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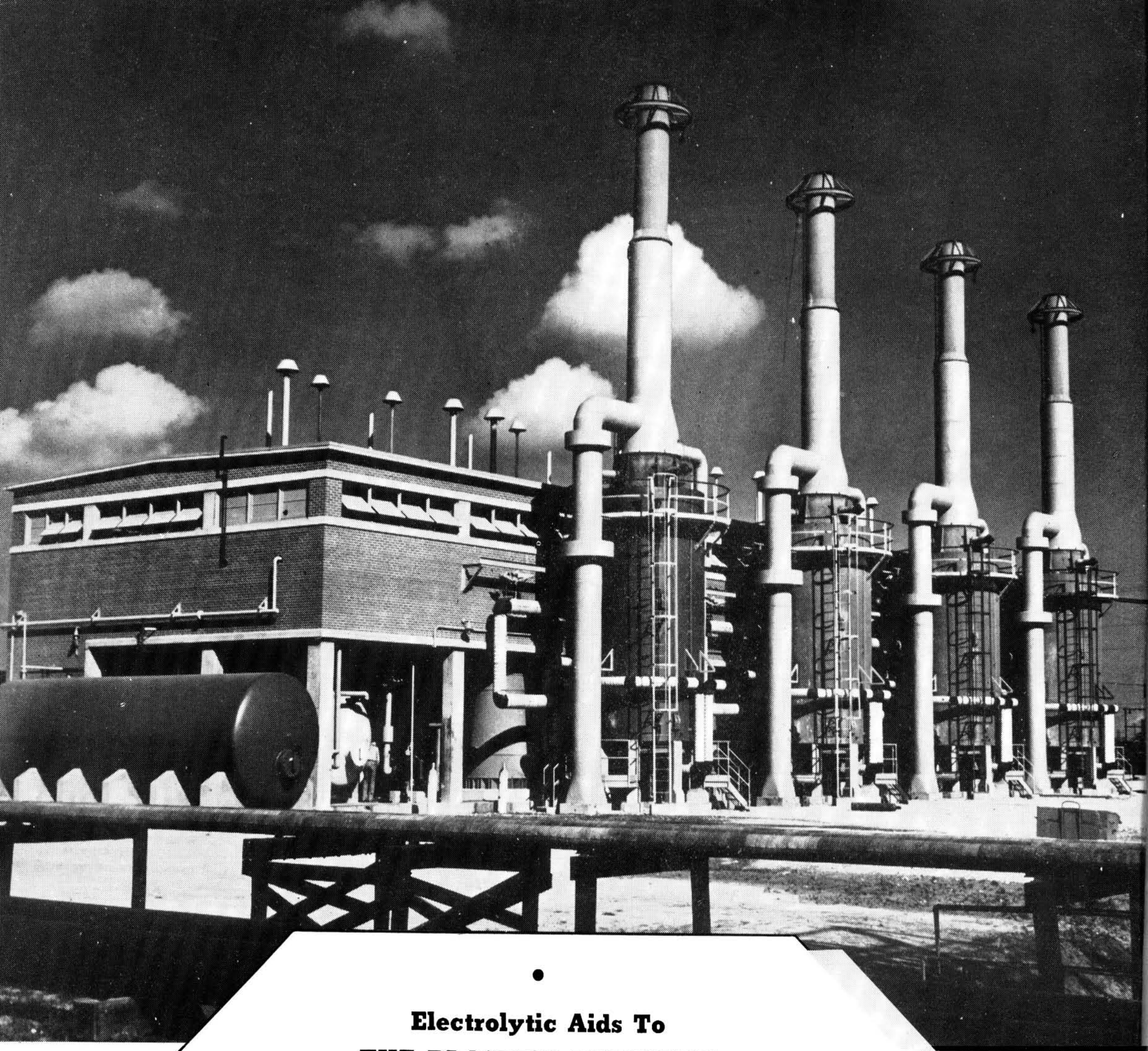
ELECTROCHEMICAL INDUSTRY

The Chemical Shore



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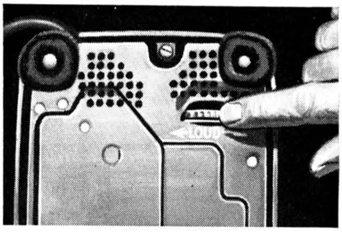
It adds miles to your voice

New "500" telephone. It has already been introduced on a limited scale and will be put in use as opportunity permits, in places where it can serve best. Note new dial and 25 per cent lighter handset.



Adjustable volume control on bottom of new telephone permits subscriber to set it to ring as loudly or softly as he pleases. Ring is pleasant and harmonious, yet stands out clearer.

For years the telephone you know and use has done its job well—and still does. But as America grows, more people are settling in suburban areas. Telephone lines must be longer; more voice energy is needed to span the extra miles.

Engineers at Bell Telephone Laboratories have developed a new telephone which can deliver a voice ten times more powerfully than before. Outlying points may now be served without the installation of extra-heavy wires or special batteries on subscribers' premises. For shorter distances, the job can be done with thinner wires than before. Thus thousands of tons of copper and other strategic materials are being conserved.

The new telephone shows once again how Bell Telephone Laboratories keeps making telephony better while the cost stays low.

QUICK FACTS ON NEW TELEPHONE

Transmitter is much more powerful, due largely to increased sound pressure at the diaphragm and more efficient use of the carbon granules that turn sound waves into electrical impulses.

Light ring armature diaphragm receiver produces three times as much acoustic energy for the same input power. It transmits more of the high frequencies.

Improved dial mechanism can send pulses over greater distances to operate switches in dial exchange.

Built-in varistors equalize current, so voices don't get too loud close to telephone exchange.

Despite increased sensitivity of receiver, "clicks" are subdued by copper oxide varistor which chops off peaks of current surges.

BELL TELEPHONE LABORATORIES

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

Editorial

Productive Professional Activity

THE *INDUSTRIAL* activity in the Cleveland area, as detailed elsewhere in this issue, is evidence of the important part played by the scientist and engineer in our present economy. Yet there is grave concern in many quarters over the inadequacy of our present supply of technical personnel and the failure of our schools to furnish enough graduates to meet current needs, either in pure or applied science.

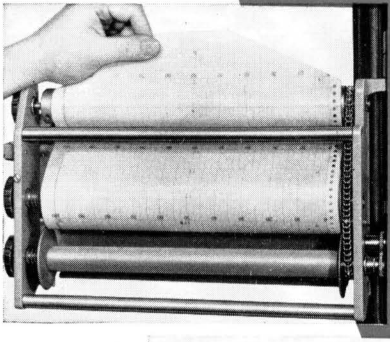
In the U. S. A. the present demand for graduates in engineering alone, we are told, is 30,000 per year and sharply rising. The supply, on the other hand, has now dropped from a peak of approximately 50,000 per year in 1949–50 to a level of 20,000, and is still declining. Perhaps some 4000 will graduate this year in chemical engineering, but of these only a very few will have had specialized training in electrochemistry. Undoubtedly an increase in our educational effort, in pure as well as in applied science, is needed to maintain our present rate of technological progress.

Nevertheless, it would be well to consider to what extent our present difficulty is due to inefficient utilization of our technical resources rather than to extreme shortages of adequately trained personnel. Many of our technical graduates—estimates run as high as 50 per cent—are not immediately available for professional employment, chiefly because of military service requirements. Although this tends to aggravate the immediate shortage, a permanent loss to the profession is not involved. More serious, and perhaps equally difficult to avoid, is the waste of man-power due to duplication in government and academic work and in industrial competitive effort.

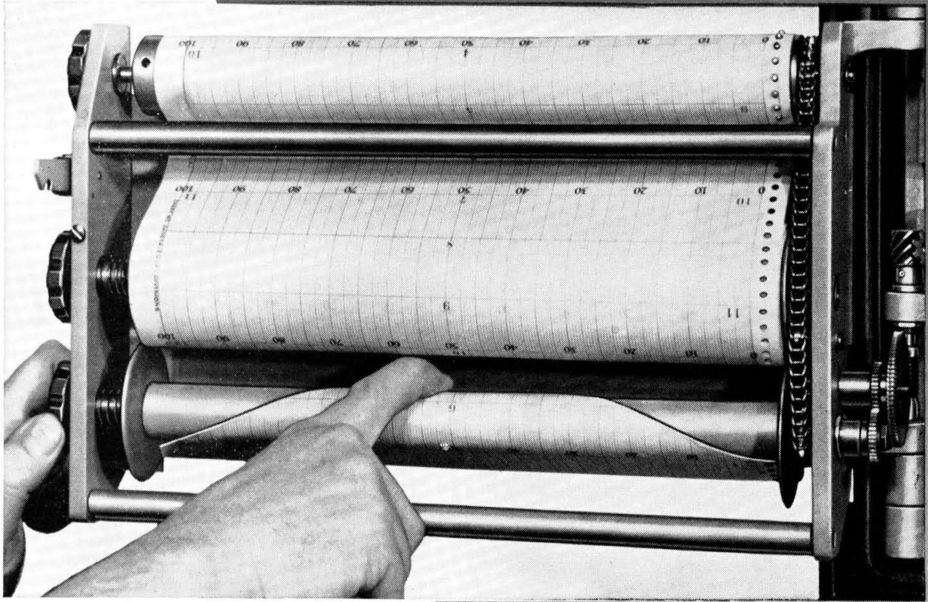
Perhaps the greatest gains might accrue from efforts to reduce to a minimum the diversion of scientists and engineers to other than technical work in their fields of specialization. Less than ten per cent of our chemical engineers are reported as engaged in the work of design, construction, and installation. The records of engineering societies indicate that more than thirty per cent of their members are in executive or administrative positions. Employment prospectuses emphasize the opportunities for advancement in terms of promotion in the corporate organizations; technical schools point with pride to their illustrious alumni who have become business executives; far too often even the young graduate considers his profession as a steppingstone to material success rather than as a career in itself.

No doubt greater recognition of technical achievement will be required to attract and hold career men. Meanwhile, it is the problem of the employer, the school, and of the technical man himself to demonstrate the possibility of achieving a successful and intellectually satisfying career without departure from the level of productive professional activity. Perhaps it is in this direction, as well as in the promotion of electrochemical education, that the Society can exert its influence to advantage.

—G.W.H.



You install charts this simple way!

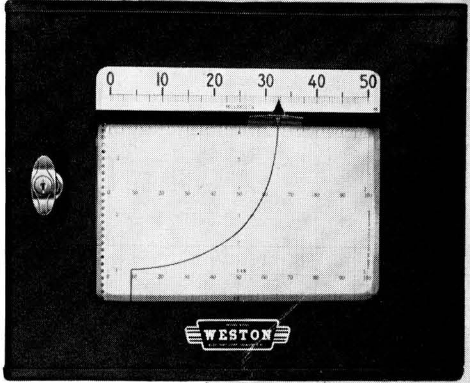


NEW Simplified Recording Potentiometer by WESTON!

Chart changing is a simple 1-2 operation on the Weston Recording Potentiometer. First, note that the chart frame has swung wide open . . . *a full 180°* . . . for complete accessibility. You then insert the chart supply in the frame, draw the chart over the timing drum and down across the front of the frame as illustrated. There are no loose pieces to handle . . . and the whole operation takes but a few seconds!

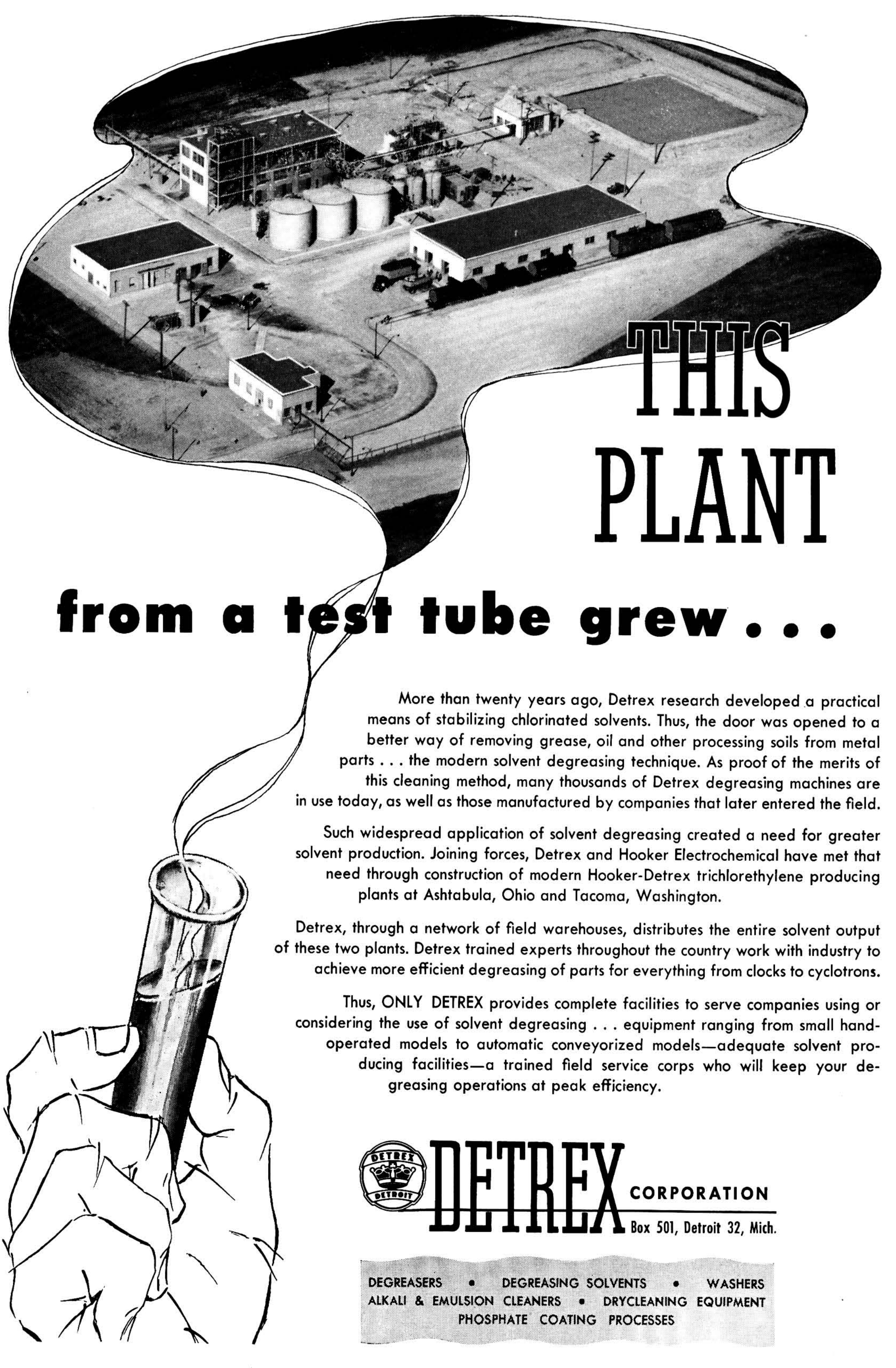
And there are many more features that make this the simplest, most flexible and efficient recorder available. You change chart speeds, for example, by a simple screwdriver adjustment. You change ranges by simply inserting the desired range standard. To service the amplifier, you quickly remove it by taking out two screws and pulling two plugs.

The whole story about this simple and dependable high-speed recorder is available in booklet form. Ask your local Weston representative or write . . . WESTON Electrical Instrument Corp., 617 Frelinghuysen Ave., Newark 5, New Jersey.



WESTON TAG 1628

WESTON *Instruments* . . . INDICATE—RECORD—CONTROL



THIS PLANT

from a test tube grew . . .

More than twenty years ago, Detrex research developed a practical means of stabilizing chlorinated solvents. Thus, the door was opened to a better way of removing grease, oil and other processing soils from metal parts . . . the modern solvent degreasing technique. As proof of the merits of this cleaning method, many thousands of Detrex degreasing machines are in use today, as well as those manufactured by companies that later entered the field.

Such widespread application of solvent degreasing created a need for greater solvent production. Joining forces, Detrex and Hooker Electrochemical have met that need through construction of modern Hooker-Detrex trichlorethylene producing plants at Ashtabula, Ohio and Tacoma, Washington.

Detrex, through a network of field warehouses, distributes the entire solvent output of these two plants. Detrex trained experts throughout the country work with industry to achieve more efficient degreasing of parts for everything from clocks to cyclotrons.

Thus, ONLY DETREX provides complete facilities to serve companies using or considering the use of solvent degreasing . . . equipment ranging from small hand-operated models to automatic conveyorized models—adequate solvent producing facilities—a trained field service corps who will keep your degreasing operations at peak efficiency.

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Box 501, Detroit 32, Mich.

DEGREASERS • DEGREASING SOLVENTS • WASHERS
ALKALI & EMULSION CLEANERS • DRYCLEANING EQUIPMENT
PHOSPHATE COATING PROCESSES

THE CHEMICAL SHORE

. . . product of a giant chain reaction in the Cleveland-Northeast Ohio area

Robert C. Hienton

We don't know who coined the name. It just seemed to "happen." But once introduced, it spread through the chemical industry like wildfire.

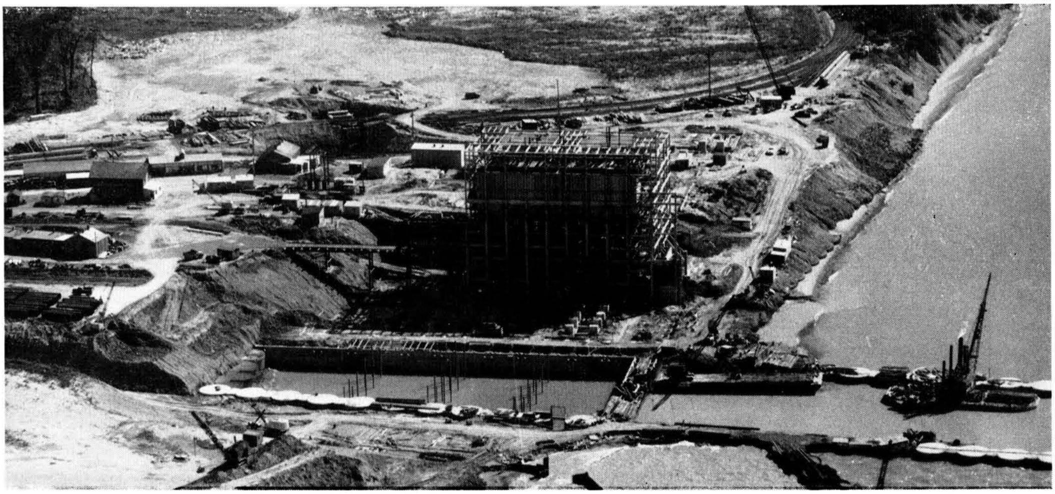
Everyone suddenly knew of The Chemical Shore, the 30-mile stretch of Lake Erie shoreline between Fairport and Ashtabula in Northeast Ohio. Since V-J Day, it has become one of the world's great chemical centers. To understand why The Shore has grown with such whopping strides, let's look first at the entire Cleveland-Northeast Ohio region, or as we call it, "The Best Location in the Nation." It extends for 100 miles along the southern shore of Lake Erie from the Ohio-Pennsylvania line to the village of Avon Lake, 20 miles west of Cleveland.

