JOURNAL OF THE

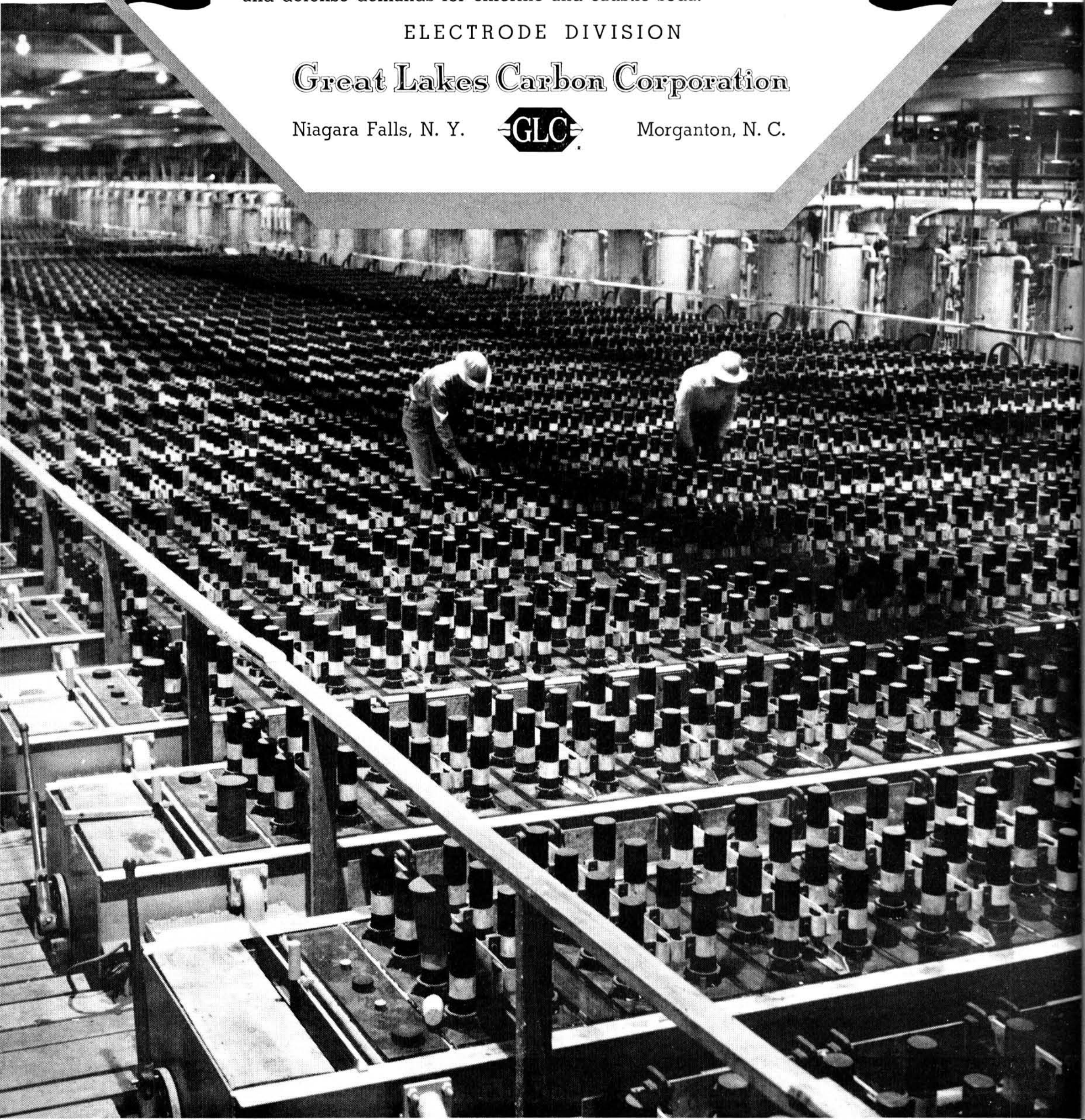
Electrochemical Society

Vol. 100, No. 5

May, 1953

ELECTROCHEMICAL INDUSTRY

The Pittsburgh Area



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Journal of the
Electrochemical
Society

MAY, 1953 **VOL. 100 · NO. 5**

CONTENTS

Regional Features

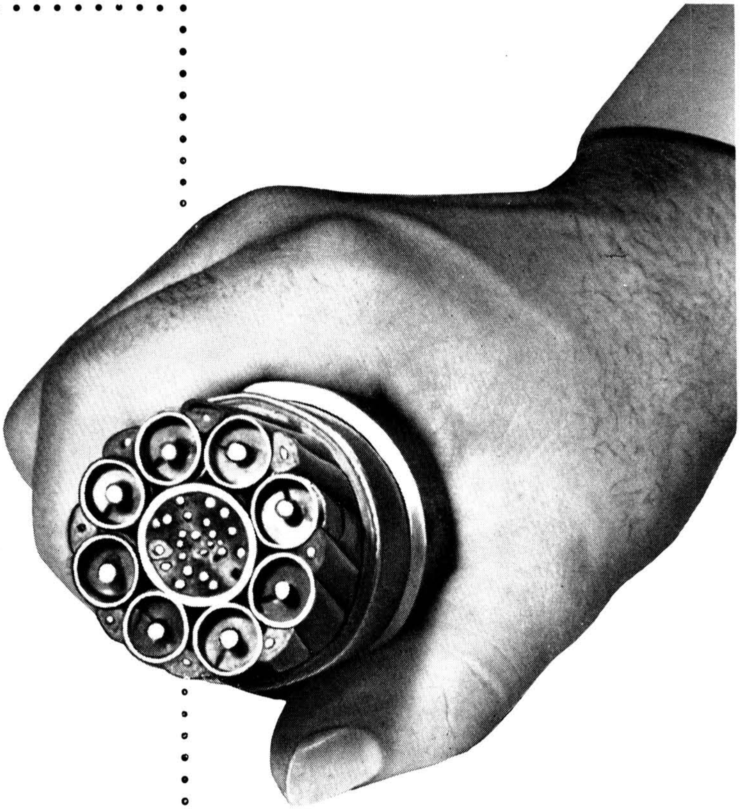
Technical Papers

Feature Section

Current Affairs

Published monthly by The Electrochemical Society, Inc., Mount Royal and Guilford Aves., Baltimore 2, Md., combining the JOURNAL and TRANSACTIONS OF THE ELECTROCHEMICAL SOCIETY. Editorial offices: 235 West 102nd Street, New York 25, N. Y. Statements and opinions given in articles and papers in the JOURNAL OF THE ELECTROCHEMICAL SOCIETY are those of the contributors, and The Electrochemical Society assumes no responsibility for them. Subscription $11.25 to members, $15.00 to nonmembers. Single copies $1.25 to members, $1.50 to nonmembers. Copyright 1953 by The Electrochemical Society, Inc. Entered as second-class matter November 15, 1947, at the Post Office at Baltimore, Md., under the act of August 24, 1912.

Pipes that grew without getting bigger



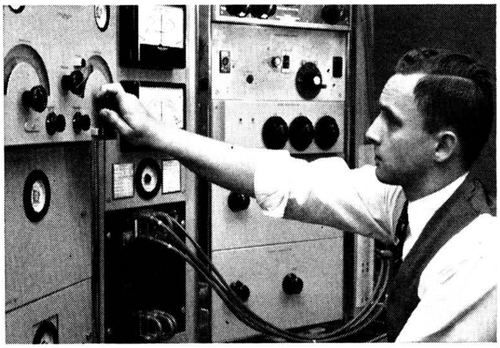
Cross-section of coaxial cable. To triple capacity, Bell Laboratories and Western Electric engineers had to make 1000 amplifiers work perfectly in tandem . . . feed repeater power along the same cable that carries messages . . . put signals on and off the line at numerous cities along the route without distortion.

Pencil-size pipes carry telephone messages and television across country through the Bell System's coaxial cable. Once, each pipe could carry 600 voices, or one television program. Now it can carry 1800 voices, or 600 voices *plus* a broadcast quality television program.

Yet the pipes aren't any larger. They are being made into triple-duty voiceways by new repeaters, new terminal equipment and other transmission advances developed by Bell Laboratories engineers.

The conversion expense is less than the cost of laying extra coaxial cables. But it calls for highly refined manufacturing procedures, made possible only by close co-operation of Bell Laboratories and Western Electric, manufacturing unit of the Bell System.

In improving the coaxial cable system they created more than 20 years ago, engineers at Bell Telephone Laboratories devised a new way to give America still better telephone service, while the cost stays low.



Laboratories engineer tests new triple-duty coaxial system. It marks the first time that telephone conversations and television can travel through the same pipes at the same time. With a wider frequency band being transmitted, big problem was to eliminate interference between the two types of signals.

BELL TELEPHONE LABORATORIES

IMPROVING TELEPHONE SERVICE FOR AMERICA PROVIDES CAREERS FOR CREATIVE MEN IN SCIENTIFIC AND TECHNICAL FIELDS

Editorial

The Need to be Different

I*N RECENT* years some Americans have criticized our native ability to develop new scientific ideas. It is often said here and abroad that Europeans create new scientific ideas and that Americans develop them into commercially useful instruments, machinery, or materials. Some of our large industrial companies support this contention. Industrial leaders are combing European universities, technical institutes, and industries for new ideas and processes. Some Americans are considering the establishment of laboratories in Europe to utilize the creative talent that they find there.

Few will question that our own university research is of a high caliber. However, it can scarcely be denied that it is somewhat channelized into the more glamorous fields of science. Thus, it would appear, for example, that every university must have a cyclotron, a radio-chemical laboratory and a low temperature laboratory. Students graduating from these institutions tend to work in fields in which they were trained. On the other hand few scientists are being trained in such fields as magnetics, inorganic chemistry, and electrochemistry. The latter subjects have been neglected in this country for years although the need for trained people in these fields is great. The industrial leader is forced, therefore, to turn to Europe for ideas and trained personnel in many borderline fields of science.

The author recently returned from a six-month visit to laboratories in nine European countries and has noted certain very interesting aspects of training and environment abroad. This channelizing of scientific activity into certain fields does not occur to the same extent in Europe as in America. The European economy does not permit the continued expansion of scientific activity where large expenditures on capital equipment are involved. Also, the European appears to have a stronger desire to work into borderline scientific fields. This is

(*Continued on next page*)

Editorial (*continued*)

especially true of the Germans. The European also tends to have a more individualistic and much less of a group approach to science.

As a most dramatic example, the French people have the reputation of offering a most fertile soil for all types of ideas. Yet this appears to be not so much due to a rigorous technical training as to a highly individualized approach. At times it appears difficult to find two Frenchmen who will agree on a scientific theory even though they were trained in the same school. The Frenchman prefers his own ideas to his neighbor's and, incidentally, French to foreign ideas.

It is true that this approach has made it difficult for the French to work as a group. Also, many practical problems are never solved except in principle. The French, it is said, tend to assume that one can solve a problem by an idea alone and that once the idea is found the problem disappears. Despite these admitted weaknesses, the desire to think and to think for himself has made the French scientist highly productive of theoretical concepts.

America could use more people with this approach. Conformity should not be our watchword. The desire to be different should be deliberately cultivated in our schools and universities. Only by intelligent individualism can we hope to be successful in producing new creative ideas.

—EARL A. GULBRANSEN

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E. H. Sargent & Co., the manufacturer of Polarographs, offers three different Polarographs—the Model XXI Visible Chart Recording; the Model XII Photographic Recording, and the Model III Manual.

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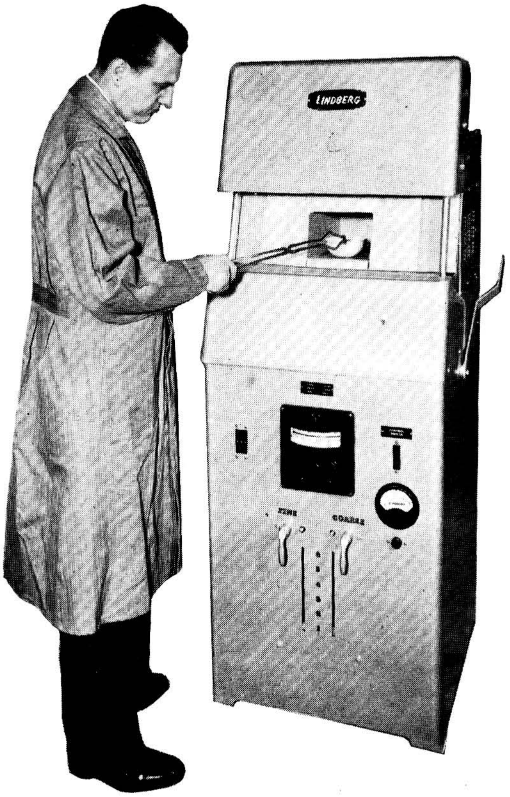

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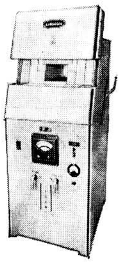

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THE PITTSBURGH INDUSTRIAL AREA

Paul Fugassi[1]

The Pittsburgh Industrial Area is located in the vicinity of the Allegheny, Monongahela, and Ohio rivers and their numerous tributaries. It is localized mainly in Allegheny County, although important sections are to be found in the adjoining counties: Westmoreland, Washington, and Beaver counties to the east, south, and west, respectively.

Allegheny County

Allegheny County has a land area of 725 square miles and a water area of 33 square miles. This is about 1.5 per cent of the area of the state of Pennsylvania. In this region are located 4 cities, 78 boroughs, and 48 townships. As of January 1, 1952, the assessed value of real estate in the county as used for taxation purposes was $2,262,187,620. This figure is about 20 per cent of the total assessed value of real estate for the entire state of Pennsylvania. The assessed valuation of personal property for the inhabitants of Allegheny County was $617,683,050. This assessment is made on all interest or dividend paying investments except bank accounts, obligations of corporations chartered in Pennsylvania, obligations of those out-of-state corporations which pay a franchise tax, and tax-exempt securities. The Allegheny County personal property assessment is about 22 per cent of the personal property assessment for the entire state. In 1950 the population of Allegheny County was 1,515,237 or about 14 per cent of the population of Pennsylvania. In population Allegheny County is eighth in the United States and ranks second in Pennsylvania. Its population is greater than the population of seventeen states. In the county there is one automobile for each four persons and one telephone for each three persons. According to the latest available figures (1948), Allegheny County produced products valued at $3,162,100,000 and had 247,749 persons employed, earning an aggregate salary of $800,750,900.

Although Allegheny County is highly industrialized, it is estimated that about 92,000 acres in the county are capable of being farmed and actually 79,500 acres are under cultivation, representing about 17 per cent of land area of the county. Of the remaining land, a considerable portion is represented by steep hillsides, ravines, etc., so that actually the industrialized area is concentrated and is located near or at the river system.

The river system comprises three major streams: the Allegheny, Monongahela, and Ohio rivers. The Allegheny River enters the county from the northeast and joins the Monongahela River, which enters the county from the southeast, to form the Ohio River at the Point in Pittsburgh. The Ohio River leaves the county in a northwest direction, connects with the Beaver River in Beaver County, and then turns southwest to eventually join the Mississippi River at Cairo, Illinois. The rivers are of reasonable size and fairly wide. At Pittsburgh, the Allegheny and Monongahela are 800 feet wide on the average, and the Ohio is about 1100 feet wide.

Many streams and creeks flow into the three major rivers through valleys, ravines, and gullies. The terrain is quite hilly. Valleys in most cases are narrow and deep; depths of 100 feet are not uncommon. Such terrain poses many difficulties for construction and it is inevitable that utilization of land of this type necessitates the construction of many bridges. The Allegheny County Department of Works has a Division of Bridge Maintenance which takes care of 264 major and minor bridges over rivers and named streams and some 346 minor structures. The city of Pittsburgh maintains some 150 bridges. Some bridges are under supervision of the state and others are privately owned by railroads, railways, etc. Altogether there are about 800 bridges in Allegheny County.

Pittsburgh

Pittsburgh is located at the junction of the Monongahela, Allegheny, and Ohio rivers and is the largest city in Allegheny County. It covers an area of 47 square miles and has a population of 676,806. Its assessed valuation of real estate is $1,043,592,185 and the personal property assessment of its inhabitants is $464,728,920. These figures correspond to 50 per cent of the real estate valuation and 75 per cent of the personal property assessment of Allegheny County.

Although the Ohio Valley was explored by the French explorer, Robert de La Salle, in 1679, the first structure, Fort Prince George, was started at the Point by the English in 1754, captured by the French before its completion in the same year, and renamed Fort Duquesne. After several unsuccessful attempts, the French were driven out in 1758 and the fortifications were reconstructed and named Fort Pitt. It served as an important frontier outpost and guard against the Indian raids until the Indians were defeated in 1763 at Bushy Run. As the Indians left Western Pennsylvania and the frontier moved westward, Fort Pitt lost its importance and was abandoned after the Indians were completely defeated at Fallen Timbers (Ohio) in 1794.

The initial importance of Pittsburgh was that it served as the gateway to the vast interior waterways of the United States. As the frontier moved westward, opportunities arose for river trade with the settlements along the Ohio River. Because it was difficult and expensive to transport eastern goods over the mountains, manufacturing started in Pittsburgh. Iron ore was discovered on the western slope of the Allegheny Mountains in 1780. Coal had been found previously. The first blast furnace to be erected in the city of Pittsburgh was built in 1792 but was in operation for only two years. Smelting operations for a number of years were conducted near the ore supplies. The first successful furnace

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[1] Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

Courtesy, Pittsburgh Chamber of Commerce

This view of "The Point," Pittsburgh, shows the site for the new Point Park, in the foreground, the first three buildings of Gateway Center, and the "Golden Triangle."

in the city of Pittsburgh was constructed in 1859 and was operated until 1927. By 1865 Pittsburgh had 46 iron factories, 7 steel manufactories, and 31 rolling mills, and had been recognized as an iron and steel center.

Natural Resources

The continued growth of the Pittsburgh Area is undoubtedly due to the abundant mineral and fuel resources present in the district.

Coal was discovered very early in Pittsburgh. A visitor to Fort Pitt in 1760 described a coal mine located opposite to the Fort on the south bank of the Monongahela River. The famous Pittsburgh Bed starts at Pittsburgh and extends south into West Virginia. The eastern limit is in Westmoreland County and the western limit in the State of Ohio. The Pittsburgh Bed averages 7 feet in thickness and the bed is sufficiently close to the surface so that drift mines can be used or, in some cases, strip mines. Another important bed near Freeport called the Thick Freeport Bed has an area of 115 square miles and has been mined for many years. Other beds are also known, but because of their depth have not been developed. After nearly 200 years of mining, the district still has adequate coal resources.

Petroleum and natural gas resources were first developed in 1858. The Pittsburgh Area is in the center of the Appalachian Field. This field starts in New York State and extends southwest through Pennsylvania and Ohio into West Virginia and Kentucky. Both gas and oil pools are found in this field. In some respects the city of Pittsburgh stands on the dividing line between oil and gas wells. Wells to the north and west of Pittsburgh give oil with little gas. Wells to the south and east of Pittsburgh give mainly gas with a little oil. Natural gas was first used in the steel industry in 1874. Although the gas fields in the Pittsburgh area are still producing, local consumption exceeds the local production, and it is necessary to import natural gas from the southwest. Local petroleum production is also exceeded by the local demand and importation of petroleum and petroleum products is necessary.

Limestone and sandstone deposits are found in the Area. A practically inexhaustible source of sand and gravel is furnished by the river system. Millions of tons of sand and gravel are dredged from the rivers each year. Adequate supplies of clay are available for refractories.

Transportation

The Pittsburgh district is served by 22 railroads. Six of these are trunk lines and the other 16 are industrial and terminal-switching railroads. The principal lines are: Baltimore and Ohio; Bessemer and Lake Erie; Buffalo, Rochester, and Pittsburgh; Pennsylvania; Pittsburgh and Lake Erie (New York Central); and Pittsburgh and West Virginia.

Heavy tonnages are shipped by the river system. The Ohio River is navigable over its entire length. The Allegheny and Monongahela Rivers are navigable to a considerable distance upstream from the city of Pittsburgh. In 1951, 44,000,000 tons of freight travelled on the Allegheny, Monongahela, and Ohio rivers. Of this tonnage 70 per cent was coal, 13 per cent was sand and gravel, 8 per cent petroleum products, 5 per cent iron and steel, and the remaining 4 per cent coke and miscellaneous materials. Shipment of steel products by river was started in 1921. The northernmost city to which such shipments have been made is Minneapolis, and the southernmost city is, of course, New Orleans. River traffic on the Monongahela in 1951 was about 32,000,000 tons, maintaining its reputation as "the busiest little river in the world." The same year river traffic on the Allegheny was 4,250,000 tons. River transportation has been of importance since the earliest days. Regular shipping of coal by river boat started in 1817. Because of the river system, shipbuilding has been an important industry. In the early eighteen hundreds, sailing vessels were constructed at Pittsburgh and cleared from the Port of Pittsburgh for Europe. This procedure could be followed only once as the vessel could not ascend the Mississippi and Ohio river systems and had of necessity to clear from other ports for future trips. The construction of ocean vessels was not resumed until the second World War when many landing craft were constructed here. The shipbuilding industry normally is concerned with river tugboats and barges. In 1952, 173 vessels were launched Of this number 116 were coal barges carrying 1,000 to 2,500 tons. At times a serious transportation problem is solved by use of the river system. The coils for the cyclotron at the Carnegie Institute of Technology were constructed at the Brooklyn Navy Yard and because of their bulk and weight could be transported neither by rail nor by truck. They were sent via the Atlantic Ocean and the Gulf of Mexico to New Orleans and transhipped there to a river boat which brought them up the Mississippi, Ohio, and Allegheny rivers to a point a few miles away from their final destination.

Electric Power

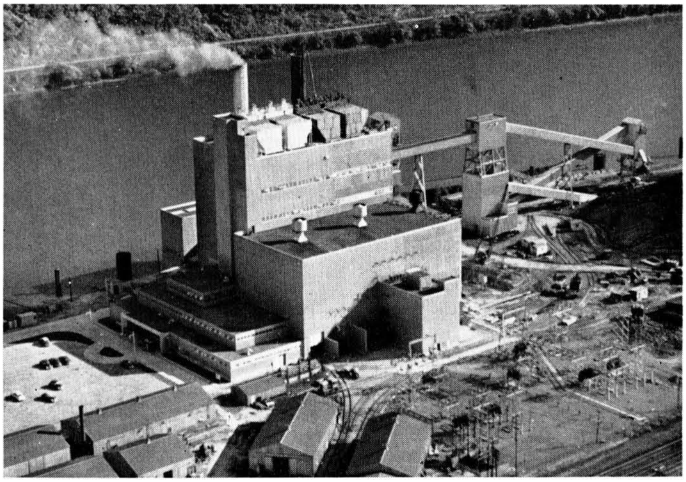
In Allegheny and Beaver counties, power is supplied by the Duquesne Light Company. The counties to the north, east, and south of Allegheny County are supplied by the West Penn Power Company. The Duquesne Light Company system is quite limited in area. Its 66,000-volt transmission ring has a circumference of only 81 miles. It has, however, a large power capacity which is at present about 1,000,000 kw. The Duquesne Light Company is in the seventh year of a nine-year expansion program, scheduled for completion in 1955 at which time its capacity will be 1,225,000 kw. All of its power is obtained from steam, using coal as the fuel. The Duquesne system is tied in with the Pennsylvania Power Company system in the north, the Ohio Power Company system in the west, and the West Penn Power system on the east. About 120,000 kw can be obtained from these other systems. Many companies in the Pittsburgh Area generate all or part of their power requirements. Some of these private power installations are tied in with the Duquesne system and can, in emergencies, furnish power to the network. The United States Steel Company plants could furnish about 60,000 kw and the gigantic butadiene-styrene plant of the Koppers Company at Kobuta can furnish about 25,000 kw. Altogether about 100,000 kw of additional power are available from such sources. Of the power sold by Duquesne Light Company, 66 per cent is for industrial use, 14 per cent for miscellaneous commercial use, and 20 per cent for residential use.

The West Penn Power Company is part of a system which supplies power in Maryland, West Virginia, and Pennsylvania. It serves an area of about 24,000 square miles and has transmission rings over 1000 miles in length. Its closest power station to the Pittsburgh district is at Springdale on the Allegheny River, 17 miles from the city of Pittsburgh. The major portion of its power is steam-generated but it does have several hydroelectric stations. The Springdale Station has a capacity of 315,000 kw and is being expanded to an ultimate capacity of 450,000 kw.

Distribution of Industries

In 1948, according to the Pennsylvania Industrial Survey, Allegheny County produced goods valued at $3,162,100,000 Of these goods, 90 per cent fell in the following five categories metals and metal products, 68 per cent; food and kindred products, 12 per cent; chemical and allied products, 5 per cent; paper and printing, 3 per cent; mine and quarry products, 2 per cent. These figures illustrate the importance of iron production for Allegheny County as it is the only metal produced in quantity. When it is considered that the chemical industry is closely connected with the steel industry in this district because of by-product coke ovens, and the mining industry also is closely connected with coke and power production, the importance of steel production to industrial activity in Allegheny County is obvious.

Another way of determining the distribution of industrial activity is to examine the distribution of employees by industries. In November 1952, the percentage distribution of employees by industry in the Pittsburgh Area, which comprises Allegheny, Beaver, Washington, and Westmoreland counties, was as shown in Table I (see next page). Inspec-



The new Elrama Power Plant of the Duquesne Light Company, supplier of electric power in Allegheny and Beaver counties. The exterior and interior surfaces of the building are aluminum sheet.

Courtesy, Duquesne Light Company

TABLE I. *Distribution of employees by industry in Pittsburgh Area*

Industry	% of Total employed
Primary metal	44.4
Electrical machinery	9.9
Fabricated metal	9.5
Machinery (other than electrical)	7.2
Glass, clay, stone	6.7
Food	6.1
Petroleum and coal products	3.1
Transportation equipment	2.1
Printing and publishing	2.1
Chemicals	2.0
Instruments	1.9
Textiles and apparels	0.9
Lumber and furniture	0.8
Paper and paper products	0.8
Other	2.5
	100.0

tion of the figures shows again the importance of iron and steel production in the Pittsburgh Area.

Iron and Steel Production

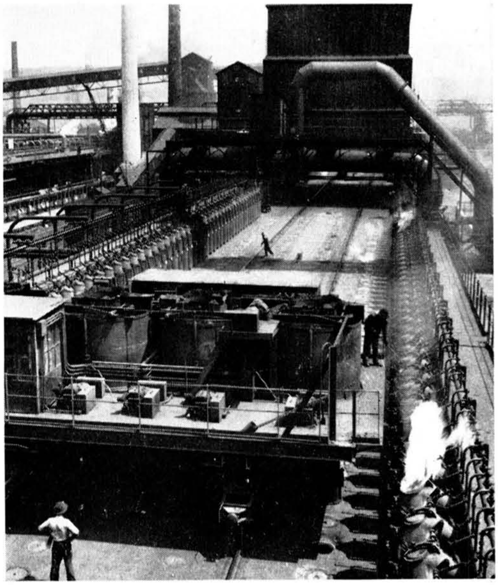
In the Pittsburgh Area there are 48 blast furnaces of which 45 were reported in operation in November 1952. These furnaces have a yearly capacity of over 14,000,000 tons, most of which is pig iron with a relatively small production of ferroalloys. The number of by-product coke ovens is about 2600. These are of the Koppers or Koppers-Becker type. Over 1500 of these ovens are located at the Clairton plant of the United States Steel Company, making it the largest coking plant in the world. The annual production of by-product coke is about 12.6 million tons. During the last war appreciable quantities of coke were made in the old type beehive ovens. Coke is still being produced in this way.

There are in the Pittsburgh Area 176 open-hearth installations, 6 Bessemers, and 24 electric furnace and crucible steel installations. The yearly capacity of the electric furnace-crucible steel furnaces is about the same as that of the Bessemer converters; each is about 0.6 million tons a year. The open-hearth capacity is near 14 million tons per year.

The area has adequate rolling-mill and fabrication facilities so that the steel and iron produced in the district is shipped in all possible forms: structural beams, plates, rod, sheet, wire, pipe, etc. Steel clad with metals such as copper, silver, etc., is also produced, together with galvanized and tin products.

Chemical By-Products

When coal is heated in a by-product oven, one ton of coal gives about 1,500 pounds of coke, 1000 cubic feet of coal gas, and around 10 gallons of coal tar. Coal gas contains principally hydrogen and methane, but many other compounds are present such as benzene, toluene, naphthalene ammonia, hydrogen sulfide, hydrogen cyanide, and cyanogen. After poisonous components have been removed, the gas is an excellent fuel. Ammonia is removed as ammonium sulfate. Hydrocarbons of low volatility can be removed by scrubbing the gas with oil. Coal tar is a very complex mixture from which over 150 compounds have been isolated to date. The components of coal tar fall into three categories: (*a*) neutral compounds such as hydrocarbons; (*b*) tar acids such as phenol and cresols; and (*c*) tar bases such as pyridine. Tar acids are soluble in dilute aqueous solutions of sodium hydroxide and the tar bases are soluble in dilute aqueous solutions of sulfuric acid. Extraction methods and distillations serve to separate the various components. From coal tar can be separated benzene, toluene, naphthalene, phenanthrene of the neutral compounds, phenols, cresols, and xylenols of the acid compounds, and pyridine of the basic compounds. The large production of coke in the Pittsburgh Area results in a large supply of chemical compounds which have direct uses or can serve as the basis of the production of other products such as styrene, phthalic anhydride, etc.



Courtesy, U. S. Steel Corporation

View of the by-product coke ovens at the Clairton Plant, United States Steel Corporation, the largest coking plant in the world.

Each pound of pig iron produced in a blast furnace is accompanied by the production of about 0.5 pound of slag. Disposal of slag is not an insignificant item in the cost of pig iron. The principal use for slag is the manufacture of cement. Two plants in the area prepare cement from slag, but the amount of slag produced far exceeds the amount used in cement manufacture. Slag, in granulated form, prepared by quenching molten slag in water, or in lump form, is used for fills, as a gravel substitute, or as a soil conditioner for lightening heavy soils. Such uses consume only small amounts of the yearly production and the excess is stored in large dumps covering many acres. In the war years slag dumps were "mined" to recover scrap iron.

Electrochemical Industries

The largest application of electrochemistry in the Pittsburgh Area is to found in the production of tin-plated steel. To a lesser extent electrothermics is represented in the production of electric furnace steel and in the production of zinc.

No electrolytic reduction processes are in operation in this area. Although the Aluminum Company of America has several large plants at New Kensington, these units are mainly fabricating plants. A number of electrochemical treatments are used there to provide decorative and protective finishes to a variety of aluminum products. Alumilite coatings formed by electrolytic oxidation of the aluminum surface in a sulfuric acid electrolyte are applied to Kensington Ware, aircraft parts, and other articles. Oxide coatings formed in a chromic acid electrolyte are also applied to some tanks and aircraft parts. Two electrochemical processes are used to make highly reflecting aluminum sheets employed as specular reflectors for lighting applications. These involve electrolytic brightening of the surface in a fluoboric acid electrolyte to obtain high reflectivity and subsequent application of a clear transparent alumilite coating to protect these surfaces.

Tin Plating

In a recent summary of electrolytic tin plating, D. A. McArthur[2] listed the electrolytic tinning lines in existence or under construction in June 1952. The total number of lines in the world was 41 with an annual production of 4,755,000 tons of 0.5-lb plate. Tin plate rated as 0.5-lb plate contains 0.5 lb of tin coated on both sides of 217.78 square feet of steel (one base box). Of the world total, 33 lines are located in the United States with a production of 3,845,000 tons per year of 0.5 lb plate. In the Pittsburgh Area 6 lines are in operation; 3 at the Aliquippa plant of Jones and Laughlin Steel Corporation, and 3 at the Irvin plant of the United States Steel Corporation. The annual production of these six lines is about 1,000,000 tons of 0.5-lb plate.

Electrolytic tin plating became a necessity with the outbreak of war in the Far East because of the limited supply of tin available to the United States. Before this time the production of electrolytic tin plate was very small and most tin plate was prepared by hot dipping. The standard coating for hot-dipped tin plate was 1.50 lb of tin per base box. To conserve tin supplies it was necessary to reduce the thickness of the tin coating. It was discovered that the thinnest practical coat obtainable by the hot-dip process was 1.25 lb of tin per base box. Electrolytic lines could be operated to produce coatings between 0.25 lb to 1.00 lb of tin per base box. Tin plate was standardized at 0.5 lb per base box which was equivalent to saving one pound of tin for each base box of plate produced. The 0.5 lb per base box plate is only 0.00003 inches thick and in many cases must be covered with a suitable lacquer to have the desired corrosion resistance.

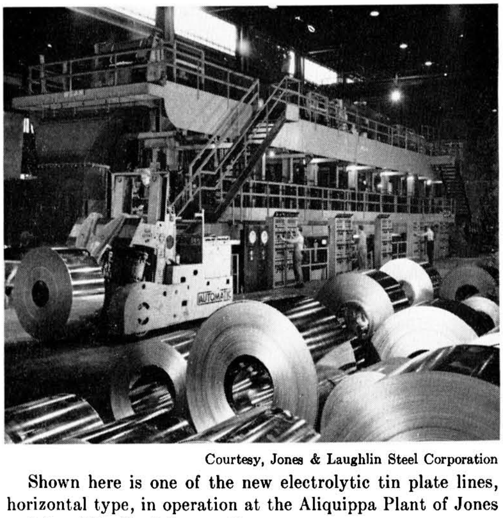
Practical tin plating installations use either alkaline plating baths (Crown) or acid plating baths (Ferrostan or Weirton). In the Crown and Ferrostan lines, the continuous sheet, in being plated, moves vertically up and down through the plating bath while in the Weirton line the continuous sheet runs horizontally through the plating bath. Theoretically, the acid baths are more efficient and permit higher current densities to be used. On the other hand, alkaline plating baths involve fewer corrosion problems and require less cleaning of the sheet steel before plating. According to McArthur's table more acid lines have been installed in recent years than alkaline lines. The present ratio of acid to alkaline lines in the United States is 20 to 13. All foreign installations are of the acid type. All three types of lines are in operation in the Pittsburgh Area.

Excluding the mechanical operations at the beginning and end of a tin plate line, all lines consist of three sections: (*a*) a pickling section where the surface of the sheet is cleaned; (*b*) a plating section; and (*c*) a melting section to fuse the electrodeposited tin plate.

In alkaline lines the cleaning operation consists of an acid pickling in 10 to 15 per cent sulfuric acid at 150° to 160°F. No alkali cleaning is necessary because of the alkalinity of the plating solution. In acid lines the sheet is first cleaned in an alkaline bath and electrolytic action is employed using current densities of 50 to 400 amperes per square foot. After alkali cleaning, the sheet in acid lines is acid pickled in sulfuric acid. In the acid pickle either a 20 to 25 per cent sulfuric acid at 200° to 220°F is used or, if supplementary electrolytic cleaning is employed, more dilute acid can be used and also lower temperatures. Electrolytic cleaning reduces the necessary immersion time by one-half or more.

In the plating section of an electrolytic tin line, a number of precautions must be taken in order to produce satisfactory tin plate economically. The linear speed of the continuous strip must be closely controlled in order to obtain a plate of uniform thickness. The motors moving the strip are of the d-c constant speed type. The linear speeds used depend on the mechanical arrangements utilized at the exit side of the line. If the line is equipped with shear and stacking units, the linear speed cannot exceed 900 feet per minute or about 10 miles per hour. If the continuous plated strip is recoiled, higher linear speeds are possible. In fact, linear speeds up to 2,500 feet per minute or about 28 miles per hour have been used.

In all types of line the electrical current is led into the continuous strip by means of conductor rolls. In acid lines the conductor rolls are copper; steel is used in alkaline lines. In acid lines the electrolyte is circulated, while in alkaline lines the electrolyte is not circulated. Smaller current densities must be used on the tin electrodes in the alkaline type lines, and the tin electrodes are larger than those in acid type lines. All tin-plating lines require large amounts of low voltage direct current for the plating, electrolytic cleaning, and electrolytic pickling. Early installations had a capacity of 45,000 to 60,000 amperes at 6 to 12 volts. Later installations have current capacities up to 180,000 amperes with voltages between 15 and 18 volts. In practically all installations the necessary d-c voltage is obtained from motor-generator sets. Rectifiers have not found any considerable use. All plating sections are furnished with current regulators to handle variations in the linear speed of the strip. Such regulators must function over wide ranges of linear speed as the line



Courtesy, Jones & Laughlin Steel Corporation

Shown here is one of the new electrolytic tin plate lines, horizontal type, in operation at the Aliquippa Plant of Jones and Laughlin Steel Corporation.

