mixing solutions in water and in glycerol, each of the required concentration.

Determination of the Solubility of Cu^{++}

Copper was dissolved anodically to give slightly supersaturated solutions. After standing at 25°C for some months, the solutions were filtered and the Cu^{++} estimated electrolytically.

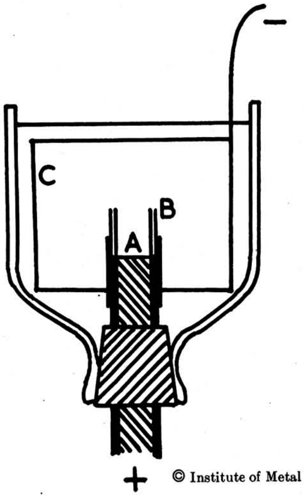

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FIG. 1. Cell. A, anode; B, glass shield; C, cathode

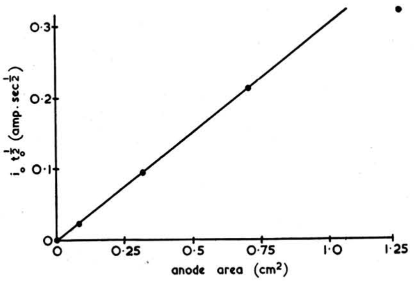

FIG. 2. Dependence of $i_o t_o^{\frac{1}{2}}$ on anode area

Determination of Viscosities

Viscosity was measured on an arbitrary scale by determining the time taken for 20 ml of solution to flow through a standard capillary tube immersed in a thermostat at 25°C. The solution reservoir was fitted with a constant head device which was adjusted to make the head inversely proportional to the specific gravity of the solution under test.

Results

To insure that the metal dissolved anodically could be equated without error to the current passing through the cell, the loss in weight of a copper anode was compared with the gain in weight of the cathode of a copper coulometer in series. At voltages below that corresponding to visible gas evolution, the dissolution of copper as Cu^{++} was found to proceed with complete efficiency.

Constancy of $i_o t_o^{\frac{1}{2}}$

Within the range of conditions investigated, $i_o t_o^{\frac{1}{2}}$ was found to be nearly independent of i_o for a given cell, although there was a tendency for $i_o t_o^{\frac{1}{2}}$ to be slightly greater than the mean (5% maximum for ¼-in. diameter anode) at the highest and lowest values of t_o.

Dependence of $i_o t_o^{\frac{1}{2}}$ *on Anode Area*

For anodes of diameter ⅛, ¼, ⅜, and ½ in., $i_o t_o^{\frac{1}{2}}$ was determined in 75 per cent phosphoric acid at 25°C. The mean values are plotted against anode area in Fig. 2. The points fall on a straight line, which passes through the origin; this confirms that $i_o t_o^{\frac{1}{2}}$ is proportional to A. There is a discrepancy with the largest anode which cannot readily be accounted for, and in view of this the ¼-in. diameter anode was used in subsequent experiments.

Dependence of $i_o t_o^{\frac{1}{2}}$ *on Phosphoric Acid Concentration, Solubility of Copper, and Viscosity*

The mean values of $i_o t_o^{\frac{1}{2}}$ for phosphoric acid solutions of concentrations between 30 and 100 per cent by volume are given in Table I.

The decrease in $i_o t_o^{\frac{1}{2}}$ with increasing acid concentration confirms the result obtained by Elmore who states that this "is to be expected, for the solubility limit, c_m, of copper should be less when there is more acid present." The meaning of the term solubility limit is not clear, but, although it may not perhaps be identified with the normal bulk solubility, it is not unreasonable to assume that the two are related.

TABLE I. $i_o t_o^{\frac{1}{2}}$, Cu^{++} *solubility and* η *for phosphoric acid solutions*

Phosphoric acid % by vol	$i_o t_o^{\frac{1}{2}}$ amp sec$^{\frac{1}{2}}$	Solubility of Cu^{++} g/l	η sec/20 ml	$i_o t_o\ \eta^{\frac{1}{2}}$
30	0.240	114	31.7	1.35
40	0.210	120	42.4	1.37
50	0.174	106	54.9	1.29
60	0.133	96	81.6	1.20
70	0.099	84	125	1.11
80	0.071	72	191	0.98
90	0.051	—	315	0.91
100	0.036	—	513	0.82

Approximate figures for the solubility of copper are set out in the third column of Table I. At concentrations of phosphoric acid greater than 80 per cent, the rate of dissolution of copper was so slow that it was not possible to prepare satisfactory solutions. Even allowing for the possibility of a fairly large error in the solubilities, it is clear that no direct relationship exists between $i_o t_o^{\frac{1}{2}}$ and the solubility of copper. One probable reason for this is that Elmore assumes D, the diffusion coefficient, to be constant. However, the solutions differ greatly in viscosity and this must be accompanied by a variation in the diffusion coefficient. For a spherical particle of radius r in a medium of viscosity η, the Stokes-Einstein equation is $D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}$. Therefore, for a given ionic species (constant r) at constant temperature, D is proportional to $\frac{1}{\eta}$. An alternative form of Elmore's equation is therefore, for constant anode area, $i_o t_o^{\frac{1}{2}} \eta^{\frac{1}{2}} = k.c_m$.

The viscosities of the phosphoric acid solutions, determined on the arbitrary scale, are given in Table I and the plot of $i_o t_o^{\frac{1}{2}} \eta^{\frac{1}{2}}$ against the solubility of copper in Fig. 3. A fair straight line is obtained, demonstrating the importance of viscosity variation and indicating that c_m is related to the solubility of copper.

Relation between $i_o t_o^{\frac{1}{2}}$ and Solubility of Copper in Solutions of Constant Viscosity

If η is constant, $i_o t_o^{\frac{1}{2}}$ should be proportional to c_m.

In equalizing viscosities by the addition of glycerol, the assumption is made that the glycerol will not adversely affect the copper ion itself nor tend to be preferentially adsorbed on the anode surface. The solubility of copper is reduced by such additions and it was necessary to redetermine solubility in the modified solutions. The results are given in Table II for three solutions; the viscosities of the 50 per cent and 25 per cent solutions were adjusted to equal that of the 75 per cent solution.

Fig. 4 shows $i_o t_o^{\frac{1}{2}}$ plotted against the solubility of copper. The slope of the line is almost as expected, but the range of solubility is too restricted for the results to be convincing. In solutions of lower concentration than 25 per cent, however, it was not possible to measure t_o accurately since current and voltage changes were not sufficiently sharp.

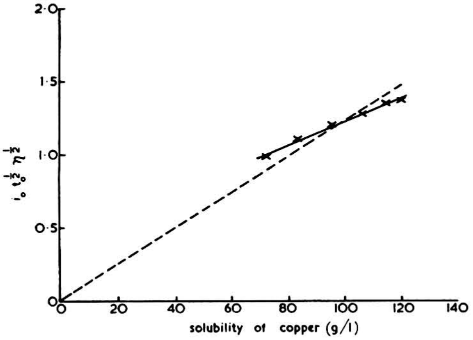

FIG. 3. Relation between $i_o t_o^{\frac{1}{2}} \eta^{\frac{1}{2}}$ and solubility of copper

Dependence of $i_o t_o^{\frac{1}{2}}$ on Concentration of Cu^{++}

The relationship between c_m and the solubility of Cu^{++} can be investigated directly by determining $i_o t_o^{\frac{1}{2}}$ for cells containing known concentrations of Cu^{++}. Elmore suggests that t_o is the time necessary for the concentration to build up near the anode to the solubility limit. If, therefore, Cu^{++} is present in the original solution, $i_o t_o^{\frac{1}{2}}$ should be less and should, in fact, be zero if the solution contains Cu^{++} up to the solubility limit.

Preliminary experiments with phosphoric acid solutions containing Cu^{++} (dissolved as the phosphate) at concentrations up to and exceeding the normal solubility showed that $i_o t_o^{\frac{1}{2}}$ decreased with increasing Cu^{++} concentration. The effect was comparatively slight, however, and it seemed likely that it was caused solely by the increase in viscosity which accompanied the increase in copper concentration. The fact that $i_o t_o^{\frac{1}{2}}$ did not reach zero even in solutions which were highly supersaturated showed conclusively that c_m is not the normal bulk solubility. To test the importance of viscosity changes, the viscosity of a solution of 100 grams $Cu_3(PO_4)_2 \cdot 3H_2O$ in 1 liter of 50 per cent H_3PO_4 was adjusted to that adopted as the standard in Table II, i.e., viscosity of 75 per cent phosphoric acid in water. With this solution, two separate determinations of $i_o t_o^{\frac{1}{2}}$ gave the results 0.096 and 0.102. The mean value is now seen to be very near that of solutions of the same viscosity containing no Cu^{++}. Thus:

	$i_o t_o^{\frac{1}{2}}$
(*a*) 75% acid	0.096
(*b*) 50% acid adjusted to viscosity of (*a*)	0.096
(*c*) 50% acid and 100 g/l phosphate adjusted to viscosity of (*a*)	0.099

The effect of Cu^{++} additions, therefore, appears to be confined to their influence upon viscosity, i.e., c_m bears no relation to Cu^{++} concentration.

This result was checked on solutions containing copper dissolved anodically and no added glycerol, correcting for viscosity differences by calculating the values of $i_o t_o^{\frac{1}{2}} \eta^{\frac{1}{2}}$. These values should be independent of Cu^{++} concentration if the conclusion reached above is correct. The results are listed in Table III for 50 per cent phosphoric acid solutions containing between 85 and 5 g/l of Cu^{++}.

TABLE II. *$i_o t_o^{\frac{1}{2}}$ and solubility of copper in solutions of constant η*

Phosphoric acid % by vol	Solubility of Cu^{++} g/l	$i_o t_o^{\frac{1}{2}}$ amp sec$^{\frac{1}{2}}$
75	81	0.096
50(+glycerol)	82	0.096
25(+glycerol)	49	0.067

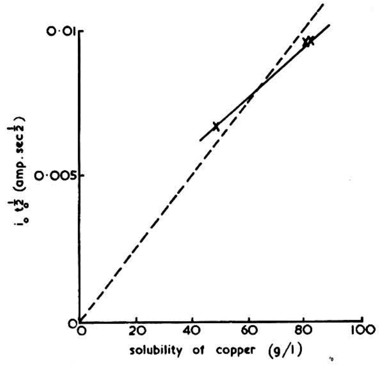

FIG. 4. Relation between $i_o t_o^{\frac{1}{2}}$ and solubility of copper in solution of constant viscosity.