The nerve center of this 1700-square mile area is Cleveland—seventh largest city in the United States and one of the nation's busiest and fastest growing metropolitan areas. The area's tremendous productivity depends upon many things—its natural resources, its manpower, its markets, its transportation network—but most of all, the area runs on electric power. As supplier of that power, The Cleveland Electric Illuminating Company has a deep interest in the area's development. We sincerely believe it is the "best location" for many firms and we consider the electrochemical industry one of our blue-chip growth industries.

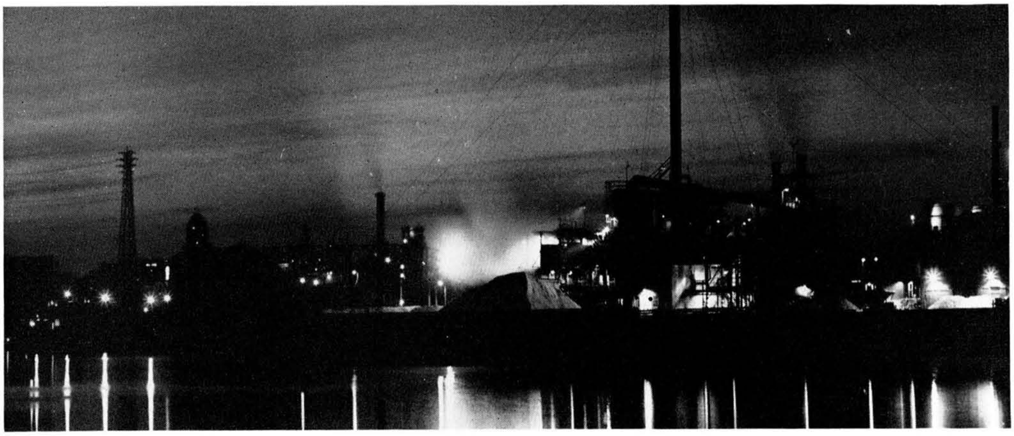
During the past seven years, American industry has committed more than *$1.5 billion* for widely diversified expansion in Cleveland-Northeast Ohio. This is more than three per cent of the nation's total, yet the region contains only one per cent of the nation's population. The steel industry has just completed a 50 per cent expansion in productive capacity. Cleveland today makes eight to ten per cent of all American-made steel strip, sheet, and plate. Approximately 8 per cent of the nation's wire drawing is done in Cleveland. There are now

ROBERT C. HIENTON

Manager of Marketing,
The Cleveland Electric
Illuminating Company,
Cleveland, Ohio



The Eastlake power plant of The Cleveland Electric Illuminating Company will be one of the world's largest, with an ultimate capacity of one million kilowatts. When finished, the plant will cost more than $100 million.



The Cleveland Works of the Du Pont Company's Grasselli Chemicals Department silhouetted against the sky, with the sulfuric acid unit making a background for the illuminated sulfur pile.

3500 manufacturing companies here. Brief as that over-all picture is, it will give some idea of this area's vast industrial expansion during the last seven years.

Of the \$1½ billion invested in the area since the end of World War II, the chemical industry has accounted for more than \$235 million, or 15.3 per cent of the total. More than half of this amount has been declared since the outbreak of the Korean war. This huge investment by the top names in the industry has set off a giant chain reaction.

When producers of basic chemical supplies, such as Diamond Alkali and the Electro-Metallurgical Division of Union Carbide and Carbon Corporation, built multimillion dollar plants in the Cleveland-Northeast Ohio area, satellite industries moved in quickly to process the output of the basic chemical producers.

Raw Materials

The trigger for this giant chain reaction is the area itself. It is rich in the natural resources which the chemical industry requires.

Salt.—Along the Lake Erie shore, at an average depth of 2000 feet, are from 150,000 to 200,000 tons of rock salt per acre. Natural brines of magnesium and bromine are found both above and below the salt stratum. This huge resource is all the more valuable because of the unlimited supply of raw water nearby.

Water.—In Lake Erie, chemical producers have an unlimited supply of raw water for processing and plant uses. The lake is one of the few remaining sources of good quality water which can be obtained at an economical cost. The average water temperature is 51.5°F with a minimum of 33°F in the winter months. During July and August, the probable maximum is 80°F, depending upon the depth at which water is taken from the lake. Readings of lake water temperatures indicate stratification of water in the lake, especially during the summer months. Evidence indicates that it will be possible to get an unlimited supply of extremely cool water by running a submerged intake out to a 50-foot depth in the lake. This is of major importance during the summer months when cooler water can reduce, to a considerable degree, the number of condensers needed.

One of the key factors in the decision of the National Distillers Chemical Corporation to build in The Illuminating Company's service area was that ultimately National Distillers may need *more than 10 million gallons of water per day.* The chemical analysis of Lake Erie is as follows:

	Parts per million
Alkalinity (in terms of $CaCO_3$)	85.0
Permanent hardness (in terms of $CaCO_2$)	29.0
Total hardness	114.0
Calcium (Ca)	34.1
Magnesium (Mg)	8.6
Iron (Fe)	0.24
Silica (SiO_2)	3.1
Carbon dioxide (CO_2) free	3.1
Hydrogen ion concentration, *p*H	7.5

Silica.—The supply of silica in Northeast Ohio is virtually inexhaustible. Most of this vast deposit (estimated at 100 million tons) is in Geauga County, which is southeast of Cleveland. The deposit was left there by two prehistoric glacial systems. Mining operations are carried on in the county at Thompson and Chardon.

Limestone.—Limestone is readily available to chemical producers from the upper lakes and is delivered by lake carriers at low rates. Diamond Alkali brings in about 1½ million tons of limestone every year. Dolmitic limestones are obtained from the northwestern part of Ohio. At one time, the Ohio counties of Sandusky and Seneca produced more dead burned dolomite than all the rest of the United States combined.

Coal.—Coal for fuel and processing is available from 17 major coal beds within overnight hauling distance.

Oil.—Millions of barrels of oil are known to be in reserve in Ohio. More than half of this reserve is top grade Pennsylvania crude.

Soybeans.—Ohio has over a million acres of soybeans under cultivation.

Electric Power

The heart of any industry, and especially the electrochemical industry, is electric power.

For every two to three dollars spent on electrochemical facilities it may be figured that one dollar must be spent to enlarge power supply facilities. And the electrochemical industry grows almost unbelievably fast. Many segments of the industry grow at a cumulative rate of eight to nine per cent per year.

To keep well ahead of industry's needs for electric power, The Cleveland Electric Illuminating Company is continuing a vast power expansion program which has been the largest—both from dollars invested and the number of people affected—of any company in the area.

Total investment in plant and property now exceeds $315 million. Investment in new facilities is speeding along at $2½ million a month. The Avon power plant now generates 420,000 kw. The Ashtabula power plant at the eastern end of the service area has a capacity of 240,000 kw. The Lake Shore power plant located in Cleveland has a generating capacity of 484,000 kw. All three plants are interconnected.

A fourth power station, at Eastlake, 20 miles east of Cleveland at the mouth of the Chagrin River is now being completed. Two 125,000-kw turbogenerators will go "on the line" next year, and a third 125,000-kw unit will be installed early in 1954. The fourth generator, a 208,000-kw unit, will be available for service by 1956. When the first section of the new plant is in operation, The Illuminating Company's total power capacity will be 1½ million kw—nearly double the system capacity of three years ago.

Markets

While electric power is the heart of the electrochemical industry, the continued growth of the industry depends upon chemical product markets. A chemical plant located in the Cleveland-Northeast Ohio area is in the heart of one of the largest, fastest-growing, and most diversified markets in America.

Metal fabricating industries.—As the steel and other metal fabricating industries expand, the demand for chemicals expands. Today production and fabrication of ferrous and nonferrous metals employ 75 per cent of the people working in Cleveland industry. This area's steel-making capacity is being expanded by 50 per cent, which is almost *three times* the present national rate of increase. As stated earlier in this article, Cleveland now produces eight to ten per cent of all American-made steel strip, sheet, and plate. Total cost of new steel-making capacity being added in the area will exceed $150 million, increasing Northeast Ohio's steel output 50 per cent. Republic Steel is currently putting $100 million back into this area with a huge expansion program which will build the world's largest strip mill, a 1400-ton blast furnace, and four open-hearth furnaces with a combined output of 1000 tons of steel per heat.

Paint manufacturers.—This area has frequently been called "the paint capital of the world." Almost 100 manufacturers of paints, varnish, and lacquer are located here, including: The Sherwin-Williams Company, The Glidden Company, The Patterson-Sargent Company, Arco Manufacturing Company, Ferbert Schorndorfer Company, and Forbes Finishes Division of Pittsburgh Plate Glass Company.

Rayon.—Two rayon producing plants are in the area.

Paper.—The area has two mills making paper, pulp, and paperboard. One is the Jaite Paper Company in Jaite, the other is the Chase Bag Company in Chagrin Falls. Thirty-three others are located in the state.

Plastics.—Fourteen plastics products producers are located here. The total for Ohio is 76.

Rubber products.—The area has 14 rubber products manufacturers; and nearby Akron, only 30 miles south of Cleveland, is the rubber center of America.

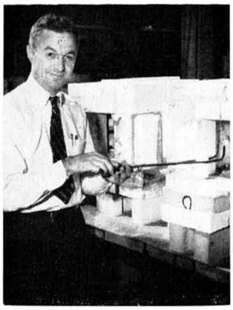
Fertilizers.—There are 37 plants producing fertilizer in Ohio. The American Agricultural Chemical Company, Stadler Products Company, and Swift & Company are all located in the Cleveland-Northeast Ohio area.

It is also interesting to note that more than two-thirds of all United States product classifications are produced in the "best location." Certainly most, if not all, of these product classifications depend upon the chemical industry in some way.

Transportation Services

Located at the market center of America, the Cleveland-Northeast Ohio area is also the heart of a great transportation network. Nine railroads serve the area, along with more than 150 motor truck lines. Nine airlines maintain regular flight schedules in and out of Cleveland, which could be of special importance to the chemical industry for speeding liaison work. Pipelines can also be classified as one of Northeast Ohio's important transportation mediums. A growing list of products

The Diamond Alkali Company's plant produces more than 150 different chemicals, using 100 million gallons of water per day.



Eugene Wainer
Horizons Incorporated

A. O. Thalacker
Hooker-Detrex Corporaton

such as hydrogen chloride, chlorine, and acetylene are now being exchanged in the area by pipeline.

Coal transportation by pipeline will soon be a practical reality in Ohio according to representatives of the Pittsburgh Consolidation Coal Corporation. That company has already invested more than half a million dollars in the development of a coal-carrying pipeline. A three-mile line built by the company in the southern part of Ohio has been used experimentally during the past year. The line itself is made of 12 ¾-in. steel pipe. Before going into the line the coal is crushed to fine size. It is then mixed with water about 50–50 to form a slurry and pumped through the pipeline under pressure. It moves as readily as oil or gasoline. At the receiving end, the coal is separated from the water in a drying machine. The crushed coal is then ready for pulverizing and firing. As the water is clean it can be pumped into rivers or lakes. The 12 ¾-in. line, say the Pittsburgh Consolidation engineers, is big enough to pump through 7000 to 9000 tons of coal a day. That is 2½ million to 3 million tons a year. Needless to say, this experimental work is being watched with considerable interest, and it is believed that coal-carrying pipelines will be a cost-cutting reality within the very near future.

Low-cost water transportation to all Great Lakes ports is readily available. Approximately 80 per cent of the freighter fleet operating on the Great Lakes is controlled from the Cleveland area. Forty-one foreign ships maintain scheduled service between Cleveland and Europe and North Africa, via the St. Lawrence River. Northeast Ohio ports transship more iron ore than any other area in the world.

Of special importance is the 241-mile Ohio Turnpike, which will connect with the Pennsylvania Turnpike on the east and the Indiana State Line on the west. Construction was started October 1952, financed by a $326-million bond issue.

Plant Sites

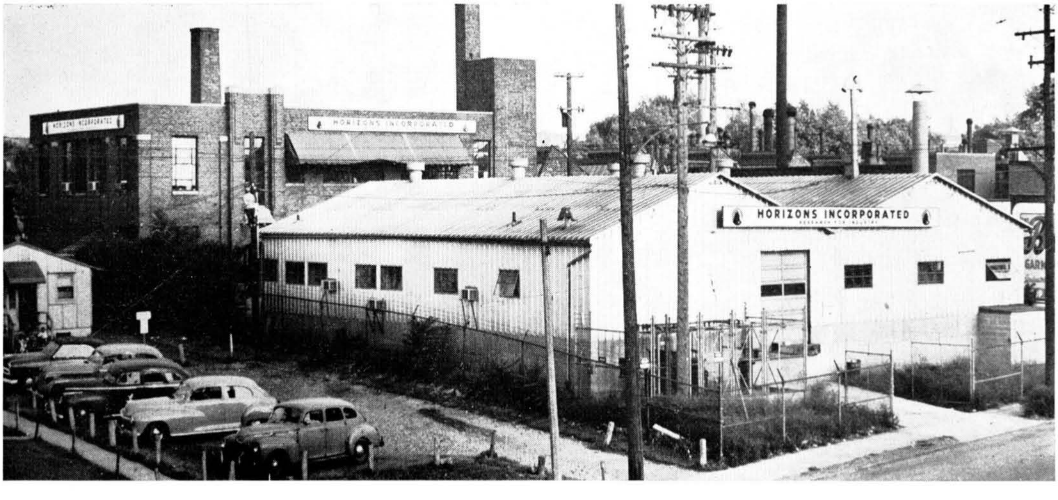
Despite the area's unprecedented growth since V-J Day, Cleveland-Northeast Ohio has thousands of acres of land ideally suited for electrochemical development. This acreage is available in city, village, and rural areas, inland and lakefront, on main highways and railroads.

The area has virtually unlimited sites for new chemical plants on main lines of principal railroads. Chemical firms which rely on motor transportation can find many excellent sites along main trucking highways. Construction cost increases in the area since 1946 are below the average for the nation's 30 largest cities. Undeveloped land for large industry sites is priced between $350 and $1000 per acre. Water pumping is easy and cheap because of level land at lake's edge, 50 to 60 feet above water level. Because the area has a solid shale foundation about 40 feet below the surface, plant sites have excellent load-bearing characteristics.

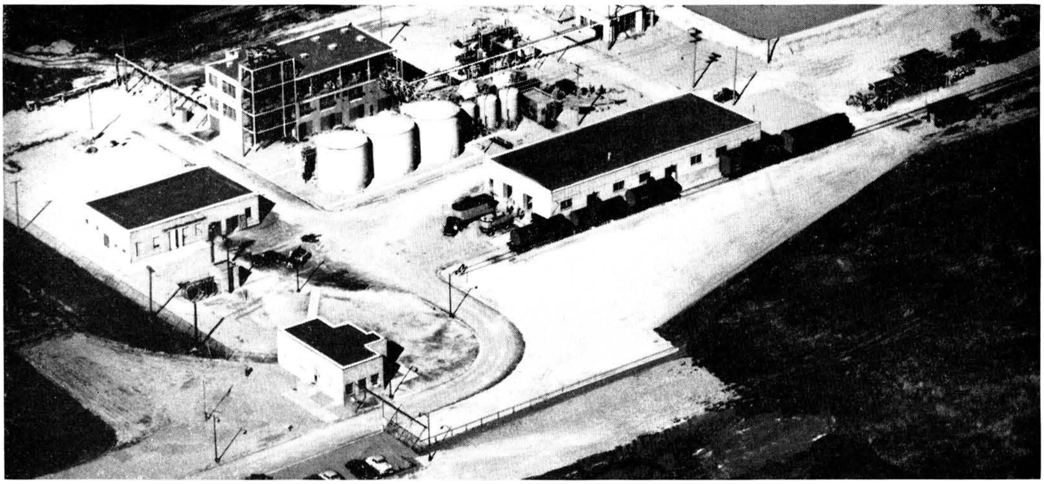
The Illuminating Company recently purchased three sites, totaling 954 acres of farmland, in the heavily developed industrial area extending east of Painesville. This acreage which includes 5800 lineal feet of Lake Erie frontage was purchased for ultimate resale as industrial plant sites.

Within a five-mile radius of the site in Lake County are plants of Industrial Rayon Corporation, Diamond Alkali Company, A. E. Staley Manufacturing Company, Diamond Magnesium Company, the Naugatuck Chemical Division of the U. S. Rubber Company, and Stauffer Chemical Company—all of which have undertaken substantial expansions in the past two years.

The second site, in Ashtabula County, is located three miles east of The Illuminating Company's Ashtabula power plant and two miles east of the Union Carbide & Carbon properties, where the Electro-Metallurgical and Linde Air Products divi-



Laboratory of Horizons Incorporated, Cleveland, Ohio



Hooker-Detrex Corporation plant at Ashtabula, Ohio

sions are now spending over $35 million in post-Korea expansions. The third site is also in Ashtabula County, ½ mile south of the Illuminating Company's Ashtabula plant.

In the same general area, new plants were recently erected by National Distillers Chemical Corporation and by the Hooker-Detrex Company.

Labor Force

Northeast Ohio's labor force numbers about 700,000 workers. Less than half are presently employed in industry. By tradition, environment, school training, and by the very nature of the area's highly diversified industrial structure, the labor resources of Cleveland-Northeast Ohio rank with the best to be found in the world. The area has long been a center for the manufacture of precision products. Many generations of skilled workers and technical specialists have plied their trades here. The climate has had much to do with the heavy concentration of skilled and semiskilled personnel in this area.

Located on the southern shore of Lake Erie, The Chemical Shore is milder in the winter and cooler in the summer than many other areas at the same latitude. There are fewer extremes in temperature, yet the regular cycle of four seasons prevails. This combination provides the environmental conditions ideally suited for active, precise, highly-skilled work—the type of work typified by the chemical industry.

Cost of Living

The U. S. Bureau of Labor Statistics reports that it costs less to live in Cleveland than in 23 other major American cities. Cost of living varies considerably among the four counties of Northeast Ohio, with Cleveland generally above the four-county average.

Housing

Housing activity in Cleveland is extremely high. Reversing the trend in most other cities, the Cleveland building industry scored a 24-per cent increase in activity in the first quarter of 1952, compared with the first quarter of 1951. In 1951, the Cleveland construction industry had its second largest year in the area's history. Since 1946, more than 80,000 new dwelling units have been completed in the area, providing housing for over 100,000 workers.

Educational and Research Facilities

Ohio has more colleges than any other state in the Union. Many of these colleges are training scientists for the growing chemical industry. Some, such as Western Reserve University, Case Institute of Technology, and Fenn College, are closely allied with the chemical industry and conduct many research projects for them. Because of the nucleus formed by these and other institutions, the area is developing as one of the nation's great chemical research centers.

A recent addition was the B. F. Goodrich Company's main research and development laboratory where over 200 scientists are exploring rubber, plastics, and other chemical products.

The Diamond Alkali Company has just opened a new research center in Painesville. Others with research and development laboratories in the area are Harshaw, The Standard Oil Company of Ohio, Lubrizol, National Carbon, and the Brush Development Company.