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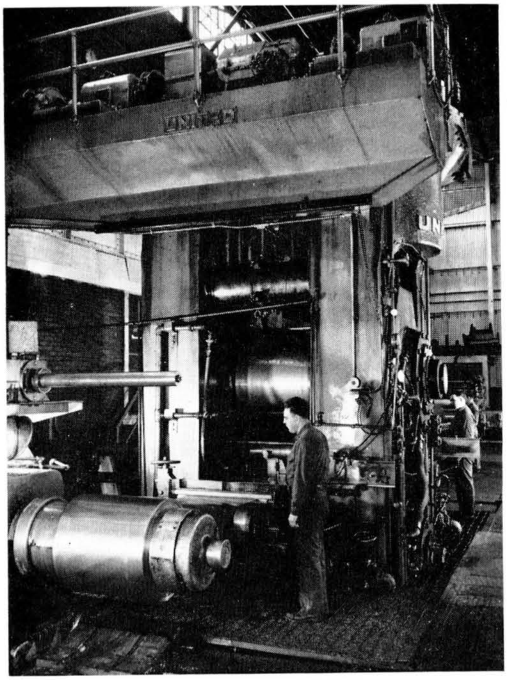
[2] D. A. McArthur, "Electrolytic Tin Plate," Wean Engineering Company, Inc., Warren, Ohio.

at times must be slowed down for welding or other mechanical operations.

A satisfactory tin plate is produced only if the tin coating is fused, and every tin-plating line has a melting section where this is done. Fusion of the tin coating improves adherence of the tin to the steel and also reduces the porosity of the tin coating. Three types of heating have been employed; inductive, radiant, and conductive. In inductive heating the continuous strip passes through a series of coils energized from vacuum tube oscillators operating at a frequency of 175 kilocycles. The energy output of such oscillators in some installations has been as high as 1800 kw. This capacity far exceeds that used even in the largest radio station. Inductive heating is expensive but can handle sheet operating at any practical linear speed. It is also possible to regulate the output very closely by relatively simple electronic methods using a photoelectric tube scanner to maintain a fixed position for the flow line of the molten tin. In radiant heating the continuous strip is passed through electric or gas-heated furnaces. Radiant heating produces a satisfactory product but cannot be controlled with the same flexibility as electrical heating. For this reason radiant heating has been used in only a few tin-plating lines. In conductive heating a low-voltage, high-amperage current is passed directly through the steel strip. Conductive heating from the standpoint of flexibility and cost is comparable to inductive heating.



Courtesy, Allegheny-Ludlum Steel Corporation

Facilities for rolling titanium strip are shown at the West Leechburg Plant of Allegheny-Ludlum Steel Corporation.

After melting of the tin coating, the strip is subjected to rinsing and chemical treatments which clean the surface. Electrolytic action, with the sheet in turn as anode and cathode, sometimes supplements chemical treatments.

In looking at the production of tin plate in the United States over the ten-year period, 1941–1951, it is interesting to note that the production of hot-dip tin plate was about 3.2 million tons in 1941 and had dropped to about 1.6 million tons in 1943. The production of hot-dip plate has remained at about that figure for nine years. In 1941 the production of electrolytic tin plate was practically nothing and reached about 0.8 million tons in 1945. Since 1945 continuous expansion of electrolytic tin plate production has taken place and in 1951 the production was about 2.9 million tons. It has been stated that 80 or 90 per cent of the total tin plate production will be electrolytic tin plate but other predictions are that all tin plate will be produced electrolytically. It should be noted that electrolytic tin plate having 1.0 lb of tin per base box has been successfully produced and that this material is competitive with hot-dip tin plate of 1.25 lb of tin per base box. The recent suggestions for "differential tin plate" are of interest. In this type of plate one side of the sheet has a heavier tin coating than the other side. For food packs the heavier coating is used for the inside of the can and the lighter coating is the outside. "Differential tin plate" is in production and is available in practically all possible combinations. A differential tin plate designated as 1.00/0.25 has a coating of 1.00 lb of tin per base box on one side and 0.25 lb of tin per base box on the other side. "Differential tin plate" cannot be prepared by the hot-dip process.

Future Developments

As a fuel center, the utilization of coal for the production of gaseous and liquid fuels and as a starting material for the production of chemicals is an item of interest to industry in the Pittsburgh district. The Bruceton (Pa.) Station of the United States Bureau of Mines has been doing extensive research work on the production of liquid fuels from coal. Other research units are interested in other phases of coal utilization. Considerable advance has been made in lowering of coal mining costs by mechanization. As with other producers of steel and iron, the companies in the Pittsburgh Area are prospecting for new sources of iron ore and for economical methods of utilizing the lower grade iron ores available on the Mesabi Range and also iron ore deposits not worked extensively since the discovery of the Mesabi Range. The metallurgy of titanium is under development in the district. In the near future tin will not be available and work is progressing on the development of protective coatings, which will give, with use of suitable lacquers, a satisfactory and economical substitute for tin plate.

Because of its river system, the Pittsburgh Area has adequate water resources. However, with such a system stream pollution becomes a very important problem. Strip mining and other coal mining operations contribute large amounts of sulfuric acid to the water system. The sulfuric acid arises from oxidation of sulfur containing residues left after removal of the coal. Both water and air are essential for the reaction. Proper arrangement of drainage facilities, sealing of worked-out coal mines, and other arrangements have been used to reduce sulfuric acid pollution. Waste-disposal receives serious attention, but considerable research work still needs to be done. A rigid smoke control law has reduced the smoke and fog to a considerable degree.

In recent years, several large users of steel products have erected fabricating plants in the Pittsburgh Area and it is to be expected that some additional diversification of industrial activity will result. With the active interest now displayed and the expenditures being made on research, it can be anticipated that the Pittsburgh Area will continue its growth for many years.

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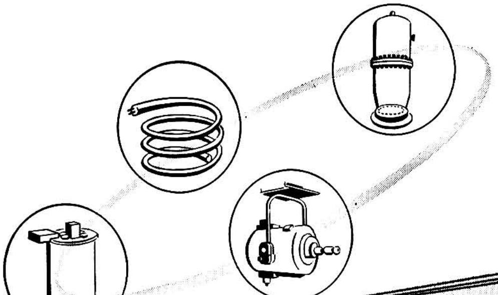

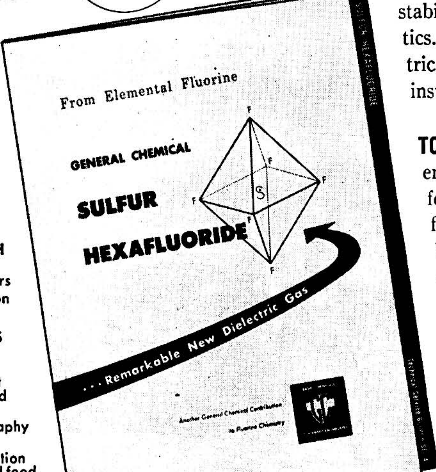

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The Inhibition of the Corrosion of Iron by Some Anodic Inhibitors[1]

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National Research Council, Ottawa, Canada

ABSTRACT

Inhibitors having relatively strong oxidizing anions, such as sodium chromate and nitrite, passivate iron both in the presence of air and in deaerated solutions. Much weaker oxidizing agents such as sodium tungstate and molybdate behave similarly to chromate and nitrite in the presence of air but do not prevent corrosion in deaerated solutions despite the fact that potential/time and polarization curves indicate that slow film formation is occurring. Tungstate ions, however, are effective oxidizing agents toward iron when discharged anodically at high current density.

Solutions of sodium acetate, benzoate, carbonate, hydroxide, orthophosphate, and silicate, which do not contain oxidizing anions, passivate iron only when they contain dissolved air. When these solutions are deaerated they attack iron very slowly, potential/time and polarization curves indicating that this attack is mainly under cathodic control.

It is postulated that oxygen dissolved in solution is mainly responsible for passivity by virtue of its heterogeneous reaction with surface iron atoms to form a thin film of γ-Fe_2O_3, approximately 200 Å[2] thick, in a manner similar to that by which oxide films are formed in air. This film, if kept in constant repair, prevents iron ions from the metal passing into solution. It is considered that, in inhibitors containing oxidizing anions, the passivity film is formed mainly by dissolved oxygen, whereas in other inhibitors, which do not contain oxidizing anions, the oxide is formed entirely by dissolved oxygen.

INTRODUCTION

Previous research was carried out in order to obtain more comprehensive information concerning the reactions occurring when solutions of sodium nitrite (1, 7, 8), sodium chromate (2), sodium hydroxide (3), and sodium orthophosphate (4, 5, 6), saturated with dissolved air, inhibit the corrosion of iron. In all cases passivation of initially film-free iron resulted in the formation of a thin invisible film which was mainly composed of γ-Fe_2O_3. It was suggested that the oxide resulted from the adsorption of oxygen dissolved in solution followed by reaction with the iron surface and growth of the film, until a limiting thickness was obtained. Chromate and nitrite, which are themselves oxidizing agents, were believed to contribute to the formation of oxide by adsorption on the surface followed by oxidation of the iron and reduction of the inhibitor anion. This contention was supported by the observation that, in deaerated solution, iron was still passivated by chromate (3) but suffered slow corrosion in sodium phosphate (5) and sodium hydroxide (3) which are not oxidizing agents with respect to iron.

Since the formation of a protective oxide film was not instantaneous, very slow corrosion initially accompanied the growth of oxide. The corrosion was believed to be localized, presumably at discontinuities in the oxide film, and was mainly under anodic control. This was supported by the detection of small inclusions of corrosion product in the passivity film, lepidocrocite (γ-FeO·OH) in the case of sodium hydroxide (3) and sodium nitrite (8), and strengite ($FePO_4 \cdot 2H_2O$) in the case of sodium phosphate (9) by the combined use of electron microscopy and electron diffraction. The detection of phosphate was later confirmed by a radioactive tracer method (6). The mechanism of inhibition put forward for these four inhibitors was essentially similar, bearing in mind the one major difference that chromate and nitrite ions are oxidizing agents with respect to iron and that chromate, at least, can passivate this metal in deaerated solutions, whereas phosphate and hydroxyl ions are nonoxidizing agents and attack iron very slowly in deaerated solutions.

Lochte and Paul (10) previously pointed out that sodium phosphate, hydroxide, carbonate, and borate behaved similarly in that the electrode potential of iron exposed to deaerated solutions of these compounds was much more negative than in similar solutions containing dissolved air. Furthermore, Robertson (11) showed that sodium chromate, nitrite, tungstate, and molybdate passivated iron at similar concentrations in the presence of air.

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[1] Manuscript received June 19, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

[2] Estimated on the apparent surface area of the specimens.

The purpose of the research described below was to determine whether one mechanism of inhibition could be advanced to explain the passivation of iron by anodic inhibitors in general, since their behavior toward iron was similar in so many aspects. The inhibitors investigated were sodium acetate, benzoate, silicate, carbonate, tungstate, and molybdate in addition to the four inhibitors sodium chromate, nitrite, hydroxide, and phosphate previously investigated.

The major part of the research was directed toward investigating the effect of deaeration on the weight losses of iron specimens, the weight loss/concentration curves, and the potential/time curves. Polarization curves, determined in deaerated solutions, indicated whether the corrosion was under anodic or cathodic control. Experiments were also carried out to ascertain whether inhibitors that were extremely effective in distilled water were, of necessity, also very effective in solutions containing potassium chloride. The effect of carbon dioxide on the corrosion rate was also determined.

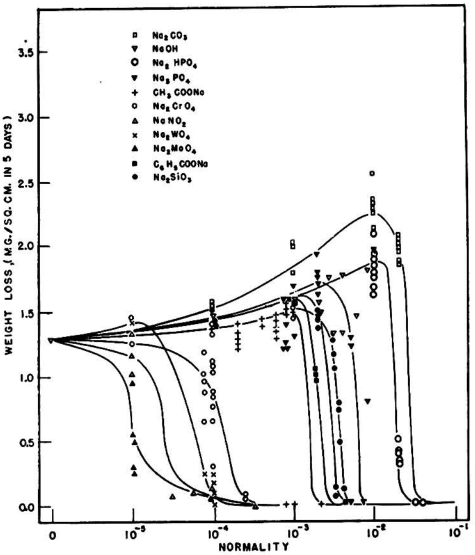

FIG. 1. Variation of weight loss/cm² in 5 days with concentration of 11 inhibitors in the presence of air.

EXPERIMENTAL AND RESULTS

Materials.—The iron was in the form of annealed sheet 0.02 cm thick and had the following analysis: C, 0.052 per cent; Si, trace; S, 0.013 per cent; P, 0.028 per cent; Mn, 0.20 per cent; Ni, 0.04 per cent; Cr and Cu, not determinable.

This sheet was used in all experiments except those carried out to determine the effect of concentration on weight loss in the presence of air and the effects of chloride and carbon dioxide. The sheet used in these experiments was on auto-body steel 0.1 cm thick having the analysis: C, 0.12 per cent; Mn, 0.32 per cent; Si, 0.02 per cent; S, 0.01 per cent; P, 0.014 per cent. Specimens, 2.5 x 2.5 cm, cut from these sheets were thoroughly degreased with benzene, abraded with 3/0 emery paper, swabbed with acetone, dried, weighed, and exposed to the solutions as quickly as possible.

The inhibitor solutions under investigation were made from C.P. chemicals and distilled water.

Variation of Weight Loss with Concentration in the Presence of Dissolved Air

The relationship between weight loss and concentration was determined in aqueous solutions of the following compounds: sodium carbonate, hydroxide, dibasic and tribasic phosphate, acetate, benzoate, nitrite, chromate, tungstate, molybdate, and silicate.

The specimens were suspended from glass hooks, by a hole near the center of the top edge, in 200 ml of the solution under investigation in such a manner that their upper edges were 1 cm below the water line of the solution. Experiments were carried out for five days at 25° ± 0.5°C with a high relative humidity to reduce evaporation from the solutions. At the end of the experiment the specimens were removed from the solutions; adherent corrosion products were removed, carefully washed with distilled water, and dried in a desiccator. The specimens were then pickled for 2 minutes in inhibited 1:1 hydrochloric acid; exposure of a clean panel to this treatment resulted in a weight loss of less than 0.2 mg. The specimens were finally washed with water, dried with acetone, and reweighed, the results being expressed as weight loss/cm² in five days (Fig. 1).

The corrosion products were subjected to x-ray analysis using a cobalt target and an iron filter. The results are shown in Table I.

Variation in Weight Loss with Concentration in Deaerated Solutions

This examination was carried out as previously described (5) using the deaeration technique involving the very large decrease in gaseous solubility on freezing an aqueous solution. The apparatus previously used was modified so that specimens measuring 4 x 3 cm and 50 ml of solution could be used. In a typical experiment a specimen was exposed to 50 ml of deaerated solution for five days, the apparatus being placed in a water bath maintained at 25° ± 0.05°C. At the end of this period the apparatus was removed from the bath and opened to the air; the specimen was removed from solution, cleaned 5 seconds with inhibited 1:1 hydrochloric acid, washed, dried, and reweighed; exposure of a clean specimen to this treatment resulted in a weight loss of less than 0.1 mg.

TABLE I

Inhibitor	Conc N	Form of corrosion	Corrosion product	Relative intensities of strongest lines for corrosion products containing more than one compound
NaOH	10^{-3}	General attack	γ-FeO·OH, Fe_3O_4 and α-FeO·OH	100:25:10
	10^{-4}	General attack	γ-FeO·OH, Fe_3O_4 and α-FeO·OH	100:40:1
Na_2CO_3	10^{-2}	Localized attack	α-FeO·OH	—
	10^{-3}	General attack	γ-FeO·OH	—
Na_2HPO_4	10^{-2}	Localized attack	$Fe_3(PO_4)_2 8H_2O$	—
	10^{-3}	General attack	γ-FeO·OH	—
Na_3PO_4	10^{-3}	General attack	γ-FeO·OH	—
	10^{-4}	General attack	γ-FeO·OH and Fe_3O_4	100:5
CH_3COONa	10^{-3}	General attack	γ-FeO·OH and Fe_3O_4	100:80
	10^{-4}	General attack	γ-FeO·OH and Fe_3O_4	100:100
C_6H_5COONa	10^{-3}	General attack	Fe_3O_4 and γ-FeO·OH	100:90
	10^{-4}	General attack	Fe_3O_4 and γ-FeO·OH	100:90
Na_2CrO_4	10^{-4}	General attack	γ-FeO·OH, Fe_3O_4 and α-FeO·OH	100:80:1
	10^{-5}	General attack	Fe_3O_4 and γ-FeO·OH	100:90
$NaNO_2$	10^{-4}	General attack	Fe_3O_4, γ-FeO·OH and α-FeO·OH	100:90:3
Na_2MoO_4	10^{-4}	General attack	α-FeO·OH,γ-FeO·OH and Fe_3O_4	100:75:10

The concentration range examined was $10^{-5}N$ to $1.0N$ for the two inhibitors, disodium phosphate and sodium acetate; blank experiments were carried out to determine the weight loss in distilled water. The results are shown in Fig. 2. Even at the lowest concentration of phosphate examined ($10^{-5}N$) small quantities of crystalline ferrous phosphate were observed adhering firmly to the iron. On the other hand, specimens immersed in the acetate solutions had a slightly dulled appearance and no solid corrosion product could be seen. However, on admitting air to the apparatus the sodium acetate solution first became a brownish-yellow color and later a small quantity of brown hydrated oxide of iron was precipitated.

Weight Loss Determinations in Deaerated Solutions

These determinations were carried out as described above in deaerated $0.1N$ solutions of all inhibitors under investigation in this research. It was found that iron suffered slow corrosion in deaerated $0.1N$ solutions of all inhibitors with the exception of sodium chromate and sodium nitrite. However, weight losses were so low in solutions with pH values higher than about 10.5 that it was not possible to determine them with any degree of accuracy by this method, but the solutions, on subsequent exposure to air, became yellowish and later minute quantities of brown hydrated ferric oxide were precipitated. This indicated that, although the weight losses were too small to measure accurately, the specimens had undoubtedly undergone very slow corrosion. The weight losses in deaerated solutions with pH values below 10.5 were such that they could be measured to a reasonable degree of accuracy (see Table II). Portions of the original air-

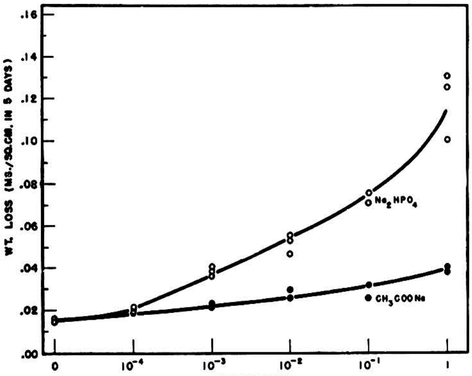

FIG. 2. Variation of weight loss/cm² in 5 days with concentration in deaerated solutions of disodium phosphate and sodium acetate.

formed oxide film were frequently undermined and could be observed suspended in the solutions. Under the microscope the films exhibited abrasion marks. Specimens immersed in sodium molybdate solution grew films of interference color thickness but, in addition, iron also passed into solution. Only specimens immersed in deaerated solutions of disodium phosphate had a visible solid corrosion product [$Fe_3(PO_4)_2 8H_2O$] adhering to the iron. In all other cases, with the exception of sodium molybdate, the specimens either appeared bright or had a slightly etched appearance despite the fact that appreciable dissolution of iron had occurred.

TABLE II

Solution *N*	Wt loss/cm² in 5 days (mg)	*p*H value
0.1 Na_2HPO_4	0.075, 0.070	8.5
0.1 CH_3COONa	0.025, 0.031	8.5
0.1 C_6H_5COONa	0.027, 0.033	8.6
0.1 Na_2MoO_4	0.021, 0.029†	8.7
0.1 Na_2WO_4	0.021, 0.016	9.2
0.1 Na_2CO_3	Very small*	10.6
0.1 Na_3PO_4	" "	11.7
0.1 Na_2SiO_3	" "	12.5
0.1 NaOH	" "	12.8
0.1 Na_2CrO_4	Passive	8.5
0.1 $NaNO_2$	"	8.7
0.1 KCl	0.021, 0.019	
H_2O	0.015, 0.017	

† First order interference colors observed on the specimens.

* Weight loss too small to determine accurately but iron passes into solution and precipitates out as hydrated oxide on exposure of solution to air.

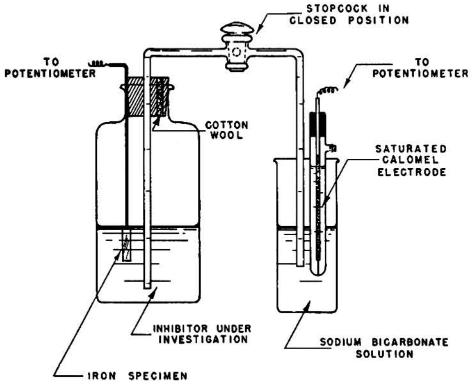

FIG. 3. Apparatus for determination of potentials in the presence of air.

Potential Measurements in the Presence of Air

The variation of the electrode potential of abraded iron specimens with time was determined continuously over a five-day period in 0.1*N* inhibitor solutions.

The apparatus used for these determinations is shown in Fig. 3. Specimens were in the form of strip 0.5 cm wide with a total of 2.5 cm² area exposed to the electrolyte. 300 ml of the solution under investigation were placed in a 600-ml glass bottle and shaken thoroughly in contact with the atmosphere in order to ensure saturation with respect to dissolved air. A small hole through the cork for the bottle was loosely packed with cotton wool to reduce evaporation while still permitting access to the air. Electrolytic contact to a saturated calomel electrode placed in an auxiliary vessel containing saturated sodium bicarbonate solution was effected through a stopcock kept in the closed position. This stopcock was greased with a stiff paste consisting of a mixture of bentonite,[3] glycerine, and water which prevented contamination of the inhibitor solution but maintained excellent electrolytic contact. Separate experiments showed that the resistance of a stopcock treated in this manner was initially of the order of two megohms, but fell in a few hours to a value of approximately 250,000 ohms and remained constant for several weeks; furthermore no diffusion of colored solutions through the stopcock could be detected in one month under a hydrostatic head of one foot.

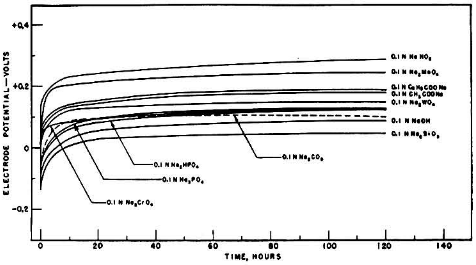

FIG. 4. Potential/time curves for 0.1*N* solutions of 11 inhibitors in the presence of air.

In a typical experiment the specimen was degreased and abraded as described previously; it was then exposed to the solution under examination; potential difference readings were recorded continuously over the five-day period of the experiment by means of a Leeds and Northrup "Micromax" recording potentiometer.

Potential/time curves,[4] determined at 25° ± 0.5°C in 0.1*N* inhibitor solutions are shown in Fig. 4. Experiments were carried out either in duplicate or

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[3] A hydrous aluminum silicate which swells on the addition of water.

[4] All potentials in this paper are expressed in relation to the Standard Hydrogen scale.

in triplicate with a control in each series—consisting usually of a redetermination of the curve for 0.1N sodium chromate. The results obtained were reasonably reproducible (±10 mv) if careful attention was paid to such factors as saturation of the solutions with dissolved air, absence of vibration, and similarity of surface treatment of the specimens.

Potential/time measurements were also carried out in more dilute solutions of these inhibitors. Fig. 5 and 6 show some typical results. In all cases, dilution of the inhibitor resulted in a more positive (noble) potential as long as the specimens did not corrode. When the final potentials are plotted against the pH value of the solution it can be seen that the steady values to which the passive potentials settle become more negative with a rise in pH (Fig. 7). The points not lying on the curve are the phosphates and sodium silicate.

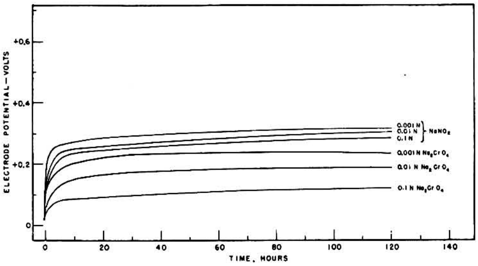

FIG. 5. Potential/time curves in diluted inhibitor solutions in the presence of air.

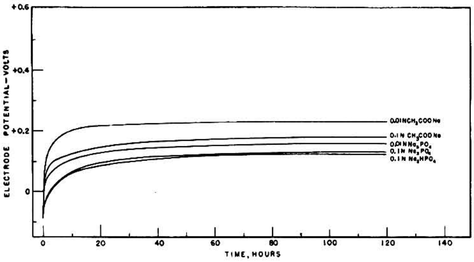

FIG. 6. Potential/time curves in diluted inhibitor solutions in the presence of air.

Potential Measurements in Deaerated Solutions

Potential measurements in deaerated solutions were carried out using the method and apparatus described in a previous paper (5). Specimens measuring 2.5 x 0.5 cm which had been degreased and abraded as described above were exposed to 5 ml of the deaerated 0.1N inhibitor solution to which had been added 10 ppm chloride ion, in the form of potassium chloride, so that the chloridized silver wire could take up a steady potential characteristic of the concentration of chloride ions in solution.

Potential difference measurements were recorded continuously for the five-day period of the experiments in all 0.1N inhibitor solutions with the exception of sodium chromate in which the silver/silver chloride electrode was not stable. Previous work (3), however, had shown that the potential of iron in deaerated 0.1N K_2CrO_4 was initially zero and became slowly more positive (noble) with time. The potential of the chloridized silver wire was determined separately at the end of each run and the electrode potential of the specimens calculated. The original air-formed oxide film appeared more stable at pH values above 11.0 and was therefore first destroyed by two minutes' treatment with deaerated 0.1N hydrochloric acid. The results are shown in Fig. 8.

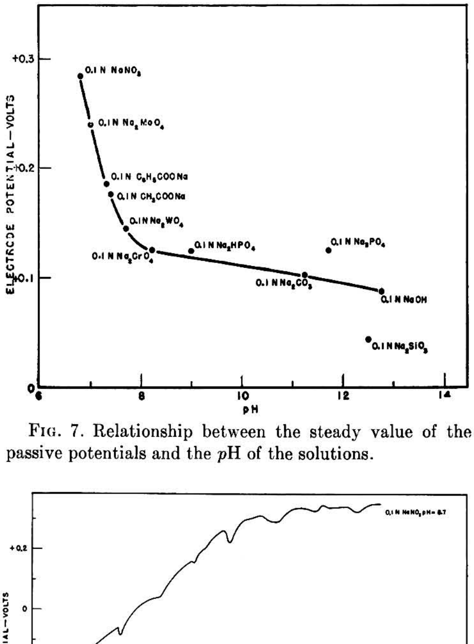

FIG. 7. Relationship between the steady value of the passive potentials and the pH of the solutions.

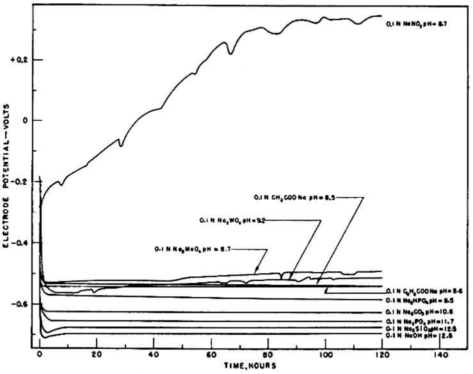

FIG. 8. Potential/time curves in deaerated 0.1N inhibitor solutions.

It can be seen that, with the exception of sodium nitrite, tungstate, and molybdate, the potential/time curves are either flat or become slightly more negative (active) with time. Chromate and nitrite are known to be oxidizing agents with respect to iron, but recently doubt has been raised as to whether tungstate and molybdate behave in a similar manner (11). Accordingly, experiments were carried out to investigate this point.

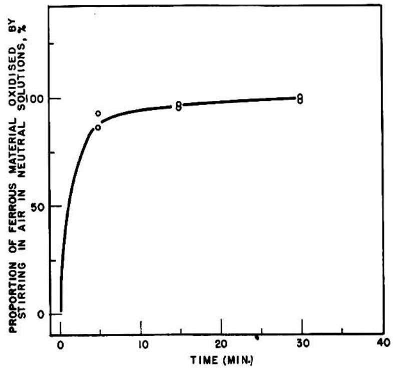

Fig. 9. Relationship between time and the percentage oxidation of a neutral ferrous solution by dissolved air.

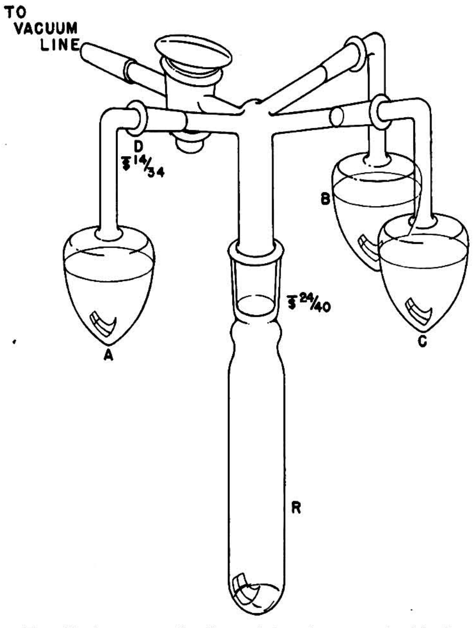

Fig. 10. Apparatus for determining the rates of oxidation of deaerated ferrous solutions.

Rate of Oxidation of Ferrous Solutions at Neutral pH Values by Sodium Tungstate, Molybdate, and Dissolved Air

The rate of oxidation of ferrous ions by dissolved air was determined by stirring 25 ml of acidified $0.0072N$ $FeSO_4$ solution, neutralized to a *p*H value of approximately 7.0 by the addition of strong NaOH solution. The concentration of residual Fe^{++} in solution was determined at different intervals of time by acidifying the solution with concentrated sulfuric acid, which dissolved the hydrated oxides of iron and stopped further oxidation of the ferrous ions, the concentration of which was then determined by an electrometric titration with $0.1N$ $KMnO_4$ from a microburette. The results (Fig. 9) show that oxidation is 95 per cent complete in five minutes and 100 per cent complete in thirty minutes.

Since the rate of oxidation of ferrous ions by air in neutral solution is so high, any attempt to determine the rate of oxidation by tungstate and molybdate must be carried out in the absence of air. Accordingly experiments to this end, the preliminary results of which have been previously reported (12), were carried out in the apparatus shown in Fig. 10. Twenty five ml of $0.0072N$ $FeSO_4$ in NH_2SO_4, together with excess (4 ml) $0.1N$ sodium tungstate or molybdate, were contained in the bulb, A. Robertson (11) has shown that this mixture is stable in air. The bulb, B, contained sufficient N sodium hydroxide solution to neutralize the acid in A and bring the *p*H of the mixture to approximately 7.0, while C contained 20 ml of $3N$ sulfuric acid. The three solutions were then deaerated as described above. When the deaeration was complete, the contents of A were transferred to the reaction chamber, R, by rotating the bulb about the joint D. The contents of B were then added to neutralize the excess acid and to bring the solution into the neutral *p*H range. Reaction was then allowed to take place at 25°C. At the end of the required period the acid in C was added to the solution in R. The hydrated oxides of iron were dissolved and the ferrous ions in solution stabilized by the excess acid. The ferrous ion concentration was then determined by electrometric titration as described above.

Experiments were also carried out in which no oxidant was added to the ferrous solution. Owing to incomplete drainage and perhaps to some decomposition of the ferrous hydroxide (13, 14), although this point is very doubtful (15), a small decrease in the ferrous ion content of the final solution was observed. This blank reading, which appeared to be independent of time, was subtracted from all values obtained with tungstate and molybdate present. The results, expressed as the percentage of weight of ferrous material oxidized, are shown in Fig. 11. They demonstrate that both tungstate and molybdate are very mild oxidizing agents with respect to ferrous compounds; the effect, however, would be masked in neutral solutions by oxidation with dissolved air, if this was present. It was also observed that excess potassium chromate completely oxidized ferrous ions in the presence of 1N sulfuric acid extremely rapidly.

Determination of Polarization Curves

Anodic and cathodic polarization curves were determined in deaerated 0.1N solutions of some anodic inhibitors using the method described in a previous paper (5). The iron electrodes, measuring 2.5 x 0.5 cm were suspended 1 cm apart in 5 ml of the deaerated inhibitor solution containing 10 ppm chloride ion in the form of potassium chloride. The potentials were measured against a chloridized silver wire also suspended in the solution. The applied current ranged between 0–10 microamps/cm^2 of specimen. The results are shown in Fig. 12. It can be seen that the slopes of the cathodic polarization curves increase with a rise in pH and in all cases are greater than those of the anodic polarization curves. The slope of the anodic polarization curve for sodium tungstate is, however, somewhat greater than that of other inhibitors at a similar pH value.

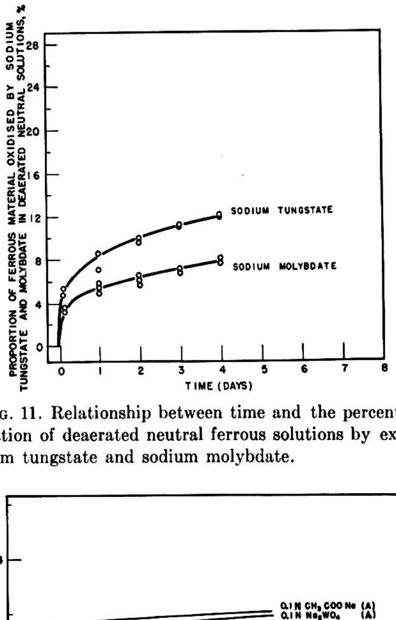

FIG. 11. Relationship between time and the percentage oxidation of deaerated neutral ferrous solutions by excess sodium tungstate and sodium molybdate.

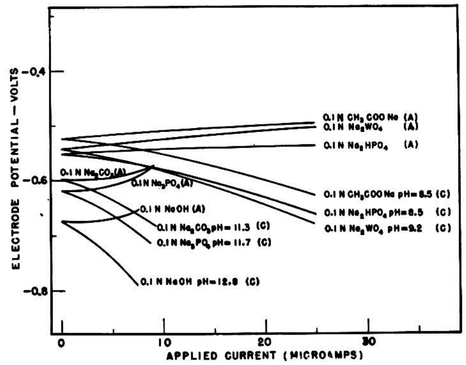

FIG. 12. Anodic and cathodic polarization curves in some deaerated 0.1N inhibitor solutions. A, anodic polarization curves; C, cathodic polarization curves.

A further investigation of the anodic curve for sodium tungstate was, therefore, carried out as follows. At the end of one determination the current was switched off and the specimen left in contact with the solution for 24 hours. The anodic curve was then redetermined in a similar manner and the current switched off once more. The procedure was repeated several times over a period of five days. The rise in potential of the specimen, with time, following anodic polarization was much more rapid than that of a specimen simply exposed to deaerated 0.1N sodium tungstate as shown in Fig. 8. After several redeterminations the anode became passive (Fig. 13), whereas the potential of the cathode remained close to the original value. This behavior is quite different from that exhibited by deaerated 0.1N disodium phosphate in which the anodic

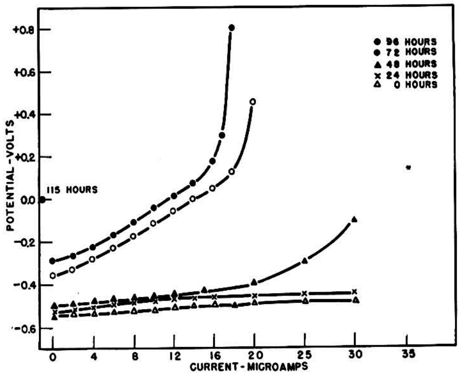

FIG. 13. Effect of repeated redetermination on the anodic polarization curve of iron on deaerated 0.1N sodium tungstate solution.

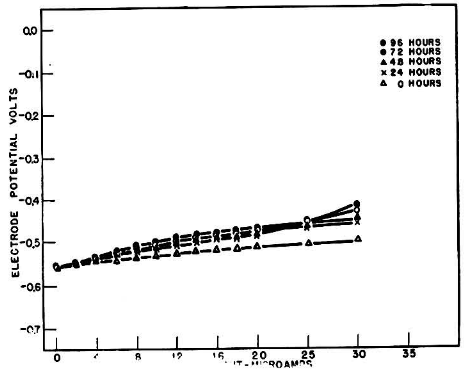

FIG. 14. Effect of repeated redetermination on the anodic polarization curve of iron in deaerated 0.1N disodium phosphate solution.

polarization curve was little affected by repeated redetermination (Fig. 14).

Effect of Chloride Ions on Inhibition

A series of experiments was carried out in order to determine the concentration of chloride ions, added as potassium chloride, required to break down the passivity resulting from immersion in 0.1N inhibitor solutions.