TABLE III. *Dependence of $i_o t_o^{\frac{1}{2}} \eta^{\frac{1}{2}}$ on concentration of* Cu^{++}

Cu^{++} conc, g/l	$i_o t_o^{\frac{1}{2}}$ amp sec$^{\frac{1}{2}}$	η sec/20 ml	$i_o t_o^{\frac{1}{2}} \eta^{\frac{1}{2}}$
0	0.174	54.9	1.29
5	0.168	57.9	1.28
10	0.164	61.7	1.29
15	0.159	65.9	1.29
20	0.154	70.8	1.29
25	0.151	76.0	1.32
30	0.146	80.5	1.31
35	0.142	85.1	1.31
40	0.136	89.4	1.29
45	0.132	94.6	1.28
50	0.129	98.6	1.28
55	0.124	103	1.26
60	0.120	109	1.25
65	0.117	113	1.24
70	0.114	119	1.25
75	0.108	128	1.22
80	0.102	133	1.18
85	0.100	142	1.19

The constancy of $i_o t_o^{\frac{1}{2}} \eta^{\frac{1}{2}}$ is good, confirming that the establishment of polishing does not depend upon the attainment of a critical concentration of Cu^{++} at the anode surface.

Further evidence that copper dissolution is not controlled by the Cu^{++} concentration was obtained by electropolishing a copper anode in 50 per cent phosphoric acid, the anode and cathode being separated by a porous pot. The Cu^{++} concentration built up to a value far greater than the normal solubility, but polishing still continued. Even when considerable crystallization of salt had occurred on the anode, it was still brightly polished at the edges and between the crystals on the faces.

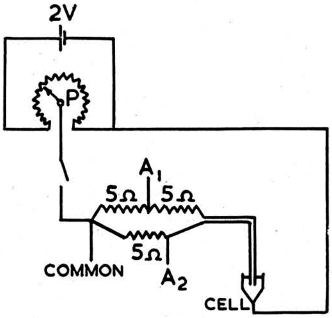

FIG. 5. Circuit (A)

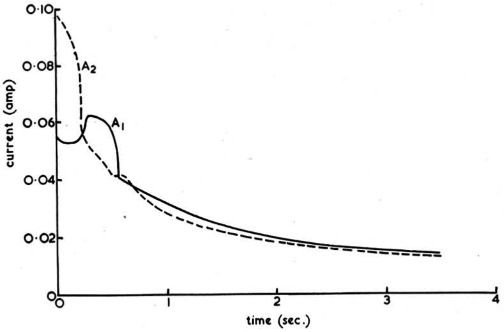

FIG. 6. Current-time curves on laminated anodes (A)

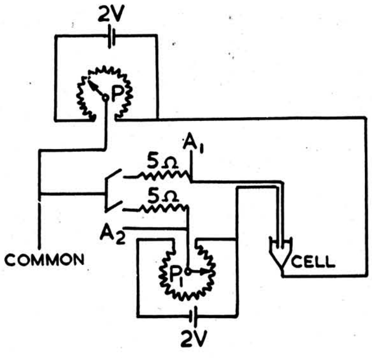

FIG. 7. Circuit (B)

Current Distribution over a Surface of Non-Uniform Potential under Polishing Conditions

It is suggested in the discussion below that the effect of slight potential variations over the anode surface is suppressed on attaining polishing conditions. This has been tested by means of a laminated anode used in the smoothing studies reported in Part II. The details of construction are described in that paper. The anode consisted of a stack of leaves of copper foil glued together with intervening leaves of mica and having alternate copper leaves connected together. The anode face was flat so that the two sets of leaves were level. In the two experiments described below, different means were chosen for maintaining a small potential difference between the two sets of leaves.

Potential Difference by Additional Resistance in One Lead

The circuit is shown in Fig. 5. The cell contained the laminated anode and 150 ml of 50 per cent by volume phosphoric acid. The potential difference between the two leads is variable but can be readily calculated from the current flowing through them. It becomes zero only when the current through the A_2 lead is twice that through the A_1. Current-time curves were photographed directly on a double beam oscillograph. The curves reproduced in Fig. 6 were obtained when a total of 1.8 volts was applied to the potentiometer *P*. Calculation shows the potential difference to be approximately 0.1 volt both at the beginning and end of the traces, although it rises well above that value in between. Within the accuracy of the oscillograph amplifiers, the current through both leads is the same after the final fall in current which indicates the establishment of polishing conditions.

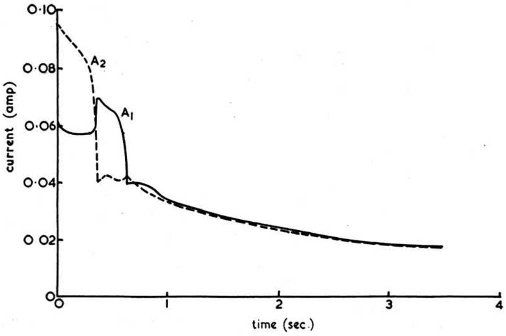

FIG. 8. Current-time curves on laminated anodes (B)

Potential Difference by Auxiliary Supply

The circuit is shown in Fig. 7. The cell was the same as before. The double-pole switch was included to prevent a current flowing between the two sets of leaves before the application of the voltage across the cell. P_1 was a low resistance (1Ω) potentiometer so adjusted as to give a potential difference between the two leads of 0.2 volt (on open circuit). The curves reproduced in Fig. 8 were obtained when 1.8 volts was applied to the A_2 lead and 1.6 volts to the A_1. Once again the current flowing through the two sets of leaves is seen to become the same when polishing conditions are established.

Discussion

The influence of changes in viscosity and the fact that the length of the transition period before polishing begins is approximately inversely proportional to the square of the current density indicate that diffusion is the controlling factor in electropolishing and that the attainment of a critical concentration at the anode surface of some constituent of the solution is responsible for the onset of polishing. However, it is clear from the experiments described above that Elmore's hypothesis is incorrect in attributing this effect to dissolved copper.

An equation similar to Elmore's was derived first by Sand

(2) to express the time necessary to reduce the concentration of ions discharging at an electrode surface to zero in an unstirred solution. This equation was verified for certain cathodic processes under conditions such that convection was small (3). Even where great care was not taken to avoid convection, the relation was found to apply fairly well for currents appreciably higher than the limiting value in the oxidation of ferrous and the reduction of ferric ions (4). By analogy with these cases a tentative explanation of electropolishing is developed below based upon the view that the controlling process is the depletion of the anode layer with respect to "acceptors," i.e., those ions or molecules with which the metal ions are combined in solution.

In many electropolishing electrolytes, the metal dissolves as a complex ion and, in these cases at least, the concept of acceptors (which could be anions or even water molecules, for instance) is plausible. Another explanation of the results reported in this paper is possible, however, in terms of hydrogen ions. These are removed from the anode layer not by discharge or combination but by migration toward the cathode. An equation of the same form as Elmore's would express the time necessary to reduce their concentration at the surface to a critical low value at which the metal ions would be insoluble and a hydroxide or basic salt might be formed; this could be the point at which polishing conditions are established. The acceptor hypothesis is preferred, however, since it is simpler on this basis to account for the principal characteristics of electropolishing. If further experimental work established the importance of hydrogen ion migration, much of the acceptor mechanism should still hold with only minor modification.

Acceptor Hypothesis

Since copper phosphate is insoluble in water but soluble in phosphoric acid, it seems reasonable to assume that the acceptors present in the copper-phosphoric acid cell are phosphate ions of some sort. It is postulated that upon the application of a voltage, these ions are used up by combination with Cu^{++} at a rate determined by the current and the number of such ions per Cu^{++} in the copper complex, their concentration at the anode thereby decreasing. If the current is low, a steady state diffusion layer may be set up such that the rate of supply of acceptors is able to balance their rate of combination with cupric ions. At higher currents, however, the concentration at the anode will ultimately reach zero. After this point the rate of dissolution of copper will be determined solely by the rate at which the phosphate ions arrive at the anode. The current can therefore no longer be maintained by the dissolution of copper alone, and the anode potential will consequently increase and the current fall. If the anode potential reaches that required for oxygen evolution, this process will intervene and the remaining voltage be taken up in the ohmic resistance of the cell once more, the discharge of hydroxyl ions permitting the additional current to pass. If this potential is not reached, the current will be established at a value corresponding to the rate of arrival of acceptors, and variation of the voltage within this range will not alter the current, i.e., the current-voltage curve will have a horizontal portion, typical of electropolishing cells of this kind. This is because the acceptors, being large ions or neutral molecules in the presence of small fast-moving cations which carry most of the current, are brought up to the anode by diffusion and convection but not, to any great extent, by electrolytic migration.

The attainment of zero concentration of phosphate ions at the anode would be expressed by a modified version of Elmore's equation in which the solubility limit of copper is replaced by the effective concentration of phosphate ions in the bulk of the solution. It was seen in Fig. 2 and 3 that, when allowance is made for varying viscosity, $i_o t_o^{\frac{1}{2}}$ is approximately proportional to the solubility of copper in the solution.

If the fairly reasonable assumption is made that the solubility of copper is determined by the concentration of phosphate ions over a range in which the concentration of Cu^{++} is small compared with that of phosphoric acid, then the conclusion reached above is confirmed. This argument is weakened by the admitted unreliability of the copper solubility values which were not accurately reproducible and by the fact that, due to the well-known complexities of phosphoric acid and phosphate solutions, it has not been possible to produce any direct experimental evidence of a relationship between copper solubility and phosphate ion concentration. The results in Table I, showing a maximum for both $i_o t_o^{\frac{1}{2}} \eta^{\frac{1}{2}}$ and for copper solubility at a phosphoric acid concentration of 40 per cent by volume, may indicate that the acceptors are hydrated ions, so that their concentration falls off at high acid concentrations at which there are fewer water molecules, as well as at low acid concentrations at which are fewer ions.