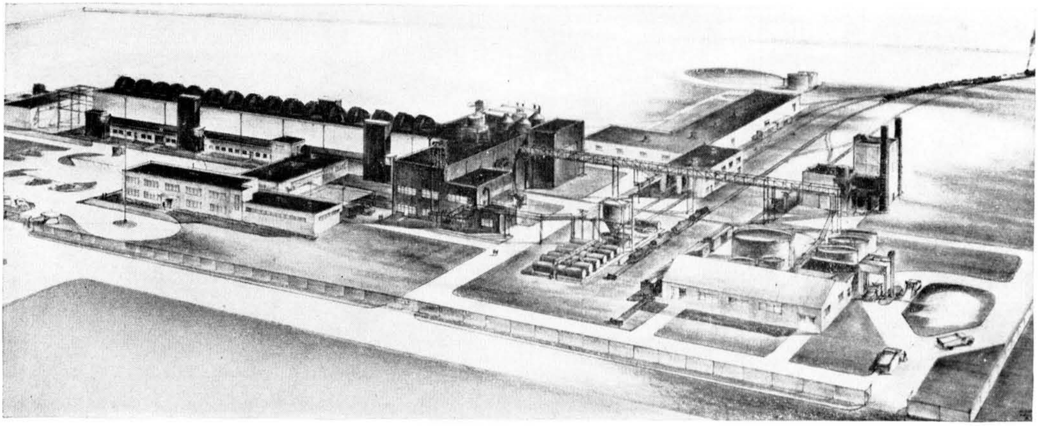
Horizons, Inc., a recent entrant in the titanium field, has a laboratory in this area. The Lewis Flight Propulsion Laboratory of N.A.C.A. has over 2500 scientists and technicians conducting research in a $66-million laboratory.

The Area's Growing Chemical Companies

Because of the many advantages the Cleveland-Northeast Ohio area offers the chemical industry, chemical companies which have already located here are constantly expanding. A cross section of their expansion offers striking evidence of faith in their industry and in this region.

THE U. S. RUBBER COMPANY—NAUGATUCK CHEMICAL DIVISION

The Naugatuck Chemical Division of the U. S. Rubber Company acquired its plant site on The Chemical Shore in two moves. In 1949 it acquired title to the Glenn L. Martin Company's vinyl resin plant and one year later acquired adjacent property of the former Buel Metals Company. Recently, U. S. Rubber announced a $3,250,000 expansion program for the Naugatuck plant, which will double the plant's capacity of Marvinol polyvinyl resin. The latest expansion program, which is expected to be completed in January 1954,



National Distillers' plant, located at Ashtabula, Ohio

will boost the plant's resin production to more than 50 million pounds annually. Construction of seven new buildings is included in the project. In addition to expanding its resin capacity, the Naugatuck plant has been conducting an intensive research and development program aimed at new and more efficient types of vinyl resins for the plastics industry. The plant recently announced Marvinol VR-21, which offers the industry a resin having the processing characteristics of the copolymers but retains the superior properties inherent in straight polyvinyl chloride resins.

NATIONAL DISTILLERS CHEMICAL CORPORATION

The National Distillers Chemical Corporation added another basic chemical plant to The Chemical Shore several years ago—their product, metallic sodium. Estimated daily capacity of the plant with all 94 Downs cells in operation is 100,000 lb of sodium and 154,000 lb of chlorine.

National Distillers produces its metallic sodium by electrolysis of fused sodium chloride. Crude sodium is further refined and cast in ingots or bricks and packed in drums for shipping. The molten sodium is drawn by vacuum into tank cars, allowed to cool and solidify, and is remelted before unloading. The low melting point (97.5°C), low specific gravity, high heat conductivity, and large scale uses of sodium make this shipping technique feasible.

The by-product is compressed and piped to the Hooker-Detrex Corporation for use in the manufacture of chlorinated solvents which find wide application in the metal degreasing and dry cleaning fields. The use of sodium hydride in the metal industry for descaling stainless steel and other special alloys makes the National Distillers' plant at Ashtabula especially valuable in this and adjacent steel producing areas. Sodium can be used in alloy formations with silver, gold, tin, mercury, cadmium, zinc, and lead, and is used in removal of antimony and bismuth from lead.

GRASSELLI CHEMICAL DIVISION OF DU PONT

One of the area's old-line companies is the Grasselli Chemical Division of Du Pont. This plant has been a part of the community life of Cleveland for 85 years. The Grasselli Chemicals Company was purchased by Du Pont in 1928 and since 1936 has operated as one of the ten industrial departments of the Du Pont Company. The Grasselli plant produces acids and heavy chemicals that are basic to much of the nation's industry. It also manufactures a wide variety of agricultural chemicals for control of insects and plant diseases, disinfecting of seeds, and control of weeds and brush. The plant occupies 55 acres, produces 65 basic products, and serves 26 individual industries. Operations of the plant give jobs to 505 men and women. Du Pont has spent approximately $2 million in expansion and new facilities for the Grasselli plant since V-J Day.

THE STANDARD OIL COMPANY OF OHIO

Two years ago, The Standard Oil Company of Ohio put into full production a new thermofor catalytic cracking unit with a capacity of 18,000 barrels of gasoline a day. Tall as a 22-story building, the new "cracker" contains two independent cracking units. The twin units operate simultaneously and continuously, but one can be shut down for inspection or repairs while the other stays in operation. Highest of all industrial structures in Ohio, the cat-cracker was erected at a cost of $4 million. Standard has been continually improving and increasing its facilities. It has spent over $25 million on new plants in Cleveland in the past several years.

GENERAL ELECTRIC WIRE WORKS

An important firm in the Cleveland-Northeast Ohio area that may not be ordinarily considered a chemical company is the General Electric Wire Works, which produces the rare gases krypton and neon. The company also uses hydrogen obtained from the chlorine-caustic cells of the Columbia Chemical Company in Barberton, Ohio.

NATIONAL CARBON DIVISION
OF UNION CARBIDE & CARBON CORPORATION

The National Carbon Division of Union Carbide and Carbon Corporation in our service area has the world's largest primary battery factory. National Carbon's research facilities, founded in 1902, cover all phases of primary batteries and carbon products. The company also researches motion picture optics, automobile antifreeze, and high polymer chemistry.

ELECTRO-METALLURGICAL DIVISION
OF UNION CARBIDE & CARBON CORPORATION

The big "Electro-Met" plant located in Ashtabula on the eastern extremity of The Illuminating Company's service area produces ferroalloys and calcium carbide. It recently expanded to double its previous capacity. This plant is one of the world's largest producers of calcium carbide, which is the basis for many acetylene hydrocarbon chemicals.

LINDE AIR PRODUCTS COMPANY

Linde Air Products Company is another division of Union Carbide and Carbon. It recently completed a $7-million tonnage oxygen plant to supply the major steel companies. When operating at full capacity, the plant will employ between 75 and 100 persons and will produce more than 100 million cubic feet of oxygen per month. The company also produces other industrial gases.

THE FERRO CORPORATION

Ferro is the world's largest producer of porcelain enamel Frit, a high temperature fired enamel coating. It also produces large quantities of colors for ceramics, glass, and plastics. A Ferro subsidiary company in Bedford, Ohio, makes metallic soaps for the paint and varnish industry. Ferro besides being one of the world's top enamel coating producers has successfully branched into allied fields such as insecticides and titanium.

SHERWIN-WILLIAMS COMPANY

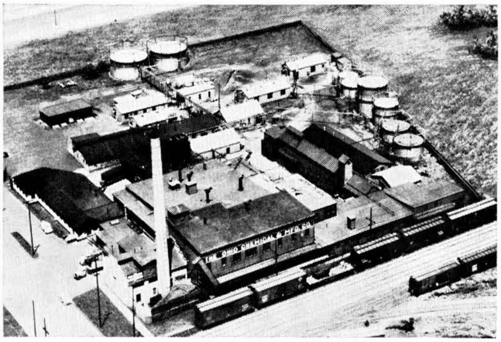
The Sherwin-Williams Company is the world's largest producer of paints, varnishes, and lacquers. The company's Cleveland plant produces many types of paints, including marine finishes and the famed "Kem-Tone." A Sherwin-Williams castor oil solvent extraction plant is also located in the Cleveland-Northeast Ohio area.

THE GLIDDEN COMPANY

The Glidden Varnish Company, producers of Jap-a-Lac, was reorganized into the Glidden Company in 1917. Glidden has branched out into many fields, but still has its main paint and varnish plant in Cleveland.

STRONG-COBB AND COMPANY

Strong-Cobb is one of Cleveland's six pharmaceutical companies. It traces its founding to 1833, although it was not until 1888 that it entered its present lines. Today, Strong-Cobb is one of the nation's largest private formula houses and has made many contributions to the medical field through its extensive research facilities.



The Cleveland manufacturing plant of the Ohio Chemical and Surgical Equipment Company.

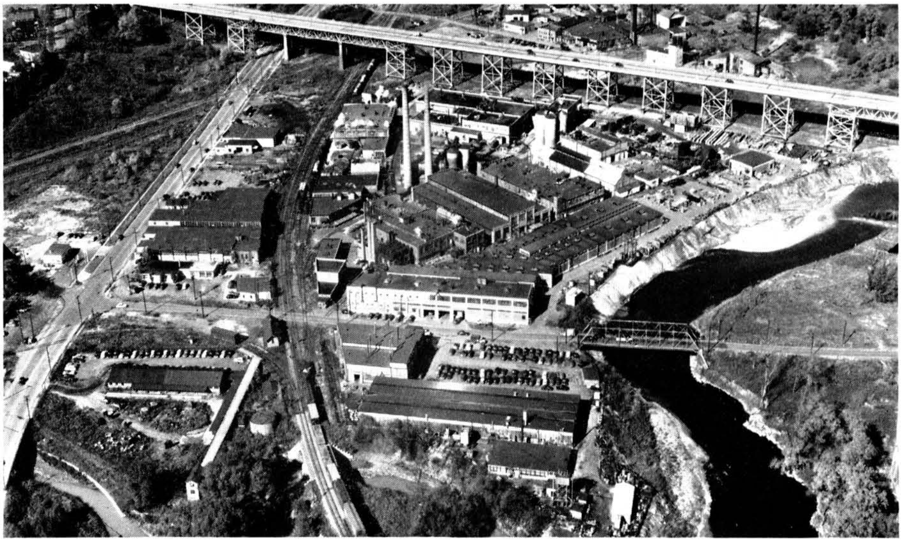
THE LUBRIZOL CORPORATION

One of the area's fastest growing chemical plants is the Lubrizol Corporation in Wickliffe. It produces additive agents for lubricants and other products for the petroleum industry. This plant, which had a small beginning only 15 or 20 years ago, has expanded regularly to meet demand requirements for transmission and crankcase lubricants, cutting oils, and other petroleum products.

DIAMOND ALKALI COMPANY

The Chemical Shore was pioneered by the Diamond Alkali Company in 1912. It started by producing soda ash for glass manufacturing. Today, Diamond Alkali is the nation's second largest producer of basic alkali and related products. Although soda ash is still the company's number one product, it also makes large quantities of caustic soda, electrolytic chlorine, sodium bicarbonate, carbon tetrachloride, muriatic acid, chromates, cement, coke by-products, and alkali specialties. The Diamond Alkali plant now employs over 3500 workers who help produce over 150 different chemicals. It uses over 100 million gallons of water a day.

Research Laboratory and Edgewater plant of the National Carbon Company, located in Cleveland; the latter has the largest primary battery factory in the world.



Aerial view of plant of Harshaw Chemical Company, one of the 'Shore's' old-line companies, which produces numerous chemicals for a variety of uses.

STAUFFER CHEMICAL COMPANY

Not far from Diamond Alkali is the $1½-million plant of the Stauffer Chemical Company. It produces carbon bisulfide which serves as a raw material for Diamond's carbon tetrachloride. Stauffer's carbon bisulfide also goes to Industrial Rayon's continuous spinning mill, which is in the neighborhood. Proof of the close integration of operations is found in the fact that Stauffer gets sulfur back from Diamond Alkali to be reburnt for more carbon bisulfide.

THE DIAMOND MAGNESIUM COMPANY

The Diamond Magnesium Company, also located near Diamond Alkali, has a rated capacity of 18,000 tons of magnesium per year. This plant, which was constructed during World War II, is one of the most efficient magnesium installations in the United States.

INDUSTRIAL RAYON CORPORATION

"Tyron" tire cord and fabrics are made in Industrial Rayon plants in Cleveland and Painesville. The Cleveland plant is one of the country's oldest sources of rayon. The Painesville plant houses a completely modern continuous process method for rayon production, which it developed and perfected.

B. F. GOODRICH CHEMICAL COMPANY

Built in 1947 in Avon Lake on the far western side of The Illuminating Company's service system, the B. F. Goodrich Chemical Company has continually expanded to meet increasing demand for its chemical products. The plant itself is divided into five sections. The first section to be completed was the pilot plant, which works exclusively with newly developed chemicals; the second section makes Geon resins, which includes Geon polyvinyl chloride; Good-rite plasticizers are made in the third section of the plant; and general chemicals are produced in the fourth section. In the fall of 1950, a sales service laboratory was completed at the plant and this laboratory does all the development work for the company's chemical sales department.

HOOKER-DETREX CORPORATION

A by-product of the metallic sodium process, chlorine gas, is compressed and piped from National Distillers to the Hooker-Detrex Corporation, where it is used with acetylene piped from Electro-Met in the manufacture of chlorinated solvents. These solvents find wide application in the metal degreasing and dry cleaning fluids. Hooker Electrochemical Company and Detrex Corporation joined forces to construct and operate the Hooker-Detrex plant. The entire output of trichlorethylene from the plant is distributed to industry through a network of Detrex Corporation field warehouses.

HARSHAW CHEMICAL COMPANY

The Harshaw Chemical Company, one of The Chemical Shore's old-line companies, produces a diversified line of chemicals. Its major products are fluorides, hydrofluoric acid, opacifiers, paint dryers, pigments, and electroplating chemicals and anodes.

MCGEAN CHEMICAL COMPANY

Cleveland's prominence in the plating field is further advanced by the McGean Chemical Company. This firm produces a widely diversified line of electroplating chemicals plus a large supply of chemicals for the ceramic and paint industries.

OTHER PROGRESSIVE CHEMICAL COMPANIES

The Harris-Seybold Company manufactures lithographic chemicals. The Ohio Rubber Company, with its large plant in Willoughby, is one of the area's leading producers of rubber goods. The Ohio Chemical and Surgical Equipment Company, a division of Air Reduction, makes anesthetic and therapeutic gases. Industrial gases of many types are produced by Air Reduction and the Burdett Oxygen Company. Both of these companies make oxygen and acetylene for the large metal working market in Cleveland. The Barium Chemicals Company produces high-purity barium and strontium compounds. The Cleveland division of the Archer-Daniels-Midland Company is the world's largest manufacturer of core oil. This plant supplies 50 per cent of America's and Canada's core oil requirements. Core oil is the varnish-like liquid used by foundries to bind cores together. The plant also makes liquid partings, which keep sand cores from adhering to the molds

What's Ahead for The Chemical Shore

At The Illuminating Company, it is firmly believed that chemical development in the Cleveland-Northeast Ohio area is still in its inceptive stages.

The future for the electrochemical industry in this area is bright. The resources are here. The transportation, the markets, the industrial potential are here. And available land is here—good land—for future-minded chemical companies. Approximately $40 million has already been committed for chemical expansion here during the next two years. That means those expanding companies will need much more electric power; it will be available to meet their increased demand.

Also we are glad to provide the location engineering services of our Development Department to *any* industrial firm interested in our area as a possible site for a new plant or for expansion of an existing plant. We provide these services free and without obligation on the part of the user.

What we strive for are industries that will strengthen the economy of our area, upbuild levels of business and industry, increase employment and job opportunities, and enhance payrolls and profits.

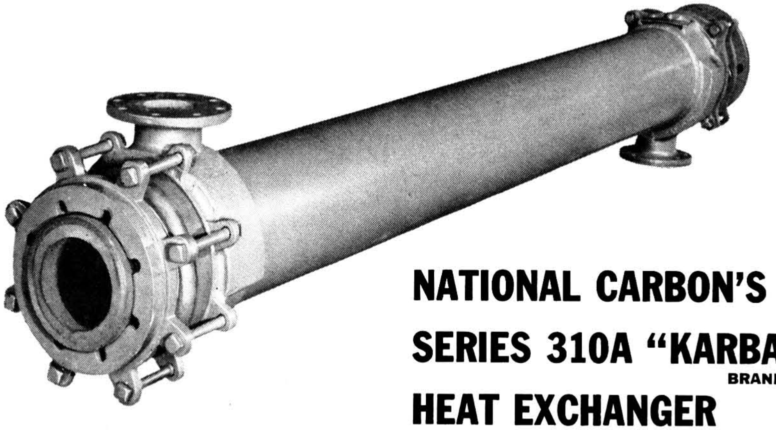
We believe that community growth is dependent, above all else, on growth of local industry. I hope this article has outlined some of the advantages which we feel make the Cleveland-Northeast Ohio area "the best location in the nation" for the chemical industry.

Because of this area's advantages, we believe the outlook for the successful production of the following products is especially favorable: synthetic resins, pharmaceuticals, solvents, rayon, soap and detergents, metallurgical products, paints and pigments, fluorinated compounds, antiknock compounds, and special agricultural chemicals.

Small chemical companies are encouraged to locate here as well as larger ones. Small industry is every bit as important to this area's development as big industry. The well-balanced area must have both.

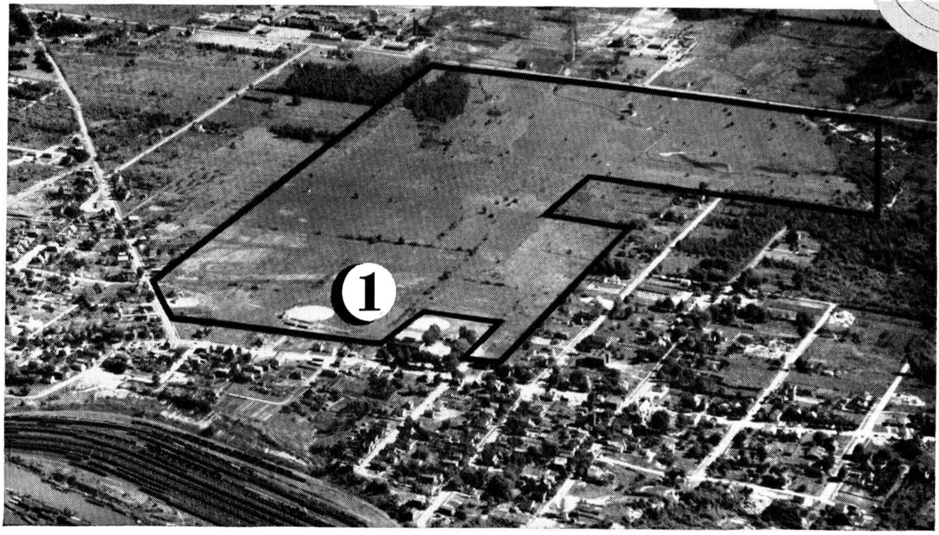
The Cleveland Electric Illuminating Company welcomes the growth in our area of chemical companies—large and small. It helps our area grow, helps support the best possible standard of living, and, more important, the chemical industry is a bulwark of our national economy. Its products are vital to the national security and to international peace.

There is no foreseeable limit to the development of the chemical industry in the Cleveland-Northeast Ohio area.