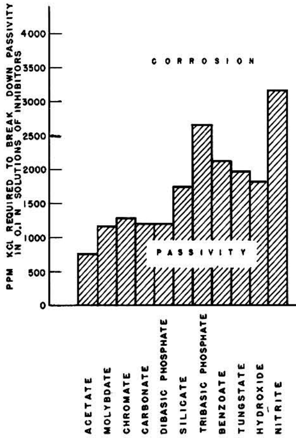

FIG. 15. Diagram showing the concentration of potassium chloride required to initiate corrosion in 0.1N inhibitor solutions in the presence of air.

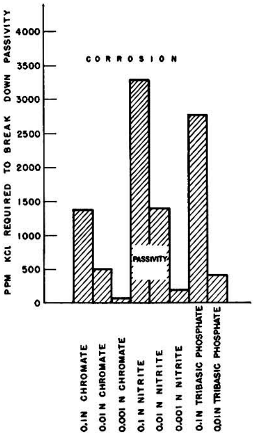

FIG. 16. Diagram showing the concentration of potassium chloride required to initiate corrosion in more dilute inhibitor solutions in the presence of air.

The specimens were in the form of sheet measuring 10.0 x 2.5 cm and were partially immersed in 200 ml of solution contained in open 250 ml beakers. Experiments were carried out for periods of up to one week, but it was generally found that, if a specimen was going to corrode, the corrosion would become evident within the first 24 hours. The results are shown in Fig. 15.

Several experiments were carried out in a similar manner to determine the effect of dilution on the concentration of chloride required to initiate corrosion. The inhibitors investigated in this manner were sodium chromate, nitrite, and tribasic phosphate. The results are shown in Fig. 16.

Effect of Carbon Dioxide on the Rate of Corrosion of Iron

The deaeration technique described above removed all dissolved gases from solutions. The weight losses were, therefore, determined not only in the absence of oxygen but also in the absence of carbon dioxide which has an appreciable effect on the pH value of unbuffered solutions. As a result, the experiments are not strictly comparable with the weight losses determined in the open beaker experiments (Fig. 1) where the solutions did contain carbon dioxide. A series of experiments was therefore carried out to determine the weight losses in solutions saturated with dissolved air but freed from carbon dioxide.

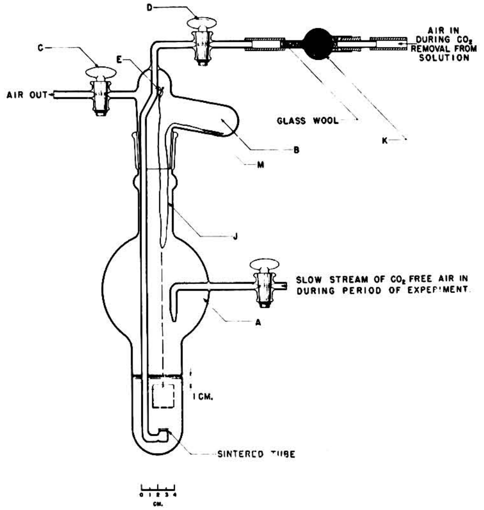

FIG. 17. Apparatus for determining weight loss in the presence of air freed from carbon dioxide.

The apparatus used is shown in Fig. 17. The carbon dioxide present in solution was removed by bubbling for two hours with air freed from CO_2 by passing through the tube K filled with ascarite. The air left the apparatus through C. During this period the specimen M was situated in the side-arm B. After the solution and apparatus had been freed from carbon dioxide the stopcock D was closed and air freed from CO_2 passed in through F and out through C, at constant pressure, for the period of the experiment. The apparatus was tilted so that the specimen, which was attached by the thread J to the glass hook E, fell 1 cm below the waterline of the solution. Banks of six similar apparatuses were placed in a constant temperature enclosure operating at 25° ± 0.5°C. Blank experiments were carried out in which a similar procedure was employed, except that the air was not freed from CO_2.

The specimens were in the form of sheet 2.5 x 2.5 cm with a small hole located at the center of the upper edge. They were degreased, abraded, and weighed as described above. At the end of the experiments, which lasted 5 days, the corrosion products were removed by treatment with inhibited 1.1 HCl and the specimens washed, dried, and reweighed. Two hundred ml of solution were used in all experiments. The inhibitor investigated by this method was disodium phosphate. The results, together with the blank experiments in which CO_2 was not removed, are shown in Fig. 18.

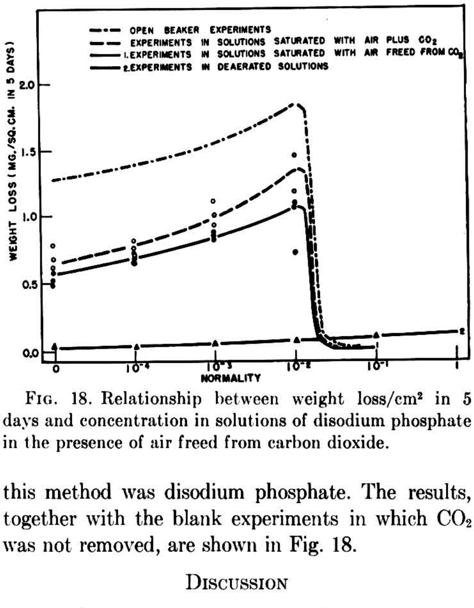

FIG. 18. Relationship between weight loss/cm² in 5 days and concentration in solutions of disodium phosphate in the presence of air freed from carbon dioxide.

DISCUSSION

All inhibitor solutions described above are capable of behaving as oxidizing agents toward iron when they contain dissolved oxygen. However solutions with nonoxidizing anions, e.g., sodium hydroxide, carbonate, silicate, acetate, benzoate, dibasic and tribasic phosphate, lose this property when deaerated. The remaining solutions, sodium chromate, nitrite, tungstate, and molybdate, which contain oxidizing anions of various degrees of effectiveness, do not completely lose their oxidizing powers on deaeration, although it has been shown (Fig. 11) that, in deaerated, neutral solutions, tungstate and molybdate are only very mild oxidizing agents. These two classes of inhibitors show rather different properties and will, therefore, be considered separately in the following discussion.

Inhibitors Having Nonoxidizing Anions

These inhibitors behave very similarly to that described previously for sodium hydroxide (3) and orthophosphates (4, 5) in that passivity is only obtained when the solutions contain dissolved air (Fig. 1 and 2, Table II). In deaerated solutions, iron corrodes very slowly, the rate of corrosion decreasing with a rise in *p*H, with the exception of disodium phosphate which exhibits an anomalously high weight loss; this point is discussed later. At high *p*H values the rate of corrosion is very slow and of little practical consequence.

The curves of Fig. 2 are not strictly comparable to the equivalent results obtained in the open beaker experiments (Fig. 1) since the solutions then contained carbon dioxide in addition to air, whereas the deaeration removed both air and carbon dioxide. From Fig. 18 it can be seen that although the removal of CO_2 reduces the weight losses slightly it does not affect the form of the curves. By comparison with the curves in Fig. 2 it can be seen that the removal of dissolved air greatly reduces the rate of corrosion at low inhibitor concentrations since the cathodic reaction is no longer depolarized by dissolved oxygen. At higher concentrations the weight losses in the presence of air begin to decrease rapidly and reach zero as the specimens become passive, whereas in deaerated solutions the weight losses continue to increase.

The potential/time curves of passivated specimens (Fig. 4–6) all fall largely within the range 0 to +0.35 volt. If the solutions are deaerated, however, the potentials of specimens in solutions having nonoxidizing anions become much more negative (Fig. 8) and either remain constant or become slightly more negative with time; the final value of the potential also becomes more negative with rise in pH, with the exception of disodium phosphate which exhibits an anomalously low potential. Weight loss determinations (Table II) indicate that the specimens are corroding very slowly and the form of the potential/time curves suggests that this corrosion is under cathodic control. This is confirmed by polarization curves[5] in deaerated solutions (Fig. 12) which show that, at the low current densities operative during this slow corrosion, the anodic polarization curves are practically flat whereas the cathodic polarization curves have a much greater slope which increases with rise in *p*H.

In a corroding system of low resistance the com-

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[5] It should be noted that these polarization curves are the continuation of the curves representing a corroding specimen.

promise potential of the specimen and the corrosion current are given by the potential and current intercepts at the junction of the anodic and cathodic polarization curves (Fig. 19a). At the low current densities operative during the cathodically controlled slow corrosion in deaerated solutions, the compromise potential of the specimen is very close to that of the anodic reaction and is given approximately by the Nernst equation:

$$E = E_0 + \frac{RT}{2F} \log_e [\mathrm{Fe}^{++}] \qquad \text{(I)}$$

where $E_0 = -0.44$ volt.

At the steady state in solutions of relatively high *p*H the ferrous ion concentration is that in equilibrium with ferrous hydroxide, except in solutions of disodium phosphate where the corrosion product is ferrous phosphate (5). The ferrous hydroxide corrosion product in deaerated solution is a whitish gelatinous product and is difficult to observe in very small amounts. However, conditions of *p*H and the rate at which iron passes into solution necessitate its formation. The concentration of ferrous ions, once ferrous hydroxide is formed as a corrosion product, is given by

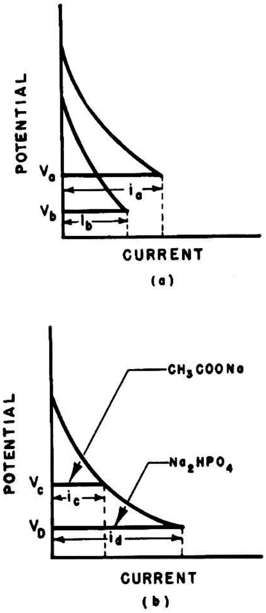

FIG. 19. Potential/current diagrams showing the effect of (*a*) *p*H and (*b*) ferrous ion concentration on the corrosion current and potential.

$$\mathrm{Fe}^{++} = \frac{S_{\mathrm{Fe(OH)_2}}}{[\mathrm{OH}']^2} \qquad \text{(II)}$$

where $S_{\mathrm{Fe(OH)_2}}$ is the solubility product of ferrous hydroxide.

The open-circuit potential of the cathodic reaction

$$2\mathrm{H}^+ + 2e' = \mathrm{H}_2 \qquad \text{(III)}$$

varies with hydroxyl ion concentration in a similar manner, at constant pressure of hydrogen, so that the open-circuit potential difference between anodic and cathodic reactions should remain constant despite the fact that a rise in *p*H results in a shift of both potentials in the negative direction. When current is drawn from this corrosion cell the cathodic reaction polarizes much more than the anodic reaction and this polarization increases with a rise in *p*H (Fig. 12). Thus, as the *p*H of the solution is raised, the compromise potential of the specimen shifts in the negative direction, e.g., from V_a to V_b, while the corrosion current falls, e.g., from i_a to i_b (Fig. 19a). If the Nernst equation is accurately obeyed, a unit increase in *p*H should result in a 59 mv decrease in potential. This appears to be true when the equilibrium concentration of Fe^{++} does not exceed a value of approximately 10^{-5} gm ions/liter. Thus calculation of the solubility product of ferrous hydroxide from the equilibrium potential of iron in deaerated 0.1*N* CH_3COONa (*p*H = 8.5) gives a value of $10^{-14.5}$ which is the same value as that obtained by Shipley and McHaffie (16). At higher *p*H values, when the $[\mathrm{Fe}^{++}]$ is less than 10^{-5} gm ions/liter, the Nernst relationship appears to be no longer obeyed and the change in potential for a unit rise in *p*H is less than 59 mv.

Iron exposed to deaerated disodium phosphate exhibits an anomalously low potential and high weight loss. At *p*H 8.5, however, the corrosion product in deaerated 0.1*N* disodium phosphate is not ferrous hydroxide but ferrous phosphate, and consequently the ferrous ion concentration in equilibrium with ferrous phosphate must be lower than that in equilibrium with ferrous hydroxide. The potential of the anodic reaction will, thus, be lower in deaerated disodium phosphate than in a deaerated solution of similar *p*H in which the corrosion product is ferrous hydroxide, e.g., 0.1*N* sodium acetate. The cathodic polarization curve will be the same in both cases with the result that the compromise potential in disodium phosphate (V_D) will be lower than in acetate (V_C) (Fig. 19b), while the corrosion current (i_d) will be greater than acetate (i_c). At *p*H values above 10, ferrous hydroxide should be more insoluble than ferrous phosphate and it is interesting to note that crystalline ferrous phosphate is not observed as a corrosion product in deaerated solutions above this *p*H value. Presumably the potential of iron in deaerated trisodium phosphate is controlled by the precipitation of ferrous hydroxide, despite the fact that ferric phosphate is found in the passivity films formed on iron immersed in trisodium phosphate containing dissolved air (9, 6). Calculation from potential data, the pH value of the solution, and dissociation constants of the orthophosphate ions (17), leads to an approximate value of 10^{-25} for the solubility product of ferrous phosphate.

It appears that inhibitors having nonoxidizing anions behave in a similar manner and that the mechanism of inhibition is like that put forward for orthophosphates (4, 5). Inhibition is due primarily to oxygen, dissolved in solution, which has been shown to be a powerful oxidizing agent in neutral solution (Fig. 9). The oxygen, dissolved in solution, is believed to adsorb on the surface of the iron and react with surface iron atoms forming a thin, invisible film of γ-Fe_2O_3, of the order of 200 Å thick, in a manner similar to that by which oxide films are formed in air. Film formation is, however, not instantaneous and very slow corrosion, leading to the production of inclusions of corrosion product, accompanies the early stages of passivation. A more detailed account of the mechanism will be given later.

Inhibitors Having Oxidizing Anions

Sodium chromate and sodium nitrite are well-known oxidizing agents and Fig. 11 shows that tungstate and molybdate ions have mild oxidizing powers in neutral solutions. These inhibitors show many points of similarity to the inhibitors having nonoxidizing anions; for instance the films formed by passivation of initially film-free iron specimens in chromate and nitrite are composed mainly of γ-Fe_2O_3 (2, 8) and films formed by nitrite also contain small quantities of lepidocrocite (8), although its distribution throughout the film was not determined. It is probable that the films formed by chromate also contain small quantities of lepidocrocite in addition to small amounts of chromium compounds (18, 19, 20). The method of electron diffraction previously used to examine these films (2) was, however, not sufficiently sensitive to detect very small amounts of other compounds.

The possibility of oxidizing inhibitors contributing to the formation of the oxide film cannot be dismissed. It was found previously (3), as well as during this research (Table II), that 0.1N sodium chromate passivates iron in deaerated solutions. Also 0.1N sodium nitrite, a milder oxidizing agent, behaves similarly (Table II) except that the potential of an iron specimen in deaerated solutions (Fig. 8) takes longer to reach the passive range. Sodium tungstate and sodium molybdate are much weaker oxidizing agents toward ferrous solutions (Fig. 11), although these experiments do not necessarily represent their oxidizing powers with respect to an iron surface. However, tungstate and molybdate are not sufficiently powerful oxidants to build up a protective oxide film in deaerated solution, at least during the period of the experiments, and so appreciable quantities of iron pass into solution (Table II). Fig. 8, however, provides definite evidence of increasing anodic polarization with time—which is quite different behavior to that shown by deaerated inhibitors with nonoxidizing anions. Presumably some oxide is being formed by adsorption of the tungstate (or molybdate) ion followed by oxidation of the iron and reduction of the inhibitor anion, but the rate of formation is not sufficiently high to form a protective film. Similar behavior is exhibited by tungstate during determinations of the polarization curves in deaerated solution (Fig. 12) where it is observed that the gradient of the anodic polarization curve is slightly greater than that of nonoxidizing agents at similar pH values.

Despite the fact that tungstate and molybdate are such weak oxidizing agents, they passivate iron in solutions containing dissolved air at similar concentrations to chromate and nitrite (Fig. 1), an effect previously noticed by Robertson (11). In order to explain this, the significance of Fig. 13 must first be considered. Successive redetermination of the anodic polarization curve in deaerated 0.1N sodium tungstate solution results in passivation of the anode in a comparatively short time, whereas similar treatment of an iron anode in a deaerated inhibitor with nonoxidizing anions, such as disodium phosphate, results in very little change in the anodic polarization curve (Fig. 14) and the potential of the anode always returns to the equilibrium value. The fact that the potential of the cathode remains at the equilibrium value in both experiments indicates that oxygen was not evolved at the anode. Apparently the tungstate ions are more effective oxidizing agents when discharged at the anode under conditions of high current density. In the later redeterminations the anode is probably so largely covered by oxide that the local current density is very high at the anodic areas.

When an abraded specimen is immersed in a passivating solution, the surface is initially largely covered with oxide formed by exposure to the atmosphere. Under these conditions the already small areas available for anodic reaction become even smaller due to the progressive growth of oxide in solution. It was previously suggested (5) that under such conditions a high local current density was developed at the anodic areas. If this is the case, the anions of such a weak oxidizing agent as sodium tungstate would be discharged at high current density and would then prove a relatively rapid and efficient oxidizing agent. This may explain the great similarity between the four oxidizing inhibitors of unequal oxidizing powers.

Thus the mechanism of inhibition for these four inhibitors is essentially the same as described in the previous section. Inhibition is primarily due to a thin film of γ-Fe_2O_3 probably formed mainly by oxygen dissolved in solution. The importance of the oxidizing inhibitor seems to be confined mainly to the reactions taking place at discontinuities in the oxide film where slow corrosion is occurring. In the absence of air, oxidizing anions react with the iron surface to form iron oxide, the rate of this reaction being sufficiently high with chromate and nitrite to form a protective film. A more detailed account of the mechanism of inhibition will be given later in the discussion.

Effect of Chloride on Passivity

It can be seen from Fig. 1 and 15 that those inhibitors which passivate iron at low concentrations are not necessarily more effective in the presence of chloride. For instance, the concentration of chloride required to make $0.1N$ sodium carbonate and disodium phosphate corrosive is very similar to that required to make $0.1N$ sodium chromate and molybdate corrosive despite the fact that, in the absence of chloride, the former do not inhibit the corrosion of iron until their concentration is of the order of $10^{-1}N$ whereas the latter inhibit at $10^{-3}N$. It is probable that film breakdown initially starts at inclusions of corrosion product in the passivity films and that the concentration of chloride that can be tolerated is related in a complex manner to the pH changes at the anodic areas.

Nature of the Passive Potentials

One of the surprising features of Fig. 4, 5, and 6 is that specimens exhibit more positive potentials in more dilute inhibitive solutions despite the fact that these solutions are poorer inhibitors, in that a much lower concentration of chloride is required to make them corrosive (Fig. 16). Furthermore, with the exception of sodium silicate and the phosphates, the steady value of the passive potential becomes more negative with rise in pH (Fig. 7). It is believed that the potential of a passive specimen is the potential of the very slow corrosion occurring at discontinuities in the oxide film.

Mechanism of Inhibition

It appears that a mechanism, based on the concept of protective films of γ-Fe_2O_3 maintained in constant repair, can be put forward to explain inhibition by anodic inhibitors. The oxide film is believed to be formed entirely by dissolved oxygen in inhibitors which do not contain oxidizing anions and mainly by dissolved oxygen even when the inhibitor contains oxidizing anions. The film is believed to be formed by adsorption of oxygen, followed by heterogeneous reaction and thickening until it reaches an equilibrium thickness of approximately 200 Å when it is sufficiently thick to prevent the outward diffusion of iron ions. The mechanism of formation of the oxide film is considered to be similar to that by which oxide films are formed in dry air. However, this film must be maintained in constant repair, usually by dissolved oxygen, in order to stop iron ions entering the solution.

The formation of a protective oxide film is not instantaneous and very slow corrosion accompanies the initial formation of oxide. The oxygen dissolved in solution exhibits a dual role, since it is not only largely responsible for the formation of the passivity film, but also acts as a cathodic depolarizer for the accompanying corrosion reaction. The rate of this corrosion is controlled by high anodic polarization brought about by the very small size of the anodic areas resulting from the progressive growth of the oxide film in solution. It was previously suggested (5) that a high current density was developed at these anodic areas.

Small inclusions of lepidocrocite (γ-FeO·OH), the natural corrosion product, of the order of 1 to 2μ in diameter have been detected in the passivity films formed in sodium hydroxide (3). Inclusions of strengite ($FePO_4 \cdot 2H_2O$), of the order of 1μ in diameter have also been found in passivity films formed on iron by disodium phosphate (9). It is probable that, in the remaining inhibitors which have nonoxidizing anions, inclusions of lepidocrocite are present in the passivity films; the lepidocrocite may also contain some α-FeO·OH and Fe_3O_4 which are also oxidation products of $Fe(OH)_2$ (Table I). The precipitation of corrosion product over the small anodic areas probably retards the further lateral growth of oxide; additional anodic polarization will, however, result from thickening and consequent increase of resistance of the corrosion product. The initial corrosion is believed to become very slow after about one day when the duplex film is apparently sufficiently thick and continuous to practically prevent the further outward diffusion of iron ions. The nonoxidizing inhibitor anions do not participate directly in the formation of the oxide film; their function seems to be confined to the initial discontinuities in the oxide film where slow corrosion is occurring. The rate of corrosion must be sufficiently slow to prevent undermining of the film and the inhibitor probably ensures this condition by controlling the pH of the solution so that the anodic areas do not become too acidic.

The same general mechanism is applicable to inhibitors which contain oxidizing anions. In deaerated solutions, chromate and nitrite form an oxide film sufficiently rapidly to give inhibition while tungstate and molybdate do not form oxide sufficiently rapidly to prevent corrosion. In solutions containing dissolved air, however, the main part of the oxide film is still formed by dissolved oxygen with slow corrosion, under anodic control, accompanying the early stages of film formation. It was suggested in an earlier paper (5) that a high current density was operative at the small anodes. Even such a mild oxidizing anion as the tungstate ion when discharged anodically at high current density proves to be a relatively efficient oxidizing agent, comparable, in fact, to chromate and nitrite. This is suggested as the reason for the great similarity of behavior, in the presence of air, of the four oxidizing anions of vastly different oxidizing power. The discharge of oxidizing anions at small anodes at high current density is considered to result in the additional formation of oxide with the result that inhibition is achieved at lower concentrations than in inhibitors having nonoxidizing anions. The inclusions, which are probably thicker than the surrounding oxide film, are believed to consist of a mixture of oxide, corrosion product, and the reduction product of the inhibitor anion if this is insoluble.

It should be emphasized, however, that even after the film has become protective it must be kept in a state of constant repair either by dissolved oxygen or by an oxidizing anion or both. Under conditions leading to inhibition any local breakdown is repaired by the formation of fresh film by the inhibitor.

The formation of γ-Fe_2O_3 by dissolved oxygen should be independent of the pH of the solution. The simultaneous corrosion process is, however, dependent on conditions existing in solution and on the surface condition of the metal (6). In general, factors tending to increase this rate of corrosion will militate against passivity since it is believed that the inclusions in duplex films are points of weakness from which film breakdown may begin.

SUMMARY

Decinormal solutions of sodium acetate, benzoate, carbonate, hydroxide, orthophosphate, and silicate passivate iron only in the presence of dissolved air. If the solutions are deaerated, they attack iron slowly, potential/time and polarization curves showing that the attack is under cathodic control.

Powerful oxidizing inhibitors such as decinormal solutions of sodium chromate and nitrite can passivate iron even in deaerated solutions. Inhibitors of weaker oxidizing power such as sodium tungstate and molybdate behave similarly to chromate and nitrite in the presence of air, in that inhibition sets in at the same minimum concentration, but are unable to prevent corrosion in deaerated solution. Potential/time and polarization curves show that in deaerated solution of tungstate and molybdate some film formation is taking place, but that it is too slow to prevent iron passing into solution. However, tungstate and probably molybdate ions when discharged anodically at high current density are effective oxidizing agents toward iron.

The view is put forward that oxygen dissolved in solution is mainly responsible for passivity by virtue of its heterogeneous reaction with surface iron atoms to form a thin, self-repairing film of γ-Fe_2O_3, of the order of 200 Å thick, in a manner similar to that by which oxide films are formed in air. Oxidizing inhibitors assist in the formation of the passivity films by acting as film repairing agents at discontinuities present during the early stages of film formation.

ACKNOWLEDGMENTS

The authors are indebted to Dr. W. H. Barnes and Mrs. H. Shepard for carrying out the x-ray examination of the corrosion products and to Mr. P. Marier for assistance with some of the experimental work.

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

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Amount of Oxygen on the Surface of Passive Stainless Steel[1]

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ABSTRACT

The amount of oxygen on the surface of 18-8 stainless steel was obtained by pickling the alloy with HCl-H_2SO_4, washing with nitrogen-saturated water, then exposing the metal to water of known dissolved oxygen content. The decrease in dissolved oxygen for a definite period of exposure was a measure of the oxygen taken up by the 18-8 surface.

The take-up of oxygen was rapid the first few minutes, then proceeded slowly, reaching a maximum, after 6 hr, of 1.1 microgram/apparent cm^2 of metal surface. No further oxygen was consumed up to a maximum exposure of 48 hr. The alloy attained maximum passivity after about 3 hr in aerated water, as shown by potential measurements. When 18-8 was pickled with HNO_3-HF, the oxygen consumed was only 0.33 μg/apparent cm^2 of surface. This smaller value is related to the decreased true surface area of 18-8 so pickled (roughness factor = 1.2) compared with the HCl-H_2SO_4 pickle (roughness factor = 4.0).

The maximum amount of oxygen on passive 18-8 based on so-called true surface area is 0.27 μg/cm^2. This value is equivalent to a supposed Cr_2O_3 film only 17 Å thick. On the other hand, an equivalent adsorbed oxygen film consists approximately of 1 layer of atoms over which a close-packed layer of oxygen molecules is adsorbed. The data are not inconsistent, therefore, with the adsorbed film theory of passivity, and, accordingly, the mechanism of passivation by oxygen need not be considered different from that produced by carbon monoxide in hydrochloric acid saturated with this gas, where the adsorption theory heretofore has provided the only plausible explanation.

The point of view is proposed that oxide films previously isolated from stainless steels by several investigators were produced by reaction of the adsorbed film with the metal, the reaction being induced by polishing and abrading, presence of halogen ions and water in the stripping solution, or by high temperatures. Such oxide films, however, are considered to be of secondary importance in accounting for passivity as measured by corrosion resistance and by a noble potential.

INTRODUCTION

Stainless steels are defined as iron-base alloys containing at least 12 per cent chromium. The most widely used composition is the 17–19 per cent chromium, 8–10 per cent nickel, remainder iron alloy called 18-8. All these alloys are phenomenally corrosion resistant despite their high iron content, and because of this property, plus a noble galvanic potential in the order of silver or platinum, are called passive.

The property of passivity resides in certain films on the surface, the nature of which depends on properties of the base metal. According to one viewpoint, the passive film on stainless steels is composed of metal oxides, predominantly chromic oxide, acting as a diffusion barrier layer between the metal and its environment and kept in repair by an oxidizing environment. This film is supposedly thick enough to allow its isolation by chemical means (1–3), accomplished, for example, by immersing the metal into iodine or bromine dissolved in methyl alcohol. This reagent reacts preferentially with the metal directly beneath any oxide film allowing the oxide to "float" to the surface of the liquid, after which it can be examined optically or analyzed chemically.

A second viewpoint (4–6) ascribes passivity to a chemisorbed film on the alloy surface, which satisfies residual affinities of the metal for its environment, and which makes up a dipole layer with negative charge on the outer surface. The satisfaction of chemical valence forces plus the dipole layer account for diminished reactivity of the alloy, in addition to a noble galvanic potential.[2] The important source of passivity, by this viewpoint, is a film in the order of a monolayer in thickness, and, therefore, too thin to be seen and handled. Thicker oxide films which may form subsequent to formation of the adsorbed film are considered to be of secondary importance in the passivation mechanism, and are not necessary to the observed corrosion resistance.

It has been difficult to distinguish experimentally

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[1] Manuscript received May 6, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952.

[2] To a first approximation, the change of potential in the noble direction by such a dipole layer is given by the expression $4\pi n\rho$, where $n\rho$ is the electric moment per unit area of metal surface.

between these two viewpoints, especially since a thick oxide film under certain conditions may be present on a stainless steel and, by circumstantial evidence, would seem to accompany its corrosion resistance, in the same sense as the thick oxide film on aluminum appears to accompany its corrosion resistance. One distinguishing experiment is possible, however, which depends on the fact that an adsorbed film is appreciably thinner than a diffusion barrier oxide film and, hence, contains less oxygen. Therefore, a measure of the minimum amount of oxygen on the surface of a stainless steel necessary to make it corrosion resistant, and to impart to it a noble potential, may serve as a critical experiment. It is the results of this experiment that are described herewith.

PROCEDURE

The procedure consisted in pickling a stainless steel sheet out of contact with air to remove all films from the surface. The pickled sheet was then washed with nitrogen-saturated water, followed by contact with aerated water for a definite time. The drop in oxygen content of the water was a measure of the amount of gas taken up by the metal surface. The procedure is similar to that described previously by Forrest, Roetheli, and Brown (7), with the refinement of an all-glass vessel to minimize contamination by air, and with greater emphasis on general quantitative features of the experiment. The "true" surface area of the stainless steel on which oxygen was taken up was also measured, since without this a calculation of film thickness cannot be made.

Commercial 18-8 sheet, (0.045% C, 18.50% Cr, 9.43% Ni) supplied by courtesy of Armco Steel Corporation, measuring 0.010 in. thick and 1744 cm^2 in area (both sides) was formed into a 3½- by 2½-in.-diameter coil. This was placed inside a 565 ml glass vessel. A glass cover with ground glass surface fitted over the bottom portion of the vessel and was held in place by a clamp (Fig. 1). A magnetic stirrer insured renewed contact of liquid with all portions of the alloy sheet.

An acid pickle from a separatory funnel entered the vessel by way of inlet B. This consisted of 25 vol per cent commercial concentrated HCl and 25 vol per cent commercial concentrated H_2SO_4 at 35°C in contact with the alloy for 10 min. Hydrogen bubbles escaping from all portions of the metal surface indicated uniform attack and removal of surface films. The metal coil and glass vessel were then washed with nitrogen-saturated water by filling the vessel successively 3 times through B, each time using purified nitrogen supplied through inlet A to force the water out through efflux E. The nitrogen-saturated water was prepared by bubbling the gas through a large volume of distilled water for 5 hr or longer, using a sintered glass bubbler, and gave a negative Winkler test for oxygen. The nitrogen used for this purpose was purified by passing it over copper turnings at 400°C, the path of which was 3 ft long. Distilled water of known oxygen content was then admitted to the cell through D (about 30 sec for filling), and allowed to remain, with continuous stirring, in contact with the stainless steel for a definite time. Finally, a sample of water was removed from the vessel and analyzed for oxygen by the standard Winkler method.

Because a small amount of oxygen from the aerated water was lost to the nitrogen atmosphere above it during filling of the vessel, a blank correction was necessary, obtained by following the procedure described above for the empty vessel. The blank, averaged for 8 separate determinations, was 0.12 ± 0.04 ppm oxygen, and was independent of the length of time, ranging from 15 min to 25 hr, that the aerated water remained in the glass vessel. This value is 3.5 per cent of the maximum oxygen taken up by the pickled stainless steel surface after contact with aerated water and, hence, was not critical.

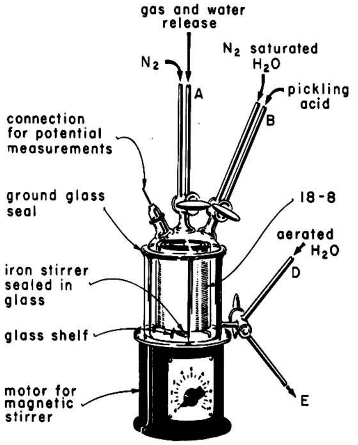

FIG. 1. Glass vessel for measuring oxygen take-up by pickled 18-8 stainless steel.

Potential measurements were made by connecting the coil to a tungsten wire sealed in a glass stopper at the top of the vessel which, in turn, made connection to a vacuum-tube potentiometer. The second electrode was a miniature calomel cell immersed in the water above partially opened stopcock A.

Effect of Varying Pickle and Washing Time

There is always the possibility that nitrogen-saturated water may have carried some small amount of dissolved oxygen, or the water itself may have reacted directly with the alloy to form an oxide. To check this, the pickled sheet and glass vessel were washed 3 times with nitrogen-saturated water as usual, and compared with a run employing 6 washes, and with runs when nitrogen-saturated water remained in contact with the metal as long as 1 hr. Also, the time of pickle was varied from the usual 10 min to double this time to insure that the surface was free of films. Differences in oxygen take-up were largely within the experimental error, as shown by data of Table I. The low value for 6 washes may be evidence of some residual oxygen in the water, indicating that oxygen take-up values, if anything, are slightly low.

TABLE I. *Effect of variation in pickling and washing time, and phosphorus addition to pickle, on oxygen take-up of 18-8.* $HCl-H_2SO_4$ *pickle, 15-min contact with aerated water*

Pickling time (min)	Washes	Washing time (min)	O_2 Take-up ($\mu g/cm^2$)
10	3	5	0.69 (normal proced.)
20	3	5	0.68
20	3	5	0.73
10	3	15	0.65
10	3	15	0.64
10	6	10	0.60
10	3	60	0.70
10, P addition	3	5	0.71
10, P addition	3	5	0.65

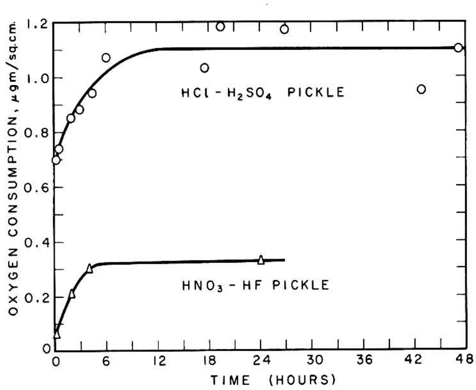

FIG. 2. Oxygen take-up by pickled 18-8 stainless steel after various times of exposure to aerated water.

RESULTS

Data showing take-up of oxygen by the pickled 18-8 stainless steel are plotted in Fig. 2. Oxygen is consumed rapidly the first few minutes of contact with aerated water, then more slowly for about 6 hr. After this, no further change occurs within the limit of reproducibility for the longest period of exposure equal to 48 hr. The maximum consumption is equal to 1.1 ± 0.1 μg oxygen/cm^2 of apparent metal surface. The true surface of stainless steel is appreciably greater than the apparent surface, as discussed later, and, hence, the variation of the true surface with each pickling operation probably accounts for the observed scattering of data over long periods of exposure. For shorter periods, and before the surface takes up maximum oxygen, the effect of true area is less important and in this region, therefore, the data scatter less.

Data are included in Table I for addition to the pickle of yellow phosphorus dissolved in CS_2. This pickle before use was filtered through a sintered glass funnel to remove any particles of phosphorus. The phosphorus addition markedly increases absorption of hydrogen by iron and alloys of iron during pickling (8, 9) and, hence, is expected to increase hydrogen absorption by 18-8.[3] Any hydrogen so absorbed would increase oxygen consumption because of its reaction with dissolved oxygen to form water. However, using this pickle did not increase oxygen consumption, so that presumably, very little hydrogen was absorbed by the alloy in a 10-min pickle.

The pickle was next replaced by one in which hydrogen is apparently not a reaction product and, hence, no hydrogen is expected to enter the stainless steel lattice during the pickling operation. This pickle was 15 vol per cent HNO_3, 10 vol per cent HF, based on the commercial concentrated acids, used at 90°C for 10 min. Oxygen consumption was now much less than in the case of the $HCl-H_2SO_4$ pickle. Data are included in Fig. 2 showing that maximum oxygen consumption amounts to about 0.33 $\mu g/cm^2$ of apparent surface. The lower oxygen consumption, however, was not due to less hydrogen absorbed by the alloy, as further investigation proved.

Forrest, Roetheli, and Brown (7) reported that maximum consumption of oxygen by an 18-8 stainless steel occurred within 3 min of pickling, instead of 6 hr as found here. The cause for this difference is not clear. It is possible that their use of a hot water wash to remove hydrogen from the pickled alloy allowed a more rapid access of oxygen to the metal surface, although this seems improbable. The difference is not a function of dissolved oxygen content of the water, because a single run using oxygen-saturated water gave an oxygen take-up, corrected by an appropriate blank, of 0.86 $\mu g/cm^2$ for 20-min

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[3] Less so than in the case of iron, because the rate of diffusion of H_2 into the face-centered cubic 18-8 lattice is much less than into the body-centered cubic iron lattice.

exposure, compared with the interpolated value of 0.71 µg/cm² for air-saturated water (Fig. 2), both values being less than the maximum oxygen that can exist on the surface. Significantly, potential measurements of the pickled coil during exposure to aerated water showed a slow, rather than a rapid trend toward a passive noble potential, the maximum occurring at about 3 hr after pickling. Previous potential measurements by one of us also showed that maximum passivity of pickled 18-8 exposed to aerated water required several hours (10). The rate of consumption of oxygen, therefore, illustrated by Fig. 2, is approximately in line with potential-time measurements.