This hypothesis seems to explain adequately why there should be a sharp change in electrical conditions without the separation of a new phase. At the end of the transition period the layer of electrolyte immediately in contact with the anode does contain a limiting concentration of dissolved copper but only because there are no more phosphate ions at that instant to dissolve more and not in any absolute sense, as appeared from Elmore's hypothesis. Thus, after this point, the copper concentration will probably increase, since the diffusion away of the complex ions is likely to be slower than the arrival of new phosphate ions, on account of the larger size of the former. Since the controlling factor is the diffusion of phosphate ions and not of dissolved copper, it can be seen why it is possible to polish even in a saturated solution in which the concentration gradient of dissolved copper must be very nearly zero, and why $i_o t_o^{\frac{1}{2}}$ is practically independent of copper concentration in solutions of constant viscosity.

Elmore supposed smoothing to be accounted for by the differences in concentration gradient adjacent to high and low points on the surface. The alternative view given above (as to which is the controlling diffusion process) would still permit this mechanism to operate. However, full discussion of this point is deferred to Part II of this paper in which the results of quantitative experiments on smoothing action are reported.

The other characteristic feature of electropolishing, viz., the suppression of crystallographic etching, may be accounted for on the basis of the acceptor mechanism. Since the acceptors in the electrolyte arrive at the anode surface under the influence of diffusion and possibly convection but not, to any great extent, of electrolytic migration, their distribution over the surface will be unaffected by slight potential differences due to crystal structure, i.e., their distribution will be random. Now, if, as postulated, the concentration of acceptors at the surface after the transition period is zero, then every acceptor which arrives at the surface must be regarded as immediately removing that copper atom with which it comes in contact. Consequently, dissolution will be independent of crystal structure and no etching will result. However, in the condition before polishing is established there will be an excess of acceptors on the surface so that the relative rates of dissolution at different points on the surface will be determined by the potential energies of the copper atoms at those points. Dissolution will be influenced, therefore, by crystal structure, and etching will be expected.

Piontelli's (5) explanation of this feature was rather similar to the above, but he appeared to claim that low acceptor concentration at the anode would be sufficient to prevent etching, whereas the suggestion now made is that the concentration must actually reach zero. Hoar and Mowat (6) suggested that the random distribution of vacant lattice sites in a solid film on the anode surface could insure the suppression of etching, but this explanation takes no account of the presumed tendency of metal atoms with higher potential energies (due to crystal structure) to pass preferentially into the lattice. However, the existence of an oxide film on an anode surface, which did not prevent the continued dissolution of the metal, might well be accompanied by polishing, since the formation of the film would be expected to depend upon the prior attainment of zero concentration of acceptors at the surface (with consequent shift of potential to that required for hydroxyl ion discharge).

It has already been mentioned that since the current under polishing conditions depends solely on the rate of arrival of acceptors at the surface, it is independent of the applied voltage within this range. The above explanation of the suppression of etching is an extension of this principle, i.e., the rate of dissolution from various areas on the same surface is likewise independent of potential differences existing between them. This fact has been confirmed by the experiments described above, using a composite anode with externally applied potential differences.

The tentative hypothesis given above has been developed with particular reference to the copper-phosphoric acid cell, but it is felt that similar considerations could apply to all electropolishing (and chemical polishing) systems. The main differences would lie in the existence of simultaneous secondary processes (gas evolution, film formation, etc.) incidental to the controlling process, although in some cases perhaps helping to maintain it. In chemical polishing, the substitution of electron-accepting anions for an external voltage need not modify the essential mechanism of polishing.

Acknowledgment

The author wishes to record his thanks to the Director and Council of the British Non-Ferrous Metals Research Association for permission to publish the account of this work. Grateful acknowledgment is also made to Dr. G. L. J. Bailey and Mr. E. A. Ollard for many helpful discussions.

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Current Affairs

Wrightsville Beach Offers Many Attractions for Fall Meeting

The fall meeting of The Electrochemical Society will be held at Wrightsville Beach, near Wilmington, North Carolina, from September 13 through 16. This will be the 104th meeting of the Society. The location is ideal for a convention as it offers all the charm of a resort but is small and intimate enough to permit members to meet easily for either social or scientific visits.

Harbor Island, the home of International Nickel Company's Marine Laboratory and Testing Station, is but two city blocks from famous Wrightsville Beach, and is connected with a modern causeway bridge. Located ten miles east of the historic city of Wilmington, and primarily a residential ocean resort on U. S. Highways 74–76, Wrightsville offers many attractions including the charm of the vast Atlantic Ocean and the cordial welcome that is always extended. There is an excellent white sandy beach where surf bathing is very popular. For those who wish to swim, Wrightsville Sound is perfect. Wrightsville Beach has a superb climate, with an average temperature during September of 75°.

This island beach is self-contained with its own stores, hotels, cottages, churches, movie theater, club, and many other attractions. The sound, the surf, and off-shore fishing is most popular for channel bass, sail fish, bluefish, mackerel, and other game fish. Chartered boats are availalbe.

Headquarters

The Ocean Terrace Hotel at Wrightsville Beach will serve as convention headquarters where registration, social functions, and most of the technical sessions will be held. As usual, reservations of hotel accommodations at an early date is strongly recommended. These should be mailed direct to The South Eastern North Carolina Beach Association, P. O. Box 698, Wilmington, N. C., attention Mr. Jack Farrell.

Chairmen

F. L. LaQue of International Nickel Company is General Chairman of the meeting and F. A. Lowenheim is Chairman of the Finance Committee. The local staff of International Nickel Company at Wrightsville Beach will take charge of the details for all meeting arrangements. Committee members are R. B. Teel, *Hotel* and *Plant Visits Committees*; W. G. Dawson, *Registration* and *Local Transportation Committees*; H. T. Paterson, *Entertainment Committee.*

F. L. LaQue
General Chairman

Technical Sessions

The Society will hold technical sessions from Monday, September 13, through Wednesday, September 16. In addition, the annual meeting of the Sea Horse Institute will be held during the same week, September 16 to 18.

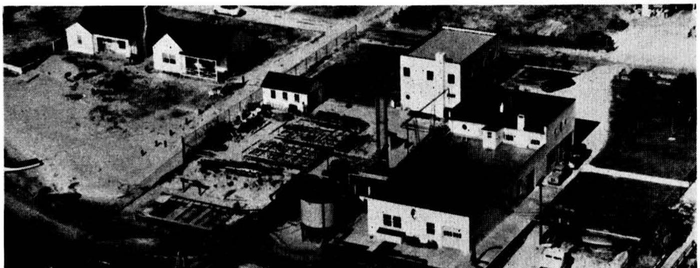
The Corrosion Division of the Society has planned two special symposia: (1) Marine Corrosion, and (2) Titanium Corrosion. Also, corrosion papers of general interest will be presented. Corrosion sessions will be held on Wednesday, September 16, which will coincide with the first day of the annual meeting of the Sea Horse Institute.

The Electrodeposition Division is arranging several sessions dealing with general electrodeposition problems.

The Battery Division plans two round-table discussions on the following topics:

1. "Low Temperature Performance of Primary Batteries"—with J. J. Coleman of Burgess Battery Company as moderator.
2. "Corrosion of Positive Grids in Lead-Acid Storage Batteries"—with J. C. White, Naval Research Laboratory, as moderator.

There will be no formal papers



Air view of International Nickel Company's Marine Corrosion Testing Station located at Harbor Island.

presented by the Battery Division at this meeting.

The Electrothermic Division tentatively plans a round-table discussion.

Plant Trips

Arrangements are being made for an organized inspection of The International Nickel Company's corrosion testing station at Harbor Island, and also their atmospheric testing stations at Kure Beach, some twenty miles away. Buses will be provided for transportation to the latter.

Social Functions and Ladies' Program

A novel feature of the social functions that has been arranged is a barbeque dinner scheduled for Monday evening, September 13. The reception and banquet will take place on Tuesday evening, the highlight of which will be the awarding of the Palladium Medal (The Palladium Medal address will be given earlier in the afternoon). A general Society luncheon has been arranged for Wednesday noon, September 16. Some of the divisions are planning luncheons which will be announced.

Seventh Annual Battery Research and Development Conference

The Battery Division of The Electrochemical Society was prominently represented at the Seventh Annual Battery Research and Development Conference sponsored by the Power Sources Branch, Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey. The meeting was held at the Berkeley-Carteret Hotel in Asbury Park on May 13 and 14. It was of especial interest to the Battery Division of the Society, many of whose members took part in the discussions and presented papers.

These conferences are held annually under the direction of Grenville B. Ellis, assisted by David Linden, for the purpose of presenting the results of Government sponsored battery research and development, and to provide a means for the exchange of technical information between the Government agencies and the battery industry. Over 150 commercial and Government groups, represented by almost 400 individuals, attended.

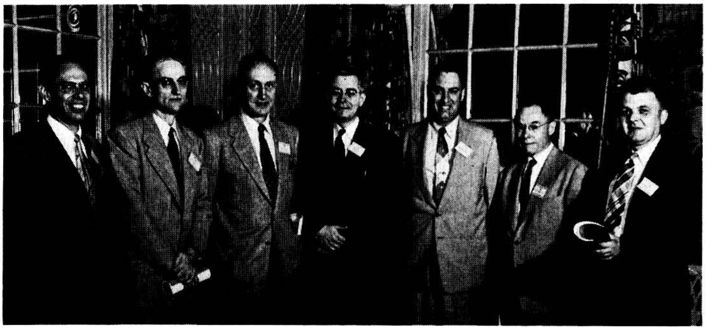
The 2-day meeting consisted of three symposia covering battery research, dry cell batteries, and special purpose batteries.

Battery Research

Under this head was "Aluminum Cell Systems," discussed by A. B. Garrett, Ohio State University; "Improved Storageability," on which investigations were reported by Olin Industries; "Dry Cell Capacity Predictor," which was the subject of a discussion by Grenville B. Ellis of SCEL; and "Solid Ion Conductor Batteries," in which W. Van der Grinten of General Electric Company described investigations being done by his company and SCEL.