BEST LOCATION IN THE NATION

Headline Industrial News from the Cleveland-Northeast Ohio Area



① *Ashtabula City Site, 175 acres, 1½ miles north of main city district near Ashtabula harbor.*

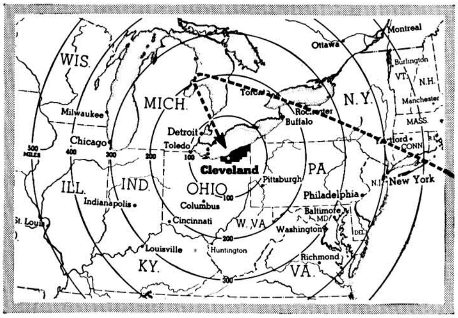
2 LARGE NEW PLANT SITES NOW AVAILABLE ON LAKE ERIE'S "CHEMICAL SHORE"

Shown on this page are two outstanding new plant sites, both located in small-city or semi-rural areas within an hour and a half drive of Cleveland.

Ideally located for chemical production as well as many types of general manufacturing, with numerous basic chemicals at hand, these sites offer easy access to mainline rail and highway facilities, soil conditions favorable to heavy structures, nearby lake ports.

Utilities—Dependable electric power supply available from Cleveland Electric Illuminating Company 1,144,000-kilowatt interconnected system. Natural gas available in area. Unlimited fresh water from Lake Erie.

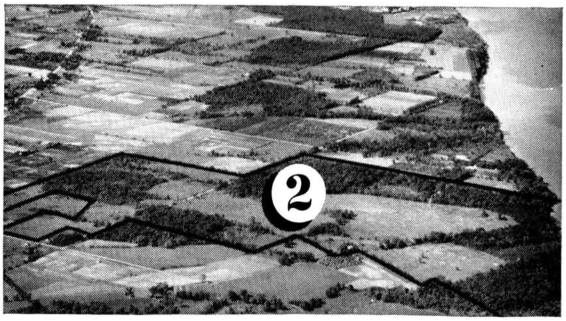
Nearby Communities—Ashtabula and Lake Counties have a combined population of 170,000. Both sites easily accessible by automobile or bus.



Low Taxes—Property taxes per $100 valuation are low in the two townships: Ashtabula $1.28; Perry $2.33. City of Ashtabula: $2.61.

A Rare Opportunity—Act Today

For complete information about either of these new sites and the opportunities for your company here, phone, wire or write Development Department, Richard L. DeChant, Manager. All inquiries held in strict confidence.



② *Perry Township Site, 368 acres, Lake Erie frontage 2500 feet, 20 miles southwest of Ashtabula, 8 miles northwest of Painesville.*

THE BEST LOCATION IN THE NATION — 81,000,000 customers within 500 miles... 3,500 manufacturer-suppliers right at hand

THE CLEVELAND ELECTRIC ILLUMINATING COMPANY

89 PUBLIC SQUARE • CHerry 1-4200 • CLEVELAND 1, OHIO

Addition Agents for Negative Plates of Lead-Acid Storage Batteries

II. Pure Organic Compounds[1]

EVERETT J. RITCHIE

Research Laboratories, The Eagle-Picher Company, Joplin, Missouri

ABSTRACT

This paper presents some of the results of an experimental study of the effects produced by the addition of pure organic compounds to the negative active material of lead-acid storage batteries. The experimental conditions used in the study were selected to show large differences between compounds of similar structure or between members of a given series. These conditions have been described since they are not standard in the industry.

The results obtained at high discharge rates at 0°F (−17.8°C) have been grouped with respect to the chemistry and structure of the compounds tested. The effect of agent solubility, its electrolytic oxidation-reduction behavior, and the effect of structural isomerism are considered.

The effectiveness of pure organic compounds as expanders appears to be directly related to the ease with which they can be degraded to "humic substances." The best results were obtained with carbohydrates and some of the homologous phenolic compounds.

INTRODUCTION

The negative-plate addition agents used commercially as "expanders" to improve the low temperature, high rate discharge performance of a lead-acid storage battery have been naturally occurring materials or products obtained from them. Among these substances woodflour, cotton and hemp fibers, paper pulp, lignin sulfonic acids, and substances classed as humic acids have been most used.

Analytical studies of wood, various plant fibers, cellulose, lignin, and humic acid preparations have demonstrated the presence of a very large number of organic compounds containing many of the recognized organic structure groups or radicals. The primary objective of this work was the evaluation of the effect of the more common organic radicals as simple compounds and in some of their combinations with other radicals. Since the physical and chemical properties conferred upon an organic molecule by the introduction of a given radical into it may vary with the position taken by the radical, it was necessary to study and evaluate the several isomeric possibilities of a number of types of compounds. As far as possible the attempt was made to evaluate each compound as a member of a family rather than as an individual.

It was necessary to devise a test cell and a method of testing and reporting the data which would give a fair picture of the effect of the agents tested.

EXPERIMENTAL METHODS

The data reported in Table IV were not obtained under the usual test conditions applied to SLI storage batteries; hence, it is necessary to describe the conditions and the methods used so that the reader may be able to evaluate the data. The negative-plate area was reduced to about 50 per cent of its usual value in order to assure sufficient positive-plate capacity to discharge the negative plate at all temperatures. Instead of 300 amp discharge at 0°F (−17.8°C), the rate on these 50 per cent negative plates was cut to 100 amp which is equivalent to a 200 amp rate on a negative plate of normal area. By reducing the rate of discharge, the time of discharge was lengthened, and the variations in the results from different agents were spread out over a longer time interval. Instead of discharging the battery to a final cell voltage as a measure of the positive-plate capacity the cells were discharged to selected final negative-to-cadmium auxiliary electrode voltages.[2] The reported cell capacities were thus

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[1] Manuscript received September 28, 1950. This paper prepared for delivery before the Buffalo Meeting, October 11 to 13, 1950.

[2] Hereafter abbreviated to N.C. voltage. As used herein a "very low N.C. voltage" means a large numerical negative value. Because the sign of the voltage measured between a cadmium auxiliary electrode and the negative electrode reverses during formation, or charge, the measured voltage decreases from an open-circuit voltage in the order of 0.17 v (in the plus direction), through zero to voltages as "low" 0.33 v (in the negative direction). This conven-

based entirely on negative-plate capacity. The details of cell construction, testing, and selection of addition agents follow.

Cell Construction

Negative plates.—The active material, composed of 1500 g milled mechanical furnace litharge, 7.5 g blanc fixe, 3.0 g lampblack, with addition agents in the test cells, was made into a paste with water and 1.325 sp gr sulfuric acid, and was hand pasted (on paper) at a paste density of 72 g/in.^{3} into conventional SLI grids of 0.090-in. (2.29 mm) thickness from which alternate rows of wires had been removed to reduce the net volume from 1.76 in.^{3} (28.8 cm^3) to very nearly 0.88 in.^{3} (14.4 cm^3) (Fig. 1). Because many of the addition agents would be lost by oven drying, the plates were treated instead by giving them a quick dip (about two seconds) in 1.250 sp gr sulfuric acid, using fresh acid for each addition agent. The plates were drained and air dried for at least 48 hours before assembly and formation.

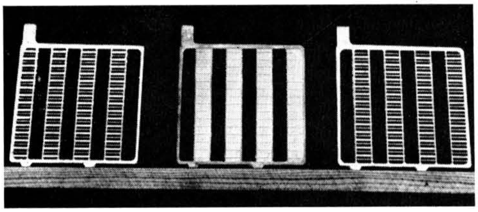

FIG. 1. Type of negative grids and plate used

Positive plates.—The active material was made from a blend of milled lead oxides containing 25 per cent red lead. Conventional SLI grids of 0.092-in. (2.34 mm) thickness and 2.00 in.^{3} (32.8 cm^3) net volume were hand pasted (on paper) at a paste density of 68 g/in.^{3} (4.15 g/cm^3), and the plates were dried in a humidity-controlled oven.

Formation.—Thirteen plate cells (7 negative, 6 positive) were assembled and separated using 0.078-in. (1.98 mm) thickness Port Orford Cedar separators. The assembled duplicate cells were formed in the end cells of three-cell glass jars which permitted some observation without disturbing the cell. Formation was carried out at 4.5 amp in 1.150 sp gr sulfuric acid until the negatives were formed. They were then removed and stored in distilled water, each pair of cells in a separate container. The formation of the positive plates was finished against dummy negatives. Nine pairs of cells were tested in each set.

Assembly.—The formed duplicate groups were reassembled in the end cells of an S-8-D (100 amp-hr) container. The center cell had holes drilled in its outer walls to promote air and water circulation and was reinforced with a wooden block to prevent warping. The electrolyte was adjusted to 1.285 sp gr at 80°F (26.7°C) after charging at 6.0 amp until the gravity was constant plus one hour. This was also the criterion of charge used on all charges before and after measured discharges.

Cell Testing Discharge Conditions

Test schedule.—Data reported in this paper are those resulting from discharges at low temperatures to observe the effect of the addition agents, and discharges at a nominal 20-hour rate at 80°F (26.7°C) to show the base capacity of the plate. It is expected, other things being comparable, that a 120 amp-hr battery will have a higher low temperature capacity than would a 95 amp-hr battery; hence, the need of low rate discharge data to give information on the development of the active material. Table I gives the schedule of measured discharges upon which the reported data were based.

TABLE I. *Schedule of test discharge conditions*

Discharge Numbers		Amp rate	Temperature		Cut off voltages, N.C., v
Initial	Cycled		F°	C°	
1,4	61,64	100	0	−17.8	+0.80
2,5	62,65	3.5*	80	26.7	+0.30
3,6	63,66	100	80	26.7	+0.60

Cycles 7 to 60 inclusive were on automatic cycling.

* This value was selected to give a discharge of about 15 to 17 hours which was more convenient to use than the usual 20-hour rate.

TABLE II. *Control cell statistics*

	Minutes at 100 amp at 0°F		Hours at 3.5 amp		Formation amp-hr to final	
	Initial	Cycled	Initial	Cycled	final N.C.	N.C. v
Mean	4.2	4.2	15.7	16.6	118	−0.18
Avg dev.	0.47	0.59	0.51	0.54	8.5	0.02
Avg dev., %	11.2	14.0	3.2	3.3	7.2	11.1
Max dev.	1.5	1.4	0.7	1.3	18	0.13
Max dev., %	35.8	33.3	4.5	7.8	15.2	44.4

Reliability of results.—The significance of the results reported in Table IV for individual agents rests heavily upon the performance of the control cells tested at the same time. Table II gives data on the control cells of the study. It will be observed that, based on the average of two discharges, the 28 sets of control cells show a reasonably uniform capacity at the low discharge rate at 80°F (26.7°C). Since

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tion is logical since the cell terminal voltage is the algebraic difference or spread between the N.C. voltage and the corresponding positive-to-cadmium voltage.

the attempt had been made to control negative-active material weight, this was as expected. The much larger percentage variation and spread in the low temperature capacity results are in part due to the greater error involved in measuring a high rate discharge and to the greater effect of some variables that did not influence the low rate capacity. It was unavoidable that a few sets of negative plates aged for as much as two weeks before assembly and use, and this may have influenced their low temperature capacity. Although preventive precautions were taken, it is possible that traces of soluble addition agents entered the control cells during the checking of electrolyte and when using the auxiliary cadmium electrode. In several instances mechanical difficulties produced abnormally low results. Since each pair of control cells was treated exactly as the eight pairs of test cells teamed with it, any deviation from the normal schedule only affected the cells of that set. The statistical study shown in Table II indicates that variations in test cell capacities with different agents do not necessarily denote real differences unless they differ from these control cells by more than the average deviation of all control cells from the mean of all the control cells.

It was expected that a litharge-blanc-fixe-lampblack negative would lose capacity after about 60 cycles. At the cold rate about half of them did. The average capacity after cycling, however, was the same as the cold rate and a whole hour greater at the low rate under the test conditions.

The rather wide variation in final N.C. voltage on formation is probably due to temperature variations, and no attempt was made to finish formation at a constant temperature. The ampere-hours reported to a zero N.C. voltage were obtained by interpolations of frequent readings made throughout formation.

Selection and Calculation of Addition Agent Concentrations

Preference was shown for those compounds which had been identified in naturally occurring organic materials, or some of their more simple degradation products. The substances selected were members of homologous series or could be compared with other compounds of similar structure. Table III lists the organic groups tested, the classes of compounds in which they are found, and the formula weights used in calculating the amount of agent to use to obtain a constant active group percentage of 0.1 per cent. Compounds were also selected because of their having been mentioned in the patent literature (1, 2).

The addition agents were used in as pure a form as was obtainable. Most of them were purchased from the Eastman Kodak Company.

As an example of the method of calculating, consider the testing of propyl alcohol with a molecular weight of 60.07 and an active group weight of 29. The amount necessary to supply 0.1 per cent of $-\underset{|}{\overset{|}{C}}-OH$ to 1500 grams of negative material is

$$\frac{60.07}{29} \times 0.001 \times 1500 \text{ or } 3.14 \text{ grams which is } 0.21$$

per cent based on the total agent weight.

TABLE III. *Organic radicals tested*

Organic structure group			Typical compounds
Formula	Name	Formula wt	
$-\overset{\overset{O}{\|}}{C}-OH$	Carboxyl	45	Acids
$-\underset{|}{\overset{|}{C}}-OH$	Carbinol	29	Alcohols (also used for phenols and naphthols)
$-\overset{\overset{O}{\|}}{C}-$	Carbonyl	28	Aldehydes, ketones
$-\underset{|}{\overset{|}{C}}-SH$	Mercaptan	45	Mercaptans, thiophenols, thionaphthols
$-\underset{|}{\overset{|}{C}}-NH_2$	Amine	28	Amines and amides
$2X(-\overset{\overset{O}{\|}}{C}-)$	Quinone	56	Quinone, naphthoquinones anthroquinones
SO_3H	Sulfonic acid	81	Aromatic sulfonic acids.

EXPERIMENTAL RESULTS

In Table IV[3] a small part of the experimental data is given in condensed form. Capacities are reported in per cent of the performance of the control

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[3] The complete Table IV has been deposited with the American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., from whom copies are available on either microfilm ($1.00) or photoprints ($1.35). Order document number 3841 directly from them. The complete Table IV contains data on 203 pairs of test cells studying 156 different organic compounds; it does not include data on the 28 pairs of control cells already discussed in Table II.

cells on the initial measured discharges. By "initial" is meant the average of discharges 1 and 4 at the cold rate and of 2 and 5 at the 3.5 amp rate at 80°F (26.7°C). By "cycled" is meant the average of discharges 61 and 64 at the cold rate and of 62 and 65 for the 3.5 amp at 80°F (26.7°C). Data are given for three commercial expanders tested under these conditions for comparison purposes.

ABRIDGED TABLE IV.[3] *Table (abridged) of relative capacities as influenced by various agents*

Agent	%	Capacity in % of initial control				Final N.C. formation voltage
		Cold rate		20-hour rate		
		Initial	Cycled	Initial	Cycled	
Acetic acid	0.13	104	104	93	95	−0.12
Benzoic acid	0.27	126	123	106	112	−0.18
o-Phthalic acid	0.19	110	105	100	101	−0.18
p-Phthalic acid	0.19	118	113	104	110	−0.15
α-Naphthoic acid	0.37	33	54	52	52	−0.28
Abietic acid	0.67	60	77	54	77	−0.33
Oleic acid	0.42	78	102	74	105	−0.29
Formaldehyde	0.10	118	89	101	94	−0.13
Propionaldehyde	0.21	100	80	97	91	−0.11
Benzophenone	0.65	76	90	91	104	−0.22
Ethyl alcohol	0.16	96	88	98	108	−0.19
Glycol	0.11	105	116	102	111	−0.18
Glycerol	0.11	113	132	105	109	−0.20
Arabinose	0.15	116	171	107	124	−0.18
Xylose	0.15	100	174	105	120	−0.20
Mannitol	0.18	110	177	107	124	−0.20
Sucrose	0.17	87	144	98	119	−0.21
Catechol	0.19	108	127	106	104	−0.16
Resorcinol	0.19	117	156	106	117	−0.16
Quinol	0.19	131	185	114	115	−0.16
α-Naphthol	0.50	173	290	96	118	−0.33
β-Naphthol	0.50	92	187	76	108	−0.25
Benzoquinone	0.19	162	225	115	129	−0.23
1–2 Naphthoquinone	0.28	107	122	69	110	−0.26
1–4 Naphthoquinone	0.28	132	100	94	72	−0.29
Anthraquinone	0.37	85	71	101	70	−0.27
α-Naphthol, 2 sulfonic acid	0.21	155	189	103	113	−0.22
α-Naphthol, 4 sulfonic acid	0.19	152	185	105	112	−0.19
α-Naphthol, 5 sulfonic acid	0.19	196	215	118	124	−0.16
β-Naphthol, 6 sulfonic acid	0.19	193	152	170	103	−0.14
β-Naphthol, 7 sulfonic acid	0.21	159	152	105	108	−0.15
β-Naphthol, 8 sulfonic acid	0.19	144	148	104	110	−0.15
Commercial neg. blends A		133	188	112	135	−0.24
Commercial neg. blends B		130	191	105	124	−0.22
Commercial neg. blends C		121	149	104	128	−0.24

The data are intended to supply answers to three questions pertinent to any study of battery addition agents: (*a*) Does the agent alter the properties of the active material to make it fragile, impermeable to the electrolyte, or difficult to form? (*b*) What is the initial effect of the agent upon the cold capacity before the electrolytic action of the battery has had opportunity to modify it? (*c*) What is the effect of the electrolytic action of cycling upon the agent?

The formation data were of value in screening out unsatisfactory agents. The "final" N.C. voltage appeared to be rather characteristic of a given agent, although subject to some variation with temperature and formation schedule.

The current required for the N.C. voltage to reach an arbitrary value, here selected as 0.0 volts, and expressed as a percentage of the current required by the control cells, was diagnostic of the nature of the formation taking place.[4] When only a small

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[4] These values are included in unabridged Table IV.

amount of current was required, the final N.C. voltage frequently was of the order of -0.30 volts, and the initial capacities were low. With a number of agents, however, the N.C. voltage after dropping to a low value would slowly rise to a more normal final value. The explanation apparently lies in the effect of the agent upon the active material. If the product was difficult to wet, or if a definite impermeable surface film was present, the N.C. voltage read was largely due to the insulating surface. By repeated partial cycles this film could be formed and the N.C. voltage would rise toward a more normal value as the surface film was formed. Where incomplete formation had reduced the initial capacities, the low rate capacity was also effected, and after cycling a definite improvement was noted. Several hydroxy compounds which were most effective as expanders also interfered the most with the formation. The volatility of some of the agents influenced the results obtained with them by an undetermined amount.

The test data are in most instances for a single concentration of addition agent. With pure compounds, the expander effect appears to be sensitive to small changes in agent concentration and also to be much influenced by small variations in plate or cell preparation. Each separate compound could thus be made the basis for a study of concentration vs. preparation variables. The data of Table IV are, therefore, to be considered as indicating the possibilities, showing the relative value of the agents under the described conditions, rather than giving data obtained at optimum conditions. The more important radicals are discussed below and some of the more important relations are pointed out.

The carboxyl radical.—The aliphatic acids had very little effect upon the initial cold capacity, but many improved with cycling. Formic and oxalic acids, perhaps because of their reducing properties, had some beneficial action. The aromatic acids gave definite initial improvement but with cycling the effect was reduced and even detrimental.