True Surface Area of Pickled 18-8

In order to convert oxygen consumption in µg/cm² to thickness of an oxygen or oxide film, it is necessary to know the true surface area of the pickled stainless steel. Measurements of this kind were obtained by O'Connor of this laboratory using the Brunauer-Emmett-Teller method (11–13). Ethane was adsorbed on 40.5 cm² of 18-8 cut from the same sheet as used in the above experiments and pickled identically. The adsorption isotherm was obtained at liquid oxygen temperatures (−183°C). Helium, after passing through a charcoal trap at −196°C, was used to calibrate the volume of the adsorption system. The area of the ethane molecule was taken as 21.5 Å² derived from x-ray data. This is in good agreement with a separate calibration made in this laboratory using glass beads of known diameter, for which the roughness factor is assumed to be unity. It is apparent from results given in Table II that the true surface area of stainless steel pickled with HNO_3-HF is only ⅓ that of 18-8 pickled with HCl-H_2SO_4.

Additional experiments showed that a pickling time of 20 min decreased the true area of the stainless sheet by 3 per cent compared with a 10-min pickle, and a 50-min pickle decreased the total area 9.5 per cent. The same sheet of stainless steel could be used, therefore, for several runs without large change in the true surface area.

Thickness of Oxygen Layer or Oxide Layer on 18-8

From the true surface area, the thickness of an adsorbed oxygen or of an oxide layer on the alloy surface equivalent to the measured oxygen take-up was calculated. Calculations assumed a chemisorbed close-packed oxygen atom layer of covalent atomic radius 0.7 Å, with the area per atom equal to $(\text{diam}^2)\sqrt{3}/2$. The oxide composition, on the other hand, was assumed to be Cr_2O_3 with density 5.2. The results are given in Table III.

Whatever the assumed composition of the oxide, this has only minor effect on the calculated thickness. The gas film is reported as atom layers, because of the fact that oxygen on tungsten appears to adsorb atomically (14), and the affinities of tungsten and chromium for oxygen are similar (heat of formation for WO_3 = 196 Cal/mol; for CrO_3 = 140 Cal/mol). On this basis, the calculated second layer of atoms over the first is not entirely complete or, alternatively, the atoms in pairs can be assumed to have greater than close-packed atomic spacing. The structure can also be considered to be a close-packed atomic layer over which molecular oxygen is adsorbed. If molecular oxygen is assumed to have a radius of 1.2 Å, and atomic oxygen 0.7 Å, both in close-packed layers, the weight of total oxygen/cm² corresponds exactly to the observed 0.27 microgram/cm². This structure, therefore, is in good agreement with the facts, in addition to being a plausible structure based on present knowledge of chemisorbed and physically adsorbed gas films.

TABLE II. *True surface area of pickled 18-8 stainless steel sheet*

Pickle	Roughness factor (true area/apparent area)
HCl-H_2SO_4, 35°C, 10 min	4.10
HCl-H_2SO_4, " "	3.90
HNO_3-HF, 90°C, 10 min	1.21

TABLE III. *Thickness of oxygen or oxide films on 18-8 stainless steel*

Pickle	Roughness factor	Oxygen take-up µg/cm		Equiv. thickness of	
		Apparent surface	True surface	Close-packed oxygen layer	Oxide as Cr_2O_3
HCl-H_2SO_4	4.0	1.1	0.27	1.8 atom layers (or 1 atom layer + 1 molecule layer)	17 Å
HNO_3-HF	1.2	0.33	0.27	1.8 atom layers	17 Å

It is of interest to note that the amount of oxygen adsorbed from the gas phase by iron is very close to that reported here for 18-8. Values obtained from gas adsorption determinations by several investigators (15–17) are within the range 0.2–0.4 µg oxygen/cm² of apparent surface, including measurements using the microbalance (18). These measurements are largely for hydrogen-reduced iron surfaces for which the apparent surface and the so-called true surface are not greatly different. Another similarity is found in the rapid initial adsorption of oxygen by both iron and 18-8 followed by a slower rate of oxygen consumption. The slow rate is a logarithmic function of time for iron (16) and appears also logarithmic for 18-8. Data of Fig. 2 transferred to a semilogarithmic plot in Fig. 3 follow the equation:

$$\mu g\ O_2/cm^2 = 0.188 \log \left(\frac{t}{\tau} + 1\right)$$

where τ is equal to 0.19 sec. This equation indicates that half the total oxygen adsorbed by 18-8 (0.55 $\mu g/cm^2$) occurs within about 2.7 min, which is in qualitative agreement with our observation that a large fraction of gas is adsorbed before measurements are possible.

The logarithmic relation is sometimes interpreted as evidence of oxide growth in accord with the similar equation expressing oxidation of several metals at elevated temperatures. However, the logarithmic relation may also apply to rate of chemisorption, where the first layer of gas molecules is rapidly adsorbed physically, followed by slow conversion to dissociated atoms which are chemisorbed. As chemisorption proceeds, more gas, less tightly bound than the first layer, is adsorbed at a rate dependent upon the rate of chemisorption.

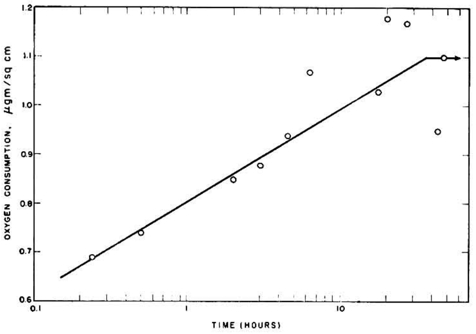

FIG. 3. Oxygen take-up by HCl-H_2SO_4 pickled 18-8 vs. time of exposure to aerated water.

DISCUSSION OF DATA

It appears that most of the hydrogen from the HCl-H_2SO_4 pickle is washed off the 18-8 surface by the nitrogen-saturated water, since the HNO_3-HF pickled surface consumes as much oxygen per true unit area as does the HCl-H_2SO_4 pickled surface. The fact that phosphorus added to the HCl-H_2SO_4 pickle gave about the same consumption of oxygen per unit area of metal surface is further evidence along these lines. Had considerable adsorbed hydrogen been present and later oxidized, this might, presumably, have given rise to small quantities of H_2O_2 in the aerated water. A check was made for hydrogen peroxide after contact of pickled 18-8 with aerated water for 1, 2, 4, 6, and 15 min using the yellow color reaction occurring with $TiOSO_4$ in dilute H_2SO_4. Although a very faint yellow first appeared and then quickly faded, comparative tests showed that any hydrogen peroxide must have been present in quantity less than 0.3 $\mu g/ml$ and, hence, was insignificant.

The amount of oxygen in the order of 0.27 $\mu g/cm^2$ of true surface, as reported herewith, is adequate to impart full passivity to 18-8. This was proved by potential measurements of the 18-8 coil and absence of visible rusting. The potential after 23 hr exposure was 0.15 volt more noble than the saturated calomel half cell. On the other hand, 5 min after exposure to aerated water, the coil was more active in potential than the saturated calomel half cell by 0.03 volt. Potentials of similar 18-8 specimens immediately after pickling in HCl-H_2SO_4 and washing indicated a value 0.5 to 0.6 volt more active than the calomel half cell, leaving no doubt that passivity is destroyed by the acid. The potential of 18-8 is similarly shifted in the active direction several tenths volt by the HNO_3-HF pickle, and again becomes noble as oxygen is taken up by the surface.

The potential data removed the possibility that a major passive film could have been built up during the nitrogen-saturated water wash by direct reaction of the metal with water to form oxide plus hydrogen. Had such an oxide formed, a noble potential might have been expected after the water wash instead of an active potential.

Since the alloy is fully passive after a few hours' exposure to aerated water, the small amount of oxygen on the surface, even after 48 hr, is consistent with a thin so-called passive film, in accord with ideas expressed by previous investigators. The maximum thickness of a supposed oxide film is about half that of the thinnest film (30 Å) isolated by Vernon *et al.* for polished 18-8. It should be noted in this connection, however, that it is not at all certain that isolated oxide films have any relation to those of concern here, because the oxide films were obtained from polished specimens, whereas our specimens were pickled. Polishing and abrading operations produce high local temperatures sometimes reaching the melting point of the metal (19) and, hence, can easily produce an oxide where none existed before. In this connection, it is pertinent that, so far, an oxide film has not with certainty been isolated from a pickled 18-8 surface, where the techniques employed have clearly avoided formation of oxides by the stripping solution itself. Vernon *et al.* (2) showed that the halogen methyl alcohol solution must be free of water and oxygen. Fontana presented similar evidence (20).

It seems reasonable to conclude that if an oxide film is present on pickled 18-8, it is extremely thin and not more than a few molecules thick. There is some question how thin a film can be and still act as a reliable diffusion barrier of the kind that matches the observed corrosion resistance of the stainless steels. On the other hand, the measured oxygen on an 18-8 surface, treated as an adsorbed film, is in the order of a monolayer. Therefore, the present data can be interpreted as being consistent with the adsorbed film theory of passivity, where the primary passive film is made up of a monolayer of oxygen atoms over which a layer of molecular oxygen is adsorbed. A structure of this kind is in quantitative agreement with the measured amount of oxygen on the surface whether the steel is pickled in $HCl-H_2SO_4$ or in HNO_3-HF and, hence, is probably true generally.

If this conclusion is valid, it indicates that the mechanism of passivity in stainless steels by oxygen is no different than that by carbon monoxide, where the adsorption theory heretofore (21) has been the only reasonable explanation for the passivity of 18-8 in hydrochloric acid saturated with this gas. It also indicates that the thin or thick oxide films, sometimes observed on stainless steels, are produced by reaction of the adsorbed oxygen film with the metal, stimulated by polishing and abrading, by presence of halogen ions and water, or by high temperatures. These oxide films, however, are of secondary importance in accounting for passivity, as measured by corrosion resistance or by a noble potential.

ACKNOWLEDGMENT

The authors are pleased to acknowledge joint support of this research by the Office of Naval Research on Contract N5-ori-07815 and by the Shell Fellowship Committee of the Shell Companies in the United States. They also wish to acknowledge the assistance of Henry Paige and James Forstner in obtaining preliminary data.

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

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Distribution of Conductivity within Dielectric Films on Aluminum[1]

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ABSTRACT

The characteristics of the dielectric film itself are substantially linear to alternating current within the limits listed. Since these characteristics are linear, the electrolytic capacitor appears equivalent to the characteristic of: (*a*) the conventional model of an electrolytic condenser film consisting of a capacity, which is determined by formation voltage, together with a high "leakage" resistance in parallel with that capacity; and (*b*) another capacity which is not so determined, with a relatively lower resistance in parallel, and in series with the conventional model indicated in (*a*).

It is concluded that conductivity within the film is not homogeneously distributed through it; assumption of an interface stratum is needed to render an adequate electrodynamic picture justifiable by a physicochemical concept.

INTRODUCTION

The purpose of this communication is to present an outline of some studies made to determine the electrical performance of the condenser film on anodized aluminum, (*a*) by constructing a model circuit which would reproduce the electrical characteristics of the actual electrolytic condenser; and (*b*) by drawing a correlation between the physical components of the condenser and the electrical elements of the model circuit. Regarding the first point, it should be noted that the simple model of a resistance in series with a parallel resistance-capacity combination is still being used (1), but more elaborate models have been presented in various publications over the last 15 years (2, 3).

GENERAL EXPERIMENTAL PROCEDURE

In order to have a well-defined electric field between anode and cathode of the electrolytic condenser, the construction of Fig. 1 was used. The specimen consists of a thin filmed aluminum anode 3 in. x 4 in. inserted between two interconnected nonfilmed cathodes held ¼ in. apart. Separators were used to keep the anode centered without hindering the passage of current. Each such assembly was put in a sealed Pyrex jar containing the electrolyte made up of boric acid and borates.

In every case referred to here the rule was followed that at all times the anode be kept at a positive potential with respect to the electrolyte. This condition is met by biasing the anode as in the circuit (4) of Fig. 2, which is made symmetrical either by using two identical electrolytic condensers or by combining the electrolytic condenser with a paper oil condenser decade adjusted to give equal a-c voltages across the decade and the electrolytic condenser. Nearly all films studied were formed to 180 v DC and operated as in Fig. 3 on 55 volts RMS AC with a 90-volt d-c bias, corresponding to the operation of a complete condenser on 110 v AC.

The d-c leakage current on our test condenser was usually of the order of 50–300 μa.[2] This current was measured on a microammeter inserted in the center branch, while the power dissipation was measured by a wattmeter, as shown in Fig. 3. To confine the alternating current to the outside branches, a resistor of 3000 ohms was inserted in the center branch with the effect that a 1 per cent unbalance in the impedances of the condensers allows less than 0.1 per cent of the alternating current to flow in the center branch, while lowering the effective bias voltage less than 1.5 v. The "excess" bias of more than 5 v fulfills the indicated condition that the anode be kept positive with respect to the electrolyte. Since the leakage current depends, among other things, on small local imperfections in the filmed anode, it may only with due caution be considered significant in discussing the basic nature of the film.

The purposes of the present investigation called for the knowledge of the performance of the condenser as a function of frequency, as part of its experimental foundation. Observations were made within the range from 20–10,000 cps.[3] The test

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[1] Manuscript received June 24, 1952. This paper was prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952.

[2] Much smaller leaks are obtainable in other types of electrolytic condensers which, however, are less suitable for the present experiments.

[3] Measurements of this kind are to be found in a paper by C. Wachenhusen (3). Although Wachenhusen's point of view was different from ours, some of his observations make it highly probable that the conclusions reached by us would hold true over the extended frequency range he used.

equipment included an audio oscillator, audio amplifier, a-c bridge, and a cathode ray oscilloscope high gain detector. The bridge was a General Radio 740-B, modified to be operated with an external generator and detector. The amplifier driving the bridge was a single-ended push-pull amplifier similar to that designed by Petersen (5). This in turn was fed from an audio oscillator built in our laboratory and calibrated against the 60-cycle line frequency by the Lissajou figure method. The condenser to be tested was thus operated with a ripple voltage of about 3 v RMS. When the condenser is thus operated at 60 cps the bridge measurements check the wattmeter measurements of Fig. 3. For all frequencies other than 60 cps the bridge measurements were used exclusively, because operation as shown in Fig. 3 was not feasible at the higher frequencies.

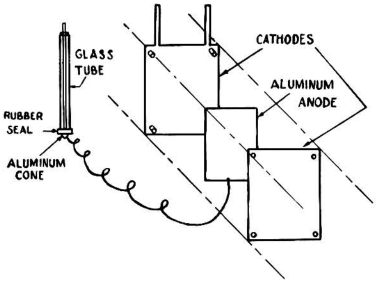

FIG. 1. Construction of typical condenser

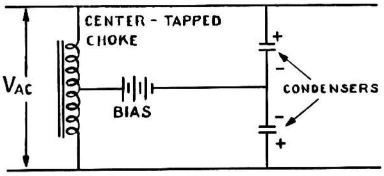

FIG. 2. Test circuit

OBSERVATIONS AS FUNCTION OF FREQUENCY

A typical set of measurements is shown in the plot of Fig. 4. In every case, the bridge unbalance was less than 0.7 per cent residual harmonics. Most of the harmonics were undoubtedly caused by amplifier mismatch, particularly at the higher frequencies. Therefore, we may consider the loss due to dielectric hysteresis as negligible and thus the electrolytic condenser may be represented as a combination of linear circuit elements.[4] These conclusions are corroborated by observations of a different kind presented below.

Electrolyte Resistance Independent of Frequency

The equivalent series resistance and capacity of a typical electrolytic condenser were measured as functions of frequency. The results are shown in Fig. 5. The effective series resistance is seen to be asymptotic to a value R_e (resistance of the electrolyte) at high frequencies. To determine the nature of R_e two tests were made. First, a geometrical substitute of the electrolytic condenser cell was made, in which the filmed aluminum anode was replaced by a geometrically identical silver foil. When this cell is operated with the same electrolyte as the condenser, the effective series resistance vs. frequency is observed as seen in Fig. 6. The second set of tests was made on an electrolytic condenser starting in pure boric acid; and then adding sodium borate in stages. After each such addition, the condenser was operated for 24 hours to insure uniform concentration in the electrolyte. The specific resistance of the electrolyte was then determined by

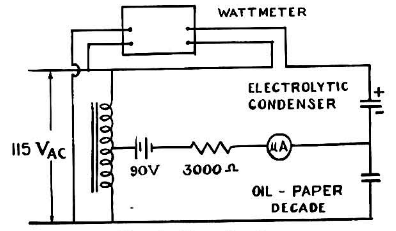

FIG. 3. Test circuit

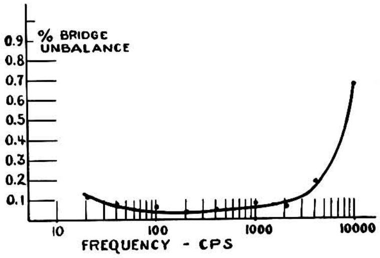

FIG. 4. Per cent bridge unbalance vs. frequency

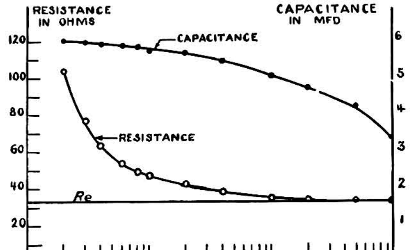

FIG. 5. Measurements on condenser #161

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[4] This statement is to define the relation between voltage and current, in each individual element, as linear.

a bridge measurement between platinum electrodes of a dip cell, while R_e was determined by the high frequency method. When the corresponding sets of these two values are plotted against each other the straight line of Fig. 7 results. Consequently, the value R_e represents within the limits of measurement the effective series component of resistance due to the condenser electrolyte, and as such R_e ought to be independent of frequency. This is confirmed by our observations inasmuch as the straight line of Fig. 7 passes through the origin. Obviously if R_e depended on frequency then the graph would intersect the axis of abscissae at some positive value $R_e - n$. Conversely, inasmuch as the electrolyte resistance is known to be frequency independent, a finite value n would correspond to dielectric losses *in the film*, and the fact that $n = 0$ does not contradict an earlier conclusion that the dielectric loss in the film is negligible.

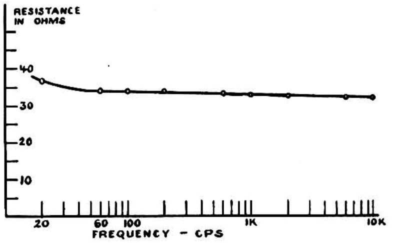

FIG. 6. Resistance of silver duplicate sandwich vs. frequency. Electrolyte resistance vs. frequency-silver anode sandwich copper end plates. Electrolyte tested 43 K in L. & N. conductivity cell.

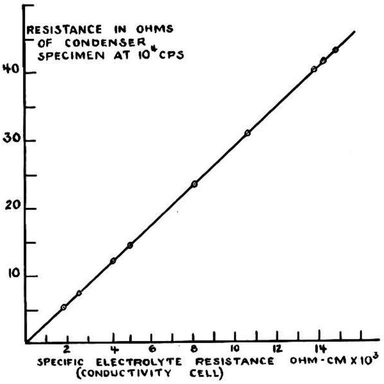

FIG. 7. Resistance of condenser specimen as determined by bridge at 10,000 cps vs. the specific electrolyte resistance as determined by conductivity cell. The function was obtained by varying the concentration of the electrolyte.

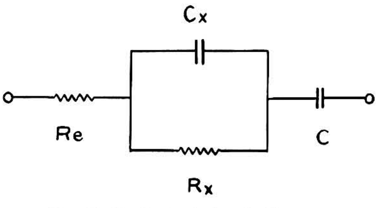

FIG. 8. Equivalent circuit diagram

Equivalent Circuit of Electrolytic Condenser

The preceding observations may be correlated by means of the equivalent circuit of Fig. 8, which will reproduce the electrical characteristic of the electrolytic condenser. It is not the only possible model, but it is the simplest one accounting for the measurements shown in Fig. 5. This may be seen by considering the behavior of the circuit of Fig. 11 at the frequency extremes; as the frequency approaches zero, the current path will be through C, R_e and R_x giving limiting values of C and $R_e + R_x$ as the capacity and resistance values measured on the bridge; and correspondingly, at high frequencies, the current path will be through R_e, C_x, and C, giving respectively R_e and $C_x\ C/C_x + C$ as the limiting values.

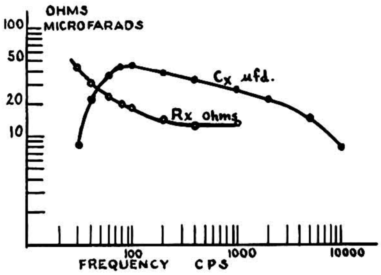

FIG. 9. C_x and R_x vs. frequency for condenser #161

Considering the circuit of Fig. 8 and postponing the consideration of a possible correlation between this circuit and the physical condenser, we can calculate these values from the above presented actual bridge measurements in which the electrolytic condenser as a unit is balanced at various frequencies against a resistance in series with a capacity. From these quantities can be calculated the elements C, C_x, and R_x of Fig. 8. The problem, however, is indeterminate unless one of the elements C, C_x, or R_x is postulated as being independent of frequency. We choose C as such an element.

The resultant value of C_x and R_x for a typical condenser are plotted in Fig. 9. The physical justification of the assumption that C is frequency independent is based on the observation that leakage current and dielectric hysteresis losses are negligible for the entire electrolytic condenser. Thus the physical counterpart of C contains a dielectric free of such losses (compare above), and as such is not likely to be frequency dependent.

Physicochemical Interpretation

Now it is possible to propose a hypothetical picture of the physical counterparts of the elements composing the circuit of Fig. 8. The quantities measured are not due to polarization effects, as such polarization capacities are relatively enormous compared to those due to the anodized film. Thus the film may be thought of as consisting of two strata. The first stratum, best thought of as adjacent to the metal surface, contains a good dielectric relatively free of conductivity and dielectric hysteresis losses. The second stratum consists of a compound with a rather high conductivity and it is best thought of as superimposed on the first stratum. It is referred to hereafter as the "interface stratum."

This picture would be more appealing if it could be shown that the first, good, dielectric stratum grows in proportion to the peak formation voltage, while the second stratum is not determined by that voltage. Conclusive observations to this effect are not available yet except that comparative tests on films formed to 180 v and 360 v make this probable.

OBSERVATIONS AS FUNCTION OF FORMATION VOLTAGE

In this connection, reference can be made to plots like those shown by Deely (6) of formation voltage vs. elastance, which is the reciprocal of capacity, (in Deely's case in.^{2}/mfd vs. formation voltage). Such plots were made with one of our specimen condensers. The formation voltage was varied in steps, and in each step formation was carried to completion. Then the effective capacity was measured at 60 cps with the bridge setup mentioned before. The plot is shown in Fig. 10. With the conventional model of the electrolytic condenser, this plot would consist of a straight line through the origin. However, from both our plot and that of Deely, there is[5] a finite value of capacity at zero voltage, of the order of magnitude of 50 μf. An obvious interpretation is that the film consists of two strata; one, of the first kind, determined by the formation voltage; and the other one, of the second kind, not so determined. The graph of Fig. 10 does not, however, produce any evidence for the hypothetical interface stratum to be part or all of the stratum of the second kind. In order to ascertain this, it has been shown that the interface phenomenon can be produced on a nonanodized surface.

This simple experiment was performed by using one of the specimen condenser cells in which, however, the aluminum foil was neither preformed on d-c nor at any other time positively biased with respect to the electrolyte. In series with this cell was connected a 6 μf paper-oil condenser. Then the usual measurements were taken within the full range of frequencies. The plot of Fig. 11 reproduces measurements which appear typically the same as in Fig. 5. The "interface" capacity at 200 cps in Fig. 11 is 37 μf, while in Fig. 5 it is 40 μf. Thus the hypothetical interface stratum may be regarded as the "stratum of the second kind."[6]

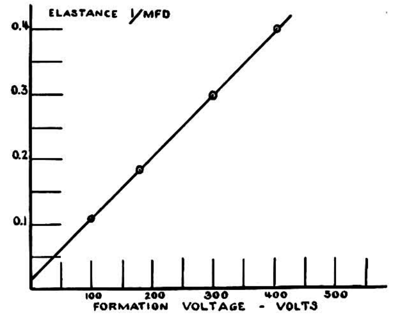

FIG. 10. Inverse microfarads vs. formation voltage

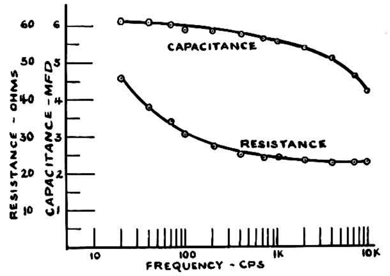

FIG. 11. Impedance of nonformed aluminum anode in series with 6-μf oil condenser.

The latter experiment not only corroborates our interface hypothesis but also, by substituting a paper-oil condenser in place of the dielectric C of the film, it supports the previous assumption that the physical counterpart of C exhibits a capacity substantially independent of frequency.

Experiments of the latter kind are scheduled to be extended more widely over a variety of conditions

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[5] This is estimated by extending the rectilinear part of the plot to its intersection with the $\frac{1}{C}$ axis. A precise determination of the point of intersection presents serious experimental difficulties.

[6] Strictly speaking the question remains open as to whether or not the interface stratum is all or part of the stratum of the "second kind." The answer to this question can, of course, be found by experiment, for instance, by a more elaborate determination of such graphs as Fig. 10.

and we expect that they will contribute substantially to our knowledge of anodized films.

SUMMARY

1. It is concluded, on the basis of experimental observations, that an electrodynamic model of the film is feasible containing a finite number of linear elements.

2. The simplest such model to reproduce the observed frequency dependent characteristic is proposed (Fig. 11) and it is shown that one of the elementary capacities,—the main capacity C—does not depend appreciably on frequency.

3. A correlation is established between the elements of the model and the here-proposed structure of the film: the film to consist of two strata, one of a good dielectric, capacity C; and the other one of a poor dielectric, capacity C_x, in parallel with a relatively small resistance R_x, and with a correspondingly high power loss.

4. It is shown that C_x, R_x are functions of frequency, but are not determined by peak formation voltage. Indeed they may be reproduced on a non-anodized surface, substituting for stratum C a paper-oil condenser.

5. While the above, No. 1 to 4, refer to relations observed with frequency as variable, the conclusions arrived at are corroborated by measurements, at a constant frequency, of the specific capacity of the film while varying the peak formation voltage.

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

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Electrodeposition of Copper from the Monoethanolamine Bath[1]

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ABSTRACT

Copper has been electrodeposited on steel by using a complex copper-monoethanolamine solution. This does not deposit copper on steel by immersion. The deposits are smooth, fine grained, bright, and adherent, and the bath is comparable to the cyanide bath. The inclusion of rochelle salt considerably improves its performance. The optimum conditions are: copper oxalate 60 g/l, monoethanolamine 60 ml/l, rochelle salt 60 g/l, 2.4–4.8 amp/dm^2 (22.3–44.6 amp/ft^2), *p*H 9.5, and 24°C. The addition of nitrates has some beneficial effect.

INTRODUCTION

Some attempts have been made to evolve a substitute for the commercial cyanide bath used in the electrodeposition of copper in view of its poisonous nature, instability, and low current efficiencies. Work has been done on solutions like thiosulfate, iodide, thiocyanate, amine, oxalate, tartrate, sulfammate, pyrophosphate, thiourea, fluoborate.

The electrodeposition of copper from complex solutions containing mono-, di-, and triethanolamines has been studied by Brockman and coworkers (1, 2, 3), Schweig (4), and Levin (5). The present investigation formed part of the general program on the electrodeposition of metals and alloys from cyanide-free baths. In a previous communication from this laboratory (6), it has been shown that the silver iodide bath gives satisfactory deposits of silver. The electrodeposition of copper and brass from the ethanolamine baths has been briefly reported in preliminary notes by Rama Char and coworkers (7–9). This paper describes in detail the work on the deposition of copper from monoethanolamine solutions. Electrodeposition from di- and triethanolamine baths will be reported in subsequent papers.

THE PLATING BATH

When 1 ml of monoethanolamine was added to 1 g of copper oxalate suspended in water, a clear blue solution was obtained indicating the formation of a complex. The salt:amine ratio remained the same at all concentrations. The concentration of copper oxalate in the bath was in the range 15–120 g/l (6–48 g/l of copper). These solutions are simpler than those attempted before.

EXPERIMENTAL

The monoethanolamine (technical) and copper oxalate were of the British Drug House make. The other chemicals were made by British Drug House or Merck. The amine had a specific gravity of 1.019 at 24°C. It had a strong smell of ammonia and its *p*H was 13.75. It distilled off completely at 170°C.

The cathodes were cut from a mild steel sheet of $\frac{1}{32}$ in. (0.08 cm) thickness. Each cathode was 1 in. x 3 in. (2.5 cm x 7.5 cm) and submerged to a depth of 2 in. (5 cm) in the bath, the submerged electrode surface area being 4 in.^{2} (25 cm^2). Two Canning's rolled copper anodes of the same dimensions as the cathode were used, at a distance of 0.75 in. (1.9 cm) on either side of the cathode.

Rust, scale, and other oxides were best removed by pickling the cathodes in hot (60°C) dilute hydrochloric acid (1:1). The cathodes were dried after cleaning with water, and then rubbed with smooth emery. They were further cleaned by cathodic treatment for about 1 min in a hot alkaline bath containing: trisodium phosphate 100 g/l, sodium carbonate 80 g/l, and sodium hydroxide 20 g/l, at 6 amp/dm^2 and 6–8 volts. The cathodes were finally rinsed in water and alcohol, dried, and kept in a desiccator for use.

The experiments were carried out in 100 ml beakers. The plating time was 2.5 min and the temperature 24°C. The rest of the experimental procedure was the same as described before (6).

EXPERIMENTAL RESULTS

Copper Ion Concentration

The copper (cupric) ion concentration in the plating solutions was determined by the emf method

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[1] Manuscript received April 10, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952. This paper is based on part of the thesis submitted by N. B. Shivaraman for the Associateship of the Indian Institute of Science in partial fulfillment of the requirements for the Diploma of the Indian Institute of Science in Chemical Engineering.

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and was of the order of 10^{-11} to $10^{-13}N$. The addition of 60 g/l rochelle salt decreased the metal ion concentration of the bath 60 g/l copper oxalate, 60 ml/l amine from 1.90×10^{-11} to $3.16 \times 10^{-13}N$, indicating that further complexes are formed. In the cuprocyanide bath the cuprous ion concentration is of the order of $10^{-30}N$. The ethanolamine solutions did not deposit copper on steel by chemical displacement due to the low metal ion concentration.

TABLE I

*p*H: 9.15–9.20

Copper oxalate g/l	Amine ml/l	C.D. amp/dm²	Bath tension volts	Cathode efficiency %	Appearance of electrodeposit
15	15	0.4	2.5	96	Bright
		0.6	3.8	93	Bright
30	30	0.8	8.1	96	Nonuniform
		1.2	5.2	100	Fairly bright
		1.6	6.7	93	Bright
		2.0	9.6	93	Partly burnt
45	45	0.8	2.5	90	Nonuniform and dull
		1.6	5.3	93	Dull
		2.0	7.5	94	Fairly bright
		2.4	8.4	98	Partly burnt
60	60	2.4	4.3	90	Dull
		3.2	5.5	95	Fairly bright
		4.0	6.9	91	Bright
		4.8	9.2	90	Bright
75	75	2.4	4.5	95	Dull
		3.2	5.2	93	Fairly bright
		4.0	8.5	91	Bright
		4.8	10.2	90	Bright
90	90	2.4	4.0	90	Dull
		3.2	4.8	98	Dull
		4.0	5.7	100	Fairly bright
		4.8	6.7	94	Fairly bright
		5.6	9.0	93	Bright
		7.2	10.0	90	Burnt
120	120	4.8	5.2	86	Dull
		6.4	7.2	90	Fairly bright
		8.0	10.0	90	Bright

Electrodeposition

Variation of concentration.—Electroplating was carried out over a wide range of concentration and current density and the results obtained are given in Table I.

The cathode efficiency ranged from 86 to 100 per cent and was 90 per cent and above in the bright C.D. range. The plating range for good deposits was from 0.4–8.0 amp/dm². Increase in the concentration of metal (complex) increased the limiting C.D. for bright deposits. But, at concentrations above 90 g/l of copper oxalate the bath tended to crystallize out and the anode corrosion was not good at high C.D. In view of the dragout losses and the fact that a decrease in the metal ion concentration causes finer grained deposits, it was not advisable to raise the copper concentration above 24 g/l. The optimum concentration was that of the bath containing copper oxalate 60 g/l and amine 60 ml/l (60:60). The bath voltage, ranging from 2.5–10.2 volts, was rather high as compared with the cyanide bath. The deposits were treed at high C.D. The adherence of the electrodeposits to the base metal, as found from bending and breaking tests, was good. Addition of 10, 30, and 60 ml/l of excess amine to the optimum concentration bath did not improve the quality of the deposit.

Rochelle salt bath.—It was found that the addition of rochelle salt as one of the constituents of the bath considerably improved its performance. Rochelle salt facilitated anode corrosion by preventing blackening of the anodes at high C.D.; reduced the bath voltage and minimized the fluctuations in voltage and current; increased the C.D. range, conductivity, cathode polarization, and throwing power; and yielded better quality deposits by eliminating treeing and increasing the brightness. It also reduced the copper ion concentration. Table II gives the results with the rochelle salt bath.

Even at high concentrations, copper oxalate 120 g/l, amine 120 ml/l, rochelle salt 120 g/l (120:120:120), the bath did not crystallize out at room temperature. The optimum concentration was 60:60:60. The deposits were brighter than those obtained from the rochelle salt-cyanide bath. There was no change in the bath performance on allowing the bath to age for a period of 4 months. It was possible to go up to 10.0 amp/dm².

Temperature.—Higher temperatures were not conducive to the good working of the bath with and without rochelle salt.

Addition agents.—In order to see whether the rochelle salt-amine bath could be further improved, some inorganic salts were added to the optimum concentration bath 60:60:60. Ammonium, potassium, and sodium nitrates (5 g/l) increased the brightness of the deposits and raised the limiting C.D. from 4.8 to 6.0 amp/dm² but considerably decreased the cathode efficiency to 58–80 per cent (2.4–6.0 amp/dm²). Ammonia (5–40 ml/l) eliminated the brittleness of the deposits but the bright C.D. range decreased and the anodes tended to blacken. Ammonium sulfate, chloride, and carbonate (5–15 g/l) decreased the C.D. range. The deposits were unsatisfactory with ammonium carbonate. Sodium chloride (5–15 g/l) decreased the C.D. range considerably and the anode corrosion was poor at higher C.D.

Conductivity, cathode polarization, and throwing power.—Table III gives the conductivity, cathode polarization (range), and throwing power of the bath, with and without additions. The polarization values give a general idea of the variations but should not be considered as very accurate in view of the difficulties in reproducibility. The throwing power of the bath was fairly good. Satisfactory deposits were obtained on the reverse side of the cathode when only one anode was used and the plating solution threw well into the recesses of irregularly shaped cathodes. The values given below were calculated according to the equation of Schlotter-Korpiun (10).

An increase in the metal concentration increased the conductivity and decreased the polarization and throwing power. Excess of amine decreased the polarization. Rochelle salt increased the conductivity, cathode polarization, and throwing power. Addition of nitrates had little effect on the conductivity but in some cases slightly increased the polarization and throwing power at higher C.D. The cathode polarization at which burning occurred was of the order of 0.9 volt.