Special Purpose Batteries

The symposium on special purpose batteries featured a round-table discussion on the zinc-silver oxide electrochemical system. Taking part was John B. Conn of Merck & Company, who proposed a reaction mechanism for the zinc-silver oxide battery in which silver (II) oxide functions as a reservoir of silver (I) oxide, furnishing capacity without contributing to the potential of the cell.



Battery Division members of the Society attending the Seventh Annual Battery Research and Development Conference at Asbury Park were (*left to right*) J. C. White, Naval Research Laboratory; E. J. Ritchie, Eagle-Picher Company; U. B. Thomas, Bell Telephone Laboratories; E. Willihnganz, Gould National Battery Company; A. F. Daniel, Signal Corps Engineering Laboratories; C. C. Rose, Willard Storage Battery Company; and A. G. Hellfritzsch, Naval Ordnance Laboratory.

SCEL and the Eagle-Picher Company reported that the interim standard line of "A" and "B" zinc-silver oxide batteries has been completed and is now available on an off-the-shelf basis for supplying the power required by the various equipment designers of rockets, missiles, and other special applications.

Arthur Fleischer, of Nickel Cadmium Battery Corporation, reported on investigations to improve the negative plate performance of the sintered plate storage battery. The symposium was concluded with a discussion by J. A. Mas of the Vibration Research Laboratories, Inc. on the use of vibrators and dynamotors as "B" supplies in lieu of batteries.

Dry Cell Batteries

This subject covered "Magnesium Batteries," in which Roy C. Kirk of the Dow Chemical Company and J. Hovendon of SCEL presented the results of the last year's efforts in the field of magnesium dry cell batteries. Investigations on "Miniature Low Drain Long Life Cell" were concerned with the improvement of the shelf life characteristics of the battery and the design of fabrication equipment which will be satisfactory for laboratory scale production.

The conference concluded with a discussion of "Manganese Dioxide and Carbon Black," two of the more important components of the dry cell battery. Edward W. Samoden of the Tennessee Corporation reported on experimental investigations on the development of methods of electrolytically synthesizing manganese dioxide to give optimum battery performance when discharged under certain specified conditions, and A. V. Peppard of Godfrey L. Cabot reported on investigations leading to the development of a domestic source of battery grade carbon black.

* * *

Papers presented at the conference, because of their restricted nature, are not available in published form.

Highlights of the Board of Directors' Meeting

(Held April 12, 1953)

The Secretary reported that the finances of the organization were satisfactory. The primary reason for the improved financial picture has been due to four causes: (1) an increase in nonmember JOURNAL subscriptions, (2) the increase in dues, (3) the large increase in the number of Sustaining Memberships (this is a direct result of Mr. Walter Prine's efforts), and (4) the increase in advertising revenue as a result of Mr. Bain's activities.

Mr. Bain gave a rather comprehensive report on his activities, and then requested help from the membership in obtaining contracts with several key companies. He feels that if these key companies can be persuaded to take contracts, the combined effect of this and the selling campaign that he is now waging will result in considerable increase in our advertising revenue.

The President proposed the following Nominating Committee:

George Heise, *Chairman*
Harold Read
Norman Hackerman
John Gall
Ralph Hunter
Harry Copson, *Alternate*

This appointment was approved.

The Treasurer reported on the Consolidated Fellowship Funds, and it was decided that a residue would be left in the National City Bank to make it possible to handle further income to this fund in a more expeditous fashion.

The possibility of publishing abstract cards was discussed. This suggestion was received from N. C. Cahoon of the Cleveland Section. No decision was made at this meeting, but it was agreed that the proposition would be studied.

The Secretary reported that to date we have 261 prepaid orders and 110 statements to the effect that the signers will purchase the Ten-Year Index when published. On the basis of this return, the Board authorized the Secretary to proceed with publication of the Ten-Year Index.

General discussion of future meetings of the Society was held. The meetings are as follows:

Fall, 1953—Wrightsville Beach, Sept. 13–16, Ocean Terrace Hotel
Spring, 1954—Chicago, May 2–6, La Salle Hotel
Fall, 1954—Boston, October 3–7, Statler Hotel
Spring, 1955—Cincinnati, May 8–12, Sheraton-Gibson Hotel
Fall, 1955—Pittsburgh, October 9–13, William Penn Hotel
Spring, 1956—San Francisco
Fall, 1956—Cleveland

The Local Section Advisory Committee reported that it is nearly ready to make formal application to the Board of Directors to change the setup of that committee. The Ways and Means Committee is cognizant of the proposed changes which will be announced formally when final decision is made.

The Young Author's Prize winner, W. E. Kuhn, The Carborundum Company, and the Francis Mills Turner Memorial Award, Sponsored by the Reinhold Publishing Corporation, winner, P. T. Gilbert, The British Non-Ferrous Metals Research Association, were announced.

The Palladium Medal Committee announced their recommendation of Professor N. H. Furman of Princeton University as Palladium Medalist. This recommendation was accepted.

President Warner outlined the current situation at the National Bureau of Standards with respect to the dismissal of Dr. Astin. He requested that Dr. Burns, Dr. Hunter, and Mr. McKay collaborate with him in preparing a proposal to bring to the Tuesday afternoon session of the Board.

At the conclusion of the business of this meeting, the Secretary announced that he had completed the first term of service on an appointed basis, and since it is his feeling that such appointment should be made for one year, and that the Board should be placed each year in a position where a change could be made readily, he formally resigned from the position of Secretary and withdrew from the proceedings. Action of the Board followed, reappointing Henry B. Linford as Secretary for the next year.

The meeting recessed at 5:15 p.m. until 4:00 p.m., Tuesday, April 14.

* * *

Resumption of Board of Directors' Meeting, April 14, 1953

The Secretary requested permission to deal expeditiously with the rental of the National Office. Since, undoubtedly, rates will be increased, he felt that it would be well to be placed in a position where he could, on advice from Dr. Burns, Mr. McKay, and others in the immediate area, move the National Office if more advantageous quarters could be found. Since this move would have to take place before July 1, it was necessary to have this enabling action.

The Nominating Committee reported as follows:

"Your Nominating Committee, on the basis of a meeting held April 13, 1953, recommends the followin gcandidates for office in The Electrochemical Society:

For President:
Marvin J. Udy
For Vice-President:
Norman Hackerman
John R. Musgrave
Fred A. Lowenheim

"Each of these men has verbally signified his willingness to stand for office and to serve if elected.

Respectfully submitted,
(Signed) H. R. COPSON
J. F. GALL
R. M. HUNTER
H. J. READ
G. W. HEISE, *Chairman*"

On the motion of Dr. Hunter, it was voted that the Board accept the report of the Nominating Committee.

President Warner then brought up the matter of a formal protest prepared since the Sunday Board meeting regarding the Astin dismissal. It was then agreed that the protest, as published in the June issue of the JOURNAL, be sent to the following people:

1. Sinclair Weeks, Secretary of Commerce
2. Dr. Allen V. Astin
3. Senate Small Business Committee
4. President Eisenhower
5. George Vinal
6. Walter Hamer
7. Paul Howard
8. Senate Committee on Commerce and Industry

The remainder of the time was spent with Mr. Bain, going over 41 companies in which he requested help in approaching the advertising managers. Members were assigned to make the contacts for Mr. Bain and to work with him in these particular companies.

The meeting adjourned at 5:15 p.m.

HENRY B. LINFORD, *Secretary*

Correction

In the article by J. O'M. Bockris which appeared in the December 1952 JOURNAL, pp. 366*C* and 367*C*, in equations (IV), (V), (VI), (VII), (X), (XI), and (XII), "exp" should be substituted for "e."

Atomic Industrial Forum Being Organized

Incorporation papers for an organization of businessmen, engineers, scientists, and educators interested in the industrial development and application of atomic energy for peaceful uses have been filed with the Secretary of State in Albany.

Presidents or key atomic energy executives of 13 corporations and institutions of higher education were named as directors of the group, which will be known as the Atomic Industrial Forum, Inc. The Forum will have its present headquarters in the Engineering Societies Building, 29 West 39th Street, in New York.

A broad membership of all businessmen, engineers, scientists, educators, and others involved or interested in atomic energy as a new and promising industry will be sought by the Forum, it was stated by its founders. There will be two classes of membership. Regular memberships will be open to individuals who are lawfully entitled to access to any "restricted data" as defined in the Atomic Energy Act of 1946. Special membership will be open to individuals, corporations, associations, partnerships and trusts which are now or expect to be engaged in research, development, or operations in atomic energy. Regular members only will have voting privileges and be eligible to serve on the Forum's board of directors.

Dr. T. Keith Glennan, president of Case Institute of Technology, in proposing an association, declared it "should provide a forum in which industry might develop its best thinking in the interest of the advancement of the peacetime uses of atomic energy; a forum in which industry might develop an informed voice to be heard at governmental levels as new atomic energy policy is hammered out; a forum, not to serve the narrow interests of a few, but to stimulate the industrial development of atomic energy for the good of all."

Later in his speech Dr. Glennan declared "there is no question but that the enlightened self-interest of competitive enterprise in the course of atomic energy development is also the public interest, and I don't think I am alone in this belief. For evidence of this, I need only point to the atomic energy law of this country, which declares that one of the principal objectives of the atomic energy program is the stimulation of free competition in private enterprise."

AIC Gold Medal Presented to J. C. Warner

The Gold Medal, highest award of the American Institute of Chemists, was presented in May to J. C. Warner, president of Carnegie Institute of Technology, and 1952–53 president of The Electrochemical Society. The presentation took place at the Benjamin Franklin Hotel in Philadelphia.

Dr. Warner has made outstanding contributions to science in the fields of corrosion of metals, the carbonization of austenite, the heats of mixing of nonelectrolytic solutions, the kinetics of ionic reactions, and the acid-base properties of mixed solvents. He is the author of more than 50 technical articles and is coauthor of a number of important chemical texts. During World War II, Dr. Warner headed government research on the purification and metallurgy of plutonium for the Manhattan Project. He is currently a member of the Atomic Energy Commission's General Advisory Committee, appointed for a 6-year term.