A few of the acids produced the most fragile active materials of the entire study, giving plates that shed badly on formation and which also appeared to be water repellent. The high molecular weight acids such as stearic, undecylic, α-naphthoic, and abietic were among the poorest of all compounds tested but even these showed some improvement with cycling.

The results obtained with acetic acid, which showed it to have little effect although it is recognized as being deleterious, have not been satisfactorily explained. Perhaps since these tests were carried out on a strict time schedule and the cells were never allowed to stand idle in a discharged state, the expected acetic acid damage could not occur at the concentration tested.

Only a few of all the carboxyl-containing agents had an effect upon cold capacity of more than 20 per cent, either before or after cycling, and the maximum initial benefit was only 26 per cent. Although the carboxyl group is frequently present in expanders derived from natural products, it is evidently not the effective structural group in expanders producing the desired cold capacity improvement.

The carbonyl radical.—This radical is present in many natural substances because it is an intermediate product in the oxidation of primary and secondary alcohols and in the reduction of carboxyl groups. The group is also present in ring structures as quinones, and can also occur as a diketo structure. In many compounds a dynamic equilibrium exists between the keto form and its tautomeric enol isomer, an unsaturated alcohol. In aromatic compounds tautomerism is an important part of the explanation of the mechanism of oxidation of monosubstituted compounds to quinoid structures.

With so many different reaction possibilities, it was somewhat surprising to find that except for benzoquinone, all of the carbonyl compounds were ineffective as expanders. Without exception, the aldehydes tested gave better capacities initially than after cycling. Most of the ketones showed slight improvement with cycling but were still near the control cell level. Of the quinones the benzoquinone was very good initially and improved with cycling, while anthraquinone was poor to start with and got worse. The naphthoquinones were intermediate with the 1–2 form resembling benzoquinone, and the 1–4 isomer similar to anthraquinone with respect to the effect of cycling.

The conclusion may be drawn that the carbonyl group as an aldehyde may supply some initial expander action but that it is soon spent; as a ketone it is of little effect; and as a quinone it is of lasting benefit only when in certain special structures.

The carbinol radical.—The hydroxyl group is present in most natural materials used as expanders. Because the hydroxyl groups are formed, or introduced, as the result of both oxidation and reduction and also by hydrolysis and biochemical action, most plant substances contain complex structures in which the hydroxyl portion is a large percentage by weight. The complex polyhydroxyl compounds, such as the starches, sugars, cellulose, and lignin, have many reaction possibilities and have had long use as expanders.

The simple aliphatic alcohols are relatively stable and resistant to oxidation and reduction. It is not surprising that as addition agents they showed very little effect. The polyhydroxy aliphatic compounds tested showed very little initial influence on cold capacity, but without exception they showed large gains after cycling. This is in qualitative agreement with practical experience using such compounds as expanders.

The aromatic and condensed ring hydroxyl compounds include those agents found to be of greatest effectiveness as expanders. Phenol itself was without significant initial effect, but a second hydroxyl gave a definite improvement related to the position taken and increasing in the order ortho, meta, para. This is also the order of increasing reducing properties. A third hydroxyl in either the vicinal or unsymmetrical positions produced no further improvement. All of the phenolic compounds improved with cycling. It is interesting that the meta and para dihydroxy benzenes after cycling should reach values of about the same order as the starting value for benzoquinone, which improved to a still higher value with cycling.

The hydroxy toluenes were much less effective than the hydroxy benzenes but all showed improvement with cycling. Only the orthocompound had an initial beneficial effect, the others were initially detrimental and their improvement with cycling was only to the control cell level. It is interesting that benzyl alcohol, which is isomeric with the cresols, should be definitely superior to the meta and para and equalled only by orthocresol.

The hydroxy naphthalenes were effective expanders but the active material was difficult to form. The best results were obtained when the hydroxyl group was in the alpha position. With two hydroxyls opposite (the 1–5 positions) the results were intermediate between those for a single hydroxyl group in the alpha and beta positions. Because of the formation difficulties it was not surprising that most of the naphthols should improve with cycling.

Since the hydroxy anthracenes are easily oxidized to anthraquinone, they were not tested. The hydroxy anthraquinones were all better than anthraquinone, and the 1-2-3 trihydroxy compound (anthragallol) was a good expander when properly formed.

The aromatic sulfonic acids.—The wide variation in results obtained when duplicate tests were made at different times demanded an explanation since the largest spread was obtained with the most effective agents. The cause appeared to lie in the way that the electrolyte wetted the surface of the plate. Many of the effective hydroxy derivatives seemed to produce a somewhat water-repellent active material.

It was assumed that the reaction between the addition agent, the leady material, and the pasting and dipping acid had resulted in an insoluble and nonporous active material, at least on the surface of the plate. Repeated partial cycles would form them eventually, but such procedure could never be put into practice and the operator was never quite certain that the process was complete. The problem was that of finding more soluble derivatives of the more effective agents that gave trouble on formation. Since the introduction of a sulfonic acid group into an organic compound ordinarily increases the water solubility and gives a compound which is stable in dilute sulfuric acid, it was logical to study a number of sulfonic acid derivatives.

The results were most interesting. In nearly every instance the presence of a sulfonic acid group resulted in (*a*) a higher N.C. voltage (more nearly that of the control) after the passage of a normal amount of current on formation, and (*b*) a higher initial cold capacity which indicated more normal formation of the active material. The active material appeared to have normal wetting properties when the agent contained sulfonic acid groups.

The position in the molecule occupied by the sulfonic acid group had a definite influence upon the cold rate. Compounds in which the sulfonic acid group was the only substituent were ineffective. The sulfonic acid-containing agents had initial cold capacities at or near their maximum and several of them, upon cycling, dropped below the control level to values indicating a definite detrimental effect.

Nitrogen and sulfur analogs.—The three compounds H_2O, H_2S, and H_3N form three series of derivatives that have many related properties. These compounds may be considered as the replacement of the oxygen in H_2O with sulfur or the —NH— group, or the replacement of the —OH group by —SH or —NH_2. A number of such compounds were tested because of the occurrence of these compounds in natural materials used as expanders.

In general, the oxygen compounds were the better expanders with the nitrogen analogs tending to give lower negative-to-cadmium potentials. A number of xanthates were studied and found to have very little effect on cold capacity although they did raise the final N.C. formation potential toward zero (by about 0.05 volts).

When agents containing nitrogen, either as amines, amides, or nitro groups, were being studied, frequent tests of the electrolyte were made in an effort to detect nitric acid which perhaps could result from electrolytic action. In no instance was it possible to detect the presence of nitric acid even when the agent contained a nitro group.

Effect of addition agents upon plate expansion.—The final apparent thickness of the tested negative plates (after about 70 cycles) compared to the thickness of the control negatives showed that there was no relation between the addition agent effect upon cold capacity and the apparent thickness of the negative plate. Some addition agents that produced the greatest expansion gave the lowest cold capacities. On the other hand, some effective agents gave less expansion than the control negatives. Plate expansion data, however, are not precise because of their dependency upon the tightness of the assembly of the elements in the cell.

DISCUSSION OF RESULTS

In a previous paper (1) a point of view on expander action was developed from a study of the literature of addition agents, which in effect said that the actual beneficial agent was produced *in situ* by the electrolytic action of formation and cycling upon the organic matter added to the negative plate. Proper treatment of the organic matter before adding it to the active material of the plate would greatly increase its initial effect, and perhaps reduce any possible gain in effectiveness with cycling. Regardless of the source or nature of the organic material added to the negative plate the previous paper concluded that, the final material, or the active agent in the plate, appeared to be of such nature to be best described as a "humic substance."

The experimental data reported here lend support to this point of view, although there are yet many unexplained relations. It is recognized that the degradation of carbohydrates and the oxidation of phenols and their homologes yield products characterized as "humic substance." From these two classes of pure compounds came the most effective agents tested in this study.

Compounds with marked reducing properties as the aldehydes, quinones, and some of the aromatic hydroxyl compounds showed beneficial effects initially. The relatively stable carboxyl acids, the alcohols, and the ketones were of little effect either before or after cycling. The aldehydes which are easily reduced to alcohols or oxidized to acids, both of which are of little effect, lost most of their beneficial action with cycling. The carbohydrates, which, although soluble, apparently were only slowly attacked under the conditions of their use in this study, had little initial effect but showed large gains by cycling.

Solubility of the agent, if accompanied by reducing properties, appears to have made for good initial effects. Insoluble agents gave poor initial results because they interfered with the development of the active material, and their low solubility also reduced the rate at which the electrolytic action of the battery might modify the original compound to an effective form. The influence of a solubilizing sulfonic acid group upon an otherwise difficultly soluble compound was to facilitate formation and increase the initial effect, although after cycling the effect may be reduced.

It is logical to believe that the effectiveness of lignin sulfonic acid derivatives, both initially and after cycling, are related to the reducing properties of their phenolic groups, and the solubilizing action of the sulfonic acid group.

ACKNOWLEDGMENT

The author wishes to express his appreciation to the Eagle-Picher Company for permission to publish this study.

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

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The Effect of Humidity upon the Insulation Resistance of Alkyd Molding Compounds[1]

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ABSTRACT

There are a large number of plastics available to the electrical engineer for consideration as dielectrics. Current electrical requirements are much more rigorous than those of former years, consequently some of the older, well-established plastics fail to meet them. The property in which there is much interest is the behavior of insulation resistance with variations in humidity.

Among the new plastics being tested for insulation resistance are alkyd molding compounds. These compounds deteriorate slowly under high humidities due to the hydrolysis of the polyester linkages. By judicious choice of acids and glycols in the resin and by careful selection of the fillers used, the effect of humidity is drastically reduced.

INTRODUCTION

This paper presents data on the deterioration of the insulation resistance of new, commercially available, thermoset alkyd plastics after exposure for increasing periods of time to high humidities and temperatures. For purposes of comparison and control, data on well known and commercially accepted phenolic and melamine plastics are included. The plastics chosen for testing were: Resimene 803A; Melmac P592; Durez 12810; Resinox 7934; Bakelite BM64; Plaskon 420; and Plaskon 422.

Resimene 803A is a cellulose-filled melamine formaldehyde molding compound specifically designed for electrical connector inserts.

Melmac P592 is a mineral-filled melamine molding compound recommended for electrical insulation applications.

Durez 12810 is a special grade phenolic molding compound designed for use where good electrical properties are necessary.

Resinox 7934 is a superior grade low-loss phenolic molding compound for electrical usage.

Bakelite BM64 is a general purpose phenol-formaldehyde molding compound.

Plaskon 420 and 422 are alkyd molding compounds designed for industrial and electrical applications.

Pertinent physical properties of these plastics are listed in Table I.

TABLE 1. *Physical properties of plastics tested**

	Resimene 803A	Resinox 7934	Durez 12810	Melmac P592	Bakelite BM64	Plaskon 420	Plaskon 422
Specific gravity	1.45	1.76	1.89	1.70	1.40	2.20	2.20
Water absorption 24 hr, %	0.60	0.03	0.02	0.50	0.55	0.14	0.08
Flexural strength, psi	10,000	9,000	9,500	6,000	10,000	9,000	8,000
Impact strength (Izod)ft lbs/in. of notch	0.32	0.37	0.34	0.32	0.30	0.33	0.33
Heat distortion, °C	149	—	143	—	160	191	191
Arc resistance, sec	125	3	3	133	5	190^+	180^+
Dielectric constant 10^6 cycles	6.70	4.30	—	5.65	5.4	4.70	4.20
Dissipation factor 10^6 cycles	0.050	0.008	—	0.040	0.04	0.017	0.014
Dielectric strength, short time test per ASTM D-149, volts per mil	400	425	400	535	330	475	420

* Data are an average of published ranges.

TEST METHODS

The effect of temperature and humidity on insulation resistance was determined according to ASTM Specification D257–38. To facilitate the expression of results of these tests, it became necessary to devise a new electrical term "insulation life." The insulation life of a dielectric is the length of time required for the insulation resistance to fall below an arbitrary figure under a given set of ambient conditions. For example, the 1000 megohm insulation life at 74°C and 95 per cent relative humidity would

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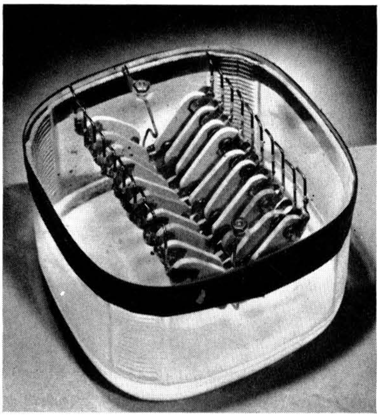

FIG. 1. Special humidity testing jar

TABLE II. *Insulation life of commercial polyesters*

Name of polyester	Catalyst concentration, %	100,000*M* insulation life, days
Plaskon 911-11	2	45
Plaskon 947 laminating resin	2	53
Selectron 5003	2	49
Paraplex AP43	2	31
Laminac 4128	2	70
Laminac 4126	2	105
Interchemical 86	2	45
Plaskon 947 laminating resin	0.1	48
Selectron 5003	0.1	48
Paraplex AP43	0.1	48
Laminac 4128	0.1	35
Laminac 4126	0.1	105

TABLE III. *Insulation resistance in megohms at 38°C and 95% relative humidity*

Type of material	20 Days	60 Days	80 Days	100 Days
422	1800	400	260	230
803A	400	140	120	110
P592	1000	75	41	14
7934	180	33	19	12
BM64	1.9	—	—	—

TABLE IV. *Insulation resistance in megohms at 71°C and 95% relative humidity*

Type of material	2 Days	6 Days	12 Days	16 Days
422	5000	2500	1600	1200
12810	380	190	120	105
803A	300	160	110	100
P592	1000	25	2.5	1.5
420	60	2	—	—

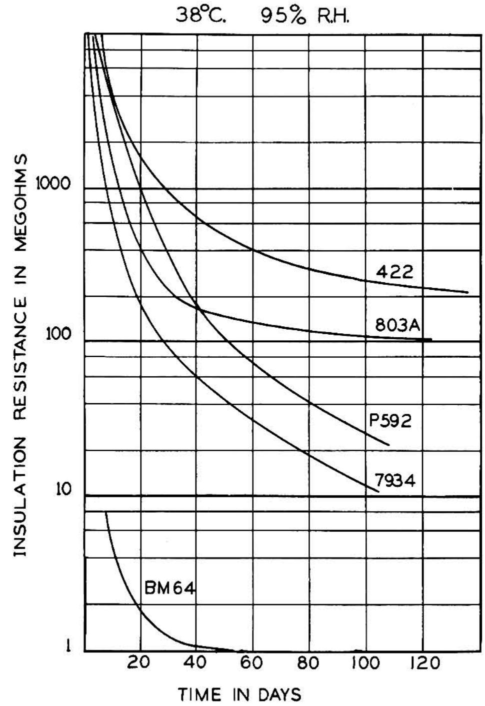

FIG. 2. Insulation resistance at 38°C and 95 per cent relative humidity.

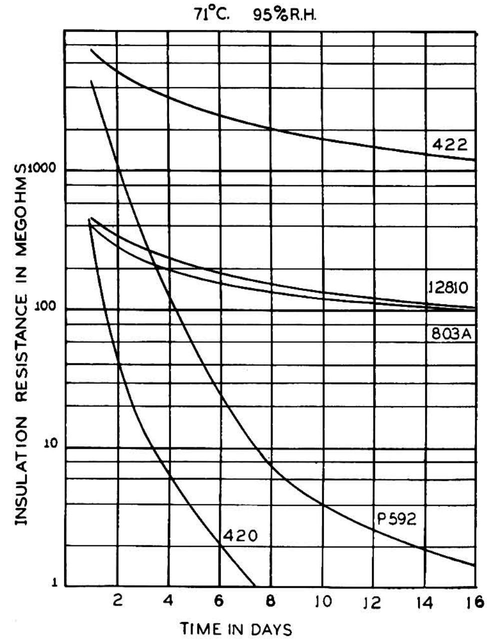

FIG. 3. Insulation resistance at 71°C and 95 per cent relative humidity.

be the time in days required for the insulation resistance to fall below 1000 megohms.

A special oven or conditioning chamber was employed.[2] Covered jars (Fig. 1) containing the test specimens were placed in the chamber and tested *in situ* by using a probe to contact each test specimen. Specimens were made by inserting 0.3175 cm machine screws into holes drilled 3.175 cm apart in molded disks 0.3175 cm thick. The test conditions were 38°C and 95 per cent relative humidity for one series and 74°C and 95 per cent relative humidity for the other.[3]

CONCLUSIONS

The insulation life of unfilled polyester resins is satisfactory for most dielectric needs (Table II). When any of these resins are compounded with fillers and other components to make molding compounds, the insulation life deteriorates rapidly at high humidities and temperatures. By carefully controlling the type of filler and surface treatments thereof, concentration ratios of alkyd component and modifying monomers, type and concentration of catalysts and methods of processing, molding compounds result which have a good insulation life. Data are listed in Tables III and IV and are plotted as graphs in Fig. 2 and 3.

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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[2] The authors will be pleased to forward blueprints of the oven to those interested.

[3] A saturated solution of K_2SO_4 maintained the requisite humidity within the jars.

The Testing of Magneto Insulation for Arc Resistance and Resistance to Spark Atmospheres[1]

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ABSTRACT

Experience gained in the production of ignition equipment, electrical connectors, and associated items indicates that certain tests are significant in predicting the performance of dielectric parts. It is our intention to discuss the methods and equipment used to conduct these tests and the interpretation of the results.

INTRODUCTION

Aircraft ignition equipment necessitates the harnessing of high voltages in the smallest possible space under operating conditions present at altitudes up to 65,000 ft. Under these conditions two factors have been found to be of more importance in the selection of insulating materials than would normally be the case. These are arc resistance and the resistance of the material to spark atmospheres.

MAGNETO ARC RESISTANCE

In this laboratory, materials which are being considered for magneto or other ignition applications are tested under a spark gap similar to that used in the original A.S.T.M. method (1), but fired by a high tension magneto. The magneto arc consists of a series of sparks, each differing in polarity from the one preceding. The frequency of sparking is regulated by the speed at which the magneto is operated. Only at the higher speeds does this series of sparks develop the characteristics of a true arc or ionized gap. At the lower spark frequencies each spark is very distinct from those immediately preceding and following it, and the test is very sensitive in eliminating those materials which Olyphant (2) has described as "tracking sensitive" and which normally carbon-track under the first few sparks. The materials which are not tracking sensitive do not carbon-track at the low frequencies although tests have been extended for several hours. At the higher spark frequencies, the test tends to separate "tracking insensitive" materials into classes more or less the same as the A.S.T.M. procedures (1, 3).

Effects on arc resistance of the decreased air pressures.—These effects are presented in Fig. 1 for four materials extensively used as magneto insulation. Tests were conducted under a bell jar at air pressures simulating those present at the altitudes under consideration. The conical, pointed electrodes, having a one-half inch spacing, were fired by a magneto producing 3000 sparks per minute.

The increase in arc resistance as the altitude increases lies in the visible lifting of the center of the arc off the surface of the material. This occurs regardless of whether the arc is placed in the normal position on the top surface of the specimen or is reversed so that the arc is beneath the specimen. It results from the release of gaseous materials from the specimen, instituted by the heat of the arc and accelerated by the low ambient pressure. The results indicate that arc resistance at higher altitudes cannot be predicted from values obtained at sea level.