TABLE II

pH: 9.4–9.7

Copper oxalate g/l	Amine ml/l	Rochelle salt g/l	C.D. amp/dm^2	Bath tension volts	Cathode efficiency %	Appearance of electrodeposit
30	30	30	0.8	2.2	100	Dull
			1.2	2.7	97	Bright
			1.6	3.4	90	Bright
			2.0	4.1	88	Bright
30	30	60	0.8	1.8	96	Dull
			1.2	2.6	97	Bright
			1.6	2.6	92	Edges rough
60	60	30	2.4	3.2	96	Dull
			3.2	4.0	93	Bright
			4.0	4.6	90	Bright
			4.8	5.0	88	Bright
60	60	60	1.6	2.2	94	Dull
			2.4	2.9	94	Brighter
			3.2	3.6	92	Brighter
			4.0	3.9	90	Brighter
			4.8	4.3	90	Brighter
			5.6	4.6	87	Burnt
60	60	120	1.6	2.2	92	Bright
			2.0	2.4	91	Brighter
			3.2	3.0	90	Brighter
			4.0	3.6	90	Edges burnt
			4.8	4.0	87	Burnt
90	90	90	1.6	1.9	90	Dull
			3.2	3.0	96	Bright
			4.0	3.6	100	Brighter
			7.2	4.4	86	Brighter
			8.0	4.9	94	Bright
			10.0	6.5	90	Burnt
90	90	180	1.6	1.6	95	Dull
			2.4	2.4	93	Brighter
			3.2	2.6	90	Brighter
			4.0	2.9	90	Brighter
			6.0	3.8	89	Bright
120	120	120	2.0	2.2	60	Dull
			3.2	2.8	83	Bright
			4.0	3.2	90	Bright
			5.6	4.0	91	Bright
			7.2	4.4	100	Bright
			8.0	4.8	100	Bright
			8.8	5.0	95	Bright
			10.0	5.3	92	Bright

TABLE III

pH: 9.15–9.50

Copper oxalate g/l	Amine ml/l	Rochelle salt g/l	Addition agents g/l	Sp. conductivity mhos/cm^3	Cathode polarization range volts (C.D. 1.6–4.0 amp/dm^2)	Throwing power at 3.2×10^{-2} amp/cm^2
30	30	—	—	0.0090	—	—
60	60	—	—	0.0141	0.38–0.72	1.28
60	120	—	—	—	0.26–0.60	—
90	90	—	—	0.0183	0.20–0.36	1.17
60	60	30	—	0.0299	—	—
60	60	45	—	0.0347	(C. D. 1.6–4.8 amp/dm^2)	
60	60	60	—	0.0398	0.71–0.82	2.01
60	60	75	—	0.0430	—	—
60	60	60	KNO$_3$ 5	0.0394	0.26 –0.89	2.03
60	60	60	NH$_4$NO$_3$ 5	0.0417	0.49–0.98	2.11
60	60	60	NaNO$_3$ 5	0.0392	0.39–0.83	1.95

TABLE IV

Composition	*Ethanolamine* Copper oxalate, 60 g/l Mono amine, 60 ml/l Rochelle salt, 60 g/l	*Cyanide* Copper cyanide, 40 g/l Sodium cyanide, 50 g/l Sodium carbonate, 30 g/l Rochelle salt, 60 g/l
pH..........	9.5	11.4
Temp, °C....	24.0	60.0
(Cu) g/l......	24.0	28.4
(Copper ion) g ion/l...........	3.16×10^{-13} (Cu^{++})	2.29×10^{-20} (Cu^{+})
Sp. conductivity, mhos/cm^3......	0.0398	0.0987
Bright C. D. range amp/dm^2............	2.4–4.8	2.0–2.5
Cathode polarization, volts (0.8–5.6 amp/dm^2)...........	0.24–0.82	0.65–1.11
Bath voltage volts	2.9–4.3	0.9–4.0
Cathode efficiency, %	90–94	70–76
Throwing power.	Fairly good	Good
Quality of deposit	Brighter	Bright

The throwing power was less than that of the cyanide bath where it is of the order of 4. In the amine bath, it can be improved to a value of 3 under certain conditions. It was also calculated from the equation of Gardam (11) by substituting, as an approximation, the interelectrode distance for l_2 in the equation. At a C.D. of 2.0×10^{-2} amp/cm^2

(where the cathode polarization—log C.D. relationship was roughly linear) the throwing power for the ethanolamine bath with and without additions was in the range 7–30 per cent, as against the normal value of 30–40 per cent for the cyanide bath.

Comparison between ethanolamine and cyanide baths.—Table IV will give an idea of the relative performance of the rochelle salt-copper oxalate-monoethanolamine and rochelle salt-copper cyanide baths. The values for the cyanide bath were experimentally determined under the conditions recommended by Bakhvalov (12).

The advantages of the amine bath over the cyanide are: (*a*) wider C.D. range; (*b*) higher cathode efficiency; (*c*) brighter deposits; (*d*) ability for good working at the room temperature; (*e*) satisfactory performance without the use of special additions; and (*f*) stability. On the other hand, the cyanide bath has a higher conductivity and cathode polarization, and superior throwing power.

The rate of deposition of copper from the rochelle salt-amine bath was compared with that from the "low concentration" cyanide bath (13) and "high efficiency" cyanide bath without brightener (14), at a C.D. of 2.4 amp/dm^2. It was in between the rates for the cyanide baths.

DISCUSSION

The electrodeposition of copper from the complex monoethanolamine bath yields smooth, fine-grained, and bright deposits on steel. There is no immersion deposition due to the low copper ion concentration. The high cathode efficiency, which is very near 100 per cent, is a definite advantage. Brockman and Tebeau (3) used the plating composition: copper sulfate, sodium oxalate, and monoethanolamine at cathode efficiencies from 93–111 per cent and concluded that, so far as the throwing power is concerned, the monoethanolamine bath is the least suitable of the ethanolamine baths (mono-, di-, and tri-) for copper plating. In the present work the throwing power of the monoethanolamine bath has been found to be fairly good and of the same order as that of the di- and triethanolamine baths (15).

The inclusion of rochelle salt in the amine bath improves its performance to a great extent and the beneficial effects are on the lines observed in the rochelle salt-copper cyanide bath (13). The action of this salt is probably due to its reducing nature and tendency to form further complexes. A decrease in the metal ion concentration on addition of rochelle salt is accompanied by the formation of brighter deposits. The addition of nitrates to the rochelle salt-amine bath increases the brightness and the C.D. range but reduces the cathode efficiency. This can be attributed to the inhibiting action of the nitrate ion (16, 17). It is preferentially reduced to ammonia before the hydrogen ion, preventing the formation of spongy deposits and enabling higher C.D. to be used. The effect of the addition of other ions is of a specific character. Small variations in *p*H are not of much significance.

Complex salt plating baths generally give fine-grained and bright deposits due to the low metal ion concentration. The cathode polarization and throwing power in such solutions is high. In the ethanolamine bath the copper ion concentration is low and fine-grained; bright deposits are obtained. The cathode polarization is high. But the conductivity is lower, the cathode efficiency higher, and the throwing power less than that of the cyanide bath. The polarization is increased by the addition of rochelle salt and by some nitrates (to a little extent) which act as brighteners. It is likely that cathode polarization has some significance in the electrodeposition of copper from the ethanolamine baths.

SUMMARY

1. The copper oxalate-monoethanolamine-rochelle salt bath gives smooth, fine-grained, and bright electrodeposits of copper directly on steel. The optimum conditions are: copper oxalate 60 g/l, monoethanolamine 60 ml/l, rochelle salt 60 g/l, C.D. 2.4–4.8 amp/dm^2, *p*H 9.5, and temp 24°C.
2. The beneficial effects of rochelle salt are of the same nature as in the rochelle salt-copper cyanide bath.
3. The advantages of the amine bath over the cyanide are: (*a*) higher cathode efficiency, (*b*) brighter deposits, (*c*) comparative stability, (*d*) nonpoisonous nature.
4. The bath is not suitable for plating at higher temperatures. Its conductivity and throwing power are lower than that of the cyanide bath. The bright C.D. range is of the same order.
5. The addition of nitrates increases the brightness and the limiting C.D. but reduces the cathode efficiency for deposition.

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

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Electrodeposition of Cadmium from Fluoborate Solutions[1]

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ABSTRACT

The optimum conditions for electroplating cadmium from its fluoborate solution have been arrived at by a systematic study of the effects of all types of variables on its plating characteristics. The best deposits of cadmium are obtained from a bath containing 210 g/l of cadium fluoborate, 25 g/l of sodium fluoborate, 25 g/l of boric acid, and 1 g/l of sodium-beta-naphthalene sulfonate at a *p*H of 3.2–3.6 and temperatures of 20°–30°C, and at current densities of 2.2–6.5 amp/dm^2 (20–60 amp/ft^2). The deposits which are obtained on steel, brass, or copper are uniform, bright, fine grained, adherent, and of pleasing appearance. The current efficiency of the process is 98–100 per cent cathodic and 102–104 per cent anodic. The bath is nonpoisonous, stable, and easily controlled. The new bath is slightly inferior to the cadmium cyanide bath in the throwing power and resistivity, but vastly superior in all other respects.

INTRODUCTION

In commercial electroplating practice, cadmium is almost invariably plated from a complex cyanide bath containing sodium cadmicyanide, sodium cyanide, sodium hydroxide, and some inorganic addition agents (1). This bath has proved satisfactory from many points of view, but it is not a very efficient plating medium. Its current efficiency is only 85–90 per cent and its plating range is only 1.6–3.2 amp/dm^2 (15–30 amp/ft^2). The control of the bath is not easy as the anode produces a cadmium sludge at very low current densities, and behaves as an oxygen electrode at current densities of more than 2.2 amp/dm^2 (20 amp/ft^2). The deposits obtained from this bath become brittle on certain occasions and have to be heated to a high temperature before use (2). The cadmium fluoborate solution has two definite advantages as a plating medium; it is nonpoisonous and is very stable. If some other advantages like very high current efficiency and wide plating range which are claimed for some fluoborate solutions (3) are also realized, in this case it can replace the cyanide solution in the commercial field.

In the present investigations, the effects of all types of variables on the plating characteristics of the cadmium fluoborate solutions have been studied to deduce the optimum conditions for electroplating cadmium from a fluoborate bath. As far as the authors are aware such a systematic study has not so far been attempted by workers in this field (3, 4).

EXPERIMENTAL PROCEDURE

After preliminary studies on the range of electrolyte concentration and current density giving satisfactory deposits, a detailed study was undertaken of the influence separately of (*a*) electrolyte concentration; (*b*) hydrogen ion concentration; (*c*) temperature; and (*d*) agitation, on the following factors: 1. nature of the deposit (brightness, texture, adherence, distribution, and treeing tendency); 2. anodic and cathodic efficiency; 3. limiting cathodic current density, i.e., the current density where the deposition of the metal practically ceases; 4. resistivity; and 5. throwing power of the solution.

The influence of some inorganic salts and a number of selected addition agents on the plating characteristics of the solution was studied before arriving at the best conditions for plating the metal.

Experimental Details

The plating experiments were conducted on a small scale in 200 ml beakers placed in a thermostat. Anodes of uniform size 7.62 cm x 1.27 cm x 0.32 cm (3 in. x ½ in. x ⅛ in.) were employed together with standard rectifiers, rheostats, ammeters, voltmeters, etc., which generally make up a plating circuit. Special wooden stands were made to suspend the electrodes freely and immerse them in the plating solutions to any desired mark. The immersed anode area was equal to the immersed cathode area and the interelectrode distance was exactly 2.54 cm (1.0 in.) in all the experiments.

Plating Solutions

Cadmium fluoborate solutions of varying concentrations were prepared by the method utilized for lead fluoborate solutions by Blum and collaborators

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[1] Manuscript received April 10, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952. Part of a dissertation submitted by T. R. Anantharaman and accepted for the award of the degree of Master of Science by the University of Madras.

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(5). A stock solution of fluoboric acid (approx. 5*N*) was prepared from powdered boric acid and concentrated hydrofluoric acid (48–50%). The fluoborate solutions were made up whenever required by saturating this acid with cadmium carbonate powder, filtering through glass wool and diluting the filtrate to the desired extent. Analytical reagents were employed to ensure the highest purity in the plating solutions. The cadmium content of the solutions was determined whenever necessary by the electrolytic method with the aid of the Fisher electroanalyzer.

Electrodes

The anodes were rolled cadmium specimens of very high purity and required no preparation before plating, save washing in water, rinsing, wiping, and drying.

Cathodes of brass, copper, and steel were used in the preliminary investigations. It was found that equally good deposits are obtained on any of the cathodes with suitable preliminary treatments. Brass cathodes were thereafter used, as they could be polished comparatively easily and stored for a long time without becoming tarnished.

The brass cathodes were prepared for the plating experiments as follows: (*a*) polishing up to 00 grade emery papers; (*b*) an "alkaline dip" for 30 sec in a hot solution (6) containing 15 g/l of sodium hydroxide and 60 g/l of sodium carbonate; (*c*) a wash with distilled water; (*d*) a "brightening dip" for 10 sec in an acid solution containing 435 g/l of sulfuric acid, 72 g/l of nitric acid, and 2 g/l of hydrochloric acid; and (*e*) a final wash with distilled water.

Hydrogen Ion Concentration

A *p*H meter could not be used in these studies as the fluoborate solutions attack the delicate glass electrode used in the meter. The *p*H of the plating solutions had to be measured roughly with the aid of suitable indicators and British Drug House narrow range test papers, and a Lovibond comparator. The Universal Indicator was first used to get a rough idea of the *p*H within the range 3.0 to 11.0. The *p*H of the solution was then adjusted to any value required within the range 3.0 to 6.6 with an accuracy of ±0.2 with the aid of bromophenol blue (*p*H range 3.0 to 4.6) and methyl red (*p*H range 4.4 to 6.6) and using fluoboric acid or ammonia.

Temperature and Agitation

The temperature of the plating solutions was controlled to ±1°C with the aid of an immersion thermostat. Agitation was secured by means of a variable speed electric motor rotating a glass stirrer immersed in the plating solution, at speeds up to 200 rpm. The effects of agitation were studied in detail at speeds of 100 and 200 rpm—the two types of agitation being designated "mild" and "vigorous," respectively.

Current Efficiency

The anodic and cathodic current efficiencies were determined by carefully weighing the anodes and cathodes before and after the passage of definite known currents for exactly 30 minutes. It was possible to calculate the current efficiencies fairly accurately from the ammeter reading as the current was fairly steady throughout the period of deposition. To ensure a greater degree of accuracy, however, a copper coulometer was also utilized in all the experiments.

Limiting Current Density

The limiting cathodic current density, i.e., the cathodic current density at which the deposition of the metal practically ceases, was measured by following the changes in cathodic potential with increasing current density, plotting them on a graph, and noting down the current density where the curve undergoes a sudden change. This stage was always marked by copious evolution of hydrogen at the cathode and a considerable blackening of the deposit. The cathode potential was measured at various current densities with a calomel half cell and a Tinsley General utility potentiometer.

Resistivity and Throwing Power

As the current density–cathodic potential relation was linear and as the current efficiency was very high in the cadmium fluoborate solutions, the following equation due to Gardam (7) was employed to calculate the throwing power:

$$T\% = \frac{1}{1 + \frac{2l_2}{N_1}} \times 100$$

where T is throwing power expressed as a fraction; l_2 is the interelectrode distance in cm and N_1 the throwing number $= m/\rho$, where $m =$ the slope of the current density–cathode potential curve expressed in volts per amp/cm^2 and $\rho =$ the resistivity of the plating solution in ohms/cm^3.

The cathode potential–current density curves were not strictly reproducible in these investigations, but they were made as representative as possible by taking into account a number of sets of readings (at least three) for a particular solution, using different electrodes of the same type and shape but keeping the interelectrode distance constant. The Kohlrausch method was employed to measure resistivity of the plating solutions.

It should be mentioned in passing that even very low values of throwing power (e.g., 2.5%) obtained by the Gardam equation indicate reasonably good throwing power in practice.

TABLE I. *Influence of electrolyte concentration on the plating characteristics of cadmium fluoborate solutions*

(Temp: 27°C; *p*H: 3.2–3.4; other conditions as in the paper)

Concentration		Current effy. % at 3.2 amp/dm² (30 amp/ft²)		Limiting current density (cathodic)		Resistivity ohm/cm³	Throwing power %
Normality	g/l	Anodic	Cathodic	amp/dm²	amp/ft²		
4*N*	572	104.9	97.7	14.7	136	5.2	4.3
3*N*	429	104.1	98.1	12.2	113	5.7	4.6
2*N*	286	105.0	98.9	10.0	93	7.1	4.8
N	143	103.9	98.3	6.5	60	12.2	4.4

TABLE II. *Influence of pH on the plating characteristics of cadmium fluoborate solutions*

(Temp: 27°C; concentration of the electrolyte: 1*N* (i.e., 143 g/l of cadmium fluoborate)

*p*H range	Current efficiency (% at 3.24 amp/dm²) 30 amp/ft²		Limiting cathodic current density		Resistivity ohm/dm³	Throwing power %
	Anodic	Cathodic	amp/dm²	amp/ft²		
3.4–3.6	104.2	99.1	6.5	60	12.2	3.8
4.0–4.2	103.6	99.7	6.8	63	12.2	3.6
4.6–4.8	103.8	100.1	7.2	66	12.2	3.4
5.2–5.4	104.1	99.9	7.6	70	12.2	2.8

TABLE III. *Influence of temperature on the plating characteristics of cadmium fluoborate bath*

(*p*H: 3.2–3.4; concentration of solution: 1*N*, i.e., 143 g/l; other conditions as before)

Temp °C	Current efficiency (% at 3.24 amp/dm²) 30 amp/ft²		Limiting cathodic current density		Resistivity ohm/dm²	Throwing power %
	Anodic	Cathodic	amp/dm²	amp/ft²		
30	104.2	99.2	6.7	62	12.2	3.0
50	104.4	98.9	7.2	67	9.2	2.8
70	104.7	96.1	8.2	76	7.3	2.0

TABLE IV. *Influence of agitation on the plating characteristics of cadmium fluoborate bath*

(Temp: 30°C; *p*H: 3.2–3.4; concentration of electrolyte: 1*N*, i.e., 143 g/l; other conditions as before)

Condition	Current efficiency (% at 3.24 amp/dm²) 30 amp/ft²		Limiting cathodic current density		Resistivity ohm/cm³	Throwing power %
	Anodic	Cathodic	amp/dm²	amp/ft²		
Still	104.2	99.2	6.7	62	12.2	3.0
Mildly agitated	106.4	98.0	7.7	72	12.2	1.6
Vigorously agitated	106.7	98.0	12.7	118	12.2	1.1

Experimental Results

The more important results obtained in these investigations are given in the Tables I to VI.

Summary of Results

(*a*) *The quality of the deposit.*—Highly satisfactory white cadmium deposits can be obtained on steel, brass, or copper from cadmium fluoborate solutions under a wide range of plating conditions. A *p*H of more than 4.0 makes the deposit dull and grayish, while an increase in temperature or agitation makes it coarser. The addition of 1.0 g/l of sodium beta naphthalene sulfonate or 1.0 ml/l of methyl ethyl ketone improves the brightness and texture of the deposit considerably.

(*b*) *Current efficiency.*—Under practically all conditions, the cathodic current efficiency of the cadmium fluoborate solutions is 95–100 per cent and the anodic current efficiency is 100–105 per cent.

TABLE V. *Influence of some inorganic salts on the performance of a cadmium fluoborate bath*

No marked influence on current efficiency

(Temp: 30°C; *p*H: 3.2–3.4; concentration of electrolyte: 1*N*; other conditions as before)

Salt added	Amount g/l	Limiting cathodic current density		Resistivity ohm/cm³	Throwing power %
		amp/dm²	amp/ft²		
None	—	6.7	62	12.2	3.2
NH_4BF_4	20	5.0	46	10.3	3.5
NH_4BF_4	40	4.9	45	9.8	3.6
$NaBF_4$	20	5.4	50	11.0	3.4
$NaBF_4$	40	5.2	48	10.5	3.9
CdF_2	20	7.1	66	11.3	3.4
CdF_2	40	7.7	71	10.8	3.5
NaF	20	5.2	48	11.7	3.4
NH_4F	20	4.5	42	11.6	3.2

These values are altered but little by the changes in concentration, *p*H, temperature, etc.

(*c*) *Throwing power.*—The calculated values for throwing power are not satisfactory in cadmium fluoborate solutions, but the throwing power is reasonably satisfactory in practice. It reaches a maximum value, according to calculations at a concentration of 1.5*N* (i.e., 210 g/l of cadmium fluoborate). It decreases in value with increase in *p*H, temperature, and agitation. Additions of up to 40 g/l of sodium or ammonium fluoborate generally improve the throwing power.

(*d*) *Limiting cathodic current density.*—This is fairly high in cadmium fluoborate solutions. It increases phenomenally with increase in concentration, temperature, and agitation, and very slightly with increase in *p*H. At a concentration of 1.5*N* and at a temperature of about 30°C, the value is about 8.2 amp/dm² (75 amp/ft²).

TABLE VI. *Influence of addition agents on the cadmium fluoborate bath; physical characteristics of deposits*

(Temp: 27°C; *p*H: 3.4–3.6; concentration of electrolyte: 1*N*, i.e., 143 g/l; current density: 3.2 amp/dm² (30 amp/ft²); other conditions as before)

(A: Marked improvement; B: slight improvement; C: no improvement; D: slight deterioration; E: marked deterioration)

Addition agent	Amount added	Effect on			
		Brightness	Texture	Adherence	Distribution
Gelatin	0.2 g/l	B	D	D	D
	0.5 g/l	B	D	D	C
Dextrine	0.5–2.0 g/l	C	B	C	C
Ammonium alum	0.5 g/l	C	C	C	D
	2.0 g/l	B	C	C	D
Citric acid	0.2 g/l	C	C	D	C
	0.5 g/l	C	C	D	E
Thiourea	0.5 g/l	B	B	C	C
	2.0 g/l	B	B	C	D
Beta naphthol	0.5 g/l	B	B	C	C
	1.0 g/l	D	B	C	C
Sodium beta naphthalene sulfonate	1.0 g/l	A	B	C	B
	2.0 g/l	A	B	C	D
Glycerine	0.5 ml/l	B	B	C	C
	1.0 ml/l	B	C	D	C

(*e*) *Control and maintenance.*—Cadmium fluoborate solutions can be maintained and controlled very easily as there are no complications like anode sludge formation, anode passivity, etc., during electrodeposition. Composition changes occur only very slowly in these solutions as the anodic efficiency of the process is a little more than the cathodic efficiency and this makes up for dragout losses. These solutions can be used conveniently for barrel plating at higher current densities.

OPTIMUM PLATING CONDITIONS

From the above results, it is possible to arrive at the following composition and plating conditions for obtaining excellent deposits.

Bath composition (*p*H: 3.2 to 3.6)	g/l	Operating conditions
Cadmium fluoborate	210	Temperature: 20°–30°C
(Cadmium content)	84	Cathodic current density: 2.2–6.5 amp/dm² (20–60 amp/ft²)
Sodium fluoborate	25	
Boric acid	25	
Sodium beta naphthalene sulfonate	1.0	Anode area = cathode area Anodic current effy. = 102–104% Cathodic current effy. = 98 – 100%

Anode: rolled cadmium; cathode: steel, brass or copper.

TABLE VII. *Comparison between the cyanide and the fluoborate baths for cadmium plating*

Particulars	Fluoborate bath		Cyanide bath	
Composition g/l	$Cd(BF_4)_2$ $NaBF_4$ H_3BO_3 HBF_4	210 25 25 Slight excess	CdO NaCN	40 130
Metal content g/l	84		35	
Metal content geq/l	1.5		0.6	
*p*H	3.2–3.6		Not specified	
Resistivity (ohms/cm³)	About 9.0		About 6.0	
Plating range (amp/dm²)	2.2–6.5		2.2–4.3	
Still plating (amp/ft²)	20–60		20–40	
Max. cathodic current density				
amp/dm²	About 8.1		About 5.4	
amp/ft²	About 75		About 50	
Max. anodic current density				
amp/dm²	More than 8.1		About 2.2	
amp/ft²	More than 75		About 20	
Cathodic current efficiency	98–100%		85–95%	
Anodic current efficiency	100–104%		95–100%	
Throwing power	5–6% (calculated)		20–30% (measured)	
Stability of the bath	Good		Poor	
Nature of the bath	Nonpoisonous		Poisonous	
Deposit				
brightness	Good		Good	
texture	Fine		Very fine	
adherence	Very good		Good	
distribution	Satisfactory		Very good	
Control and maintenance	Easy		Difficult	

COMPARISON WITH THE CYANIDE BATH

A study of the salient features of the newly developed cadmium fluoborate bath and the standard cyanide given in Table VII shows that the former is superior to the latter in the following respects: (*a*) plating range; (*b*) cathodic current efficiency; (*c*) rate of deposition; (*d*) general finish of the deposit; (*e*) stability; (*f*) nonpoisonous nature; and (*g*) ease of control and maintenance.

The fluoborate bath is inferior to the cyanide bath in the throwing power and resistivity. The difference in throwing power is not, however, so marked as the values denote because the value for the fluoborate bath is calculated unlike in the other case.

Considering all aspects the fluoborate bath appears to be more efficient than the cyanide bath for deposition of cadmium.

ACKNOWLEDGMENTS

The authors wish to thank the Head of the Department of Metallurgy and Dr. E. G. Ramachandran, Assistant Professor of Metallurgy, for their interest and encouragement in the course of the investigations.

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

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Electrogalvanizing from Fluoborate Solutions[1]

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ABSTRACT

The optimum conditions for electroplating zinc from its fluoborate solution have been deduced by a systematic study of the effects of all types of variables on its plating characteristics. The best deposits of zinc are obtained from a bath containing 180 g/l of zinc fluoborate, 30 g/l of ammonium fluoborate, 25 g/l of boric acid, and 1.0 g/l of beta naphthol at a pH of 5.0 to 5.4 and temperatures of 20°–30°C, and at current densities of 4.3 to 9.7 amp/dm^2 (40 to 90 amp/ft^2). The deposits which are obtained on steel, brass, or copper are uniform, fine grained, adherent, and of pleasing appearance. The current efficiency of the process approximates 98 to 100 per cent cathodic and 102 to 105 per cent anodic. The bath is nonpoisonous, stable, and easily controlled. The new bath is comparable to the zinc cyanide bath, and is vastly superior to the zinc sulfate bath.

INTRODUCTION

The only solutions used for commercial zinc plating are the acid sulfate solution and the alkaline cyanide solution. Satisfactory deposits can be obtained from either of these solutions, but the latter is preferred by platers for its excellent throwing power and wide plating range. From the commercial standpoint both solutions are highly efficient and it is difficult to imagine a better substitute for them. Previous work on zinc fluoborates has shown, however, that a fluoborate solution may have advantages of both solutions, i.e., it will be stable and nonpoisonous like the sulfate bath and will also have the good throwing power and plating range of the cyanide bath. The investigations were made to determine optimum conditions for electroplating zinc from its fluoborate solution and compare the best fluoborate bath with baths in vogue for electrogalvanizing.

EXPERIMENTAL PROCEDURE

The procedure adopted by the authors in their investigations of the cadmium fluoborate bath[3] was also followed in the present studies.

Experimental Results

Experimental results are given in Tables I to VI on page 238.

SUMMARY OF RESULTS

(*a*) *Quality of deposit.*—The quality of zinc deposits on steel, brass, or copper is of a very high order under a wide range of plating conditions. The addition of 0.5 to 1.0 g/l of beta naphthol leads to a very fine and bright deposit while higher temperatures and agitation make the deposits slightly coarser and rougher.

(*b*) *Current efficiency.*—The current efficiency of the zinc fluoborate solution is very satisfactory over a wide range of plating conditions. The cathode efficiency is very near 100 per cent and the anodic efficiency usually varies from 100 to 110 per cent. The latter is influenced appreciably by the pH of the solution, an increase in pH bringing the value to nearer 100 per cent.

(*c*) *Throwing power.*—The throwing power is higher than in the case of the corresponding cadmium fluoborate bath, but still not very satisfactory when the calculated values are considered. It reaches a maximum as in the case of cadmium bath at a concentration of 1.5N (i.e., 180 g/l of zinc fluoborate). It decreases slightly with increase in pH, temperature, and agitation. Additions up to 40 g/l of ammonium and sodium fluoborate, especially the former, improve the throwing power.

(*d*) *The limiting cathodic current density.*—The limiting current density is generally quite high in zinc fluoborate solutions. It increases phenomenally with increase in concentration, temperature, and agitation. An increase in pH also increases, although slightly, the limiting current density. At a concentration of 1.5N (i.e., 180 g/l of zinc fluoborate) and at a temperature of 30°C, the limiting current density for a still solution is about 10.3 amp/dm^2 (95 amp/ft^2).

(*e*) *Control and maintenance.*—As in the case of the cadmium fluoborate bath the control and maintenance is very easy. The zinc fluoborate solu-

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[1] Manuscript received April 10, 1952. This paper was prepared for delivery before the Montreal Meeting, October 26 to 30, 1952. Part of the dissertation submitted by T. R. Anantharaman and accepted for the degree of Master of Science by the University of Madras, Madras, India.

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[3] Published elsewhere in this issue.

TABLE I. *Influence of electrolyte concentration on the plating characteristics of zinc fluoborate solutions*

(Temp: 26°C; *p*H: 3.5; other conditions as mentioned in the paper on cadmium fluoborate)

Concentration		Current effy. % at 3.2 amp/dm^2 (30 amp/ft^2)		Limiting cathodic current density		Resistivity ohms/cm^3	Throwing power %
Normality	g/l	Anodic	Cathodic	amp/dm^2	amp/ft^2		
4*N*	480	111.2	97.8	18.8	174	5.859	4.85
3*N*	360	112.5	99.3	15.0	139	6.246	4.90
2*N*	240	110.7	99.5	12.5	116	7.235	5.51
1*N*	120	109.7	99.7	8.50	79	11.060	5.48

TABLE II. *Influence of* pH *on the plating characteristics of zinc fluoborate solutions*

(Temp: 25°C; concentration of electrolyte: 1*N* [120 g/l of zinc fluoborate])

*p*H range	Current efficiency % at 3.2 amp/dm^2 (30 amp/ft^2)		Limiting cathodic current density		Resistivity ohms/cm^3	Throwing power %
	Anodic	Cathodic	amp/dm^2	amp/ft^2		
3.5	109.7	99.3	8.50	79	11.06	4.58
4.5	106.7	99.5	9.80	91	11.06	4.33
5.5	102.3	99.7	12.30	114	11.06	4.01

TABLE III. *Influence of temperature on the plating characteristics of the zinc fluoborate solutions*

(*p*H: 5.0; concentration of electrolyte: 1*N* [120 g/l of zinc fluoborate])

Temp, °C	Current effy. % at 3.2 amp/dm^2 (30 amp/ft^2)		Limiting cathodic C.D.		Resistivity ohms/cm^3	Throwing power %
	Anodic	Cathodic	amp/dm^2	amp/ft^2		
30	103.7	99.8	10.60	98	11.07	5.03
50	103.4	99.2	12.10	112	8.33	5.45
70	104.1	99.0	14.70	136	6.52	5.58

TABLE IV. *Influence of agitation on the plating characteristics of zinc fluoborate solutions*

(Temp: 30°C; *p*H: 5.0; concentration of electrolyte: 1*N*, i.e., 120 g/l of zinc fluoborate)

Condition	Current effy. % at 3.2 amp/dm^2 (30 amp/ft^2)		Limiting cathodic C.D.		Resistivity ohms/cm^3	Throwing power %
	Anodic	Cathodic	amp/dm^2	amp/ft^2		
Still	103.7	99.8	8.5	79	11.07	3.98
Mildly agitated	105.4	99.2	10.5	97	11.07	2.20
Vigorously agitated	105.8	99.0	14.3	123	11.07	1.97

TABLE V. *Influence of some inorganic salts on the performance of a zinc fluoborate bath*

(No marked influence on current efficiency)
(Temp: 30°C; *p*H: 5.0; concentration of electrolyte: 1*N*, i.e., 120 g/l of zinc fluoborate)

Salt added	Amount g/l	Limiting C.D.		Resistivity ohms/cm^3	Throwing power %
		amp/dm^2	amp/ft^2		
None	—	8.4	78	11.07	5.00
NH_4BF_4	20	7.3	68	9.19	7.49
NH_4BF_4	40	6.4	59	8.86	8.47
$NaBF_4$	20	7.2	67	9.88	5.86
$NaBF_4$	40	5.8	54	9.49	6.99
ZnF_2	20	9.3	86	10.21	5.68

TABLE VI. *Influence of addition agents on the physical characteristics of deposits from zinc fluoborate solutions*

(Temp: 27°C; *p*H: 5.0; C.D. (50 amp/ft^2) 5.4 amp/dm^2; concentration of electrolyte: 1*N*, i.e., 120 g/l of zinc fluoborate)

(A—Marked improvement; B—Slight improvement; C—No effect; D—Slight deterioration; E—Marked deterioration)

Addition agent	Amount added	Effect on			
		Brightness	Texture	Adherence	Distribution
Gelatin	0.2 g/l	B	B	D	C
	0.5 g/l	B	B	D	C
	1.0 g/l	E	E	D	C
Dextrine	0.5 g/l	C	B	C	C
	1.0 g/l	D	B	C	C
Ammonium alum	0.5 g/l	B	C	C	C
	1.0 g/l	B	C	C	D
Citric acid	0.2 g/l	C	C	D	D
	0.5 g/l	D	C	D	E
Thiourea	0.5 g/l	B	B	C	C
	2.0 g/l	B	B	C	C
Beta naphthol	0.5 g/l	A	B	C	C
	1.0 g/l	A	B	C	C
Sodium beta naphthalene sulfonate	0.5 g/l	B	B	C	C
	1.0 g/l	B	B	C	C
Glycerine	0.5 ml/l	B	B	C	C
	1.0 ml/l	B	B	C	C
Methyl ethyl ketone	0.5 ml/l	B	B	C	C
	1.0 ml/l	B	C	D	C
Carbon bisulfide	0.01 ml/l	A	B	C	C
	0.02 ml/l	B	B	D	D
	0.03 ml/l	B	B	D	E

tions are ideally suited for barrel plating, at higher current densities.

Optimum conditions and composition

Bath composition:	zinc fluoborate	180 g/l
	(zinc content)	49 g/l
	ammonium fluoborate	30 g/l
	boric acid	25 g/l
	beta naphthol	1.0 g/l
Operating conditions:	*p*H: 5.0 to 5.4	
	Temperature, 20°–30°C	
	Cathodic current density, 4.3–9.7 amp/dm^2 (40–90 amp/ft^2)	
	Anodic current effy., 102–105%	
	Cathodic current effy., 98–100%	
	Anode area is the same as cathode area	
	Anode: pure zinc	
	Cathode: steel, brass, or copper	

ACKNOWLEDGMENT

The authors wish to thank the head of the department of metallurgy and Dr. E. G. Ramachandran, Assistant Professor, for their interest and encouragement in the course of the investigations.

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

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Factors Controlling the Combustion of Zirconium Powders[1]

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ABSTRACT

The activity of zirconium metal powders was studied by measurements of ignition temperature, burning time, and ignition energy on subsieve powders prepared by calcium reduction of ZrO_2 and on coarse powders made by grinding fused zirconium. Particle diameter of 10 microns represents approximately the dividing line between hazardous and nonhazardous powder, using 0.01–0.04 joule spark ignition energy as a criterion. Thermal ignition appears to occur by spontaneous combustion, and a theory was developed which accounts qualitatively for the dependence of ignition temperature on a number of variables. The burning time of Zr powders is related to, but not uniquely determined by, the surface area. Ignition sensitivity of Zr powders was not successfully decreased by alloying with Ti, Ni, Cu, Fe, Co, or H_2. Hazards are discussed briefly, and details of evaluation methods reported.

INTRODUCTION

Zirconium metal has increased greatly in technological importance during the past decade, and a large body of literature has consequently evolved which describes its preparation, properties, and applications. The largest proportion of scientific effort has been devoted to the metal in its massive form. The preparation of pure crystal bar by the deBoer method (1), as first represented commercially by installations at the Foote Mineral Company, and of high purity sponge by the Kroll method, as practiced by the U. S. Bureau of Mines (2), are the major developments in this field. The principal properties of pure massive zirconium which have accelerated this development are its resistance to corrosion in various media (3), its ductility (4), and its low neutron-capturing tendency (5).

In powdered form, zirconium retains to a remarkable degree its resistance to corrosion, and is, in contrast with other metal powders of commerce, stable for long periods of time under all normal conditions of storage. Coupled with this stability is a high degree of chemical reactivity at slightly elevated temperature. Absorption of gases such as O_2, N_2, and H_2 accounts for vacuum tube gettering applications (6, 7). Combustion in air or oxygen is rapid, and is accompanied by evolution of considerable heat and light. Such behavior makes zirconium powder of great use in photoflash bulbs (8) and of interest as a fuel in ammunition elements (9–11). It is the purpose of this paper to report the results of recent investigations of the combustion properties of zirconium powder.

PREPARATION OF ZIRCONIUM POWDERS

Among the objectives of this research were two essential extremes: the preparation of zirconium powders of the highest possible burning speed, and the preparation of zirconium powder of the lowest possible sensitivity to ignition by static electricity or heat. These objectives dictated preparation, on the one hand, of powder with minimum particle size, and, on the other, of powder of maximum particle size consistent with other desired qualities.

Powder of high burning speed was made by the calcium reduction of ZrO_2:

$$ZrO_2 + 2Ca = Zr + 2CaO. \qquad \text{(I)}$$

Several other reactions were considered:

$$ZrO_2 + 2Mg = Zr + 2MgO \qquad \text{(II)}$$

$$\left.\begin{aligned} ZrO_2 + 4Na &= Zr + 2Na_2O \\ ZrO_2 + 2Na &= Zr + Na_2O_2 \end{aligned}\right\} \qquad \text{(III)}$$

$$ZrO_2 + 4H = Zr + 2H_2O \qquad \text{(IV)}$$

$$\left.\begin{aligned} ZrO_2 + 2CaH_2 &= ZrH_2 + 2CaO + H_2 \\ ZrH_2 + \text{heat} &= Zr + H_2 \end{aligned}\right\} \qquad \text{(V)}$$

$$\left.\begin{aligned} &ZrX_4 + 2M = Zr + 2MX_2 \text{ (where X is Cl} \\ &\text{or F, and M is Ca, Mg, or 2Na).} \end{aligned}\right\} \qquad \text{(VI)}$$

Magnesium reduction of the oxide was incomplete, yielding powder of great sensitivity to ignition, but with low free metal content. Reaction (III) did not proceed, as predicted by thermodynamics.[2] Reac-

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[1] Manuscript received April 28, 1952. This paper was prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952. Part of the research in this paper was made possible through Philadelphia Ordnance District Contracts DA-36-034-ORD-88—388 and 389, sponsored by the Pitman-Dunn Laboratories of the Frankford Arsenal.