J. C. Warner

Acheson Nominations Due Sept. 1, 1953

Ernest G. Enck, Chairman of the Acheson Medal Award Committee, desires to receive suggestions for possible candidates for the next Acheson Medal Award, to be made in the fall of 1954.

Chairman Enck announces that the date for receiving these nominations has been moved forward (with the approval of the Board of Directors) to *September 1, 1953*. All nominations should be in his possession on or before that date.

The procedure to be followed by the membership in naming candidates was published in the March issue of the Journal, page 68C.

Electrochemistry Course in Cleveland Area

A survey course in applied electrochemistry is offered by Western Reserve University during the first term of the summer session, June 22–August 1. Topics to be covered will include electrometallurgy, the electroprocess industries, various aspects of plating and electrodeposition, electropolishing, battery technology, and corrosion. Conducting the course will be Dr. Allen G. Gray, technical editor of *Steel* magazine ande ditor-in-chief of The Electrochemical Society's forthcoming book, *Modern Electroplating*.

DIVISION NEWS

Electrothermic Division

Following the Division luncheon at the Hotel Statler in New York City on Tuesday, April 14, 1953, the annual business meeting was held.

C. H. Chappell, Chairman of the Division, called the meeting to order and requested that the secretary-treasurer's report be presented. Accordingly, I. E. Campbell presented his report as follows:

The net income for the past fiscal year was $64.00, thus increasing the net worth of the Division to $3427.88. Statistics were presented pertaining to the membership of the Division, which after a net gain of 12 for the past year, represented a total of 265.

Dr. Campbell also spoke of the proposed amalgamation of the Rare Metals group of the Electronics Division with the Electrothermic Division. Although no formal action was taken, the members of the Division expressed their approval of the proposal.

A brief report was made of progress pertaining to the Monograph on "High Temperature Material, Methods and Measurements." The first draft should be completed within two or three months.

After expressing thanks to J. S. Dewar for his efforts in organizing the meetings just concluded, Dr. Chappell read the report of the nominating committee. The committee, composed of A. T. Hinckley, Chairman, H. C. Oswald, and J. H. Brennan, made the following nominations:

Chairman—I. E. Campbell
Vice-Chairman—J. S. Dewar
Secretary-Treasurer—A. C. Haskell, Jr.
Members-at-Large on the Executive

Committee—J. W. Glasser and
M. H. Udy

As no further nominations were made from the floor, a resolution was adopted to authorize the Secretary to cast a unanimous ballot for all of the nominees.

Dr. Campbell then opened a brief discussion pertaining to the next Fall and Spring Meetings. A few subjects were proposed and appropriate committees will be selected. Additional suggestions should be sent to the Secretary-Treasurer.

A. C. Haskell, Jr., *Secretary-Treasurer*

Theoretical Electrochemistry

A business meeting of the Theoretical Electrochemistry Division was held at the New York Convention on Thursday, April 16, 1953, with H. R. Copson presiding as acting chairman. The chief item of business was the election of new officers. There were several nominations from the floor, and a vote resulted in the election of the following to serve for two years:

Chairman—J. P. Fugassi
Vice-Chairman—E. B. Yeager
Secretary-Treasurer—P. Delahay

There was then some discussion of the possibility of publication, prior to the convention, of some form of preprints of the papers on the program. The new officers of the division were requested to look into the possibility of an extended abstracts booklet, modeled after the one printed by the Electronics Division.

W. J. Hamer, *Chairman* (1952)

SECTION NEWS

Detroit Section

A dinner meeting, featured as "Students' Night," was held by the Detroit Section on April 24 in honor of Professor A. L. Ferguson of the University of Michigan and Professor D. T. Ewing of Michigan State College. The meeting took place at Wayne University Student Center.

The speakers who participated at this occasion are listed below, with their subjects:

Walter Dow, Graduate Student and Research Associate, Michigan State College, "Effect of Iron Impurities in Nickel Plating Solutions and Their Removal"

Joseph Tobin, Graduate Student and Research Fellow, Michigan State College, "Porosity of Electrolytic Nickel Deposits"

John Hoekstra, Graduate Student and Research Associate, Wayne University, "Some Studies in the Mechanism in Bright Plating"

J. M. Markowitz, University of Michigan, "Electrochemical Reduction of Halogenated Compounds."

G. V. Kingsley, *Secretary-Treasurer*

Midland Section

J. C. Warner, Society president, was the featured speaker at the April 2 meeting of the Midland Section. Ralph M. Hunter, past president, made some introductory remarks sketching the busy life of Dr. Warner.

Dr. Warner spoke on the subject of "Histories of Theories of Electrolytes." He concisely and thoroughly discussed the history behind the development of theories of electrolytes, and the talk was well dispersed with slides. The contributions of Valson were first discussed, then the five postulates of Arrhenius. The ten proposed forms of the Dilution Law from Ostwald in 1887 to Kraus and Bray in 1914 were next shown.

After 1914, the speaker said, theory

New Address

FOR

The Electrochemical Society, Inc.

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

Telephones—RIverside 9–0602 and RIverside 9–0603

The Electrochemical Society has moved its offices to larger quarters, located on the southeast corner of 102nd Street and Broadway. This is diagonally across Broadway from the former location. After July 1st, all communications to the Society and the Journal should be addressed to the new number, *216* West 102nd Street. Telephone numbers remain the same.

was supplanted by more intensive experimental work. The thermodynamic properties of electrolytes were studied by Lewis and Noyes and in 1923 the Debye-Hückel theory was presented. Noyes later interpreted the work of Debye and Hückel—contributing much to early acceptance of the theory. Later, the Debye-Hückel-Onsager theory, pertaining to electrostatic and electroviscous retarding forces, was discussed. A conductance equation for a 1–1 salt was developed. Several slides showed plots of functions of the Debye-Hückel theory.

Dr. Warner then led the discussion to dilute systems and stated that a conductivity theory from the modern point of view is very difficult. Poisson's equation was solved for two cases—high and low concentration. Another slide showed the effect of ionic diameter upon the activity coefficient. An anlaysis of organic acids, he said, would be very difficult. Dr. Warner completed his talk with a prediction that future theoretical interest would be in fused salts and nonaqueous systems.

Preceding the meeting, members of the Section gathered at the Midland Country Club for an informal dinner with Dr. Warner.

F. N. Alquist, *Secretary-Treasurer*

Philadelphia Section

The Philadelphia Section held its final meeting of the season on Saturday, May 9th. Following its custom, the Section had arranged an interesting afternoon and evening outing program to which the ladies were especially invited; approximately forty members and guests attended. The meeting was held in the Pfahler Hall of Science at Ursinus College, Collegeville, Pa.

The principal event was a most interesting and enjoyable talk, "To the Land of the Zulus," given in the evening by Ernest G. Enck, Secretary of the Foote Mineral Company and an active member of the Philadelphia Section.

In his talk, Mr. Enck related his experiences in Africa in connection with the procuring of lithium minerals and other ores for his Company's operations. Mr. Enck guided the group through the vast mysterious depth of Kruger Park and, by jeep and trekking, across the great South African veldt.

The group was impressed by the primitive character of the African mining operations. Numerous Kodachrome slides contributed to the impressions of the African scene.

In the afternoon, the group assembled at the Audubon Shrine development, Audubon, Pennsylvania, where J. D'Arcy Northwood, the curator, gave a brief talk on the Audubon lore, and also discussed the copper and lead mining operations which from time to time have been pursued on the property. The group took time to enjoy this historic site and its rural beauty and to examine the collection of Audubon color prints of birds and other natural life.

The group then went to the locally famous Lakeside Inn in Limerick for a pleasant social hour and dinner. After dinner the party proceeded to Ursinus College where a brief conducted tour of the campus had been arranged.

John F. Gall, the Philadelphia Chairman, opened the meeting with a word of appreciation to Ursinus College for kindly providing the Philadelphia Section with a very satisfactory meeting place. The Ursinus host, Professor William S. Pettit, responded with an expression of welcome.

In a short business meeting, the Philadelphia Section voted to accept in principle the proposed changes in our Society's bylaws which are intended to reorganize the Local Section Advisory Committee.

The Section then held its annual election of officers, and the following persons were elected for the 1953–1954 term:

Chairman—J. Fred Hazel
Vice-Chairman—Edgar L. Eckfeldt
Treasurer—G. Franklin Temple
Secretary—George A. Bodamer

The program proved to be very enjoyable throughout and was the highlight of the Philadelphia Section's season.

E. L. Eckfeldt, *Secretary*

New York Metropolitan Section

The final meeting of the season was held on May 13, 1953, at the Hotel Holley. This meeting was the Third Annual Ladies' Night and featured favors, door prizes, and other special attractions for the wives of the members, who turned out in good quantity (and needless to say, high quality).

The featured speaker of the evening was R. M. Bowie, Director of Engineering for Sylvania Electric Products Incorporated, who spoke in a semitechnical manner on color television. Dr. Bowie explained the principles involved in televising color and gave a short history of the various means which have been proposed to solve the problems. His talk was very well received and he was kept answering questions until a late hour.

Preceding the principal speaker, Dr. Carl Kolbe of the General Electric Company showed a short color film on the forging of molybdenum alloys in inert atmospheres.

The following officers were elected for the coming year:

Chairman—Herbert Bandes
Vice-Chairman—Martin F. Quaely
Secretary-Treasurer—Kenneth B. McCain
Members of the Executive Committee—
  Past-Chairman, A. C. Loonam, M. B. Diggin, C. V. King, and Fred P. Peters

F. A. Lowenheim, *Secretary-Treasurer*

PERSONALS

Felix E. Wormser, president of Lead Industries Association, New York, was recently appointed by President Eisenhower to be Assistant Secretary for Mineral Resources in the Department of the Interior, Washington, D. C.

Hubert M. Goldman has been appointed to the newly-created post of assistant to the sales manager and technical engineer at Enthone, Inc., New Haven, Conn. Edward F. Foley has been named research chemist in the company's enlarged research facilities.

Claire C. Balke, formerly Director of Research and Chief Engineer, Roberts and Mauder Corporation, Hatboro, Pa., is now president and treasurer of Balke Research Associates Inc., Doylestown, Pa.