RESISTANCE TO SPARK ATMOSPHERES

Resistance to spark atmospheres is a term applied to the relative resistance a material offers to chemical attack by nitric acid fumes which result from oxidation of the nitrogen in the air in the presence of moisture and which are caused by arc discharges in a confined space. Attack on a material by these fumes results in a marked decrease in surface resistivity which promotes surface creepage with possible permanent failure by carbonization. Many failures attributed to poor arc resistance have actually resulted from this condition.

The most serious attack found in this laboratory occurred on a mineral-filled material and consisted basically of a conversion of water-insoluble salts to soluble nitrates. This material, a hard rubber magneto insulation which had excellent electrical properties including humidity resistance and arc resistance, was occasionally found to suffer considerable loss in insulation resistance after long periods of service, with subsequent failure by carbonization in some cases. Accelerated endurance tests at high humidities duplicated this, the hard rubber parts showing the presence of beads of moisture on all surfaces, particularly on machined surfaces, resulting in extremely low surface resistance.

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[1] Manuscript received May 6, 1952. This paper was prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952.

The filler of this material consisted primarily of calcium carbonate and iron oxide, the former being soluble in nitric acid. An analysis of the moisture beads showed them to contain calcium nitrate. To prove our theory an experimental compound was produced in which the calcium carbonate was replaced by additional iron oxide. This material showed none of the effects previously encountered.

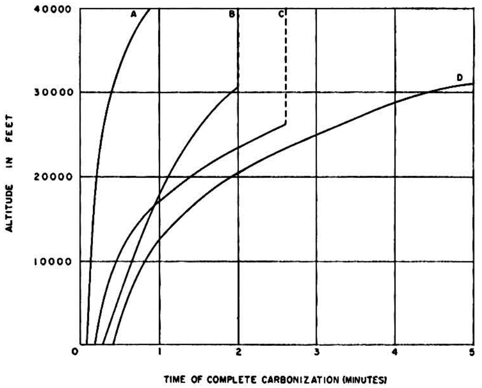

FIG. 1. Illustration of the effect of low ambient pressures on arc resistance of various dielectric materials. A—Hard natural rubber; B—Buna N hard rubber; C—Buna S hard rubber; D—Mineral filled melamine.

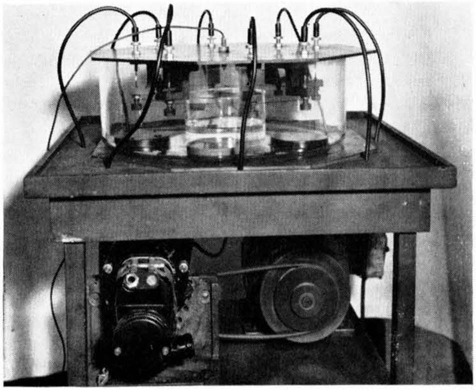

FIG. 2. Equipment used to evaluate the resistance to spark atmospheres offered by various dielectric materials.

In some infrequent cases the resin itself is affected and although the processes are apparently more closely allied with accelerated oxidation and sometimes hydrolysis, the end effects are very similar. Most materials show little more effect than under extremely high humidity, but those which are attacked by the fumes are much more seriously and permanently affected than by humidity alone.

The test equipment employed is shown in Fig. 2 and consists simply of a closed glass chamber having a laminated phenolic cover on which are mounted eight spark gaps fired by a motor driven magneto located outside the chamber. A beaker of water is placed in the chamber to maintain high humidity. The size of the chamber, number of gaps, and source of energy can be varied according to the equipment available as this test can, at present, only be conducted on a comparative basis. Results are normally indicative at the end of 24 hours, and the effects can be determined by use of standard insulation resistance measuring equipment. It is advisable to test a known good material and a known poor material as standards with the unknown material.

The above tests are primarily intended for the evaluation of materials to determine their acceptability as ignition insulation. They cover specific characteristics of vital importance which may not be found by conventional tests. They have the advantage of closely duplicating conditions present in service, thereby eliminating the necessity of attempting to predict service performance from standard tests which for reasons of expediency may vary considerably from actual operating conditions.

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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Streaming Potential Measurements and the Adhesion of Phosphors on Cathode Ray Screens[1]

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ABSTRACT

Streaming potential measurements were carried out to determine the effect of barium acetate on the zeta potentials of phosphor and glass surfaces in the presence of potassium silicate. The results are compared with previous data for sodium sulfate as the addition agent. Although widely different concentrations of the two salts were required to depress the zeta potentials to the same low values, the concentrations corresponded to those which give good adhesion of phosphor to glass. The mechanism of adhesion is discussed.

Introduction

Previous reports from this laboratory on streaming potential measurements with phosphors (1) and on the adhesion of phosphors on cathode ray screens (2) have dealt with the role of sodium sulfate as an addition agent to potassium silicate.

The present study was designed to clarify the role of barium acetate which may be substituted for sodium sulfate as addition agent. It is known that the concentration of barium salt required to produce adhesion is much lower than of sodium sulfate.

Experimental Procedure

Materials

Phosphors: Du Pont No. 1630 phosphor, zinc sulfide-zinc cadmium sulfide; R.C.A. No. 33-Z-8 phosphor, zinc beryllium silicate.

Glass

Corning No. 774 glass (crushed Pyrex—150 mesh); Corning No. 9010 glass (crushed to pass a 100 mesh screen).

Sodium sulfate, barium acetate, and potassium chloride: analytical reagent grade.

Potassium silicate: Kasil No. 1, Philadelphia Quartz Company (analysis: 7.8% K_2O, 19.5% SiO_2; sp gr 1.25; molecular ratio, K_2O: 3.92 SiO_2). Stock solutions of the silicate were prepared fresh daily.

Apparatus

The apparatus employed is shown in Fig. 1 and is a modification of the one described previously (1). Improvements were as follows. The glass tubing from the streaming cell to the calomel half-cells had an outside diameter of 10 mm instead of 4 mm. This reduced the resistance between the half-cells to a marked extent[2] and made possible the use of switches in the circuit. The comparatively low resistance of the circuit also made it possible to use a potentiometer and galvanometer for measurements of the potential even in the case of dilute solutions. All electrical connections were made with test prod wire (Belden No. 8899) and the connections near the apparatus were enclosed in rubber tubing to prevent electrical leakage.

Measurements

The powders under investigation were confined between perforated platinum electrodes using a section of rubber tubing as the cell compartment (1). The diaphragm assembly is shown in Fig. 2. Silver-silver chloride electrodes having the same shape as the platinum electrodes were substituted for the latter in a number of experiments. Since these electrodes were not polarized, they were used for potential determinations as well as for conductance measurements.

In general, the zeta potentials determined with the silver-silver chloride electrodes corresponded with those using calomel electrodes. In runs with 0.0100*N* potassium chloride and with Kasil No. 1 solutions of concentrations from 0.05 per cent to 20 per cent, zeta potentials measured alternately with the calomel and with the Ag-AgCl electrodes agreed to 1 mv. At higher concentrations the calomel electrodes appeared to have greater stability. Other investigators (3) have found Ag-AgCl electrodes to be somewhat polarized at high solution concentrations especially in the absence of chlorides.

In several series of experiments the powders were contained between platinized platinum electrodes

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

[2] With 0.010*N* potassium chloride solution the resistance was about 40,000 ohms instead of the previous 300,000 ohms.

which were employed for both potential and resistance measurements. The platinized electrodes gave reproducible potential measurements and because of their great insolubility and extensive surface area were preferred to the Ag-AgCl electrodes.

No two electrodes, whatever the type, were found to have the same potential values. Potential measurements were taken, accordingly, with no flow in order to obtain a zero correction value. The potential correction remained quite constant for a given pair of calomel electrodes but the corrections tended to change slowly with time for both Ag-AgCl electrodes and platinized platinum electrodes. The two features, constancy of potential and complete reversibility, give calomel electrodes an advantage for potential measurements in the present system.

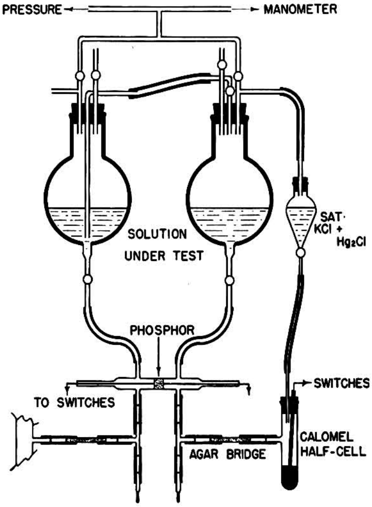

FIG. 1. Streaming potential apparatus

In the determination of streaming potentials, the solution under test was permitted to stream through the diaphragm for 15 minutes[3] at a hydrostatic pressure of 40 cm of Hg before the first potential reading was made. Four readings were taken at five-minute intervals at this pressure for each solution employed. Zero-pressure potential readings were taken before and after each streaming potential measurement, averaged, and applied as a correction to the streaming potential. Despite the fact that the correction factors varied widely for each of the electrode pairs, when these corrections were applied to the measured streaming potentials, the corrected values for the different electrode pairs were in good agreement. Illustrations are given below. Two different calomel electrode pairs are used in the illustrations.

Electrode pair	Measured streaming potential (40 cm pressure)	Potential correction (no pressure)	Corrected streaming potential
Calomel	−9.3 mv	+2.9 mv	−12.2 mv
Ag-AgCl	−13.6 mv	−1.3 mv	−12.3 mv
Calomel	−15.5 mv	−5.5 mv	−10.0 mv
Platinized Pt	−7.7 mv	+2.3 mv	−10.0 mv

The cell constants for the packed diaphragms were obtained using 0.100*N* KCl.[4] The resistance measurements necessary for the calculation were made during streaming. This procedure was decided upon when it was discovered that, with no flow, the conductance of dilute solutions in cells filled with powdered glass increased sharply with time due to solubility of the glass. The cell constant was determined before and after each series of streaming potential measurements. The two values of the cell constant, which never differed by over a few per cent, were averaged for the purpose of calculating the zeta potential.

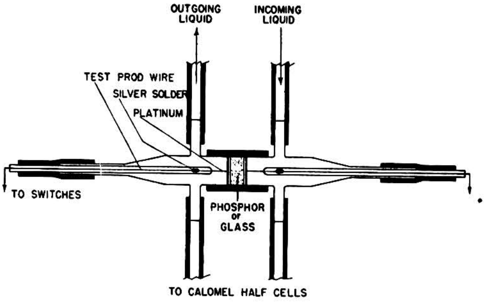

FIG. 2. Streaming potential diaphragm assembly

RESULTS

The data are presented graphically in the accompanying figures in plots of zeta potentials against concentration of potassium silicate or of added salt. The zeta potentials were calculated from a knowledge of the streaming potential, cell constant, cell resistance, and pressure difference by the method described previously (1).

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[3] Conductance data indicate that this time is more than adequate to displace the previous solution from the streaming cell.

[4] Cell constants for diaphragms filled with phosphor and with powdered glass were determined using 0.0100, 0.100, and 1.00*N* KCl and with saturated sodium chloride solution. All solutions gave the same cell constant indicating negligible surface conductance. This was not the case with more dilute solutions where appreciable surface conductance was encountered.

Effect of Potassium Silicate on the Zeta Potentials of Phosphors and Glasses

The effects of potassium silicate concentration[5] on the zeta potentials of R.C.A. No. 33-Z-8 phosphor and Du Pont No. 1630 phosphor are shown in Fig. 3. The general shape of the curves is the same and strong negative potentials are produced with both phosphors, indicating adsorption of silicate on the solid surfaces. A falling off of negative potential with increasing concentrations of silicate occurred after the initial charging. A rather unexpected result was that the Du Pont No. 1630 phosphor had a positive charge in the absence of potassium silicate. This may have been due to flux or other impurity present in it. The addition of the first small increment of potassium silicate recharged the phosphor with a negative sign.

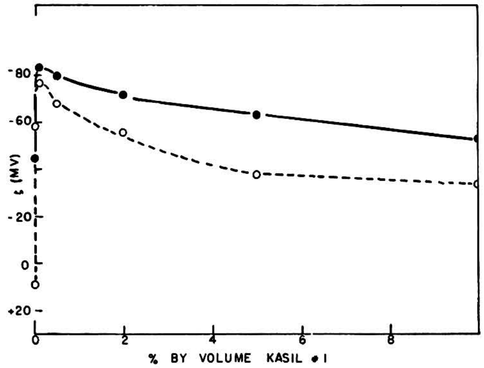

FIG. 3. Results with different phosphors. ● R.C.A. No. 33-Z-8 phosphor; ○ Du Pont No. 1630 phosphor.

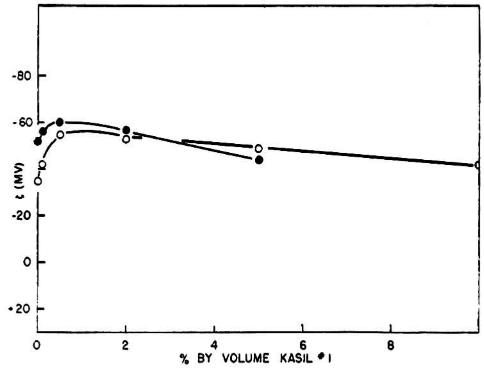

FIG. 4. Results with different glasses. ● Corning No. 774 (Pyrex) glass; ○ Corning No. 9010 glass.

Considering that different samples were used, the present results with the R.C.A. No. 33-Z-8 phosphor and potassium silicate agree substantially with those obtained by Edelberg and Hazel (1), except for the point corresponding to the highest concentration of silicate. These investigators found no drop in negative potential despite the fact that a fall in negative potential was suggested by the point corresponding to 1.2 per cent silicate. It is thought that the discrepancy is due in part, at least, to the fact that a new cell was employed by the previous workers for the measurement at the highest concentration. It has since been found that such cells give higher negative potentials than those which have been in use.

The negative potential of glass surfaces also was increased strongly at low concentrations of added silicate. This is shown by the data in Fig. 4 for Corning No. 774 glass (Pyrex) and Corning No. 9010 glass.

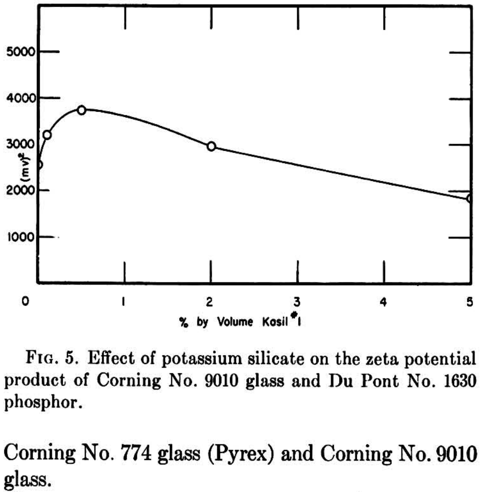

FIG. 5. Effect of potassium silicate on the zeta potential product of Corning No. 9010 glass and Du Pont No. 1630 phosphor.

Since the negative potentials of both phosphor and glass surfaces are increased in dilute solutions of silicate, the mutual repulsion between the surfaces increases under those conditions. The repulsion between the surfaces may be expressed in terms of the zeta potential of the glass surface multiplied by the zeta potential of the phosphor surface for different silicate concentrations. This plot is given in Fig. 5 for Corning No. 9010 glass and Du Pont No. 1630 phosphor.

Effect of Mixtures of Potassium Silicate and Salts on the Zeta Potentials of Phosphors and Glasses

The effect of mixtures of potassium silicate and barium acetate upon the zeta potentials of the surfaces is shown in Fig. 6. The potassium silicate was maintained at a constant value of 2040 ppm and the concentration of barium acetate varied. Du Pont No.

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[5] Potassium silicate concentrations are expressed in percentage by volume Kasil No. 1. Since Kasil No. 1 contains 3.41×10^5 ppm of solid $K_2O:3.92\ SiO_2$, a 1 per cent solution contains 3.41×10^3 ppm of this potassium silicate.

1630 phosphor and Corning No. 9010 glass powder were employed as the solid surfaces.

These data represent the average of several runs. Zeta potentials for both glass and the phosphor were found to be negative in all cases, but are plotted in opposite directions from a zero ordinate in order to show the relative repulsion under varying conditions (1). The effect of barium acetate in decreasing the repulsion between the two surfaces under these conditions is shown also in Fig. 7, in which the product of multiplying the zeta potential of the phosphor surface times the zeta potential of the glass surface is plotted against the barium acetate concentration.

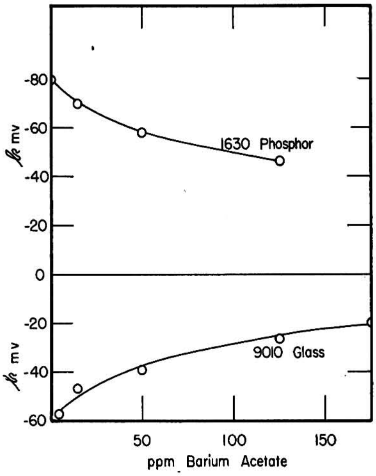


FIG. 6. The effect of barium acetate-potassium silicate mixtures on the zeta potential of phosphor and glass surfaces.

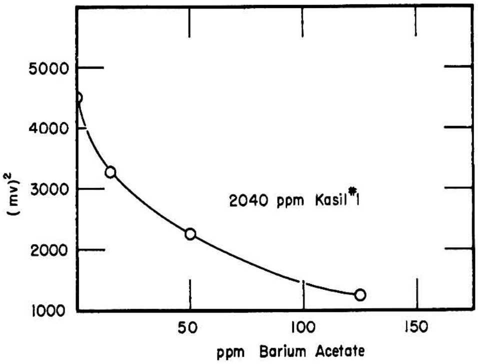


FIG. 7. The effect of barium acetate on the zeta potential product of phosphor and glass surfaces in the presence of 2040 ppm potassium silicate.

Similar results to those shown in Fig. 6 were obtained by Edelberg and Hazel on R.C.A. No. 33-Z-8 phosphor and Pyrex glass wool with potassium silicate-sodium sulfate mixtures (1). The effect of sodium sulfate in decreasing the repulsion between these two surfaces in the presence of 3600 ppm of potassium silicate is shown in Fig. 8. A comparison of Fig. 7 and 8 shows that the concentrations of these two salts required to produce a lowering of the zeta potential product to an arbitrary value of 1000 are markedly different. These concentrations are of the same order of magnitude as will give good screens, however. The data in Table I, showing the amount of salt required to reduce the value of $\zeta\zeta'$ to 1000, were interpolated from the above figures. These data indicate that the potentials of the surfaces play an important role in the adhesion in the present system.

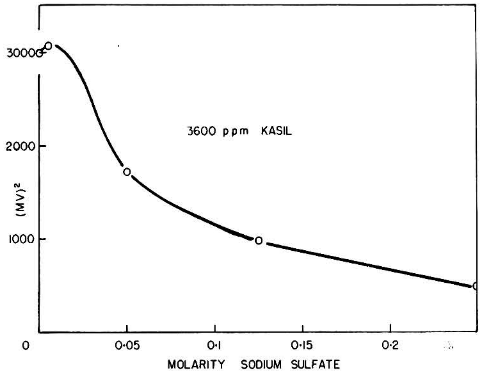


FIG. 8. The effect of sodium sulfate on the zeta potential product of phosphor and glass surfaces in the presence of 3600 ppm potassium silicate.