[2] The literature (12, 13) indicates, however, that sodium reduction occurs, possibly through intermediate zirconium halide formation, when an alkaline earth halide is included with the charge.

tion (IV) was studied by generating atomic hydrogen on a hot filament and passing it over ZrO_2, but no reduction was observed. Reaction (V), which may be written in several different ways, yields a metal powder containing more or less hydrogen depending upon conditions in the reduction cycle. It is shown later that hydrogen decreases the burning speed of the powder without appreciably diminishing its sensitivity to ignition. The reaction therefore did not appear useful for our purposes. Reductions of the type shown in reaction (VI) are sufficiently exothermic to yield sponges or fused metal, rather than powders.

Powder of maximum particle size and low ignition sensitivity was prepared by grinding fused zirconium metal resulting from the reaction

$$ZrCl_4 + 2Ca \rightarrow Zr + 2CaCl_2. \qquad \text{(VII)}$$

Grinding of fused metal, rather than sponge metal, was favored because the sponges might yield agglomerates composed of small particles. Such agglomerate powders would be expected to have the ignition characteristics of the smaller units, rather than of the larger particles of measured size. Calculation of peak temperatures reached during the reactions of equation (VI), in a manner analogous to the calculation of flame temperatures, showed that the melting point of zirconium (1830°C) might theoretically be exceeded in the sodium reduction of $ZrCl_4$, and in the calcium reductions of $ZrCl_4$ and ZrF_4. Experience in the sodium reduction of $ZrCl_4$ indicated that sponges were obtained, whereas calcium reduction yielded well-fused metal; ZrF_4 was not used because of its cost and the solubility of Zr in acidic fluoride solutions which would necessarily be present during acid-washing of the raw product.

Preparation of Subsieve Zirconium Powder by Reduction of ZrO_2 *with Calcium*

The calcium reduction process was studied by charging mixtures of C.P. ZrO_2[3] (-200 mesh) and granulated calcium, in measured excess, to a steel reduction bomb (approximately 3½ in. diameter × 7 in. high), igniting the mixture by placing the bomb in an electric furnace at 900°C, and, after cooling, removing the contents and washing the product with water and HCl. Typical yields of metal powder were in the range of 83–92 per cent. Determination of dissolved Zr showed that a loss of 5–6 per cent was incurred in the hot acid treatment used to minimize acid-soluble impurities. Small samples of powder were taken for analysis and other tests by filtering through a Büchner funnel, washing with acetone, and allowing the filter cake to air-dry at room temperature. Chemical properties of such powder have been reported previously (4).

The procedure differed from that of Rentschler and Lilliendahl (14) in that an evacuated bomb was used and cooled as rapidly as possible after reaction, instead of maintaining the reacted mass at high temperature, and under argon atmosphere, for a protracted period. The deleterious effect of extended heating on powder activity is shown in a separate series of experiments summarized in Table I.

The combustion properties of the metal powder were not a function of the purity or fineness of the calcium employed, but it was found that reaction was difficult to initiate when calcium coarser than 10 mesh was used. The $Ca:ZrO_2$ molar ratio was varied over the range of 1.8 to 4, corresponding respectively to 10 per cent deficiency and 100 per cent excess. The free metal content of the powder made with a deficiency of reductant was lower than that of other powders, as anticipated, but there was no significant dependence of the combustion properties (ignition temperature and burning time) on the $Ca:ZrO_2$ ratio. For a given oxide type,[4] the metal powder qualities appeared to be relatively independent of the state of subdivision of the oxide (Table II).

TABLE I. *Effect of extended heating of* Ca-ZrO_2 *mixtures on zirconium powder activity*

(In these experiments, Ca-ZrO_2 mixtures were ignited in graphite crucibles under argon atmosphere, and maintained at 1200°C for indicated times after completion of reaction.)

Time, min	Properties of zirconium powder, after acid-washing and drying			
	Particle size, microns, air permeability method	Burning time, sec/10 in.	Ignition temp, °C	Ignition* energy, joules
0	2.05	1.6	196	0.000045
5	2.61	6.7	201	0.000045
10	2.75	3.5	203	0.000045*
20	3.22	14.2	200	0.000045*

* Static ignition tests were performed by the Pitman-Dunn Laboratory of the Frankford Arsenal. Asterisk indicates that ignition was not followed by sustained combustion.

Preparation of Coarse Zirconium Powder

Fused zirconium was obtained by bomb reduction of $ZrCl_4$ with Ca under suitable conditions. The Zr

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[3] All Zr and its compounds mentioned in this work contained Hf(Hf/Zr = approximately 0.01).

[4] Oxides which were predominantly monoclinic yielded "fast" metal powders, whereas the tetragonal modification produced powders of long burning time. Unfortunately, there are no data on the heat of transition to indicate whether the difference is attributable to differences in the exothermic heat of reaction.

content of such fused metal varied from 96 to 98.6 per cent, the principal impurities being oxygen, calcium, minor metallic impurities present in the $ZrCl_4$, and included salt. The salt and calcium contents were sharply reduced by acid-washing the ground metal. Average oxygen content was of the order of 1–2 per cent, rendering the material sufficiently brittle for grinding.

The fused metal was crushed in a small jaw crusher equipped with a special housing permitting maintenance of an argon atmosphere. By repeated recycling of crushed metal, and "choke-feeding," it was possible to obtain metal finer than 100 mesh. The possibility of crushing to a coarser size (4 to 60 mesh), and further reducing such material to size in a high-speed hammer mill (Mikropulverizer) was also explored briefly. With extreme care in the matter of inert gas atmosphere, and using only a few hundred grams, it was possible to obtain appreciable quantities of powder finer than 100 mesh, with a minimum occurrence of fires. Crushed metal finer than 100 mesh was washed with HCl and water, and wet-sieved to produce the 100/325 cut desired as a part of this research. Subsieve portions of the ground metal were studied for various properties, as described later, in an attempt at over-all correlation of the properties of zirconium with particle size. Microscopic examination showed the crushed metal to consist of discrete particles of irregular, angular shape.

Combustion Properties of Zirconium Powders

Combustion of zirconium powders was studied by measuring the following properties.

Burning time.—Burning time was measured on a 10-in. powder train prepared in a steel mold (12 in. x 1/8 in. x 1/16 in.). No attempt was made to pack the dry powder. The train was transferred to a transite board, ignited at one end, and the time interval measured either visually with a stopwatch, or electronically by two Cetron CE2P phototubes spaced 10 in. apart. Reproducibility was approximately ±20 per cent or ±1/2 sec, whichever was the greater.

Ignition energy.—Ignition energies were measured by subjecting a small sample of metal powder to an electric spark from a charged condenser. The energy of the spark ($W = \frac{1}{2} Ce^2$, where C is the capacitance and e the instantaneous voltage) was increased stepwise until actual burning occurred. The limits of the equipment used (Pitman-Dunn Laboratory Electrostatic Discharge Tester No. 307-141) were 0.000045 to 21.9 joules. These tests were performed by the Pitman-Dunn Laboratories of the Frankford Arsenal.

Ignition temperature.—Ignition temperatures were measured by heating one-gram samples in a massive copper block (3 in. diameter x 3 in. high) with a blind 3/4-in. hole for the sample and a blind 5/16-in. hole for a thermometer. The block was set on a hot plate producing a temperature rise of 15°C per minute at the anticipated ignition temperature. Ignition was seen as a glow in the dark sample cavity, and the thermometer reading was recorded as ignition temperature. In some of the early work, ignition temperatures were determined by placing samples, in porcelain crucibles, in an oven. The rising oven temperature was read by thermometer. This method was discarded because better conditions for uniform heat transfer existed in the massive copper block. Duplicate readings generally agreed within 2°C.

Particle size.—Particle sizes were measured by three techniques: gas elutriation with a Roller particle size analyzer (15); settling in water by the hydrometer method (16); and air permeability, read

TABLE II. *Dependence of zirconium powder properties on particle size of oxide*

(ZrO_2—Commercial C.P. product, predominantly monoclinic. Ca—10 mesh, 10% stoichiometric excess.)

Experiment no.	Oxide treatment	Average ZrO_2 particle size, hydrometer method, microns	Free Zr (a) %	Avg part. size, hydrometer method, microns	Ignition temp, °C	Burning time, sec/10 in.	Photoflash bulb peak time, m. sec (b)
1	Sieved through 200 mesh	7.7	91.3	6.6	181	1.3	6.1
2	Sieved through 200 mesh	7.7	90.8	6.8	186	1.2	6.3
3	None	6.9	88.0	5.8	192	1.6	6.0
4	Air-milled	1.1	91.0	5.9	181	1.3	5.4
5	Ball-milled	<1.	91.3	6.1	181	12.2	8.8

(*a*) Determined by weight gain on ignition.

(*b*) Peak time is the time taken for the light emitted from the photoflash bulb to reach maximum intensity. Typical light emission curves are shown in reference (19). Values cited were provided through the courtesy of Dr. W. C. Fink, Sylvania Electric Products Company.

on a Fisher subsieve sizer (Fisher Scientific Company, Catalog No. 14-312). As a safety precaution, argon instead of air was used as a fractionating medium in the Roller analyzer.

IGNITION ENERGY AND PARTICLE SIZE

Zirconium powder can be ignited in two ways: by elevating its temperature, or by adding to it a minute amount of electrical energy. From the industrial standpoint, the ignition energy, which is the minimum energy required to ignite the powder, is probably the more important property. Hartmann (17) states that electrostatic spark energies of the order of 10 millijoules might be built up and discharged from a human body under some conditions. By this criterion, any metal powder which can be ignited by a spark less energetic than 0.01 joule would present serious hazards in dry handling. Corresponding approximately with this statement is the fact that commercial magnesium powder, having a spark sensitivity of 0.045 joule, can be handled with relative safety. Fine zirconium powder, on the other hand, having a spark sensitivity of 0.00004 joule, must generally be handled wet to obviate danger of inadvertent combustion.

TABLE III. *Combustion properties of ground fused zirconium powders and commercial magnesium powder*

	Zirconium (GZ) 200/325 mesh, by sieving	Zirconium (GZ) 10 to 44 μ, by decantation	Zirconium (GZ) 2 to 10 μ, by decantation	Commercial ground magnesium
Particle size range, μ, estimated	44–74	10–44	2–10	Screen analysis: 100/200 mesh 37% 200/325 30% through 325 33%
Average particle size, μ, air permeability method	33	18.3	3.15	12.4
Free Zr, %	86.4	84.5	72.5	—
Ignition temp, °C	378	312	199	412–490
Burning time, sec/10 in	414, 397	127, 165	21.5, 23.5	54, 46
Ignition energy, joules	12.5*	0.0200–0.0378*	0.000125–0.000225	0.045–0.046

* Ignition not sustained.

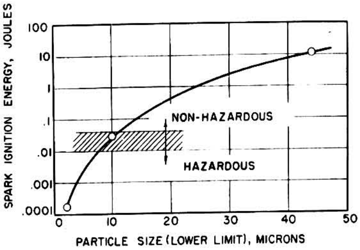

FIG. 1. Spark ignition energy as a function of particle size (ground fused Zr).

The crushed, fused zirconium was split into three fractions by screening between the limits of 200 and 325 mesh (Tyler sieve series), and treating the subsieve portion to repeated suspension and decantation after times computed from Stoke's Law (18). Ignition energy, burning time, and ignition temperature for these three fractions, and also for a commercial ground magnesium sample, were measured as described above, with the results shown in Table III. It is worth noting that the finest sample of this series had a higher order of spark energy than that characteristic of metal powder made by oxide reduction (Table I). The ignition energy data, plotted in Fig. 1, show that particle diameter of 10 microns represents approximately the borderline between safe and hazardous zirconium powder, on the basis of the criteria previously cited. The practical significance of this conclusion, that zirconium in the sieve range (44 microns and greater in effective particle diameter) can be handled dry without danger of ignition by static discharge, requires one important qualification: the size limit refers only to discrete particles, and not necessarily to particles which are essentially agglomerates of finer units. Ground sponges nominally coarser than 325 mesh may be static-sensitive, if they consist of agglomerates of particles smaller than 10 microns.

IGNITION TEMPERATURE

When zirconium powder is heated, it is found that sudden ignition occurs at some reproducible external temperature, here defined as the ignition temperature. The literature indicates that zirconium has the lowest ignition temperature of the commercially available metal powders.

Certain interesting regularities were observed in the determination of ignition temperatures (Fig. 2). The increase of ignition point with water content (Fig. 2B) is ascribed to a slight oxidation of the zirconium by water near the boiling point. Physical dilution of the zirconium powder raises the ignition temperature (Fig. 2C), but the trend is not carried over into metal powders "internally diluted," that is, incompletely reduced metal powders. No correlation has been found between the free metal content and the ignition temperature. Indeed, some of the lowest ignition temperatures were recorded for incompletely reduced powders, such as those made by the magnesium reduction of ZrO_2.

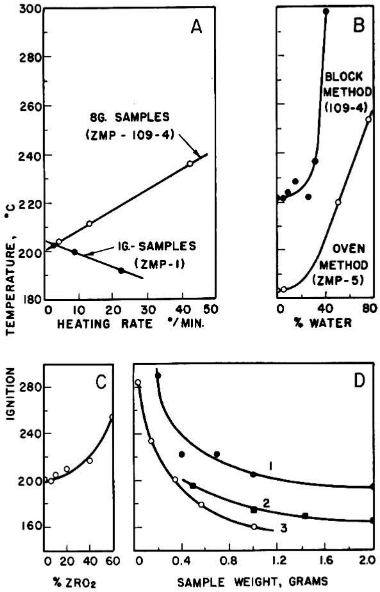

FIG. 2. Influence of several variables on ignition temperature of zirconium powder made by Ca-reduction of ZrO_2. A, heating rate. B, water content at room temperature (1-gram Zr samples). C, dilution with ZrO_2 (1-gram total weight). D, sample weight: 1—ZMP-7, copper block method; 2—ZMP-5, compacted at 14,000 psi, oven method; 3—ZMP-5 oven method.

TABLE IV. *Effect of high-temperature pumping on the ignition temperature of zirconium powder*

(Metal powder—ZMP made by calcium reduction of ZrO_2. Sample pumped at high vacuum for one hour at indicated temperature.)

Temp, °C	(No treatment)	420	900*
Ignition temp, °C	187	158	160
Burning time, sec/10 in.	8.4	7.3	8.4
Average particle size, air permeability method, μ	2.5	2.6	4.2*
Ignition energy, joules	0.000045	0.000045	0.000045

* To permit measurements on this sample, it was necessary to grind the sintered cake in a mortar and pestle.

In all cases where ignition point determinations were repeated on a given powder sample after a prolonged period, it was found that the ignition temperature had risen. The only rational explanation of this fact is that an oxide film forms which hinders subsequent oxidation. The effect can be accelerated by maintaining the powder a few degrees below the nominal ignition point for several minutes. Conversely, it was found that powders pumped at high temperatures show a decrease in ignition temperature (Table IV), because of inward migration of the surface oxide film (20).

Perhaps the most revealing variation of the ignition temperature is its dependence on the sample weight (Fig. 2D). The observed variation is consistent with a spontaneous combustion mechanism, wherein the heat of reaction within the powder mass increases the oxidation rate continuously, limited only by the rate at which the heat can be dissipated to the container. Burning from the inside of the sample to the outside was evidenced in several experiments during which internal temperature was compared with the external. The internal temperature lagged behind that of the container throughout most of the heating period. Shortly after the internal temperature exceeded the external, visible ignition occurred (Fig. 3).

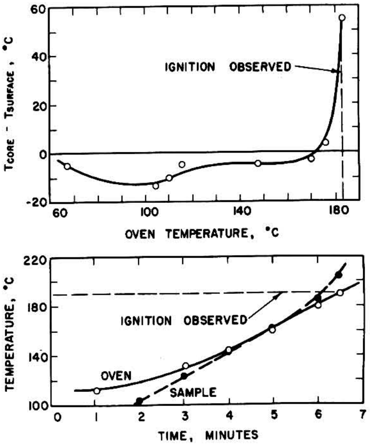

FIG. 3. Temperature differences prior to ignition of zirconium powder. Upper curve—results with differential thermocouple, one junction in center of sample, other near exposed surface; lower curve—comparison of oven and metal powder sample temperatures.

A semiquantitative explanation of these facts follows. Assume a spherical mass of zirconium powder of radius, r, in perfect thermal contact at its periphery with an infinite heat reservoir at a controlled temperature, T_1. Assume further that the mass consists of small perfect spheres, each of diameter d. At ordinary temperatures, oxidation occurs so slowly that the infinitesimal amount of heat developed is easily dissipated to the surroundings. As the temperature is raised, and the oxidation rate increases, the exothermic heat becomes appreciable and causes further temperature increase of a segment of the powder which is thermally isolated. If the rate of heat development at the center of the mass is greater than the rate at which the heat can be transported to the container, ignition eventually occurs. Then the following condition is necessary to ignition: rate of exothermic heat development > rate of heat loss.

Gulbransen (21) has shown that zirconium reacts with oxygen in the temperature range of 200°-425°C according to a modified parabolic law:

$$W^2 = Kt + C$$

where W is the weight gain of a sample of known geometric area, t is the time, and K a reaction rate constant with Arrhenius temperature dependence. The constant C expresses a slight deviation from the simple parabolic law in the initial stages of reaction, and can be omitted as negligibly small for reactions in advanced stages or metal with appreciable oxide film thickness. The reaction rate per unit area is then

$$\frac{dW}{dt} = \frac{K^{\frac{1}{2}}}{2t^{\frac{1}{2}}} = \frac{K'\mathrm{e}^{-E/2RT}}{t^{\frac{1}{2}}}$$

where E is the activation energy, reported to have a value of 18.2 kcal.

For a small mass of fixed weight at the center of the hypothetical spherical sample, the rate of heat development is obtained by multiplying the reaction rate per unit area by the total surface area and the heat of reaction ΔH. The total area per gram of a system of uniformly sized spheres is $6/\rho d$,[5] where ρ is the density and d the sphere diameter. The rate of heat generation by center element is thus

$$K'' \frac{\Delta H\mathrm{e}^{-E/2RT_2}}{t^{\frac{1}{2}}\, d}$$

where T_2 is the temperature of the central mass, and K'' includes all previous constants. Assuming that the rate of heat transport from the center element to the reservoir is of the form $k'''(T_2 - T_1)/r$, the fundamental condition for ignition becomes

$$K'' \frac{\Delta H\mathrm{e}^{-E/2RT_2}}{t^{\frac{1}{2}}\, d} > \frac{k'''(T_2 - T_1)}{r}.$$

The expression cannot be solved for T_1, the ignition temperature, in terms independent of T_2, the internal temperature. On the assumption that ignition is possible when T_2 exceeds T_1 by some small constant value, two simplifications are possible: $(T_2 - T_1)$ in the heat loss term can be taken as constant, and T_2 can be taken as roughly equal to T_1 in the exponential. The inequality then simplifies to

$$\mathrm{e}^{-E/2RT_1} > \frac{Kt^{\frac{1}{2}}\, d}{r}$$

or eventually,

$$T_1 > \frac{E}{2R \ln\left(\dfrac{r}{Kt^{\frac{1}{2}}\, d}\right)}; \qquad T_1 > \frac{E}{2R \ln\left(\dfrac{m^{\frac{1}{3}}}{Kt^{\frac{1}{2}}\, d}\right)},$$

where m is the sample mass.

Various interpretations of the time factor in this expression are possible. If it is interpreted as an inverse function of the external heating rate, then the expression predicts a decrease in ignition temperature with heating rate. This is the experimental case for small samples (Fig. 2A). In the case of larger samples, the increase of ignition temperature with heating rate is attributed to increased lag of internal temperature with respect to external temperature. The predicted increase of ignition temperature with time is in qualitative agreement with the observations that the ignition temperature can be greatly raised by keeping powder below the usual ignition point for some time. For a system of fixed particle size and shape distribution, and constant time, i.e., heating rate, the expression indicates a relationship between sample mass and ignition temperature as shown in Fig. 4. The form of this theoretical curve is very similar to those found experimentally (Fig. 2D). Likewise, the expression is in qualitative agreement with the data of Table III, as regards particle size.

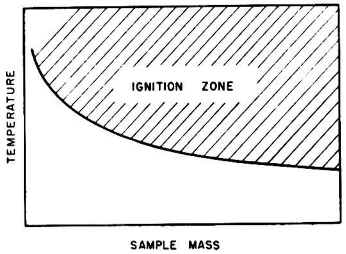

FIG. 4. Theoretical curve of ignition temperature vs. mass, for any given powder (heating rate constant).

A similar theoretical treatment for massive magnesium, developed by Eyring and Zwolinski (22), and based in part on the data of Leontis and Rhines (23), has recently been tested by Fassell, Gulbransen, Lewis, and Hamilton (24). An interesting demonstration of the dependence of ignition temperature on sample mass is cited by Hartmann (25), who found that one gram of uranium hydride ignited at 110°C, whereas 5 grams ignited after a few minutes' exposure to room temperature.

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[5] A general treatment would include a roughness factor to account for the fact that the measured surface area is greater than that calculated for smooth spheres. For a given powder lot, however, the necessity for this refinement disappears.

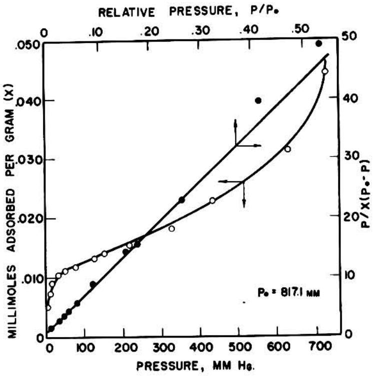

FIG. 5. Adsorption of N_2 on Zr powder (made by calcium-reduction of ZrO_2) at 77°K. Open circles—x vs. pressure; closed circles—$P/x(P_0 - P)$ vs. P/P_0.

TABLE V. *Surface areas of* Zr *and* ZrO_2 *powders and combustion properties of* Zr *powders*
(Area of N_2 molecule taken as 16.2 Å²)

Powder	Area, m²/g	Equivalent particle diameter, μ*	Ignition temp, °C	Burning time, sec/10 in.
Zr powders made by calcium reduction of ZrO_2 (ZMP)				
ZMP-41	2.90	0.32	214	1.75
ZMP-5	2.85	0.32	160	1.8
103 G-3, ball-milled	2.85	0.32	171	10.3
ZMP-19	1.10	0.85	135	2.6
ZMP 110-5				
degassed 1 hr at 20°C 0.85	1.08	0.86	222	2.3
degassed 1 hr at 200°C 1.08				
degassed 1 hr at 400°C 1.08				
degassed 1 hr at 600°C 0.41				
degassed 1 hr at 750°C 0.25				
103 G-3	0.83	1.1	281	25.5
ZMP 106-1	0.52	1.8	222	10.0
Ground fused zirconium (GZ)				
5 to 10μ fraction, by separation in Roller analyzer	1.07	0.87	200	22
10 to 44μ fraction, by separation in Roller analyzer	0.25	3.7	240	122
100/325 mesh, by screening (44 to 149μ)	0.13	7.2	>500	∞
Zirconium oxide	3.08–7.0	0.30–0.13	—	—

$$*d = \frac{6}{\rho S} = \frac{0.93}{S}.$$

SURFACE AREAS OF ZIRCONIUM POWDERS

Surface areas of various zirconium powder samples were measured by the Brunauer-Emmett-Teller nitrogen adsorption method (26). The ultimate objective of these measurements was to correlate the surface area with the burning time of zirconium powder. Although this objective was not achieved, certain other information of interest was developed. It was found that the adsorption was reversible, which, together with the S-shape of the isotherm (Fig. 5), was taken to prove that physical adsorption, rather than chemical combination, occurred at liquid nitrogen temperature. Degassing temperatures of 200°–400°C yielded reproducible areas (Table V, experiments on ZMP 110-5).

In Table V are summarized surface area results on the three categories of material studied, in the order of decreasing area. It is apparent that the magnitude of the surface area does not uniquely determine the burning speed. It seems reasonable to ascribe the failure of correlation to variations in the oxide film thickness, just as certain variations in the ignition temperature were ascribed to such films, through the time factor in the ignition temperature equation. As noted in the following section, burning time is also affected by hydrogen content. Judging from the substantial increase in area (and accompanying increase in activity[6]) on wet ball-milling zirconium powder, it would appear that porosity contributes negligibly to the surface area,

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[6] In addition to the increase in activity (decreased burning time and ignition temperature) caused by ball-milling, slight chemical change is also effected. The free metal content decreases and hydrogen pressure develops in the mill, which consequently requires periodic venting. All the changes are consistent with reduction in particle size, as is also indicated by air permeability measurements, and reaction of the freshly exposed Zr surfaces with water:

$$Zr + 2H_2O = ZrO_2 + 2H_2.$$

and that grinding results in actual particle rupture. The reduced metal surface area approaches but does not equal or exceed that of the parent oxide. This is consistent with a reduction mechanism in which the zirconium metal would have a particle size corresponding to the ZrO_2 grain size, but for a tendency to increase in size because of sintering effects at the high reaction temperature.

The surface areas of all the metal powders were substantially greater than would be inferred from the particle sizes as determined independently. The particle sizes calculated from the surface areas, on the assumption of smooth, uniform spheres, are smaller, by factors of 7 to 18, than the particle sizes as determined by sieve limits or hydrometer settling. These factors, which are due to the irregular shape of the Zr particles, are of the same order of magnitude as that calculated from the data of Guldner and Wooten (27), who compared the B-E-T particle size with microscopic measurements.

TABLE VI. *Effect of alloying constituents on zirconium powder*

Alloying Constituent (A)	% Zr	% A	Particle size or range microns	Ignition temp, °C	Burning time, sec/10 in.	Ignition energy, joules
Ti	44.7	40.0	2–8 (*a*)	228	7	0.000125
Ti	21.8	66	2–8 (*a*)	279	9.9	0.000045
Ti	11.8	73.5	2–8 (*a*)	>400	30.5	0.00045*
Ti	8.1	75.2	2–8 (*a*)	>500	45.2	0.0025*
Ti	0	86.0	2–8 (*a*)	>500	81	>21.9
Ni	87.2	6.2	<44	176	9.4	0.00016
Ni	79.1	13.8	<44	250	60	0.00036
Ni	64.5	29.9	<44	>400	202	12.5*
Ni	54.9	38.9	<44	>400	324	21.9*
Ni	34.7	54.3	<44	Would not burn		
Cu	85.3	7.7	<44	210	21.2	0.000625
Cu	72.1	15.1	<44	194	25.8	0.00125
Cu	64.0	31.4	<44	200	18.2	0.00144
Cu	49.2	46.0	<44	210	47.5	0.0025*
Fe	86.7	6.1	<44	132	31.0	0.000625
Fe	81.6	11.9	<44	162	23.4	0.000625
Co	89.0	13.5	<44	188	32.6	0.00025
H_2 (*b*)	90.0 (*c*)	0	3.77 (*a*)	218	11.8	0.00009
H_2 (*d*)	89.9	0.07	3.77 (*a*)	200	6	0.000045
H_2	89.9	0.08	3.77 (*a*)	204	11.5	0.000045
H_2	89.9	0.13	3.77 (*a*)	208	8	0.000045
H_2	89.4	0.55	3.77 (*a*)	230	42.5	0.000080
H_2	88.9	1.1	3.77 (*a*)	224	51	0.000125
H_2	88.6	1.5	3.77 (*a*)	260	73.1	0.00050*
H_2	88.5	1.8	3.77 (*a*)	>400	81	0.0225*

* Ignition not sustained.

(*a*) By air permeability method. (*b*) Degassed at 1100°C. (*c*) Free Zr, as determined by gain on ignition. (*d*) Degassed at 700°C.

ZIRCONIUM ALLOYS

Attempts were made to decrease the extreme ignition sensitivity of zirconium powder by preparing binary alloys with other elements. The results of addition of Ti, Ni, Cu, Fe, Co, and H_2 (Table VI) show that very large additions of these elements are required to reduce the ignitability materially. Furthermore, in every case for which the ignition energy was increased to values near the nonhazardous limit (of the order of 0.01 joule), the ignition temperature was high and the burning rate low. Emission of heat and light during burning was, under these circumstances, much less than that desired.

The titanium-zirconium mixtures were prepared by calcium-reducing intimate mixtures of TiO_2 and ZrO_2 in a small bomb, as described previously for the preparation of Zr powder. Prior to the preparation of these mixed metal powders, a few experiments were made in the reduction of TiO_2 with calcium.

The resulting metal powders had Ti contents varying from 86 to 91 per cent, burning times from 24 to 81 seconds, and ignition temperature over 500°C. The reaction rate constant for oxidation of Zr is some 23 times as great at 350°C as for Ti (28), and the corresponding activation energies are 18.2 and 26 kcal. The ignition temperature of Ti is thus different from that of Zr in the direction indicated by the theoretical expression developed earlier.

The other metallic alloys were prepared by vacuum melting, in graphite crucibles, appropriate mixtures of fused zirconium and powdered metal, crushing the resultant ingots, and grinding them to pass 325 mesh. No attempt was made to obtain a specific particle size, but the results are sufficient to show that the static sensitivity of Zr cannot be appreciably decreased except by use of very large proportions of the alloying metal.

The hydrided zirconium samples were prepared from metal powder made by calcium reduction of ZrO_2. A quartz tube containing a weighed amount of the powder was sealed to a glass vacuum system, and heated under high vacuum to expel hydrogen already contained. Hydrogen was then admitted to the system, and in turn admitted to the sample. Amount of hydrogen consumed was calculated from pressure decrease and the known volume of the system. After degassing at 1100°C, the sample absorbed H_2 very slowly; after degassing at 700°C, the hydrogen absorption started readily at room temperature. The absorption was exothermic and increased in rate as the sample temperature rose. A portion of the sample richest in hydrogen (corresponding to $ZrH_{1.8}$) was degassed at 1100°C, and the sintered cake ground lightly to permit burning measurements. The burning time was 9.2 sec, and the ignition temperature 216°C, essentially duplicating the values found for the original Zr powder simply degassed at 1100°C. The effect of hydriding on powder properties is, therefore, reversible. Inspection of the data indicates a slight break in burning time and ignition temperature near 0.5 atom H/atom Zr. Not until the sample had been almost completely converted to ZrH_2, however, was there a significant increase in ignition energy. Such results are in accord with the findings of Hartmann (25), who reported ignition energies of 64–320 microjoules for ZrH_2 dust layers; although slightly greater than most of the values reported for Zr powder, these spark energies still place the hydrides in the hazardous category.

HAZARDS

The hazards incident to handling subsieve zirconium powders arise because of their sensitivity to ignition by static electricity or heat. Suggestions for safe handling of such material have been published by the National Safety Council (29) and by Fink (30).

As shown in this paper, zirconium powder intrinsically coarser than 10 microns is relatively insensitive to ignition, and such powder can be safely handled dry. The statement does not apply to powders nominally coarser than 10 microns but consisting of agglomerates of particles smaller than 10 microns. Powders containing an unknown proportion of fines (particles smaller than 10 microns) should be handled with the same care as recommended by the National Safety Council, until extensive testing and experience have shown that extreme precautions are unnecessary.

CONCLUSIONS

Subsieve zirconium powder made by calcium reduction of ZrO_2 has maximum activity when the high-temperature exposure of the reacted mass is kept to a minimum. The combustion properties (ignition temperature and burning time) are not a critical function of the calcium purity, size, nor molar excess, but depend upon the type of oxide used. Magnesium reduction of ZrO_2 yielded powders of high activity but low free metal content. Fused zirconium prepared by bomb reduction of $ZrCl_4$ with calcium can be ground to discrete particles in the sieve range. Ignition energy determinations on fractions of such ground Zr showed that particle diameter of 10 microns represents approximately the dividing line between hazardous and nonhazardous powder, using 0.01–0.04 joule as a criterion of critical ignition energy. Thermal ignition appears to occur by spontaneous combustion, and the dependence of ignition temperature on several variables follows qualitatively the expression:

$$\text{ignition temperature} > \frac{E}{2R \ln (m^{1/3}/Kt^{1/2}\, d)},$$

where E is the activation energy for zirconium oxidation, m the sample mass, d the particle diameter, and t a time factor related to the oxide film thickness. Because of variations in this film thickness, the burning time of Zr powders is not uniquely determined by the surface area, as measured by low-temperature nitrogen adsorption. The adsorption experiments showed that the metal particle size approaches, as a lower limit, that of the oxide, and also that the metal particles are not appreciably porous. The ignition sensitivity of Zr could not be decreased by alloying with Ti, Ni, Cu, Fe, Co, or H_2, except by use of amounts so great that burning properties were deleteriously affected.

ACKNOWLEDGMENTS

The authors wish to thank the Frankford Arsenal, under whose sponsorship a part of this research was carried out, and the Foote Mineral Company, for permission to publish these results. Mr. Thomas Stevenson, of the Pitman-Dunn Laboratory of the Frankford Arsenal, has provided many suggestions relevant to the course of the research and supplied spark evaluations of all samples reported herein. Frequent stimulating discussions with Mr. Charles L. Scheer of this laboratory contributed to the progress of the work, and Mr. Anthony C. Demos carried out several of the experimental phases of the research.

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

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Alkaline Earth Orthophosphate Phosphors[1]

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ABSTRACT

The characteristics of new phosphors, comprising orthophosphates of calcium, strontium, and barium, and their mixtures are described. The primary (absorbing) activator is tin dissolved in the matrix and with this activator alone strontium, barium, and alpha calcium phosphate emit either in the long wave ultraviolet or the blue regions of the spectrum, while beta calcium phosphate emits mainly in the red. Introduction of manganese as a secondary activator into beta calcium phosphate or into the mixed calcium-strontium phosphate gives deep red emission. Variable color can be obtained by varying the manganese content. Beta calcium phosphate, tin activated, has an efficiency of 45 lpw in 40 watt fluorescent lamps and their color is close to 3500° White. It gives outstandingly good color rendition and represents an improvement over the red phosphor now used in the Deluxe line of lamps.

INTRODUCTION

Although halide-free phosphate phosphors emitting visible light have received some attention in the patent literature (1–3), other published information is rather scanty. Huniger and Panke are quite indefinite in their description of the matrix materials, but from the context it seems probable that they were working with meta phosphates. Tin-activated calcium phosphate, strontium phosphate, or barium phosphate were all listed as giving a medium fluorescence of blue color. McKeag deals with pyrophosphates of strontium or barium, activated by tin or tin and manganese. Kroger (4) has mentioned the preparation of doubly activated orthophosphates of calcium and strontium, containing the combinations Ce-Mn and Sn-Mn. Froelich and Margolis (5) have also published an excellent discussion of calcium orthophosphate, activated by cerium and manganese, which emits deep red light. Henderson and Ranby (6) have described a blue-green emitting barium pyrophosphate, activated by a rather large amount of titanium.

In considering the alkaline earth phosphates as phosphors, it is important to recognize clearly the multiplicity of crystal structures which may be encountered and to specify exactly which crystal structure is being used in the particular phosphor. The best summary on the crystal structures of the calcium phosphates is that of Bale, Bonner, and Dodge (7), who give x-ray powder diffraction patterns of 11 different materials. There are no equally thorough surveys of either the barium or strontium phosphate systems, though Zachariasen (8) has proposed a crystal structure for the two orthophosphates.

The present paper discusses the preparation and properties of phosphors made from the orthophosphates of calcium, strontium, and barium or from mixed orthophosphates, employing tin or tin and manganese as activators.

No previous work has been published dealing with orthophosphate phosphors,* activated by tin alone, and only the single reference by Kroger has been found for orthophosphate phosphors containing both tin and manganese. Kroger's work was limited to preparation of two specific phosphor compositions by firing in wet nitrogen, which is not suitable for most of the phosphors described in the present paper.

The primary activator in these orthophosphate phosphors is stannous ion in solid solution in the lattice, probably replacing calcium.[2] It need be present only in low concentration while the secondary activator, manganese, must be present in larger amounts before its emission will be appreciable.

METHOD OF PHOSPHOR PREPARATION

The basic raw materials used in the preparation of all of the phosphors were the secondary phosphates and the carbonates of the alkaline earths, with the activators being added generally as stannous oxide and manganous carbonate. The secondary phosphates were made by precipitation, with purified ammonium monohydrogen phosphate, of a pure chloride or nitrate solution. A small amount of am-

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[1] Manuscript received July 21, 1952. This paper was prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952.