Percy E. Landolt, Lithium Corporation of America, Inc., New York City, has been elected president of the Columbia University Engineering School Alumni Association for the 1953–54 academic year.

Richard Rimbach of Richard Rimbach Associates, Pittsburgh, left for Europe in June to visit a number of representatives of technical and scientific groups and instrument engineers in connection with the First International Instrument Congress and Exposition to be held in Philadelphia, September 13–24.

B. B. Dey has joined the Central Electrochemical Research Institute, Karaikudi, as Director.

J. V. Petrocelli, Patent Button Company, Waterbury, Conn., has been appointed Journal editor of the Corrosion Division of the Society, succeeding Michael A. Streicher, former Corrosion Division editor.

James H. Schulman has been named head of the Chemistry Branch of the Metallurgy Division of the Naval Research Laboratory, Washington, D. C. Dr. Schulman was formerly head of the Luminescent Section of the Chemistry Branch.

George A. Perley was recently presented with an Alumni Citation from the University of New Hampshire "in recognition of outstanding achievements and services in the field of chemistry."

S. Krishnamurthi has been appointed deputy engineer, Plating Shop, Indian Telephone Industries, Ltd., Bangalore.

Daniel C. Oakley of Ray-O-Vac Company, Madison, Wis., has joined the Blake Manufacturing Company, Clinton, Mass.

G. P. Contractor, Acting Director of the National Metallurgical Laboratory of India for a period of three and one-half years, relinquished his services with the Indian Council of Scientific and Industrial Research in April. Dr. Contractor has served with the Council for nearly nine years. He will leave India some time in August for Great Britain, on his way to Canada.

CHARLES F. VAUGHN

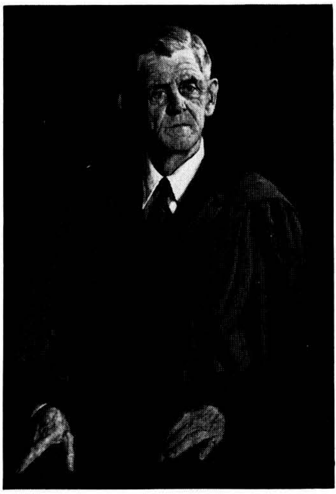
Charles F. Vaughn, retired vice-president and manager of Mathieson Chemical Corporation, died in Niagara Falls on March 30.

Charles Vaughn was born in Providence, Rhode Island, in 1874 and was graduated from Worcester Polytechnic Institute in 1896. Connected with the Mathieson Corporation for 53 years, he made many contributions to the development of batteries and perfected the Castner mercury cell. He was awarded the Schoellkopf Medal for meritorious work in the chemical field. During World War I he served with distinction as a lieutenant-colonel in the Chemical Warfare service.

Mr. Vaughn joined The Electrochemical Society in 1902, the year of its founding.

Dr. Creighton Honored at Swarthmore

A large portrait of H. Jermain Creighton, recently completed and handsomely framed, was presented to Swarthmore College by his former students and friends. A photograph of the portrait is shown below. The presentation was made on June 6 and was the occasion of many tributes to Dr. Creighton, former head of the Swarthmore chemistry department. He retired in June 1952 after 40 years of teaching at that institution. During this time his work has made him world famous and brought him many honors.



Copy of portrait of Dr. H. Jermain Creighton recently presented to Swarthmore College.

Journal readers will be interested to hear of Dr. Creighton's activities during the past year. A former Society president, he promised to travel and engage in various interesting pursuits upon retirement. Accordingly, since last June, he has visited Mexico, California, and Canada. He has threatened to leave the North American continent the next time he takes a trip.

Dr. Creighton was born in Nova Scotia and for many years he has had a summer home there, at St. Margaret's Bay. This is now his home base and he keeps a small fleet of boats there: a schooner, a motor launch, and some smaller craft—for sailing has been his lifelong recreation. In the fall, he will again follow the sun, visiting some of the warmer climates that he has not previously had the opportunity to enjoy.

NEW MEMBERS

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

Active Members

Francis Bitter, Massachusetts Institute of Technology, Cambridge, Mass. (Electronics)

S. D. Bowers, Jr., U. S. Radium Corporation, mailing add: 106 West St., Bloomsburg, Pa. (Electronics)

Vicente E. Coca, Laboratorios Quimicos Cora, mailing add: Bahia Blanca 683, Buenos Aires, Argentina (Electrothermic and Theoretical Electrochemistry)

Rolf Cransberg, N. V. Metallic Industry, Loosdrecht, Holland (Corrosion, Electrodeposition, Electro-Organic, Industrial Electrolytic, and Theoretical Electrochemistry)

Robert L. Crone, Radio Corporation of America, mailing add: 59 E. Pine St., Ephrata, Pa. (Electronics)

Robert J. Dawson, Ray-O-Vac Company, 212 E. Washington Ave., Madison, Wis. (Battery)

Joseph F. Donahue, Jr., Naval Ordnance Laboratory, mailing add: 9812 Dilston Rd., Silver Spring, Md. (Battery)

Peter J. Ensio, Quebec Iron & Titanium Corporation, mailing add: 461 Second St., St. Lambert, Quebec, Canada (Electrothermic)

Jesse J. Fuchs, U. S. Electric Mfg. Corporation, mailing add: 140–09 Jewel Ave., Kew Gardens Hills, N. Y. (Battery)

Richard H. Gale, Chemical Products Works, General Electric Company, 1099 Ivanhoe Rd., Cleveland, Ohio (Electronics)

Robert J. Good, Monsanto Chemical Company, Anniston, Alabama (Electric Insulation)

Joseph T. Gushue, U. S. Rubber Company, mailing add: 1230 Avenue of the Americas, New York, N. Y. (Battery and Electric Insulation)

William H. Highfield, General Electric Company, mailing add: 295 Heath Terrace, Buffalo, N. Y. (Electronics)

John W. Hoopes, Jr., Columbia University, Box 102, Havemeyer, New York, N. Y. (Industrial Electrolytic)

Warren E. Haupin, Aluminum Company of America, Research Laboratories, New Kensington, Pa. (Industrial Electrolytic)

Robert N. Hazelwood, Line Material

Company, mailing add: 3405 N. Hackett Ave., Milwaukee, Wis. (Electric Insulation)

Samuel Korman, Phelps Dodge Corporation, mailing add: 397 Fifth Ave., Cedarhurst, N. Y. (Electronics and Electrothermic)

Alfred Kremheller, Sylvania Electric Products Inc., mailing add: 35-05 Parsons Blvd., Flushing, N. Y. (Electronics)

Herman A. Liebhafsky, General Electric Company, mailing add: 1674 Lake Blvd., Schenectady, N. Y. (Theoretical Electrochemistry)

Lewis G. Longsworth, Rockefeller Institute, 66 St., and York Ave., New York, N. Y. (Theoretical Electrochemistry)

Leonard May, National Union Radio Corporation, 350 Scotland Road, Orange, N. J. (Electronics)

Albert Muller, Air Reduction Company, Murray Hill, N. J. (Electronics & Electrothermic)

William K. Murray, R. Wallace & Sons Manufacturing Company, mailing add: 48 Maple Ave., Meriden, Conn. (Electrodeposition)

Edward S. Naidus, United Shoe Machinery Corporation, mailing add: 29 Cypress St., Marblehead, Mass. (Electric Insulation and Theoretical Electrochemistry)

Kurt O. Otley, National Bureau of Standards, mailing add: 3435 Yuma St., N.W., Washington, D. C. (Electric Insulation, Electronics, and Theoretical Electrochemistry)

Maurice H. Pickard, Pacific Coast Borax Company, mailing add: 100 Park Ave., New York, N. Y.

Howard H. Rogers, Research Division, Allis-Chalmers Corporation, Milwaukee, Wis. (Theoretical Electrochemistry)

Keith L. Smith, General Electric Company, mailing add: 4887 Anderson Rd., Cleveland, Ohio (Electronics)

Luke Thorington, Westinghouse Electric Corporation, Research Department, Bloomfield, N. J. (Electronics)

Robert L. Westlake, Jr., National Carbon Company, Rm. 303, 292 Madison Ave., New York N. Y.

Associate Members

John Betley, Sunray Electric, Inc., 1401 Lexington Ave., Warren, Pa. (Electronics)

Edward A. Kure, Willard Storage Battery Company, mailing add: 1276 E. 172, Cleveland, Ohio (Battery and Theoretical Electrochemistry)

LETTER TO THE EDITOR

More About New Nickel-Plating Process

Dear Sir:

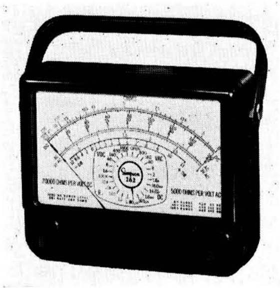
This concerns the recently announced "Kanigen" process of the General American Transportation Corporation for depositing nickel, as described on page 127*C* of the May issue of the Journal. It may not be out of order to point out that the deposition of nickel by reduction of nickel salts with hypophosphites is a development of Dr. Abner Brenner and his group at the National Bureau of Standards, and it is their process upon which the General American Transportation Corporation process is based. The Bureau deserves credit in this instance over and above any of the several companies who are currently commercially developing and applying the original disclosure.

In addition to the fact that the initial fundamental work was well done and merits recognition, it is also appropriate, at this critical time for the Bureau, to bring attention to another of the Bureau's many outstandingac complishments of the past fifty or more years to American industry and to American life.