TABLE I. *Comparison of sodium sulfate and barium acetate*

Salt	Conc of salt required to reduce $\zeta\zeta'$ to 1000	
	Ppm	Molarity
Barium acetate	100–200	3.7×10^{-4}–7.3×10^{-4}
Sodium sulfate	14,200	0.1

As expected from electrokinetic behavior the valence of the positive ion determines the concentration of salt required to reduce the potential to a given low value. The choice of cation is limited by the *p*H of the silicate system. Metals whose hydroxides precipitate at *p*H values below about 10 are eliminated from consideration; hence tri- and tetravalent cations cannot be employed. Indeed, only ions of the strongly basic metals, the alkalies and alkaline earths, are stable in solution at this *p*H.

The Adhesion of Phosphors

The effects of potassium silicate and of potassium silicate-salt mixtures in promoting adhesion of phosphor to glass may be discussed with the aid of the diagram in Fig. 9. The dotted line running from top to bottom divides the electric double layers of the solid phosphor surface (shaded area to the right) and of the solid glass surface, represented by the shaded area to the left. The surfaces are negatively charged and are kept apart by electrical repulsion. The repulsion is weak in the presence of water (indeed with the No. 1630 phosphor, which is positive in water, a weak attraction would appear to be possible, although adhesion is weak in the absence of silicate).

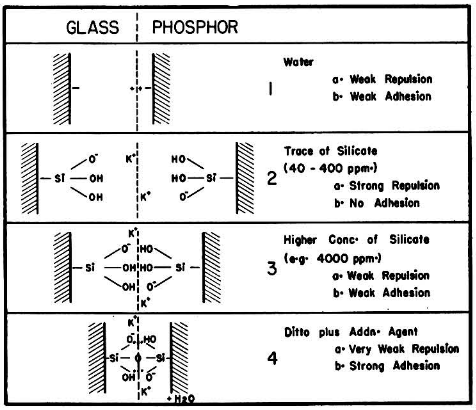


Fig. 9. Diagrammatic illustration of the effect of potassium silicate and addition agents on the bonding of glass and phosphor surfaces.

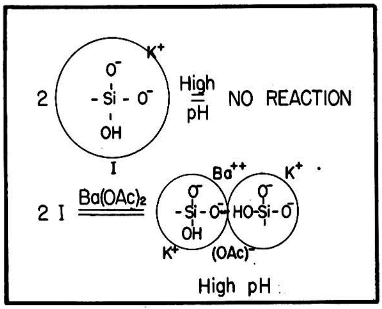


Fig. 10. Diagrammatic illustration of the effect of barium acetate on polymerization at high pH.

The addition of a trace of silicate increases the repulsion between the surfaces by increasing the negative potentials (cf. Fig. 5). At higher silicate concentrations the surfaces become saturated with silicate. The double layer is less diffuse, i.e., is thinner, under these conditions because the potassium silicate in solution tends to screen the charges in the electric double layer of the adsorbed silicate. This condition corresponds to the falling off of zeta potential at high silicate concentrations. The repulsion between the surfaces keeps them too far apart for the adsorbed silicate to polymerize, however. Not until a salt is added (condition 4 of Fig. 9) and the surface charges are more effectively screened does polymerization of the adsorbed silicate occur. The polymerization takes place preferentially at the solid surface rather than in the bulk of the solution because the silicate is concentrated by adsorption at the solid interfaces.

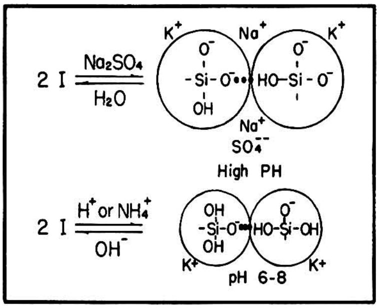


Fig. 11. Top: diagrammatic illustration of the effect of sodium sulfate on polymerization. Bottom: illustration of the effect of reduction of pH on polymerization.

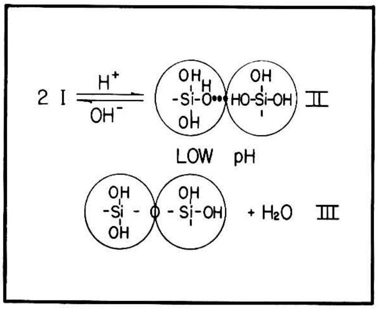


Fig. 12. Illustration of the types of bonds that may hold the polymer together at low pH.

Polymerization of Silicates

The polymerization of silicates can be discussed with the aid of Fig. 10–13. At high pH values the number of charges per silicate ion is high. The ions repel each other and the polymerization reaction is prevented. The charges can be screened by the addition of salts which crowd in the double layer and reduce the repulsion between the ions. Polymerization of the silicate then occurs. In Fig. 10 and 11 the thickness of the double layer is indicated by the diameter of the circle surrounding the silicate ion. The double layer of the silicate ion at high pH, structure I, is pictured being compressed by barium acetate, Fig. 10, and by sodium sulfate, Fig. 11. As indicated in Table I, a much lower concentration of barium salt than sodium salt is required for polymerization.

The bonds holding the silicate ions together in the polymer, or gel, at high *p*H are weak. A revealing experiment can be carried out as follows. Mix equal 25 ml portions of Kasil No. 1 and 4*N* sodium nitrate in a small beaker. A stiff gel which can be retained in an inverted beaker will form within 2 to 3 minutes. If now the gel is transferred to a beaker containing 500 ml of distilled water and stirred, it will dissolve within 5 minutes. The bonds that are present in this salt-gel are of the same nature that hold phosphor particles to glass on cathode ray screens. When water is added to such a gel, the electric double layer around the silicate ions expands. The negative charges force the ions apart and the silicate returns to the monomeric structure indicated by I in Fig. 10.

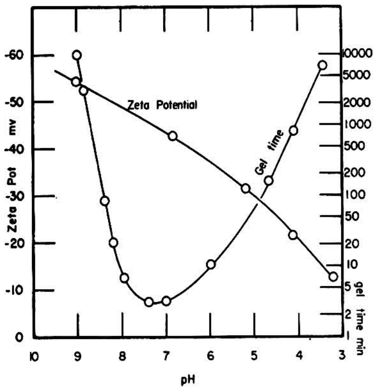
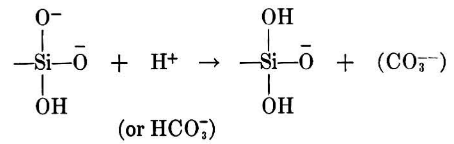


FIG. 13. Effect of *p*H on the gel time (Merrill and Spencer) and on the zeta potential (Hazel) in aqueous silicate systems.

Polymerization by Reduction of pH

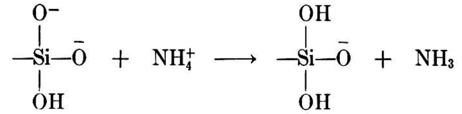
Silica gels or silicate polymers may be formed by reduction in *p*H. This may be accomplished by the addition of acids, ammonium salts, or acid salts (e.g., $NaHCO_3$ or $KHSO_4$) to silicates. The electric charges on the silicate ions are neutralized. Water will not effectively dissolve gels formed by lowering the *p*H because there are not enough negative charges in the polymer to break it up into small fragments. The reaction involved in neutralizing the charges is indicated below.



$$-\overset{\displaystyle O^-}{\underset{\displaystyle OH}{Si}}-\bar{O} + H^+ \rightarrow -\overset{\displaystyle OH}{\underset{\displaystyle OH}{Si}}-\bar{O} + (CO_3^{--})$$

$$\text{(or } HCO_3^-\text{)}$$

Acid or acid salt



$$-\overset{\displaystyle O^-}{\underset{\displaystyle OH}{Si}}-\bar{O} + NH_4^+ \longrightarrow -\overset{\displaystyle OH}{\underset{\displaystyle OH}{Si}}-\bar{O} + NH_3$$

Ammonium salt

The polymerization which occurs following the reduction in *p*H and charge is illustrated in the lower half of Fig. 11 and in Fig. 12.

Too great a reduction in charge is not desirable for maximum polymerization, a fact replete with implication concerning the type of bonds holding the polymer together. The best evidence available indicates that maximum gelation occurs when negative charges are abundant. This is shown by the data in Fig. 13. The zeta potential of silica and the gel time of silicates are both plotted against *p*H. The zeta potentials were calculated from electrophoresis measurements of silica sols at varying *p*H (4). The gel data are from the work of Merrill and Spencer who studied the effect of *p*H on the rate of gelation of sodium silicates (5). Polymerization occurs most rapidly at *p*H values between 6 and 8.[6] Since faster polymerization occurs under these conditions than at lower *p*H where fewer negative charges are present, it is suggested that the negative charges are involved in bond formation. This is indicated by the hydrogen bond designated (*a*) below. Other possible bonds are shown in the text and also in Fig. 12.

$$\equiv Si-OH\cdots\bar{O}-Si\equiv \qquad \equiv Si-O\cdots HO-Si\equiv$$
$$(a) \qquad\qquad\qquad (b)$$

$$\equiv Si-O-Si\equiv$$
$$(c)$$

Although television screens can be formed by lowering the *p*H of alkaline silicates to the range where rapid gel formation occurs, they are usually produced using a salt which does not lower the *p*H, such as sodium sulfate or barium acetate (or nitrate). This assures that an ample proportion of charged groups, $\equiv Si-\bar{O}$, are present in the system.

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[6] Potassium silicate shows a similar gel time-*p*H relationship with maximum gelation occurring in the same *p*H range. A simple experiment which will illustrate this relationship is as follows. Measure 60 ml volumes of 30 per cent Kasil No. 1 (prepared by diluting 30 ml of Kasil No. 1 to 100 ml with distilled water) into each of four 250 ml beakers. Add about 1 ml of Gramercy Universal indicator (Fisher Scientific Co.) to each. Prepare a 1.5 per cent H_2SO_4 solution by volume (15 ml of concentrated acid diluted to one liter with water). For different *p*H values, add acid as indicated below to the silicate in the beakers.

*p*H	ml 1.5% H_2SO_4
10	35
8	55.5
6	62.5
3	65

ACKNOWLEDGMENT

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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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On the Nature of Fluorescent Centers and Traps in Zinc Sulfide[1]

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ABSTRACT

The impurity levels in the energy diagram of a zinc sulfide phosphor are considered to be localized S^{2-} levels lifted above the filled S^{2-} band due to the presence of monovalent positive or trivalent negative activator ions in the lattice. Electron traps are formed similarly by the substitution of S ions by monovalent negative ions or of Zn^{2+} ions by trivalent positive ions. The energy produced when electrons recombine with trapped holes or when holes recombine with trapped electrons is either emitted directly as light or is first transferred to impurity ions. The elements of the iron group give rise to electron traps. The killing action of these elements is explained by assuming that the energy liberated by recombination between holes and electrons in these traps is transferred to the killer ions. The excited ions return to the ground state radiationless because of the presence of many electronic levels between the excited and the ground state. The effect of heat and infrared radiation on the luminescence is discussed. It is shown that, in a phosphor, energy may be transferred by electrons through the conduction band or by holes through the occupied S^{2-} band.

INTRODUCTION

There are several reasons why it seems justified to treat the impurity-activated zinc sulfide phosphors as a separate class. In many respects their properties differ from other impurity-activated phosphors such as silicates, or phosphates activated with cerium, thallium, manganese, rare earth elements, etc. In these phosphors most properties, such as spectral distribution, temperature dependence, and decay of the luminescence, etc., are determined primarily by the activator, and the basic lattice acts only as a modifying factor. In cerium-activated phosphors, for example, the emission always shows a double peak at low temperatures due to electronic transitions of the excited Ce^{3+} ion to the doublet ground state. For thallium-activated potassium chloride the shape and peak of the absorption spectrum have been calculated successfully by assuming that it is the transition from the $^1S_0$ ground state to the $^3P_1$ state of the Tl^+ ion (1). In the sulfide phosphors, however, the emission characteristics seem to be more a property of the lattice itself than of the activator.

Let us consider, for instance, the fluorescence produced by the incorporation of the elements silver, copper, gold, and "zinc." The emission bands all have nearly the same shape and width and the peaks of the bands fall in a fairly narrow range from about 4300 to 5200 Å. These peaks are all shifted to longer wavelengths by the gradual substitution of cadmium for zinc. The magnitude of the shift corresponds to a decrease of energy of about $1.9.10^{-2}$ ev/mole per cent CdS (2). The lon-gwave edge of the absorption spectrum of the pure sulfide is shifted by about the same amount (3).

In other respects, too, the zinc sulfide phosphors deserve to be treated as a separate class. For example, among the elements which have been recognized as activators are lithium (4), sodium (4), indium (5), scandium (5), and phosphorus (6) which are not known as activators in other materials.

Electron traps are formed by the incorporation of a number of elements (7), some of which also act as activators. The depths of most of these traps vary in a regular manner when zinc is substituted by cadmium. In this respect the behavior of traps is very similar to that of the luminescent centers.

In discussing the properties of the zinc sulfide phosphors the well known energy diagram given in Fig. 1 is generally used. Between the uppermost occupied or S^{2-} band and the next unoccupied or Zn^+ band there are localized levels. The levels C near the full band which are normally occupied by electrons are usually attributed to luminescent centers while the levels T, which are normally empty, are responsible for the trapping of electrons. Excitation of the phosphor with 3650 Å radiation then lifts an electron from the occupied level C into the conduction band. These electrons, moving freely through the lattice, may be captured by empty T-levels or they may recombine with empty C-levels under emission of light. The C-levels are associated with the presence of activators and have, therefore, often been considered as ground states of these activators. Luminescence then is a

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[1] Manuscript received May 21, 1952. Invited Keynote Address given before the Symposium on Luminescence at the Philadelphia Meeting, May 5, 1952.

direct property of the activator. On the other hand the author (37) has suggested that *C* levels may also arise from S^{2-} ions disturbed by adjacent activator ions. This theory of indirect activation has already been applied by Kröger (4, 5, 43) in discussing the properties of many zinc sulfide phosphors.

After a short review of the theory of indirect activation, the various activators in zinc sulfide phosphors will be discussed to see which of them may belong to this class of indirect activation. It will furthermore be argued that most of the *T*-levels in zinc sulfide phosphors likewise do not belong to impurity elements but to disturbed lattice elements.

NATURE OF FLUORESCENT CENTERS

Kröger and co-authors (5, 8) have shown that the formation of luminescent centers in zinc sulfide activated with Ag, Cu, Au, Zn, Li, or Na is governed by the principle of charge compensation. These elements can be incorporated much more easily if coactivators are also present. The coactivators can be negative ions such as Cl^- or Br^-. But they can also be trivalent positive ions such as Al^{3+}, Sc^{3+}. These facts show not only that the above mentioned activators are present as monovalent ions but also that these ions occupy lattice sites. If the activators were divalent positive ions on lattice sites, or atoms occupying interlattice sites, no coactivators would be necessary for their incorporation. If they were ions occupying interlattice positions, the fact that both negative ions and positive ions can be used as coactivators would be difficult to explain. But if a divalent Zn^{2+} ion is replaced by a monovalent positive activator ion, the missing positive charge is compensated for either by replacing a divalent negative S^{2-} ion by a monovalent halogen ion, or by replacing a second Zn^{2+} ion by a trivalent positive ion.

It is unlikely that these monovalent activator ions are further dissociated by the exciting radiations or that they are even excited. This holds especially for the alkali ions. For the free Li^+ ion the distance between ground state and the first excited state is 59 ev and its dissociation energy is 75 ev. It is hard to believe that incorporation in the zinc sulfide lattice would lower these energies to such an extent for ionization or excitation to become possible by the absorption of light quanta of only a few electron volts.

Absorption in a pure zinc sulfide crystal of radiation with a wavelength shorter than the edge of the fundamental absorption brings an electron from a S^{2-} ion to a state in which it can move freely through the lattice. One might therefore say that excitation with such radiation leads to ionization of the S^{2-} ions. One of the factors which determines the magnitude of the dissociation energy is the Madelung potential of the S^{2-} ion (9, 10). A lack of positive charge in the immediate vicinity of an S^{2-} ion, such as is created by the replacement of one of the neighboring Zn^{2+} ions by a monovalent positive ion, must raise the Madelung potential of this S^{2-} ion, and thus lower its dissociation energy. An accurate estimation of the decrease in dissociation energy is difficult to make since the lattice will try to compensate for the lack of charge as much as possible by a displacement and polarization of the ions surrounding the monovalent activator ion, but it may well be of the order of 0.5 − 1 ev.

The new absorption band appearing on the long-wave side of the edge of the fundamental absorption when zinc sulfide is activated with copper (8, 11), for example, is thereby explained. Excitation in this new absorption band, known to produce photoconductivity, may then be written as:

$$(S^{2-}A^+) + h\nu \rightarrow (S^-A^+) + \Theta$$

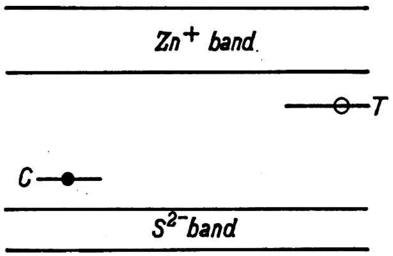

FIG. 1. Schematic energy diagram of a zinc sulfide phosphor containing two kinds of impurity levels; ● = electron and ○ = hole.

where *A* is the activator. The reverse process is responsible for the fluorescence.

One can thus understand why so many of the monovalent ions produce similar emissions in zinc sulfide, and why these emissions all shift in the same manner to longer wavelengths when cadmium is substituted for zinc. The small differences which still occur between the emissions of the various monovalent activator ions are probably caused by differences in the polarization and disturbance of the lattice around the activators.

So far it has been tacitly assumed that the activators and coactivators are distributed at random over the lattice positions. It is, however, also possible that they occupy neighboring lattice sites forming a kind of dipole within the lattice. The monovalent positive ion, forming one of the poles of such a dipole, must still raise the electronic level of a neighboring sulfur ion in the same way as was argued above for a separate activator ion. Arguments have been brought forward in support of either a dissociated or an associated center. The former is supported by the fact that the spectral distributions of silver, zinc, and copper-activated phosphors are independent of the nature of the coactivator (5). On the other hand, the fact that the line emissions of praseodymium and samarium are markedly different in the presence of different monovalent activators (5, 29) points at least to a partial association. Further experiments have to be carried out to clarify this point.

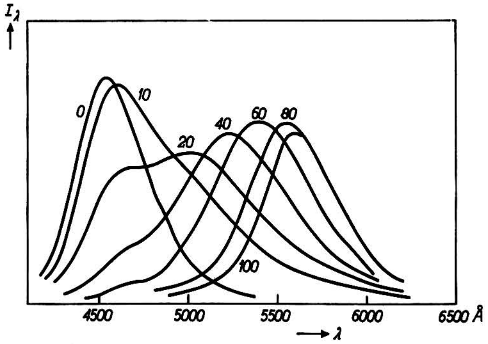

FIG. 2. Spectral distribution curves of a number of Zn(S, Se) phosphors activated with silver, fired at 900° in N_2, with 3% NaCl as flux. The numbers indicate the mole percentages of ZnSe. Excitation with 3650 Å at room temperature.