[2] In this paper "primary activator" is used for the activator capable of absorbing exciting radiation and capable also of emission. The energy absorbed may be transferred to the "secondary activator" which is not capable of absorbing the exciting radiation directly, but which may furnish the main visible emission band.

*Note added in proof: Th. P. J. Botden, has published [*Philips Research Rpts.*, 7, 197 (1952)] some data on strontium orthophosphate activated by tin.

monium chloride was sometimes added to the blend of raw materials to catalyze the diffusion of the activators into the lattice.

The powdered raw materials were dry blended and hammer milled to insure intimate mixing before firing. The blends were fired in an electrically heated furnace, in open silica crucibles, to form the orthophosphates containing the activators in solid solution in their oxidized form. These nonfluorescent white or pink powders were then converted to phosphors by firing and cooling in a controlled atmosphere, which consisted of a mixture of hydrogen with oxygen-free nitrogen. The exact mixture used was determined by the firing temperature and by the composition of the phosphor, but it generally contained from 0.5 to 10 per cent hydrogen by volume. The color of light emitted was generally independent of the composition of the ambient atmosphere, but brightness was low either with very low hydrogen content or with excessive hydrogen content, due in the first case to insufficient stannous ion being formed and in the second case to reduction to metallic tin. The temperature for the initial firing ranged from 1040° to 1200°C, while that of the second firing ranged from 925° to 1200°C.

The firing method, using carefully controlled reducing atmospheres, is quite different from those previously described in the literature. In the past, either an inert atmosphere, such as nitrogen, has been relied upon to prevent oxidation of the activators, or a strong reducing atmosphere, such as dry or wet hydrogen, has been used to insure complete reduction of the activators. Neither atmosphere is fully effective with the tin-activated phosphates, since nitrogen does not prevent oxidation by the water vapor or CO_2 evolved during firing, and pure hydrogen gives metallic tin. In contrast, controlled small amounts of hydrogen serve to reduce the stannic ion to stannous ion without formation of the free metal.

While the phosphors are designated as orthophosphates, they generally contain less than the stoichiometric amount of the alkaline earths, as materials with the theoretical amount do not fluoresce well.

The phosphors made with tin as the only activator have emission colors determined solely by the crystal structure of the matrix, with concentration of the activator having no effect. When manganese is introduced as a second activator, the emission color becomes dependent on the manganese concentration, since the emission band due to tin is gradually suppressed, while that due to manganese builds up, as the concentration increases.

The following sections of this paper will describe briefly the outstanding characteristics of the various phosphors, classified according to the alkaline earth metals used to form the orthosphosphate. The ultraviolet emission of some of the individual phosphors is described in a separate section.

The composition is expressed as gram-atoms of each metal for each two gram-moles of the PO_4 radical. Thus, a typical calcium strontium orthophosphate would have the composition:

TABLE I

Gram-atoms						Firing conditions		Figure
Ca	Sr	Ba	P (as PO_4)	Sn	Mn	% H_2	°C	
2.88	—	—	2.00	0.005	—	1.8	1200	1 (Alpha-Sn)
2.88	—	—	2.00	0.040	—	2.8	1200	1 (Beta-Sn)
2.84	—	—	2.00	0.020	0.080	3.6	1200	1 (Beta Sn-Mn)
—	0.00	2.88	2.00	0.040	—	2.8	1150	2 A
—	0.88	2.00	2.00	0.040	—	2.8	1040	2 B
—	2.00	0.88	2.00	0.040	—	2.8	1150	2 C
2.88	—	—	2.00	0.010	—	2.8	1175	3
2.64	—	0.24	2.00	0.040	—	2.8	1040	3
2.00	—	0.88	2.00	0.040	—	2.8	1175	3
2.66	0.22	—	2.00	0.040	—	1.8	1200	4
2.00	0.88	—	2.00	0.040	—	1.8	1120	4
2.00	0.88	—	2.00	0.040	0.00	1.8	1200	5
2.00	0.88	—	2.00	0.040	0.01	1.8	1200	5
2.00	0.88	—	2.00	0.040	0.08	1.8	1200	5
2.80	—	—	2.00	0.005	—	2.8	1175	6 (Alpha)
2.80	—	—	2.00	0.005	—	2.8	1065	6 (Beta)
1.60	1.20	—	2.00	0.020	—	0.3	1090	7
2.00	—	0.88	2.00	0.010	—	0.6	1175	8
2.88	—	—	2.00	0.005	—	1.4	1200	8
—	2.80	—	2.00	0.040	—	0.6	1200	8
—	—	2.88	2.00	0.040	—	0.6	1150	8

Element	Gram-atoms
Ca	1.44
Sr	1.44
P (as PO_4)	2.00
Sn	0.04
Mn	0.04

Table I lists the composition and final firing conditions of the phosphors for which emission curves are given in the accompanying figures. Except for tricalcium phosphate, as discussed below, nearly identical emission curves are obtained with a wide range of hydrogen concentrations and firing temperatures. The firing time for the controlled atmosphere firing was one hour, using a porcelain boat in a 1½-in. x 30-in. silica tube.

CALCIUM ORTHOPHOSPHATE PHOSPHORS

Three different types of phosphors have been made, based on tricalcium phosphate, and their characteristics are listed briefly in Table II. The emission curves of typical materials are shown in Fig. 1.[3]

The alpha form of the phosphate is quite readily produced by firing at temperatures above 1175°C, with low amounts of tin present and compositions near the stoichiometric amounts. Deviations from these conditions lead to the formation of the beta form, and the production of this can be made certain by the use of rather large amounts of tin and control of the atmosphere so as to only partially reduce the stannic ion. Apparently, the stannic ion inhibits the conversion to the alpha form at temperatures below 1200°C. Manganese also inhibits the conversion to the alpha form and it has proved rather difficult to obtain alpha tricalcium phosphate containing tin and manganese. However, this phosphor has a very weak fluorescence and is not of great interest.

TABLE II

Crystal structure	Activators	Emission	Peak wavelength
High temp (Alpha	0.005 Sn	Blue	4900
Low temp (Beta)	0.04 Sn	White	6300
Low temp (Beta)	0.02 Sn + 0.08 Mn	Orange	6500

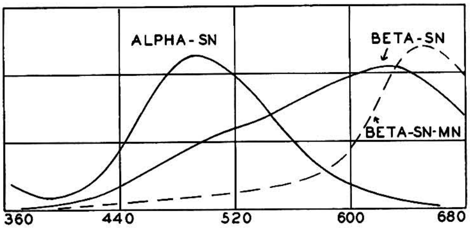

FIG. 1. Relative visible emission of calcium orthophosphates activated by tin and by tin and manganese.

The reduction processes, converting stannic ion to stannous ion and stannous ion to metallic tin, are sensitive to temperature, and the ambient atmosphere employed during firing must be changed in ratio of hydrogen to nitrogen to suit the exact time and temperature of firing.

With tin contents between 0.01 and 0.04 gram-atoms per mole of calcium phosphate, it is readily possible to produce phosphors of variable color ranging from blue to white, with the emission depending on the relative proportions of the two crystal structures present in the final product.

The visible emission of the alpha form of the phosphor, activated by tin, is a single band with a Gaussian distribution of energy against wave number. In addition, there is an ultraviolet emission band.

The visible emission of the beta form, tin-activated, is somewhat more complex and it may be analyzed into two subbands with Gaussian distribution of energy, the peaks of these subbands lying at 6300 and 4950 Å.

The introduction of manganese into the tin-activated beta structure apparently suppresses the tin emission as the concentration of manganese increases, with the development of a new emission band peaking at 6500 Å. Thus the result of the manganese addition is a gradual shift from a white to an orange-red emission. With manganese concentrations above 0.15 gram-atoms, the emission becomes quenched and intensity drops off.

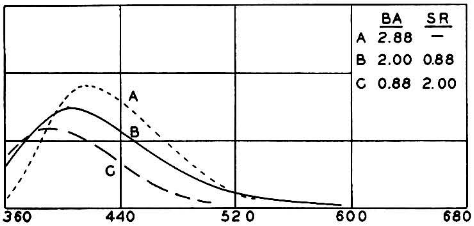

FIG. 2. Relative visible emission of tin-activated barium-strontium orthophosphates.

STRONTIUM AND BARIUM ORTHOPHOSPHATE PHOSPHORS

At the firing temperatures used for the preparation of these phosphors, only one crystal form of strontium orthophosphate and barium orthophosphate was detected, confirming previously reported data. Both phosphors show relatively simple emission spectra, that of barium orthophosphate lying in the visible with the peak at about 4150 Å as shown in Fig. 2. The color of the emission is independent of the tin concentration, but the efficiency falls off at either very low or very high concentrations. The control of the tin reduction also becomes difficult at concentrations above 0.08 gram-atoms and the powders are frequently grayish, unless the ambient atmosphere during firing is correctly chosen.

The emission of strontium orthophosphate lies completely in the ultraviolet and will be described in a later section.

Addition of manganese to the strontium phosphate results in rather poor emission in the visible with the

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[3] In Fig. 1 to 5 the relative energy scale is the same and 2537 Å radiation is used for excitation.

effect of the manganese being mainly that of suppressing the emission due to tin, though it does introduce a band peaked at 6100 Å. Barium phosphate will not dissolve manganese.

MIXED ORTHOPHOSPHATE PHOSPHORS

Use of a mixture of the alkaline earth metals in place of the single metals results in slight changes with certain mixtures and in more radical changes in the emission spectra for other systems.

Strontium-Barium Phosphates

The effect of replacing a part of the barium, in barium orthophosphate, by strontium is relatively slight with a gradual shift in the peak of the emission curve. Typical emission curves are given in Fig. 2. The change in position of the peak is quite gradual through most of the range, but as the pure strontium phosphate is approached, the change in peak emission becomes more rapid.

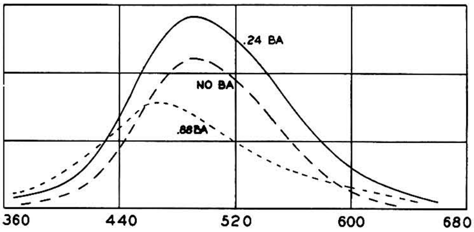

FIG. 3. Relative visible emission of tin-activated calcium-barium orthophosphates.

Strontium-Barium-Calcium Phosphates

Tin-activated phosphors containing all three of the alkaline earth metals generally gave very poor emission when moderate amounts of any of the three components were present.

Calcium-Barium Phosphates

When there is gradual replacement of calcium by barium in the alpha phosphate there is at first little change in the emission spectrum or in the crystal structure, although there is a definite change in physical properties, with evidence of a eutectic for the composition containing 2.44 gram-atoms of calcium and 0.44 gram-atom of barium. Further replacement leads to changes in both emission spectrum and crystal structure, as evidenced by powder diffraction patterns. With 2.00 gram-atoms of calcium and 0.88 gram-atom of barium, only the new powder diffraction pattern is found, and the emission curve peaks at 4700 Å. Further increase in the barium content leads to decreased emission, until the pure barium orthophosphate is approached. Typical curves are shown in Fig. 3.

Like many other systems containing barium, manganese is not soluble in the calcium-barium phosphates and useful phosphors containing manganese have not been made.

Calcium-Strontium Phosphates

This system shows rather radical changes in the emission spectra as the composition of the mixture is varied.

Starting with the beta form of tricalcium phosphate, which has a red emission band with subbands peaked at 6300 and 4950 Å, the apparent effect of strontium substitution up to 0.88 gram-atom is a suppression of the 4950 subband, without major change in the 6300 subband, and the development of a new emission band at 4000 Å. While the 6300 subband shows no major change, it does shift position slightly from 6300 to 6150 Å as shown in Fig. 4. The emission color thus shifts from a white to a red, because of the suppression of the 4950 subband and the low visual effectiveness of the band at 4000 Å. This change in emission occurs without change in crystal structure other than a slight expansion of lattice.

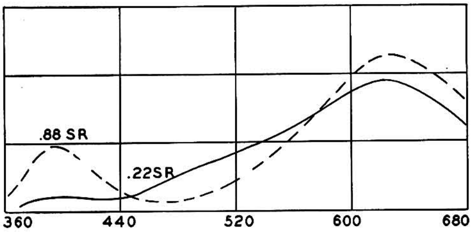

FIG. 4. Relative visible emission of tin-activated calcium-strontium orthophosphates.

Addition of manganese to a phosphor containing 2.00 gram-atoms of calcium and 0.88 gram-atom of strontium, like additions to beta calcium phosphate, results in a gradual suppression of the tin emission at 4000 Å, while the change in the red emission band may be interpreted as a suppression of the tin band at 6150 Å and the development of a new manganese band peaking at 6350 Å. This manganese band is considerably sharper than that due to tin, so the emission color is deep red. Fig. 5 shows emission curves for phosphors containing 2.00 gram-atoms of calcium and 0.88 gram-atom of strontium.

With tin activation, further increase in the strontium content above 0.88 gram-atom results in the development of a new type of crystal structure which might be described as a transition structure between calcium and strontium phosphates. However, this change of structure does not cause any marked change in the emission spectra. Surprisingly, the typical red emission spectrum persists even with compositions containing as much as 2.60 gram-atoms of strontium with 0.20 gram-atom of calcium, even though this shows the powder diffraction pattern of strontium orthophosphate. Beyond this point, there is a sharp transition to the typical ultraviolet emission of the tin-activated strontium orthophosphate.

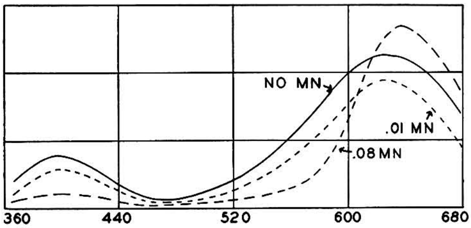

Fig. 5. Relative visible emission of calcium-strontium orthophosphate activated by tin and manganese.

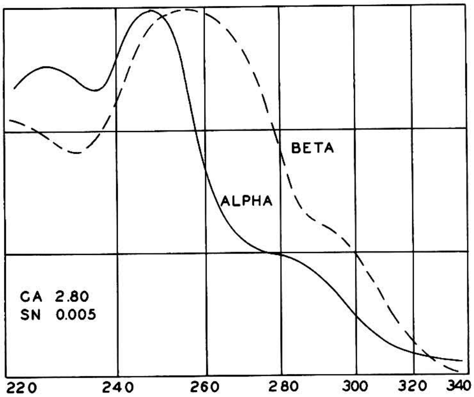

Fig. 6. Normalized relative excitation spectra of alpha and beta calcium orthophosphate activated by tin.

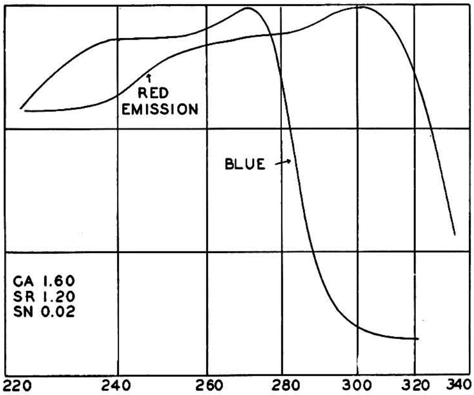

Fig. 7. Normalized relative excitation spectra of calcium-strontium orthophosphate for red and blue emission bands.

Excitation Spectra

A rather limited amount of work has been done on the excitation spectra of these phosphors and data on these spectra will be reported in a later paper. The excitation spectra are quite complex in their dependence on composition and show a multiplicity of peaks, in some cases, over a wave length range from 2200 to 3200 Å. In general, the peak of the excitation curves lies close to 2537 Å, so that the efficiency of excitation by the low-pressure mercury arc is excellent. The results on the mixed calcium strontium orthophosphates activated by tin are especially interesting since they show different excitation spectra for the red and the blue emission bands. For example, radiation of 3000 Å will excite red emission efficiently but will not cause appreciable blue emission. Some typical normalized excitation curves are given in Fig. 6 and 7.

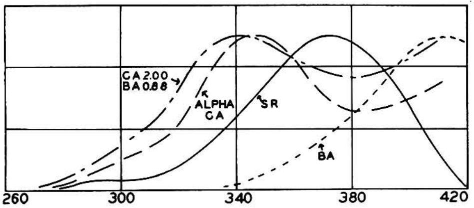

Fig. 8. Normalized ultraviolet emission spectra of various orthophosphates activated by tin.

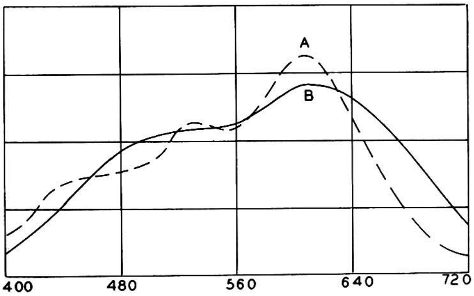

Fig. 9. Emission spectra, omitting mercury lines, of 40T12 Cool White fluorescent lamps. A, major component $CaSiO_3$:Pb,Mn; B, major component $Ca_3(PO_4)_2$:Sn.

Ultraviolet Emission Spectra

As mentioned previously, some types of tin-activated phosphate phosphors show emission in the ultraviolet. Typical examples are shown in Fig. 8. In this figure, the ultraviolet emission curves have been normalized since our method of measurement did not permit accurate intercomparison of different phosphors. However, it should be noted that the emission was much weaker than that of lead-activated barium disilicate, the best of the blacklight phosphors.

APPLICATIONS

A number of these phosphors offer considerable promise for use in fluorescent lamps, especially in Deluxe types, because of the large amount of deep red light emitted and the relatively high efficiency. Some of the blue emitting phosphors are also of interest as possible replacement for certain tungstates.

The properties of typical red phosphors when made into 20 watt lamps are listed below:

Alkaline earths	Activators	100 hr lpw	x	y
Calcium (Beta)..........	Sn	35	0.417	0.384
Calcium (Beta)..........	Sn, Mn	21	0.420	0.345
Calcium + strontium....	Sn	29	0.444	0.363
Calcium + strontium....	Sn, Mn	21	0.465	0.339

The beta calcium phosphate, tin-activated, gives lamps with a color between that of one of the soft white lamps now on the market, and 3500° White, and by blending with magnesium tungstate and zinc orthosilicate can be made to match Cool White. This improved Deluxe Cool White has a very smooth output curve for the phosphor component, with an unusually large amount of deep red light, as shown in Fig. 9. The measured output in 40 watt lamps has reached 45 lpw at 100 hours and the color rendition obtained is exceptionally close to that with natural daylight.

CONCLUSION

The system of phosphors described in this paper is not only of considerable practical interest as an addition to the growing group of deep red phosphors for fluorescent lamp use, but also of great theoretical interest because of the striking differences in emission and excitation characteristics caused by changes in crystal structure or by replacement of one alkaline earth metal by another.

At present it seems that the various emission colors obtained with tin as the only activator can be interpreted as transitions between the $^1S_0$ ground state and the $^3P_1^0$ or $^1P_1^0$ excited states with the transition probabilities and the exact location of the absorption and emission bands being determined mainly by the crystal structure of the matrix. The phosphors containing both tin and manganese, in their general behavior, resemble calcium silicate activated by lead and manganese, or calcium halophosphate activated by antimony and manganese. All are, therefore, sensitized phosphors in which the primary activator is present in low concentration. They are unlike the other well-known systems activated by cerium and manganese, where the primary activator, cerium, must be present in high concentration.

It is expected that a detailed study of the excitation and emission spectra of these new phosphors will throw further light on the mechanisms of fluorescence, and work along these lines is in progress. Further interpretation of their behavior must be deferred until this is completed.

ACKNOWLEDGMENTS

The author would like to thank Mr. R. Vogel and Mr. A. J. Oszy for data on excitation and ultraviolet emission spectra, and Mrs. V. M. B. Hannaford for x-ray powder diffraction data. He would like also to thank Mr. O. H. Biggs and Dr. E. F. Lowry for their encouraging interest in the progress of the work.

Note added in proof—See p. 250, column 2: Th. P. J. Botden has published [Philips Research Rpts., 7, 197 (1952)] some data on strontium orthophosphate activated by tin.

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

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Electrolytic Grinding or Machining of Metals[1]

O. W. Storey[2]

Electrochemistry apparently is destined to aid a metalworking industry threatened by the shortage of the diamond bort so essential in the past for the grinding and shaping of hard metals and other materials, such as the sintered carbides. Controlled anodic dissolution of these hard materials, developed as an electrolytic grinding process, has now reached the stage where it seems likely to displace diamond grinding at least sufficiently to end the critical diamond bort situation. Although two other electrochemical hard-metal-working processes (electroarcing and electrosparking) also are promising, the Minerals and Metals Advisory Board of the National Research Council, in its evaluation of the several processes,[3] held that the electrolytic grinding method was particularly promising for flat offhand grinding as applied to sharpening of single-point tools and particularly to the finishing of the sintered carbides. These grinding operations are the largest consumers of diamond bort. The report further stated that the process also seems well suited to the sharpening of milling cutters and broaches, the grinding of projectile cores, and the machining and grinding of compressor disks. It also has been used successfully in the sharpening of twist drills.

The intentional electrolytic removal of metals has been practiced for many years as in electropickling and in electropolishing. However, the controlled electrolytic removal of metal as in the shaping of metals has not been practiced commercially. The possibilities of the anodic process were demonstrated dramatically by the late Dr. C. F. Burgess at the 1941 Chicago meeting of the Society in his "Electrolick Work-Shop." In the Electrolick pamphlet that was distributed he called attention to the striking differences between the mechanical and electrolytic methods for displacing metal, the first being a method of "brute force and violence" and the second being a "cool, steady, nondeforming magic of electrolytic-anodic removal of metal." However, except for a few isolated applications, and despite its intriguing appeal, Dr. Burgess' hobby failed to develop commercially during the following decade. Although the hardest metals and the sintered carbides can be dissolved readily by anodic action at low potentials, it was found difficult both to control the action so that only unwanted metal was removed and to remove the metals at rates comparable to those obtained by mechanical methods. These two hurdles now seem to have been overcome in the grinding field.

Super-Cut, Inc., of Chicago, manufacturer of diamond grinding wheels and tools exclusively, is sponsoring the development of the electrolytic grinding method devised by George Keeleric. His method utilizes a fast-moving cathode having spaced-apart insulating particles imbedded in its surface and protruding evenly above it for spacing the cathode from the work. The method and equipment are being tested by a number of users of large quantities of sintered carbides and hard-metal tools, including Buick, Frigidaire, Ford, Excello, Chrysler, and Kenna-Metal. The development is of particular interest to electrochemists because there were utilized in the solution of the problem several phases of electrochemistry. As practiced at present, the success of the Super-Cut process is due to: (*a*) the utilization, without appreciable arcing, of high electrode current densities up to 1500 amp in.^{2} with closely spaced electrodes 0.007 in. (0.0178 cm) apart; (*b*) effective removal of insulating insoluble residues from the anode surface; (*c*) accurate spacing means between anode and cathode; and (*d*) automatic control of the voltage so that the operation is conducted at the highest possible current density at all times, that is, without causing arcs or "hot" sparking to occur.

In the process as developed, the diamond grinding wheel remains as the most important element, but its function differs essentially from the ordinary diamond grinding in that the diamonds no longer operate on the metal or other hard stock. Instead, they function primarily as insulating spacers between the stock anode and the revolving nickel cathode surface in which they are anchored, and, secondarily, as a mild abrasive to keep the surface of the anode free of films of insulating insolubles. These films, which are relatively soft, consist primarily of oxides which are formed when the carbides are anodically dissolved. The diamonds are more economical to use than aluminum oxide or silicon carbide because the latter do not stand up sufficiently long. The diamonds, therefore, are still used, but their life has been extended greatly. In one reported test in which chipbreakers were ground, the diamond wheel cost was decreased from $107.87 per cubic inch of carbide removed for conventional grinding to 68 cents for electrolytic grinding. To the 68 cents must be added 8 cents for the power required to dissolve the carbide anodically. These costs are subject to further checking but nevertheless are indicative of the conservation of diamond bort that may be effected.

The structure of the ordinary diamond grinding wheel has been modified to obtain maximum electrolytic grinding efficiency. A single layer of diamonds is used to surface the electroformed nickel cathode facing of the wheel. These diamonds are of coarser mesh than previously used for this work and the particle concentration has been increased considerably. This increased concentration helps to prevent intermittent contact between the work piece and the cathode. This would cause arcing and sparking with consequent impairment of the finish of the work and possibly erosion of both the work piece and the wheel electrode, which, in form or contour grinding, is very detrimental to the accuracy of machining. The particles must be spaced sufficiently apart to allow flow of electrolyte between the work piece and wheel.

With close spacing of the electrodes (0.007 in. or 0.0178 cm) rapid replenishment of the electrolyte is essential if the high current densities needed for rapid stock dissolution are em-

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[1] It is believed that this description of one sort of Applied Electrochemistry will be of considerable general interest to our readers. (*Ed.*)

[2] Chicago Regional Editor, JOURNAL of The Electrochemical Society.

[3] *J. Metals*, **4**, 378 (1952).

ployed. This rapid replenishment is accomplished by supplying a stream of electrolyte continuously to the rapidly rotating diamond-faced cathode wheel, its surface speed being comparable to that employed in ordinary grinding, 5000 to 6000 surface-feet per minute. It therefore has been possible to use the ordinary tool-grinding machine for electrolytic grinding after insulating the tool spindle from the rest of the machine and conveying the current to it by suitable means. It is estimated that standard grinding machines can be converted locally at a cost not exceeding $500.00 per machine.

The electrolyte used is a conductive salt solution, the salt depending upon the composition of the work piece. The highly conductive sodium salts have been mainly used. The electrolyte should not corrode the machine parts and carbide tool shanks. This requirement eliminates the highly effective chloride salts and particularly sodium chloride. Furthermore, the electrolyte should be nontoxic because of the mist which is formed by the rapidly revolving wheel. Salts of certain organic acids are now giving satisfactory results, but this is a field for continued research. Sodium silicate solution may be used as electrolyte to help decrease edge erosion as it forms a protective coating on adjacent surfaces. However, it decreases the rate of cutting. Because the electrolyte apparently can be used indefinitely, its cost per unit of metal removed is very small.

The diamond particles are anchored in the electroformed nickel cathode perimeter of the wheel during the plating operations. In the fabrication of the wheel the first step is to mount the single layer of diamonds in a very thin adhesive film on a steel ring. A thin layer of copper is plated onto this surface, followed by the nickel. The copper is plated to a thickness equal to the depth that the diamonds are to be exposed at the wheel surface. The nickel is plated to the desired thickness of about ⅛ in. (0.32 cm), completely enveloping the parts of the diamonds exposed above the copper. This composite structure is now mounted on the base wheel after which the steel ring is removed. The exposed copper deposit is dissolved anodically in a cyanide bath, thereby uncovering the tops of the diamonds which are firmly held in the underlying nickel matrix. The wheel must run absolutely true and new procedures are used to obtain this result handily.

The electroformed nickel or nickel-cobalt alloy must be a low-stress deposit. A dense, tough, hard deposit is necessary to hold the diamonds securely. It also must be a good conductor of electricity and be highly abrasive resistant. Such nickel has been found superior to the standard metal bonds and standard types of impregnation used in standard diamond wheels.

The automatic control of voltage to maintain the maximum current density without causing arcing between the nickel cathode wheel and the work piece has been effected through a rectifier of special design. Its output voltage, usually about 25 volts, is automatically controlled to give maximum voltage and thereby maximum currents at all times for any particular work operation. If too high d-c voltage is delivered to a grinder for a given spacing, sparking and arcing occur. These must be avoided. To accomplish this close control an electronic unit built into the rectifier lowers the voltage as soon as excessive or "hot" sparking occurs. The principle involved is based upon the fact that arcs and sparks produce a superimposed a-c current on top of the d-c current. This a-c current is picked up by the control unit, amplified, and rectified, and the resulting current is then used to reduce the input power to the rectifier by reducing the saturation of reactors in series with the input power line. This action takes place practically instantaneously. The control unit may be adjusted to: eliminate any sparking; allow a certain amount; entirely cut off the d-c voltage; or lower it to any desired level. For most purposes it is adjusted to allow a certain amount of cold sparking and to reduce the voltage only to such an extent that arcs cannot be maintained. The rectifier eliminates the human element in the adjustment of the voltage and also allows the operator to operate at the highest possible current density under any condition. It would be difficult or impossible to do this while manually operating the grinder without the automatic control. Consequently no additional training of personnel is required. The operator maintains only sufficient pressure on the wheel to scuff off the oxides formed in the work.

In electrolytic grinding the metal is removed at the anode substantially in accordance with Faraday's law. Using the described method and equipment it is possible to operate at such current densities that the rate of metal removal is at least no slower than in normal diamond grinding. At one shop electrolytic grinding is doubling the rate of metal removal in one specific job.

Experience to date shows that no stresses or strains are set up by electrolytic grinding in the worked piece. Because of the extremely cool grinding, no hidden cracks have been found, such as are often caused by heat generated if normal grinding is done incorrectly.

Electrolytic grinding produces a matte surface in contrast to the parallel scratches and grooves produced by normal diamond grinding. On the other hand, the matte surface finish consists of minute and slightly oval-shaped mounds. Finishes can be obtained as fine as 4 micro inches providing the diamond wheel is right and is running true.

Electrolytic grinding produces a slightly rounded edge on the part of a tool that is being ground, that is, the very top edge where the electrolyte first hits the tool. The amount of rounding varies with the type of carbide. Where a slightly rounded or chamfered edge is preferred this may not be objectionable.

At present the data indicate that tools shaped by electrolytic grinding have no shorter life than diamond-ground tools.

Experience has been too limited to provide reliable cost data and to determine the sphere of usefulness of electrolytic grinding. However, experience to date indicates that electrolytic grinding probably will effect economies in the grinding of sintered carbides and that the diamond bort shortage may be relieved by a process that will not add to production costs. Super-Cut, however, warned early in October 1952, that "until sufficient reports have been received relative to the merit of electrolytic grinding from all sources so experimenting, conclusions should be questioned."

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Current Affairs

News Notes in the Electrochemical Field

Gordon Research Conferences, June 16-Sept. 4

The Gordon Research Conferences, sponsored by the American Association for the Advancement of Science, for 1953, will be held from June 16 to September 4 at New Hampton School, New Hampton, New Hampshire. The facilities of the school have been made available for the Conferences.

The Gordon Research Conferences were established to stimulate research in universities, research foundations, and industrial laboratories. This purpose is achieved by an informal type of meeting consisting of the scheduled lectures and free discussion groups. Sufficient time is available to stimulate informal discussions among the members of a Conference. Meetings are held in the morning and in the evening, Monday through Friday, with the exception of Friday evening. Afternoons are available for recreation, reading, resting, or participation in discussion groups as the individual desires.

The object of the program is not to review the known fields of chemistry, but primarily to bring experts up to date as to the latest developments, analyze the significance of these developments, and to provoke suggestions as to underlying theories and profitable methods of approach for making new progress. No publications are prepared as emanating from the Conferences.

The morning sessions, Monday through Friday, are scheduled from 9:00 A.M. to 12:00 Noon, Eastern Daylight Saving Time. The second session of each day is held in the evening from 7:30 to 10:00 P.M., Monday through Thursday.

Those interested in attending the Conferences are requested to send in their applications to the Director, on or before May 15, 1953. Each applicant must state the institution or company with which he is connected and the type of work in which he is most interested. Attendance at each Conference is limited to 100. Communications should be addressed to W. George Parks, Director, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island. From June 15 to September 1, 1953, mail should be addressed to Colby Junior College, New London, New Hampshire.

Shown below are the programs for 1953 Chemistry and Physics of Metals Conference, and the Corrosion Conference.

Chemistry and Physics of Metals

July 13—Band Theory, Crystal Structure, and Phases.
July 14—Modification of Bands by Aperiodic Structures.
July 15—Transition Elements.
July 16—Optical Properties.
July 17—Ferromagnetism.

A Critical Review of Modern Fundamental Concepts in Corrosion

July 20—Thermodynamics in Corrosion; Electrochemical Theory of Corrosion.
July 21—Chemical Kinetics in Corrosion; High Temperature Oxidation.
July 22—Reaction Mechanisms: Intergranular Corrosion, Stress Corrosion, Pitting Corrosion, Fretting Corrosion.
July 23—Reaction Mechanisms: Corrosion Fatigue, Thermogalvanic Corrosion; Corrosion in Fused Salts and Molten Metals.
July 24—Corrosion in Non-Electrolytes.

New Nickel-Plating Process Offers Wide Use

The availability of an entirely new process of nickel plating which greatly stretches the available nickel supply, and which "may well prove to be one of the most far-reaching industrial developments since World War II" was announced recently by William J. Stebler, Executive Vice-President of General American Transportation Corporation, Chicago. General American will immediately build two new plants, one in East Chicago, Indiana, and the other in Los Angeles, California, to utilize the new process. These plants are expected to be in operation by the third quarter of 1953. Thereafter, other firms will be licensed to use the process.

The new process, named "Kanigen," requires no electrolytic equipment. It promises marked economies in many applications over customary methods, and makes it possible to plate almost any solid substance with a dependable and predictable thickness of a superior, nonporous plates.

The process, it is claimed, will plate any article uniformly, regardless of size or shape, and has proved satisfactory for the production-line plating of steel, copper, brass, bronze, stainless steel, and aluminum. Tests on plastics and magnesium indicate that these materials will prove practical for "Kanigen" plating.

Because of its greater efficiency, it is said the new process will provide important savings in critical nickel, requiring about $\frac{1}{3}$ to $\frac{1}{2}$ the nickel used with other processes. Reasons given are "Kanigen's" nonporosity, uniform plating, and because it takes 2 or 3 times more nickel to provide the same corrosion resistance with the electroplating process.

General American originally set out to develop a process for the interior coating of tank cars to carry corrosive chemicals and materials which must not be contaminated by "pick-up iron" from the tank car metal. The "Kanigen" process, developed through the reduction of nickel by the use of hypophosphites, resulted. A pilot plant was built in the summer of 1952 and has been in service since.

Since neither design nor size offers any complications to the "Kanigen" process, and because of the hardness of "Kanigen" plate, large vessels, tanks, chemical process equipment, valves, pipe structures, and similar objects can be fabricated of any desirable and easily worked material, assembled, and then given a continuous coating of nickel in whatever thickness is desired. At present this thickness may be controlled when desired to within 1/10,000ths of an inch.

Westinghouse Forms Atomic Equipment Dept.

Westinghouse Electric Corporation, Pittsburgh, has announced plans for a multi-million dollar plant to produce atomic equipment. The plant will be operated by a newly formed department in its Atomic Power Division—the Atomic Equipment Department.

The new facility, which is believed to be the first major enterprise of its kind, will be located in Hamar Township, near Pittsburgh. Purpose of the department will be to engineer, manufacture, and sell products that have been developed for atomic power plants.

Uses Wanted for Gallium—"Wonder Metal"

The "use-wanted" sign is still out for gallium, one of the most unusual performers in the family of metals. The Aluminum Company of America, a major gallium producer, widely publicized its properties more than two years ago; yet only a few minor uses have developed.

To the researcher, the attraction of any rare material, for which no significant use has been found, is great. And, should its properties be unique, its attraction to the laboratory becomes almost magnetic. Gallium is one of these. It melts at about 86°F, but doesn't boil until 3600°F or higher. Like water, it expands upon solidification. It shows marked differences in electrical resistivity and coefficient of thermal expansion along the direction of the three axes of its crystallographic structure. Its electrical resistivity variability is believed greater than for any other metal. It emits electrons at extremely low temperatures. Thus, combining its unique properties, gallium is truly one of the most unusual elements.

Exploiting the properties of gallium has been the problem. Some uses are: In dental alloys for gold restoration work, where it reduces the melting point, increases strength and ductility, and displays other advantages. It has some application as an excitant for phosphors in fluorescent lighting and luminous paint. A patent has been issued for minor use in selenium rectifiers. Gallium chloride is used experimentally as a catalyst for polymerization of vinyl ethers. Radioactive gallium has been used in the diagnosis and treatment of bone cancer. In spyrochete-caused disease it has definite preventive and curative action. The most promising application, though quantitatively minor, is as a liquid seal on the inlet system of mass spectrometers, where its liquid range and low vapor pressure make it superior to mercury in analyzing hydrocarbons with high boiling points.

Despite this list of applications, the pounds of gallium so far used commercially in any year could be counted off on one's fingers—and it is over $1000 a pound.

Many other applications have been attempted or suggested. If there were a market the price could be lower; if the price were lower a market could be found. At any rate, Alcoa still seeks uses for the weird and wonderful enigma of the metallic world.

Armour Research Forms Safety Research Group

Armour Research Foundation of Illinois Institute of Technology, Chicago, has organized a fire protection and safety research group especially for service to Midwest industry.

The objectives of the group are: (1) to prevent fire or explosions from starting; (2) to limit the spread of fire after it has started; (3) to provide for prompt detection of fires; (4) to provide for prompt extinguishment; and (5) to prevent accidents.