H. H. Uhlig
Massachusetts Institute of Technology,
Cambridge, Massachusetts

NEW PRODUCTS

Volt - Ohm - Milliammeter. New Model 262 Volt-Ohm-Milliammeter features 20,000 ohms per volt sensitivity. Very compact unit housed in a 7-inch case. Each of its 33 ranges has been customized to meet the needs of the electronic and electrical industries. Simpson Electric Co. N-13



Fiberglas Plating Tank. New seamless Fiberglas tank for use with all solutions generally used in plating—except caustic cleaner and hydrofluoric acid. Temperatures of tank contents may be as high as 220°F. Costs from 5 to 29% less than lined steel tanks and is equally impervious to chemical attack. Furnished in any size required. Hanson-Van Winkle-Munning Co. N-14

Liquid-Liquid Extractors. New type of glass apparatus, known as the Schmall Apparatus, for the extraction and determination of salts of organic bases and acids. This procedure eliminates many hand operations and facilitates sample preparation; also, extraction is automatic, washings are eliminated, and labor cost of analysis is reduced. Two types available: for solvents lighter than water and for those heavier than water. Scientific Glass Apparatus Co., Inc. N-15

Vacuum Rhodium Coating Service. A service, equipped to apply coatings of rhodium to nonconductive and conductive materials by using the vacuum technique, has been announced. It is applied on a commercial basis upon glass and other nonconductive substances to meet specifications of transmittancy and hardness. Rhodium has high resistance to chemical attack and is excellent for mirrors and reflecting surfaces when exposed to corrosive chemical atmospheres. Other metals that can be vacuum deposited, such as aluminum, gold, and silver, will also be applied. The coating service is available to technical laboratories, industrial organizations, etc.; the work is done on a job basis. Serfass Corp. N-16

Aluminum Protection. New protective coating chemical for aluminum, "Alodine" No. 1200, has been developed and its effectiveness tested in 500 hours

(*Continued on page 205C*)

Annual Report of the Board of Directors for 1952

During the year 1952, four meetings of the Board of Directors were held. Full details of the business transacted at these meetings are contained in the minutes, on file in the Secretary's Office, where they may be consulted by any member of the Society. Only the important items of business transacted during the year of 1952 are detailed here.

The Reinhold Publishing Corporation, during the year 1952, announced their desire to continue the work of one of their officers, the late Francis M. Turner, in recognizing young authors. For many years Mr. Turner has personally offered a prize to young authors publishing in the official organ of the Society. The new award, known as "The Francis Mills Turner Memorial Award, Sponsored by the Reinhold Publishing Corporation," consists of a prize of $100 worth of books from any publisher.

Your Board, this year, has established a Consolidated Fellowship Fund from the accumulated earnings of the Weston Fellowship Fund, the Roeber Research Fund, the excess earnings of the Acheson Fund, and $1,000 returned by Dr. Marden (his Acheson Award) at the time of the Montreal Meeting. (Due to the deterioration of the Weston Fellowship funds, the control of such funds was not in the hands of the Board of Directors.) It is the policy of the Board that this fund will be accumulated until such time as the Society has available sufficient yearly income from this source to justify offering a first class fellowship, at which time we again will be in a position to sponsor graduate studies in electrochemistry.

During this past year, the following awards were made:

The Acheson Award—J. W. Marden of Westinghouse Electric Corporation.

Honorary Membership—William Blum of the National Bureau of Standards, Washington, D. C.

Young Author's Prize—John T. Byrne of The Dow Chemical Company.

Turner Book Prize—Kurt H. Stern of Clark University and Charles C. Templeton, Shell Oil Company.

Prize Essay Contest—First prize — Gordon Gemmell, Cambridge, Massachusetts; second prize — Donald W. Hutchings, Oberlin, Ohio; honorable mention — Robert Auerbach, New York City.

During the year, the Board of Directors decided to change their Sustaining Membership policy, making it possible for companies to take out more than a single membership.This campaign was started in December 1952, and to date has resulted in a total of 13 multiple memberships.

The dues schedule for the members was changed so that at present our active membership dues amount to $15, associate membership $9.50, and student associate membership $3. Subscriptions to the JOURNAL will be $15.

Several changes in operation of the Society were made:

Mr. Frank LaQue resigned as Business Manager of the JOURNAL for reasons of health. Since his retirement date, the duties of the Business Manager have been conducted by the Secretary.

Richard Rimbach Associates resigned as our advertising representative, and Mr. Jack Bain has been handling this work since. As our members will note from the increased advertising activity in the JOURNAL, this has been advantageous.

Miss Eleanor Reid, our Managing Editor, resigned. This resignation was necessary since Miss Reid was married to Mr. Brian Forrow and moved to the West. Mrs. Ruth Sterns was appointed Assistant Editor, and has been handling the duties carried on by Miss Reid in an excellent fashion for the large part of the year.

The elected term of office of the Secretary was concluded in May of 1952. At the Philadelphia Meeting, the Board of Directors appointed Henry B. Linford to continue as Secretary on an appointment basis.

HENRY B. LINFORD, *Secretary*

Annual Report of the Secretary

Report on Membership for 1952

Membership as of January 1, 1952	2055	
Qualified as members in 1952	242	
Reinstated members	7	
Total		2304
Deaths during 1952	10	
Resignations and members dropped in 1952	141	151
Membership as of December 31, 1952		2153
Net Increase		98

Composition of Total Membership, January 1, 1953

	Active	Associates	Student associates	Total
United States	1787	66	30	1883
Canada	62	2	1	65
England	37	1	0	38
India	31	5	2	38
Other Foreign	126	3	0	129
Total	2043	77	33	2153
Emeritus				36
Honorary				9
Sustaining				75
Grand Total				2273

Sustaining Memberships

Sustaining member companies and total number of memberships as of May 1, 1952	66
Sustaining member companies as of April 8, 1953	81
Total sustaining memberships (including multiple memberships by some companies) as of April 8, 1953	94

Modern Electroplating

Modern Electroplating on hand January 1, 1952	82
Modern Electroplating sold during 1952	82
Modern Electroplating on hand Dec. 31, 1952	0

Report of Tellers of Election

For President: R. J. McKay, 740; 8 write-ins; 12 abstentions

For Vice-President: Hans Thurnauer, 305; Jerome Strauss, 297; 147 write-ins; 11 abstentions

In addition to the above, 10 ballots were declared illegal because of irregularities.

(Signed) HERBERT P. DENGLER, *Chairman*
IRVING MOCH, JR.
DAVID O. FEDER
Tellers of Election

The Tellers' Report was unanimously accepted and a motion was made declaring the candidates, R. J. McKay (President) and H. Thurnauer (Vice-President), duly elected.

HENRY B. LINFORD, *Secretary*

TREASURER'S REPORT* FOR 1952

* *The Auditor's Report appeared in the May 1953* JOURNAL.

Canadian Convention Fund (in Canadian Funds)

Bank Balance 1/1/52	$1,104.20
The Canadian Bank of Commerce, Toronto Transferred to the Montreal Branch June 2, 1952	
Credit: Deposits	6,970.18
	8,074.38
Debit: withdrawals to 12/11/52	5,051.30
	3,023.08
Debit: withdrawal for draft of $3,108.50 in USA—Funds—12/18/52	3,023.08
Bank Balance 12/18/52	0.00

The draft for $3,108.50 in USA funds was deposited in the National City Bank, New York City, to the credit of The Electrochemical Society.

Columbus Convention Fund

USA Gov. Bonds Series F (earmarked in safe deposit box)	400.00

CORN EXCHANGE BANK
102nd Street and Broadway, New York, N. Y.

Corrosion Handbook Fund—for 1952

Total Corrosion Handbook Fund, 1/1/1952		$12,399.83
Corn Exchange Bank		
USA Savings Bonds Series F (earmarked in safe deposit box)		10,471.37
New York Savings Bank		
Balance, 1/1/52		1,928.46
Credit: Interest for 1952	$58.43	
Royalties for 1952	1787.40	1,845.83
		3,774.29
Debit: Prizes, Travel Expenses, Medallic Art Co., etc.		491.38
Balance, 1/1/53		3,282.91
Total Corrosion Handbook Fund, Jan. 1, 1953		13,754.28

Edward Weston Fellowship Fund—for 1952

Total Weston Funds available for Fellowship 1/1/52	$2,296.91

* *Capital Funds Securities, 1/1/1953*

$11,881.88—Hanover Bank Co., Trust Fund A—purchase price 5/2/51 for 1160 units; value 1/1/1953—$12,303.19
$1,836.66—AC 1330 Brook Avenue, Bronx N. Y., N.Y.T. & M. Co.
1 —Prudence 422 34 E. 86th St., N.Y.C. allowed claims.

* The Hanover Bank, Trustees
70 Broadway, New York, N. Y.

The Hanover Bank, *Trustees*

Principal Account Balance 1/1/1952	$57.31	
Principal Account Balance 1/1/1953	57.31	
Checking Account Balance 1/1/1952		$1,460.36
Credit: Deposit from Income Acct. 9/11/52		365.92
		1,826.28
Debit: ECS Consolidated Fellowship Fund 12/23/52		1,800.00
Checking Account Balance 1/1/1953		26.28
Income Account Balance 1/1/1952		93.36
Credit: Dividends from H.B., C.T. Fd. A. for 1952		388.62
		481.98
Debit: Trustee charges for 1952	$ 19.26	
Transfer to checking acct. 9/11/52	365.92	385.18
Income Account Balance 1/1/1953		96.80
The Hanover Bank Balance for Fellowship 1/1/53		$ 123.08
Seamen's Bank for Savings		
Income Balance 1/1/1952	$1,042.35	
Credit: Interest for 1952 to 12/23/1952	13.03	$1,055.38
Debit: withdrawal for Consolidated Fellowship Fund 12/23/52		1,055.38
Income Balance, Dec. 23, 1952		0.00
Total Weston Fund Available for Fellowship, 1/1/53		$ 123.08

Edward Goodrich Acheson Fund—for 1952

*Capital Funds Securities—1/1/1953**

$ 5,000.	USA Savings Bond Series F, no interest; due 10/1/53. Registered.
10,000.	USA 2½% Savings Bond Series G due 11/1/54. Registered.
2,000.	Pennsylvania Railroad Co. 3⅛% General Mortgage Bond, Series F. Due 1/1/85.
2,000.	American Telephone & Telegraph Co. 2-¾% Debenture due 10/1/75.
52 shs.	American Can Co. 7% Cum. Pfd.
14 shs.	Corn Products Refining Co. 7% Cum. Pfd.
10 shs.	Eastman Kodak Co. 6% Cum. Pfd.
10 shs.	Ingersoll Rand Co. 6% Cum. Pfd.
25 shs.	International Harvester Co. 7% Cum. Pfd.
20 shs.	National Lead Co. Class A 7% Cum. Pfd.
1	Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Guaranteed First Mortgage Participating Certificate, Series 2-7165 Bond & Mortgage. Only remaining asset is General Claim.
1	Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Series 3-6902 due 3/1/38. 5½%
1	Sealed envelope containing Lawyers Westchester Mtge. & Title Co. Guaranteed First Mortgage Certificate in Bond & Mortgage of Chatsworth Gardens Corp. Series 6-6972 Certificate #296. Only remaining asset is General Claim against the former guarantor.