Auromet Corp., New Firm Announced

C. B. F. Young and Nathaniel F. Crisera, in cooperation with Victor G. Gottlieb and David Neustadt, have announced the formation of a new company to be known as Auromet Corporation, with offices and laboratory located at 267 Elizabeth Street, New York, N. Y.

Auromet Corporation will manufacture precious metal solutions and salts. The corporation will give particular attention to the electronics field and has developed platinum and palladium solutions which can be used to deposit very thin films of these metals on electronic parts. This will be of interest to electronic engineers engaged in this work. Also emphasized is the refining of scrap metals and solutions.

A complete service will be available by the experienced personnel of the company who were formerly connected with A. Robinson & Son, New York, in the field of electrodepositing gold, silver, platinum, palladium, and rhodium.

Trade Notes

Nuclear-Chicago

Nuclear Instrument & Chemical Corporation, Chicago, will be identified in future advertising and sales promotion as "Nuclear-Chicago," according to an announcement by the president. This step was taken because of the large number of firms having names similar to the corporate title, which has, in some instances, caused confusion among users of the company's products.

Dow Chemical Company

The Dow Chemical Company has entered into a contract with the Lehigh Warehouse & Transportation Company-Elizabeth, operator of public warehouses at Elizabeth, N. J., for the use of a 3¼ million gallon tank storage to be built at Bayonne, N. J. Lehigh expects to start construction about May 1, and most of the facilities are expected to be ready for operation in September.

Norton Company

The New York City domestic sales offices of the Abrasive Division, Grinding Machine Division, and Refractories Division of Norton Company, Worcester, Mass., formerly of 61 Broadway, have moved to Green and North Sts., Teterboro, N. J.

The office of Norton Behr-Manning Overseas Inc., will remain at 61 Broadway, New York, N. Y.

Lindberg Engineering Company

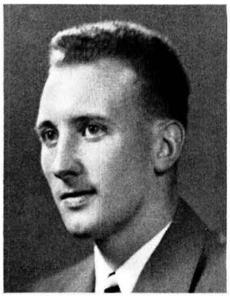
Lindberg Engineering Company of Chicago, Ill., has announced the opening of a new West Coast plant at Downey, Calif.

Hammel-Dahl Company

The Hammel-Dahl Company of Providence, R. I., manufacturers of Automatic Control Equipment, announces the opening of two California offices to be devoted to sales and service of Hammel-Dahl products. The Los Angeles office is at 3715 Santa Fe Avenue and the San Francisco office is at 607 Market Street.

Winners of Cleveland Section Contest

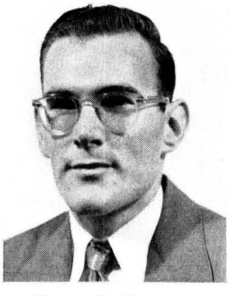
For the second year, the Cleveland Section of The Electrochemical Society sponsored a contest among ten colleges in the Cleveland area, with a view to increasing interest in the study of electrochemistry. The candidates for the contest were nominated by the heads of the chemistry departments of their respective colleges and the winners were chosen on the basis of their scholastic achievements as well as their interest in electrochemistry. Each will receive a one-year Student Associate Membership including a subscription to the JOURNAL of The Electrochemical Society.



NORMAN CRAIG

The awards this year were made to Norman Craig of Oberlin College and Keith Coultrap of the University of Akron, and were presented by G. W. Heise, Chairman of the Contest Committee.

Norman Craig is a senior at Oberlin College with a rating for excellent scholarship in his freshman, sophmore, and junior years. He was elected to Phi Beta Kappa in his junior year. He has been a member of the College Faculty-Student Conference Committee and is president of the senior class. He plans graduate work in physical chemistry and has been awarded graduate assistantships in chemistry at two nationally known universities to which he applied.



KEITH H. COULTRAP

Keith H. Coultrap served in the U. S. Army, Corp of Engineers, after graduation from high school in 1943. He entered the University of Akron in February 1946, and will be graduated with a B.S. degree in chemistry in June 1953. During part of this time he has been employed as a control and laboratory technician and, currently, as a chemist in production and technical control. He is a member of a number of fraternities and was president of Akron Colony in 1952. He is married and has two children.

SECTION NEWS

Chicago Section

"The Chemistry of Semiconductors and Transistors" was the subject discussed by Gordon K. Teal, Director of Materials Research, Texas Instruments, Inc., at the February 6 meeting of the Chicago Section.

Dr. Teal made an excellent presentation of the methods of preparing transistors of various types, discussing in particular detail in the growth of single crystals from molten germanium.

After discussing the characteristics of the various types of transistors, he demonstrated these characteristics on an oscilloscope. In addition to these demonstrations of theory, Dr. Teal showed the audience a transistor oscillator which he obtained on a galvanic cell made from a coin and using saliva as the electrolyte. This oscillator produced a signal which could be heard throughout the meeting room. Another interesting exhibit was a transistor amplifier.

Dr. Teal left his audience most eagerly awaiting the availability of transistors for nondefense application.

R. R. BANKS, *Secretary*

Cleveland Section

The March 10 meeting of the Cleveland Section was "local talent" night. Two speakers were invited to address the gathering: Richard S. Johnson, National Carbon Company, Cleveland, and John M. Finn, Jr., Horizons, Inc., Cleveland, both of whom discussed the investigations which led to their Ph.D. degrees.

Dr. Johnson, speaking on the subject "The Electrical Potential of the Manganese Dioxide Electrode," discussed the factors which determine the potential of the MnO_2 electrode. The application to dry cells was stressed. He showed that pH was not the sole effector in cells but that the activity of the NHy^+ ion is also a factor. Dr. Finn spoke on "The Electrolysis of the Alkali Metal Phosphides in Liquid Ammonia." He discussed the anode reactions of the phosphide anion in liquid ammonia.

The presentation of the Cleveland Section's Student Membership Awards was an added feature of the evening. This is reported in another column of the JOURNAL.

J. M. MARGOLIS, *Secretary*

New York Metropolitan Section

J. N. Mrgudich of the Signal Corps Engineering Laboratory, Fort Monmouth, New Jersey, spoke on the subject "Dry Battery Theory and Practice" at the New York Section meeting on March 4. Copies of the address were distributed and Dr. Mrgudich said he believed that this talk could be the basis for a paper for the Battery Manual, which he hopes the Battery Division may soom compile. A brief summary follows.

Theoretically, the speaker said, any oxidation-reduction reaction might be used to furnish an electric current, but, practically, only a few such reactions have been utilized. The familiar Leclanché cell is the most important commercially and it should be worth while to consider certain facts of its technology which have not been clearly described in the literature. Fundamentally, this cell consists of two electrodes separated by an electrolyte of ammonium and zinc chlorides. The positive electrode is manganese dioxide and the negative is metallic zinc. Zinc in contact with an aqueous solution tends to go into solution with the release of two electrons,

$$Zn \rightarrow Zn^{++} + 2e.$$

This reaction can proceed to the right only if provisions are made to remove both zinc ions and electrons. The solution acts as an electronic insulator, so electrons can move only if an external circuit is closed. Ions move by diffusion through the electrolyte. The magnanese dioxide functions as an absorbent for both electrons and ions,

$$2MnO_2 + 2e + Zn^{++} \rightarrow Mn_2O_3ZnO.$$

Dr. Mrgudich went on to discuss the

function and preparation of the components of the cell and pointed out that the depolarizing mix is the most complex and least understood part. A description of manufacturing and test procedures was given.

In conclusion, the speaker stated that it was the electrochemist's goal to produce electrical power directly from chemical reaction, but one of the problems which must be solved is the manner in which power can be generated at a sufficiently high potential. The silver iodide cell in which a number of cells can be assembled very compactly may point the way to a solution.

KENNETH B. MCCAIN

Niagara Falls Section

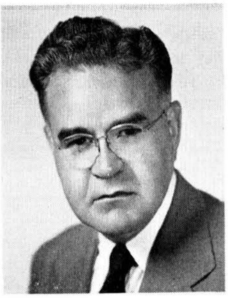
The Niagara Falls Section met on March 11 at the Red Coach Inn, Niagara Falls, New York. Twenty-six members and guests attended the dinner and thirty-five were present at the meeting following.

In a short business meeting the following officers for the 1953–1954 season were unanimously elected:

Chairman—Harry R. Oswald, Oldbury Electrochemical Company
Vice-Chairman—Warren D. Sherrow, Great Lakes Carbon Corporation
Secretary-Treasurer—John E. Currey, Hooker Electrochemical Company

The speaker of the evening was Malcolm F. Judkins, New Products Manager, Firth-Sterling, Inc., Pittsburgh, who spoke on the subject "Electromechanical Machining by Method X." This very interesting method, Mr. Judkins said, uses electrical energy directly for the machining and the "tool," which is a hollow electrode that does not touch the work, can be almost any conducting material and may be much softer mechanically than the material machined. Thus a hole can be drilled in tungsten carbide (Rockwell Hardness C78) with a brass "tool."

The principle of the method, the speaker stated, is in essence the generation between the work and the electrode of a magnetic field of force which exceeds the tensile strength of the work. Thus with a 50-volt power source, a force of 310,000 lb/in.^{2} can be attained. The work is submerged in a dielectric such as kerosense and the kerosene is forced through the hollow electrode. The latter is automatically lowered to provide a constant spacing from the work, and cutting rates of several inches per minute have recently been achieved. Advantages of the method include permitting the machining of very hard materials, of sections too thin or weak for customary methods, and the attainment of very close tolerances. Threaded ⅜-inch blind holes have been machined in tungsten carbide.



MALCOLM F. JUDKINS

The equipment for the work is leased by Firth-Sterling, Inc., and rights have recently been sold to Excell Machine Company, Detroit, Michigan.

Mr. Judkins demonstrated the method with a portable unit, cutting the letter "C" through a ⅛-inch thick piece of tungsten carbide in about five minutes.

MILTON JANES, *Secretary-Treasurer*

Philadelphia Section

The Philadelphia Section held its third meeting of the current season on March 4 in the John Harrison Laboratory of Chemistry of the University of Pennsylvania. Sixty or seventy persons in attendance heard the President of The Electrochemical Society, Dr. J. C. Warner, lecture on the history of theories of electrolytes. Dr. Warner is the president of Carnegie Institute of Technology.

Prior to the meeting, members and guests of the Section had the privilege of meeting Dr. Warner at an enjoyable informal dinner held at the Lenape Club, on the University campus. The occasion also offered a pleasant opportunity for Dr. Warner's old friends in the Philadelphia area to renew acquaintanceships.

Chairman John F. Gall presided at the meeting. Dr. Hiram Lukens reported for the nominating committee, comprising also Dr. Arthur Osol and Mr. Homer Cherry, on the committee choice of candidates for officers of the Philadelphia Section, to be voted on at the May meeting. The committee nominated the following persons, at the same

MANUSCRIPTS AND ABSTRACTS FOR FALL MEETING

Manuscripts are now being received for the Fall Meeting of the Society, to be held at the Ocean Terrace Hotel in Wrightsville Beach, N. C., September 13, 14, 15, 16, and 17, 1953. Subjects to be covered at the technical sessions will be Battery, Corrosion, and Electrodeposition.

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

time mentioning that candidates could be added to this slate by the membership prior to the May meeting:

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

Dr. Hazel reported on the plans for the May meeting of the Section to which the ladies are especially invited. Following the business meeting, Dr. Lukens presented Dr. Warner to the gathering.

Dr. Warner began his talk with comments on the present status of our Society. The Philadelphia Section was very glad to hear that the Society is in a more favorable position than it has been in for the last five or six years.

Dr. Warner next discussed the theories of electrolytic solutions, tracing them from the time when the distinction between electrolytes and nonelectrolytes was first recognized, to the present day. The successes and failures of the Arrhenius theory were outlined. This was followed by reference to the achievements of those who systematically studied the thermodynamic properties and conductance of electrolytes. Finally, the modern theories of Debye, Hückel, Milner, and Onsager to explain the physical properties and conductance of electrolytes were outlined.

Dr. Warner answered questions from the audience. In appreciation to the speaker, the Philadelphia Section closed the meeting with a rising vote of thanks.

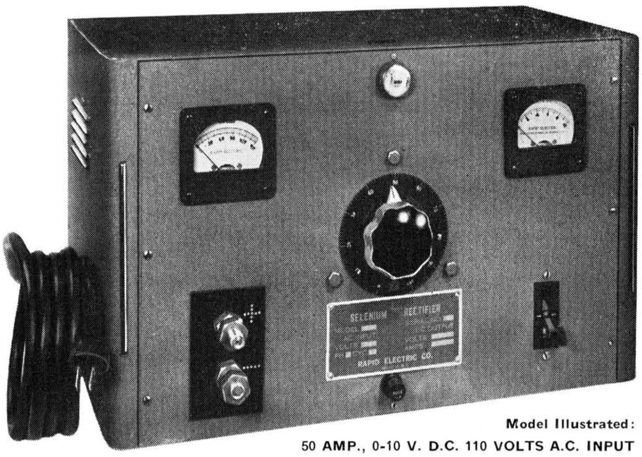
EDGAR L. ECKFELDT, *Secretary*

PERSONALS

RICHARD GLICKSMAN has accepted a position with Radio Corporation of America, RCA Laboratories Division, Princeton, N. J. Mr. Glicksman was formerly a teaching fellow at New York University, New York City.

ANDREW C. HOLM of Shawinigan Chemicals Ltd., Shawinigan Falls, Quebec, was recently appointed a Regional Editor on the JOURNAL for Canada. The current extensive developments in Canada should prove of interest to JOURNAL readers.

ARTHUR A. WINTERBOTTOM has accepted an assignment in Pakistan under the auspices of UNESCO, and will be located at UNESCO T. A. Mission, Department of Metallurgy, University of Dacca, Dacca, East Pakistan. Professor Winterbottom had been at the Metallurgical Institute, Trondheim, Norway.



W. C. Vosburgh, Department of Chemistry, Duke University, Durham, N. C., has been appointed editor of the Battery Division of the Journal, succeeding former Battery Editor N. C. Cahoon.

Lowell A. Woodbury, Department of Physiology, University of Utah, Salt Lake City, has recently joined the Atomic Bomb Casualty Commission.

Michael J. Pryor has left the Division of Applied Chemistry, National Research Laboratories, Ottawa, Canada, to join the Corrosion Laboratories, Division of Metallurgical Research, Kaiser Aluminum & Chemical Corporation, Spokane, Wash.

L. D. Thomas has joined the Libbey-Owens-Ford Glass Company, Toledo, Ohio. Mr. Thomas was previously studying at the University of Michigan, Ann Arbor, Mich.

Allen S. Russell has been appointed chief of the Physical Chemistry Division, Aluminum Research Laboratories, New Kensington, Pa., succeeding Cyril Stead Taylor who retired on March 1. Dr. Allen served as assistant Division Chief since 1946.

John B. Merrill has been appointed to the newly created post of vice-president in charge of Metallurgical and Chemical Operations at Sylvania Electric Products Inc. A vice-president of the company since 1951, Mr. Merrill now has responsibility for Sylvania's Atomic Energy Division, in addition to retaining executive direction of the Tungsten and Chemical Division.

M. Merlub-Sobel has accepted a position as research specialist at Horizons, Incorporated, Cleveland, Ohio. Mr. Merlub-Sobel had been at the Hebrew Institute of Technology, Haifa, Israel, and more recently was located in Jersey City, N. J.

G. G. Crewson, formerly chief engineer, has been named Director of Engineering at Buffalo Electro-Chemical Company, Inc., Buffalo, N. Y.

Mention the Journal

When making purchases from our advertisers, please be sure to mention that you saw the ad in the Journal.

NEW MEMBERS

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

Active Members

John C. Cessna, National Carbon Research Laboratory, mailing add: 1291 Lakeland Ave., Cleveland, Ohio (Corrosion)

S. L. Chawla, Delhi Polytechnic, Applied Science Department, Delhi, India (Industrial Electrolytic)

Harold E. David, D & M Alloy Company, Box 342, Rahway, N. J. (Electrothermic)

Ferdinand P. Heller, American Chemical Paint Company, Ambler, Pa. (Corrosion)

James O. Koehler, National Carbon Company, mailing add: 8314 Deerfield Dr., Parma, Ohio (Electro-Organic)

Clifford M. Tubb, Associated Ethyl Company, Ltd. Oil Sites Rd., Ellesmere Port, Cheshire, England (Industrial Electrolytic)

Robert W. Wollentin, Westinghouse Electric Corporation, Mailing add: 75 Martin St., Bloomfield, N. J. (Electronics)

John F. Yeager, National Carbon Company, 2034 Cornell Road, Cleveland, Ohio (Battery, Electrodeposition, and Theoretical Electrochemistry)

Reinstatement

Andrew C. Holm, Shawinigan Chemicals Limited, P.O. Box 330, Shawinigan Falls, Quebec, Canada (Electrodeposition and Electrothermic)

Associate Member

Baldev K. Sardana, D.C.M. Chemical Works, Post Box 1211, Delhi, India (Industrial Electrolytic)

Student Associate Members

Keith H. Coultrap, University of Akron, mailing add: 1799 Ninth St., Akron, Ohio (Electro-Organic)

Norman C. Craig, Oberlin College, mailing address: 6515 Barnaby St., Washington, D. C. (Theoretical Electrochemistry)

Demetrius N. Triadis, Massachusetts Institute of Technology, Room 8–206, Cambridge, Mass. (Corrosion)

William H. Wade, University of Texas, Brackenridge Hall, Room 125, Austin, Texas (Theoretical Electrochemistry)

ANNOUNCEMENTS FROM PUBLISHERS

Soluble Silicates, 2 volumes, by James G. Vail. American Chemical Society Monograph No. 116. Published by Reinhold Publishing Corporation, New York, 1953. Volume I, 370 pages; Volume II, 600 pages.

This comprehensive work deals with the history, theory, and application of the soluble silicates.

The Design of a Phosphate Smelting Furnace by Harry A. Curtis. Published by the Tennessee Valley Authority, Knoxville, as Chemical Engineering Bulletin No. 1. October 1952.

Principios de Electroquímica. Experimental y Teorica, Spanish translation by Jesus Nicolas of Malcolm Dole's book "Experimental and Theoretical Electrochemistry." Published by Editorial Alhambra, Madrid, Spain, 1952.

1950–51 Journal Electrodepositors' Technical Society, Volume 27. Published by the Institute of Metal Finishing, London, England, 1952.

This volume covers the proceedings of the Institute of Metal Finishing for Session 26.

Vacuum Tube Oscillators by William E. Edson. Published by John Wiley & Sons, Inc., New York, 1953. 476 pages, $7.50.

This book covers every phase of vacuum tube oscillator activity and phenomena and offers the latest information on oscillator design and analysis.

Tungsten—Its Metallurgy, Properties and Applications by Colin J. Smithells. Published by The Chemical Publishing Company, Inc., New York, 1953. 326 pages, plus 74 pages of illustrations, $8.50.

This is a comprehensive volume on the metallurgy, chemical and physical properties, and industrial applications of tungsten.

"Electrochemistry in the Pacific Northwest"

will appear in an early issue of the Journal—one of the series of Regional Features.

NEW PRODUCTS

INEXPENSIVE MICROMANIPULATOR. New micromanipulator of the rack and pinion type for rapid manipulation is available for under $100. Has two inches of travel in three planes; tool holder accommodates small hand vise or special tools, glass tubing, or rods. Handles Benedetti-Pischler techniques requiring precision transfer of small volumes of inorganic compounds. Microchemical Specialties Co. N-1

ULTRASONIC CLEANING. An advanced, practical method of metal cleaning through the use of ultrasonic waves, known as the Detrex Soniclean Process, features a man-made element for directing sound energy. The new element, in place of quartz crystals previously used, overcomes limitations caused by size and properties of quartz. Detrex Corp. N-2

NEW SENSITROL RELAY. New relay of the Sensitrol (magnetic contact) type, Model 723, is sealed against moisture and incorporates a newly designed, self-shielded core magnet mechanism and a built-in solenoid release device. Supplied in a variety of ranges with double magnetic contacts, or with single magnetic contacts to make contact on either increasing or decreasing values. Sensitivities as high as 2-0-2 microamperes are available, and both a-c and d-c voltage ranges can be supplied self-contained up to 500 volts, the company says. Weston Electrical Instrument Corp. N-3

ELECTRONIC LIQUID LEVEL CONTROL. The new Belmont Level Control provides adjustment of liquid level and cut-in, cut-out differential over very wide limits, based on capacitive action of liquid surrounding a porcelain-enamel-covered-electrode. In operation, the new unit consists of the probe, mounted directly at the location of the controlled liquid, a connecting cable which can be 1000 feet long if necessary, and the control unit which can thus be located for operating convenience. Thermo Instruments Co. N-4

TUNGSTEN ALLOY FOR INERT GAS WELDING. A new tungsten zirconium alloy arc-welding rod that saves time and expense on inert gas welding jobs has been announced. Called Zirtung, the new electrode features less contamination pickup on touch starting, continued steady arc, and longer working life. Ideal for use on all metals, particularly mild steel, aluminum, and magnesium. Sylvania Electric Products Inc. N-5

NEW ROSIN CORE SOLDER. A new rosin core solder, active yet noncorrosive, has recently been developed. Known as RTS 200, it has been proved in production operations to have many advantages over ordinary rosin solders; 30% greater spread, pierces retarding agents four times faster, the flux is just as active after standing for long periods. Federated Metals Division, American Smelting and Refining Co. N-6

VOLTAGE REGULATED POWER SUPPLY. The new Kepco Model #1520 features a regulated high voltage d-c power supply with excellent regulation, low ripple content, and low output impedance. The high voltage supply is continuously variable from 0–1500 volts and delivers from 0–200 milliamperes. Ripple voltage is less than 30 millivolts peak to peak. Kepco Laboratories, Inc. N-7

LITERATURE FROM INDUSTRY

ELECTRONIC WATTMETER. New 2-page bulletin describes Keithley Model 110 Electronic Wattmeter. Includes complete specifications and full description of features, which include a range of 0.3 to 9000 watts, 20 to 3000 cps response, unusual convenience and accuracy in measuring low impedance devices. Keithley Instruments. P-130

HANDBOOK FOR CHEMISTRY ASSISTANTS is a unique 32-page manual prepared and published by the Division of Chemical Education of the American Chemical Society. Designed for use by graduate and undergraduate student

Members: Please Check Your Code Numbers

Code numbers appear at the right of your name and address on mail from the Society office. For instance, $\overset{1}{\underset{B}{6}}$ means Active Member, New York Section, Corrosion Division.

A complete explanation of the code is printed below. In order to keep the records up to date, members are kindly requested to check the code numbers on recent mail from the Society and, if incorrect, please send the corrected code number to The Electrochemical Society, Inc., 235 West 102nd Street, New York 25, N. Y.

Membership Classifications

1 Active Member
2 Honorary
3 Sustaining
4 Associate Member
5 Student Associate
6 Subscriber

SECTIONS

No. *City*

1 Chicago
2 Cleveland
3 Detroit
4 India
5 Midland
6 New York
7 Niagara Falls
8 Pacific Northwest
9 Philadelphia
10 Pittsburgh
11 San Francisco
12 Washington-Baltimore
— No Section

Division Classification

A Battery
B Corrosion
C Electric Insulation
D Electrodeposition
E Electronics
F Electro-Organic
G Electrothermic
H Industrial Electrolytic
I Theoretical Electrochemistry

assistants; easy-to-read chapters on Conducting A Recitation Period; Conducting A Laboratory Period; Quizzes, Tests, Reports, etc. Fisher Scientific Co., Educational Service Dept. P-131

Vacuum Tube Electrometers are described in a new 8-page bulletin. Nineteen application diagrams are included, plus a full description of accessories, which permit measuring a wide range of d-c voltages, currents as low as 10^{-14} ampere, resistance to 10^{16} ohms. Keithley Instruments. P-132

Corrosion-Proof Structural Plastic. Complete engineering facts, including information on fabrication and design factors, physical strength and chemical resistance of unplasticized, rigid polyvinyl chloride Ampcoflex are provided in new illustrated bulletin. Includes chart showing resistance characteristics and detailed tabulation of physical properties. Atlas Mineral Products Co. P-133

Photoelectric Recorder Applications. Fully illustrated 12-page publication describes applications of the recorder with seismology, psychology, textile, metals, fatigue and research testing equipment, as an aid in the quick detection of pipeline corrosion, and in development and machinability testing, medical research, light-intensity study, etc. General Electric Co. P-134

To receive further information on any New Product or Literature from Industry listed above, send inquiry, with key number, to Journal of The Electrochemical Society, 235 West 102nd Street, New York 25, N. Y.

Please print your name and address plainly.

RECENT PATENTS

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

November 25, 1952

Aukerman, N. B., Ingram, S. A., executrix of said Aukerman, N. B., deceased, 2,619,456, Metal Recovery Apparatus

Wagner, F. W., 2,619,457, Electroplating Anode

ADVERTISERS' INDEX

January 27, 1953

Smith, A. W., 2,626,620, Regulator Responsive to the Electrical Conductivity of a Solution

Balke, C. W., 2,626,895, Electrolytic Production of Iron

Hunrath, G., 2,626,970, Thermoelectric Couple and Method of Making Same

FUTURE MEETINGS OF The Electrochemical Society

* * *

Wrightsville Beach, N. C., September 13, 14, 15, 16, and 17, 1953

Headquarters at the Ocean Terrace Hotel

Sessions on

Battery, Corrossion, Electrodeposition

* * *

Chicago, May 2, 3, 4, 5, and 6, 1954

Headquarters at the La Salle Hotel

Highlights of the Board of Directors' Meeting

(Held January 30, 1953)

For the first time in several years, the Society operated in the black during the year 1952. The audit indicates an excess of income over expenditures of $2,460.72, as shown in the Auditor's Report below.

The budget for the year 1953 was approved. In this budget the amount of $26,000 was approved for printing and mailing of the JOURNAL. This is a $2,000 increase over the previous year. The estimated income from advertising, $11,878, was that amount of advertising contracted for by January 30. A provision was made whereby the budget for the printing and mailing of the JOURNAL would be automatically increased 50 per cent of any additional advertising income. The remaining 50 per cent would go to building up Society reserves. It is interesting to note that the budget, as approved for 1953, anticipates an excess of income over expenditures of $383, while the budget for 1952, as revised in June 1952, indicated a deficit of $1,130, whereas the audit shows that we operated well in the black. Therefore, it is a much more optomistic financial picture that we are now presenting.

It was decided that, in order to make the business affairs of the Society more readily available to the local sections, copies of the minutes of the meetings would be distributed to the chairmen and secretary-treasurers of each local section.

The future meetings of the Society were discussed, and these are scheduled as follows:

New York—Spring 1953
Wrightsville Beach—Fall 1953
Chicago—Spring 1954
Boston—Fall 1954
Cincinnati—Spring 1955
Pittsburgh—Fall 1955
San Francisco—Spring 1956

HENRY B. LINFORD, *Secretary*

Auditor's Report

BALANCE SHEET

December 31, 1952

Assets		
Furniture and Office Equipment	$ 4,274.03	
Cash	14,823.31	(a)
U. S. Savings Bonds (Cost)	28,860.00	(b)
Inventory-Bound Volumes	2,691.60	
Accrued Income on Investments	5,226.00	
Accounts Receivable	184.50	
	$56,059.44	
Liabilities, Reserves and Surplus		
Accounts Payable—Suppliers	$ 4,918.12	
Taxes Withheld From Salaries	520.50	
Life Memberships	1,443.50	
Prepaid Sustaining Memberships	800.00	
Prepaid Subscriptions	4,367.20	
Reserve for Depreciation	625.79	
Deferred Income (India Section)	.70	
Surplus	43,383.63	
	$56,059.44	

(a) Includes $3,265.63 Corrosion Division funds.
(b) Includes $10,471.37 Corrosion Division funds.

CASH STATEMENT

January 1 to December 31, 1952

National City Bank		
Book balance December 31, 1951		$8,401.81
Receipts—1952 (Gross)	$77,182.82	
Disbursements—1952 (Gross)	76,389.43	
Excess receipts over disbursements		793.39
Book balance December 31, 1952		9,195.20
New York Savings Bank		
Book balance December 31, 1951		1,918.68
Interest 1952		50.93
Transferred from National City Bank	1,787.40	
Transferred to National City Bank	491.38	
Excess of transfers in		1,296.02
Book balance December 31, 1952		3,265.63
Corn Exchange Bank Trust Company		
Book balance December 31, 1951		2,117.65
Receipts—1952 (Gross)	35,476.04	
Disbursements—1952 (Gross)	35,279.44	
Excess receipts over disbursements		196.60
Book balance December 31, 1952		2,314.25
Cash on hand—Agent—December 31, 1952		48.23
Total		$14,823.31
Total accounted for as follows:		
National City Bank per bank statement		9,195.20
New York Savings Bank per bank statement		3,265.63
Corn Exchange Bank per bank statement	2,858.61	
Less outstanding checks	544.36	2,314.25
Cash on hand—Agent		48.23
Total, as above		$14,823.31

ANALYSIS OF EXPENDITURES

January 1 to December 31, 1952

Furniture and Office Equipment		$ 47.54
Publication Department		
General Expenses		
Salaries, full-time employees	$10,800.50	
Wages, part-time employees	64.00	
Rent	810.00	
Stationery and supplies	635.84	
Postage and express	650.36	
Traveling	197.86	
Miscellaneous office expenses	593.42	13,751.98

Publication Expenses		
Journal	27,057.59	
Reprints	2,114.35	29,171.94
Secretary's Department		
Salaries, full-time employees	16,114.91	
Wages, part-time employees	303.50	
Rent	810.00	
Stationery and supplies	831.23	
Postage and express	1,129.97	
Traveling	512.62	
Miscellaneous office expenses	590.90	
Audit	175.00	
Prizes	100.00	
Local Sections:		
Philadelphia	131.50	
Cleveland	129.00	
N. Y. Metropolitan	256.00	
Midland	68.00	
India	136.50	
Wash.-Baltimore	24.00	
Pittsburgh	50.00	
Publication Committee	185.71	
Corrosion Division	491.38	
Conventions	1,482.82	
Emblems	45.34	
Advertising	4,532.21	
Sale of Publications	208.65	
Surplus (1951 and 1952 Faraday)	2,096.84	30,406.08
		$73,377.54

ANALYSIS OF INCOME

January 1 to December 31, 1952

Dues:	
1948	$ 6.00
1949	10.00
1950	6.00
1951	205.00
1952	9,177.33
1953	18,527.89
Volumes:	
1952	18.00
1953	1,494.10
Publications	2,343.39
Nonmember subscriptions—Journal	14,280.78
Advertising	9,966.99
Conventions	2,691.86
Preprints	132.10
Reprints	2,731.86
Emblems	95.00
Thompson Monograph	21.10
Membership Directory	225.50
Sustaining Memberships	8,150.00
Bank Interest	50.93
Cathodic Protection	385.55
Canadian Convention Fund	1,135.40
Modern Electroplating	476.05
Journal	1,920.03
Corrosion Division	1,787.40
	75,838.26
Excess income over expenditures	$ 2,460.72

Accounted for as follows:

Surplus (increase)	$ 2,508.26
Less: Furniture and office equipment	47.54
	$ 2,460.72

(Signed) H. K. LEICHT, Auditor

PROPOSED BUDGET FOR 1953

	Income	
	Estimated Income 1953	Revised (June, 1952) Budget for 1952
Membership Dues	$33,000	$26,000
Sustaining Memberships	9,000	7,500
Sale of Publications		
Back Transactions & Journals	2,000	2,000
Reprints & Preprints	2,500	3,000
Non-member Journal subsciption	15,000	12,000
Office Sale of Journal	1,500	800
Modern Electroplating	50	400
Royalties Cathodic Protection	100	400
Convention Registration	2,000	1,500
Advertising	11,878*	10,000
Total Income	$77,028	$63,600

	Expenditures	
	Estimated Expenditures 1953	Revised (June, 1952) Budget for 1952
Printing and Mailing Journal	$26,000*	$24,000
Reprints	2,000	2,500
Publication Commission	250	250
Adv. Commission	5,200*	730
A.B.C. Rating	300	—
Salaries	33,000	27,600
Rent	1,620	1,620
Postage, Supplies & Misc	4,800	4,500
Travel	700	750
Auditor	175	180
Loc. Sec. & Div	1,000	1,000
Prize to Young Authors	100	100
Program Booklets, etc	1,500	1,500
Total Expenditures	$76,645	$64,730
Total Income	77,028	63,600
Excess Income over Expenditures	$ 383	$ 1,130

* Advertising income is estimated at $11,128. This represents actual contracts in hand to date. There is good expectancy that this item will increase markedly during the year. Since advertising agent's commission is on the basis of a minimum $5,200, this figure will remain fixed until such time as the item of advertising listed under Income reaches $20,800, at which time our representative will receive 25% of our income from advertising. Therefore, it must be considered automatic that our item of $5,200 will be the minimum. The maximum will be based on the ultimate advertising income in case the income exceeds $20,800. The proposed budget indicates an excess of income over expenditures of $383. Further advertising income above $12,000 will automatically increase the printing and mailing of the Journal budget by 50% of any additional advertising income.

2 New Developments in Precious Metal Plating

Let's talk about silver first and for silver we offer two variations

a) Mirror-Bright Silver deposits from Ronal Bright Silver Process—Na

b) Semi-Bright Silver deposits from Ronal Bright Silver Process—K

Both Silver Processes produce deposits that can be plated from clear, colorless solutions . . . at high current density (Hull cell 5 - 40 amps/sq. ft.) . . . with easy solution control . . . and without brightener breakdown. In addition to brilliance, the silver deposits obtained from Na and K silver baths are soft and ductile and have superior tarnish resistance.

As for gold, we offer the following processes; each outstandingly effective where heavy gold deposits are required.

RONAL BRIGHT GOLD "A"

For Decorative and Similar Appeals in field of Consumer Merchandise . . . in alloy and colored deposits (pink, yellow, Hamilton) . . . producing brilliant, mirror-bright deposits directly from the bath; with no subsequent buffing or coloring required; builds brightness equivalent to bright nickel.

RONAL BRIGHT GOLD "S"

For Technical and Industrial Precision Plating . . . provides smooth bright ductile deposit.

Both Ronal Bright Silver and Ronal Bright Gold Processes are simple to operate. To the best of our knowledge Ronal Bright Gold Processes are the only ones on the market that have been processed and production tested for over two years in actual plant operations.

If when planning on either of these two processes you have any questions, our technical staff will be glad to answer them. We shall, of course, be glad to provide complete details of the processes.

* Lea Silver Glo and Lea Golden Glo are marketed nationally by The Lea Mfg. Co., Waterbury, Conn. They are the trade names for the Ronal Bright Silver and Ronal Bright Gold Processes.

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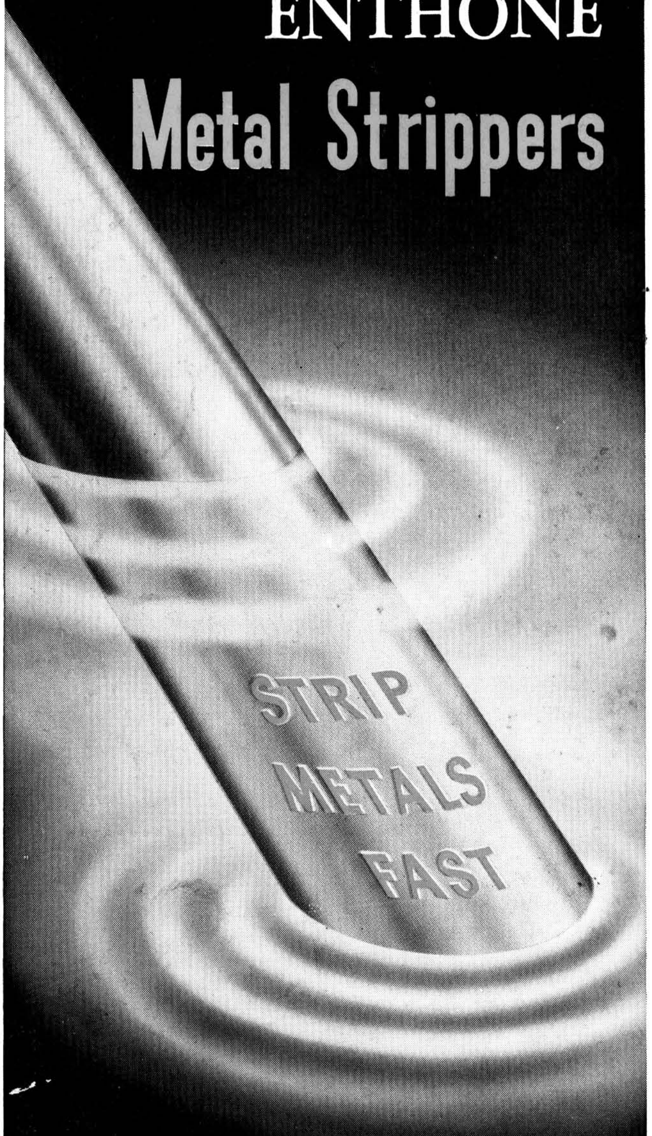
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