* Guaranty Trust Company of New York, Custodian. Fifth Ave. at 44th St., New York, N. Y.

Acheson Fund Total Balance 1/1/1952	$4,092.33

TREASURER'S REPORT FOR 1952 (*continued*)

Guaranty Trust Co., *Custodian*

Income Balance, 1/1/1952 (includes Prin. Fds. of $97.43)		3,372.99
Credit: Dividends plus interest		991.50
		4,364.49
Debit: Custodian Charges	$ 77.00	
Honorarium to J. W. Marden	1,000.00	
Medallic Art Co.	432.77	
Medallists Expenses	107.10	
Consolidated Fellowship Fund	2,000.00	3,616.87
Income Balance 1/1/1953 (includes Prin. Fds. of $97.43)		747.62

East River Savings Bank, Amsterdam Ave. at 96th St., N.Y.C.

Principal Funds Balance, 1/1/1952	719.34
Credit: Interest for 1952	17.16
Principal Funds Balance, 1/1/1953	736.50
Acheson Fund Total Balance, 1/1/1953	1,484.12

Roeber Research Fund

Bank Balance, 1/1/52	$5,209.39
Credit: Interest for 1952 to 12/18/52	58.60
	5,267.99
Debit: Consolidated Fellowship Fund 12/18/52	5,267.99
Bank Balance, 12/18/52	0.00

The Roeber Research Fund was incorporated into the Consolidated Fellowship Fund by directive of the Board of Directors. Oct. 26, 1952

East River Savings Bank
Amsterdam Ave. at 96th St., New York, N. Y.

Joseph W. Richards Memorial Fund

Bank Balance, 1/1/52	$3,657.48
Credit: Interest for 1952	73.52
	3,731.00
Debit: Consolidated Fellowship Fund 12/18/52	3,000.00
Bank Balance, 1/1/53	731.00

Central Savings Bank
Broadway at 73rd St., New York, N. Y.

(*Continued from page 202C*)

salt spray exposure. The new chemical forms an amorphous mixed metallic oxide coating of low dielectric resistance that provides high corrosion-resistance for unpainted aluminum. Also it forms an excellent paint bond. American Chemical Paint Co. N-17

LITERATURE FROM INDUSTRY

Mono-Column Demineralizer. Catalogue sheet describes Penfield's new M-100 Mono-Column Demineralizer. Photograph and schematic diagram, combined with detailed description of parts, sample specifications, and performance data, provide a concise and complete resume of essential information. Penfield Manufacturing Co., Inc. P-139

New Manuals. Two new manuals, "Constant Temperature Control" and "Constant Pressure Control," have been published. The former is a guide to control devices of specialized design; 64 pages, extensively illustrated. The latter manual explains effective means of achieving automatic vacuum and pressure control. Emil Greiner Co. P-140

Rustproofing Agent. New product to prevent rusting of steel, cast iron, and other iron alloys during storage is described in technical bulletin. The product, a free-flowing powder, is a mildly alkaline, water-soluble material used in a concentration of 1 oz/gal. Tests indicate that it will protect iron and steel against rusting in 100% humidity for several weeks or more. Available in 100- and 300-lb fiber-packed drums. Enthone, Inc. P-141

Germanium Diodes. Bulletin describes characteristics and advantages of the new line of Germanium Diodes being produced. This company is first to produce a vacuum-impregnated Diode. These are the result of two years of development and pilot production. International Rectifier Corp. P-142

Tank Rheostats. New bulletin describes and illustrates the new H-VW-M tank rheostats. Lists standard ratings and sizes of rheostats, which are used to adjust current density in plating tanks. A schematic drawing shows a typical rheostat-to-tank hookup. Hanson-Van Winkle-Munning Co. P-143

Liquid-Level Control. Folder describes a single-thyratron electronic liquid-level control operating without radio frequency from a single capacitive type probe. Illustrates the single-unit control, probe, and alternative schematic arrangements for installation. Thermo Instruments Co. P-144

Electric Heater. Bulletin describes new Glo-Quartz Electric Radiant Immersion Heater which makes it possible to heat all acid electroplating, electropolishing, pickling, and phosphatizing solutions with 100% efficiency. Long life, portability, and replaceable heating elements are some of its advantages. Glo-Quartz Electric Heater Co., Inc. P-145

To receive further information on any New Product or Literature from Industry listed above, send inquiry, with key number, to Journal of The Electrochemical Society, 216 West 102nd Street, New York 25, N. Y.

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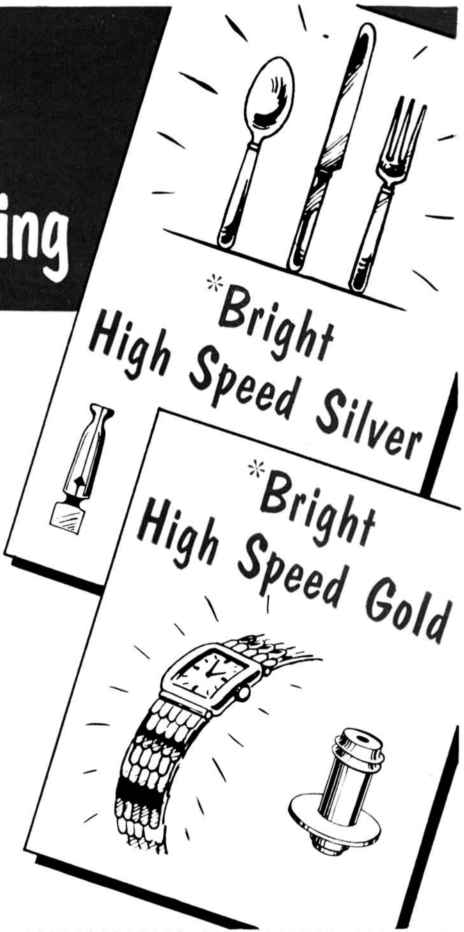
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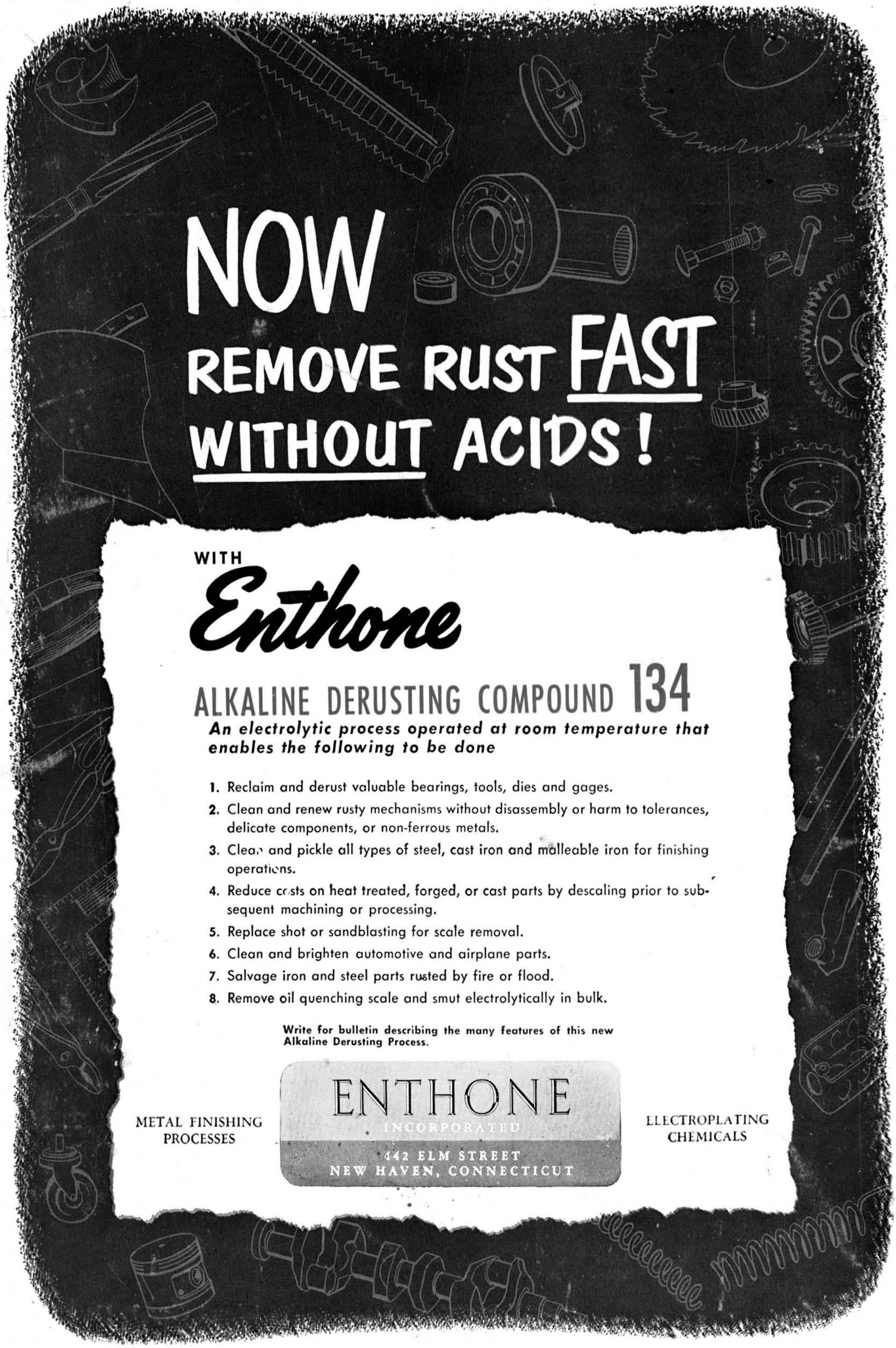

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