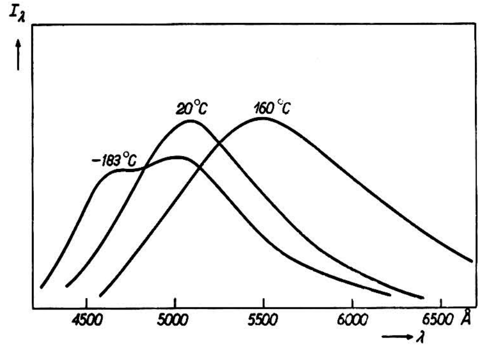

FIG. 3. Spectral distribution curves of Zn ($S_{0.8}$, $Se_{0.2}$)—Ag excited with 3650 Å at −183°, 20°, and 160°C.

It also remains to be explained why copper and gold may produce two different bands (2, 12–16).

Rothschild (12) attributes the green copper band to Cu^{2+} and the blue band to Cu^+, while Bube (15) is of the opinion that copper at interstitial places is responsible for the green band while the blue band is due to Cu^{2+} at lattice sites. Kröger and coauthors (5, 8), however, have shown that for the development of both the blue and the green copper bands chlorine or trivalent positive ions are necessary. These facts show that copper in both cases is present in the form of monovalent ions. To explain the two bands Kröger and coauthors (5, 16, 17) have assumed the green band to be due to Cu^+ ions and the blue band to Cu_2^+ ions.

Replacement of a sulfur ion by a trivalent negative ion must produce similar effects on the electronic levels of neighboring sulfur ions as the replacement of zinc by a monovalent positive ion. In this way the activation of zinc sulfide with phosphorus (6) and arsenic (18) may be explained.

Further support for the idea that impurity levels are to be attributed to disturbed sulfur ions comes from the emission of mixed crystals of sulfides and selenides activated with Zn^+ or Ag^+. The spectral distributions of a number of zinc sulfoselenides activated with silver are given in Fig. 2. They are very similar to the spectral distributions found by Leverenz (19). Substitution of selenium for sulfur not only shifts the bands to longer wavelengths, but causes new bands to appear which are also shifted toward longer wavelengths with increasing selenium content. The appearance of these new bands may be understood when it is realized that two kinds of centers may then occur, e.g., disturbed sulfur and selenium ions. Increase of temperature or of the wavelength of excitation must favor the long-wave emissions caused by transitions of electrons from the conduction band to levels lying farther above the top of the occupied band. This effect is illustrated in Fig. 3 and 4.

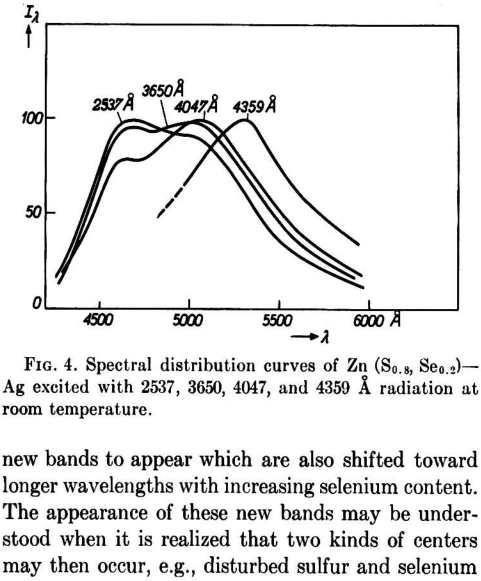

FIG. 4. Spectral distribution curves of Zn ($S_{0.8}$, $Se_{0.2}$)—Ag excited with 2537, 3650, 4047, and 4359 Å radiation at room temperature.

It is remarkable that the blue and green copper bands behave quite differently. Both bands are shifted gradually to longer wavelengths with increasing selenium content and no new bands were found to appear.

Of the activators not yet mentioned manganese is most probably present in the form of its divalent positive ion because MnS and ZnS can form mixed crystals over a large range. It is to be noted, however, that ZnS activated with Mn is hardly excited at all by ultraviolet radiation when fired in an atmosphere of pure H_2S (20). The characteristic yellow band only appears when HCl is added to the atmosphere or if aluminum is present. In the light of this evidence one might conclude that manganese is also present as a monovalent ion. On the other hand, firing with Al or HCl produces Zn^+ centers and it may well be that the excitation with 3650 Å takes place via these centers by some kind of energy transfer. ZnS-Mn without Cl is, moreover, easily excited with cathode rays.

The manganese emission seems to be characteristic of the ion itself. Substitution of zinc by cadmium or of sulfur by selenium has little effect on the spectral distribution as shown in Fig. 5 for the zinc sulfoselenides. Our results are markedly different from those of Leverenz (19). The curves of Leverenz, however, show evidence of a strong zinc band which for small selenium contents is at the short-wave side of the Mn band and for high selenium content at the long-wave side. The broadening observed in our curves is no doubt also due to the appearance of the Zn band at higher selenium contents. Among the other activators which possibly are present in the divalent state are Pb and Sn. With the incorporation of Pb (21–24) two bands are produced. Since the presence of Cl^- seems to favor the green Pb band, Smit and Kröger (22) have attributed it to Pb^+. There are also indications that Sn (20, 25, 26) produces two bands.

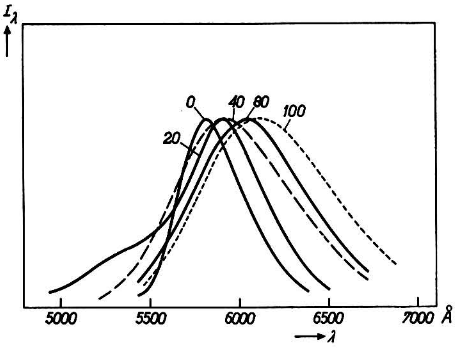

FIG. 5. Spectral distribution curves of a number of Zn(S, Se) phosphors activated with 0.5 mole % Mn, fired at 1000°C in H_2S + HCl. The numbers indicate the mole percentages of ZnSe; excitation with 3650 Å at −183°C.

NATURE OF ELECTRON TRAPS

The arguments which have led us to believe that the monovalent activator ions replace Zn^{2+} ions at lattice sites also lead to the conclusion that the coactivators must occupy lattice sites. Replacement of Zn^{2+} by trivalent positive ions and substitution of S^{2-} by Cl^- involves the introduction of an extra positive charge. This extra positive charge must lower the electronic energy level of neighboring Zn^+ ions. Electrons moving freely through the lattice will be trapped near such a positive charge. The chemical equivalent of a filled trap in a phosphor containing Cl^- as coactivator might therefore be considered to be a Zn^+ ion next to a Cl^- ion, although the electron is probably shared by several Zn^{2+} ions around the Cl^- ion. The thermal release of the electron from such a trap may then be written:

$$(Zn^+Cl^-) + E \rightarrow (Zn^{2+}Cl^-) + \ominus.$$

Some idea of the magnitude of the dissociation energy or trap depth E may be obtained from a study of the thermal glow curve. This method, first applied by Urbach (27) to halides, was later used by many others for the study of traps in zinc sulfide phosphors. The interpretation of these glow curves is difficult since nearly all published curves are rather complicated and often show many peaks. Hoogenstraaten (7), however, has shown recently that with sulfides made under carefully controlled conditions, using no flux and by firing in well defined atmospheres according to the method of Kröger (16), simpler glow curves are obtained. Oxygen must be avoided. Firing zinc sulfide in an atmosphere of H_2S and HCl, one obtains a single glow peak at approximately −90°C regardless of the nature of the activator. With trivalent ions, other characteristic glow peaks are obtained as shown in Fig. 6. This is just what one would expect, if the coactivators are responsible for unoccupied levels below the conduction band.

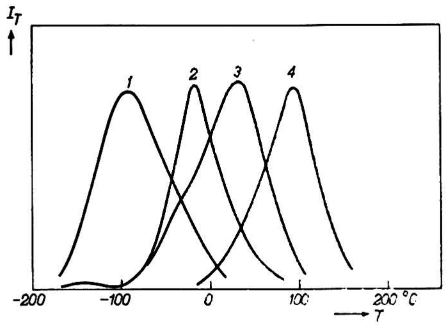

FIG. 6. Thermal glow curves for ZnS activated with Cu and different trivalent ions. (The activator concentration in Fig. 6, 8, 10, and 14 are in gram atom activator per mole ZnS.) Curve 1—ZnS − 5.10^{-5} Cu − 10^{-4} Al; curve 2—ZnS − 5.10^{-5} Cu − 10^{-4} Sc; curve 3—ZnS − 5.10^{-5} Cu − 10^{-4} Ga; curve 4—ZnS − 3.10^{-5} Cu − 3.10^{-5} In.

Riehl (28) has suggested that such levels may be filled directly with electrons from the occupied band (transition [1] of Fig. 7), for example by excitation with 3650 Å radiation. In that case there seems to be no reason why the reverse process—the recombination of a free hole with a trapped electron—should not occur with emission of light. This transition is indicated by transition [2] in Fig. 7 where the hole recombines directly with the trapped electron, or by transition [2a] if it passes through a "waiting state." Three of the trivalent coactivators Sc, Ga, and In have indeed been found (5) to be associated with broad emission bands. The theory that these emissions are due to transitions [2] or [2a] is supported by the fact that those ions which are responsible for the deepest traps also produce the reddest emissions. One would also expect Al to give an emission band, probably in the blue region, because of its shallow trap. Indications of an Al band have indeed been found on the short wavelength side of the Zn band in zinc sulfides fired with an excess of aluminum, as shown in Fig. 8. It is seen from the above that traps may also function as luminescent centers and that a distinction has therefore to be made between two types of centers in zinc sulfide phosphors. The various excitation and emission processes of these two types are indicated schematically in Fig. 9. We have:

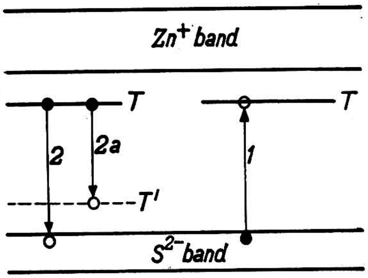

FIG. 7. Schematic representation of the emission produced by the recombination of trapped electrons and free holes.

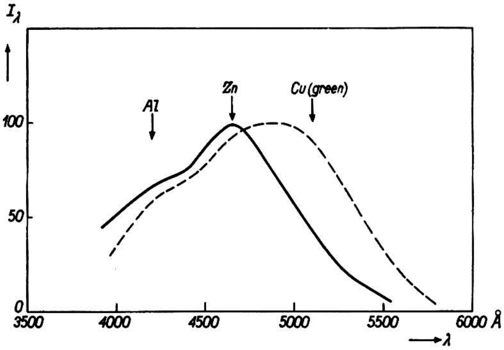

FIG. 8. Spectral distribution curves of zinc sulfide phosphors showing the aluminum band. Curve 1—ZnS fired with 10^{-4} Al at 1200° in H_2S; curve 2—ZnS – 10^{-3} Al – 5.10^{-6} Cu fired at 1300° in H_2S. Excitation with 3650 Å at −183°C.

1. *Centers represented by occupied levels C.*—On excitation some of these levels lose an electron by direct absorption [3] or by capturing a hole from the occupied band [8]. Such a hole may be obtained by lifting an electron from the full band into the conduction band [9]. Emission occurs when free electrons from the conduction band recombine with holes in *C*-levels [4]. Temperature quenching of the emission starts at temperatures where electrons may be lifted thermally from the occupied band into the empty *C*-levels or, in other words, when the holes in *C*-levels are transferred thermally to the occupied band [7].

2. *Centers represented by unoccupied levels T.*—In the excited state these levels are occupied by electrons. Excitation may occur through direct absorption [1] or by capturing an electron from the conduction band [6]. Emission is indicated by [2]. Thermal quenching starts when electrons are lifted thermally into the conduction band [5]. "Waiting states" which may be present in both types of centers have been omitted for simplicity.

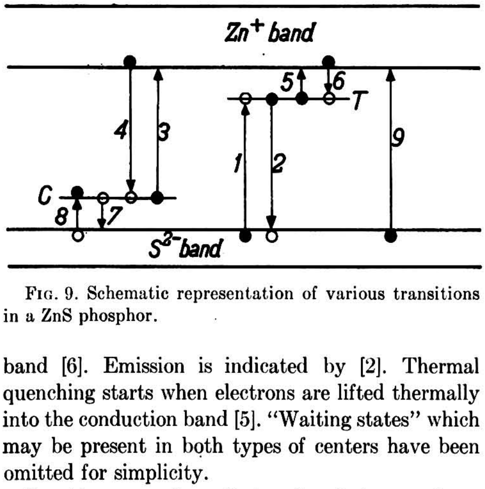

FIG. 9. Schematic representation of various transitions in a ZnS phosphor.

Consider now the effects of cadmium and selenium substitution on the *T*-levels. It has already been seen that cadmium substitution shifts the emission connected with the *C*-levels to longer wavelengths by an amount about equal to the shortening of the distance between the S^{2-} and Zn^+ band, as judged from the shift of the fundamental absorption edge. It seems, therefore, that the conduction band moves down with respect to the occupied band without affecting greatly the distance between *C*-levels and the latter. This is confirmed by a study of the temperature quenching of (Zn, Cd)S phosphors. The temperature of quenching is not lowered much by the substitution of zinc by cadmium. The distance between the *T*-levels and the full band is apparently also little affected by the cadmium substitution. This is evident from the spectral distribution of (Zn, Cd)S activated with indium (Fig. 10). The peak moves from 6100 to 6200 Å when the cadmium content is increased from 0 to 20 per cent. This corresponds to a decrease in energy of only 0.03 ev. Also, the scandium band at 5400 Å was found to be little affected by the cadmium substitution.

Since the gap between the conduction and the occupied band becomes smaller, the distance between *T* and the conduction band should diminish when cadmium is substituted for zinc. This was confirmed by Hoogenstraaten (7), who found indeed that the trap depth of various traps was lowered at a rate only slightly less than the rate at which the distance between the two bands is diminished. Another remarkable effect found by Hoogenstraaten was the appearance of new traps in zinc sulfide phosphors containing Cl^- or Al^{3+} as coactivators when zinc was gradually replaced by cadmium. This is in accordance with our theory that the traps are to be considered as disturbed cations. When the lattice contains both Zn^{2+} and Cd^{2+} ions, traps of different depth may be found depending on whether Cd^{2+} or Zn^{2+} ions, or possibly various combinations of these ions, are disturbed. This phenomenon is to be compared with the appearance of new emission bands in the spectra of zinc sulfide activated with Ag^+ when sulfur is partly replaced by selenium. Also in accordance with our theory is the fact that the selenium substitution does not produce new traps. Fig. 11 and 12 show that the Cl^- and Al^{3+} peaks in the glow curves are merely shifted to lower temperatures; no new peaks are observed in contrast to the phosphor with cadmium substitution. To follow the shifts to very low temperatures, it was necessary to cool the phosphor in liquid hydrogen. A new shallow trap was thereby observed giving a glow peak at 60°K which is not affected by the selenium substitution. The nature of this shallow trap has not been established. The Cl^- and Al^{3+} peaks move to lower temperatures with increasing selenium content until they merge into this low temperature peak.

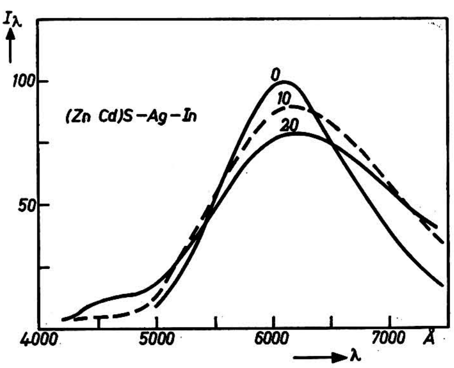

FIG. 10. Spectral distribution curves for (Zn, Cd)S fired with 5.10^{-5} Ag + 10^{-4} In at 1100°C in H_2S. Excitation with 3650 Å at −183°C.

Some of the trivalent ions active in zinc sulfide do not belong to the class of indirect activators. Samarium produces a line emission while cerium shows the double-peaked emission characteristic of all cerium activated phosphors. However, one property is found in cerium-activated zinc sulfide which is characteristic for zinc sulfide phosphors and which arises from the fact that the emission is a recombination process, namely, that the quenching temperature is a function of the intensity of the exciting radiation (5). We have therefore come to the conclusion that the first stage in the emission process of cerium is a recombination process indicated by transition [2] in Fig. 9—the Ce^{3+} ion must produce *T*-levels—and that the energy released by this process is transferred to the activator itself bringing it into an excited

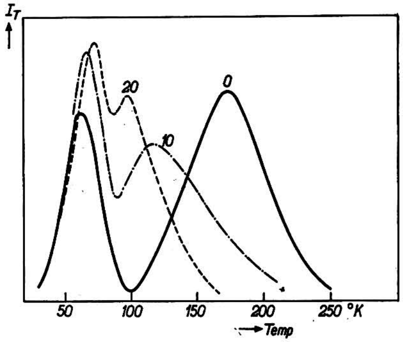

FIG. 11. Thermal glow curves of Zn(S, Se) activated with 3.10^{-5} Cu and fired in HCl at 1000°C. The numbers indicate the mole percentages of ZnSe.

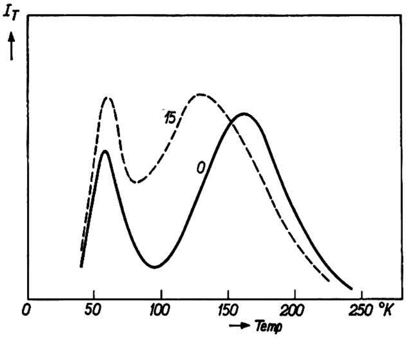

FIG. 12. Thermal glow curves of Zn(S, Se) activated with 3.10^{-5} Cu and 3.10^{-5} Al and fired in N_2 + CS_2 at 1000°C. The numbers indicate the mole percentages of ZnSe.

state. The process of emission may then be represented as:

$$(Zn^{+}Ce^{3+}) + S^{-} \rightarrow (Zn^{2+}Ce^{3+*}) + S^{2-}$$

followed by

$$Ce^{3+*} \rightarrow Ce^{3+} + h\nu.$$

Quenching of the emission probably occurs at temperatures where the electrons trapped in the T-levels belonging to the cerium center are released again by thermal agitation. On the other hand, quenching may be a property of the activator itself. This is found to occur in the ions of the iron group known as "killers." No coactivators are necessary to incorporate these ions in the zinc sulfide lattice. They are situated as divalent ions at normal Zn^{2+} positions in the lattice. Since they also produce traps (7, 33) the electronic levels of Ni^{+} and Co^{+} must be below the Zn^{+} band. Trapping can then be represented as:

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

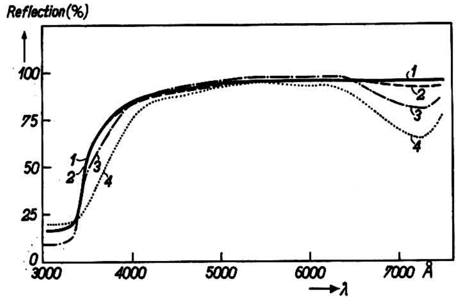

FIG. 13. Reflection spectra of ZnS—Co. Curve 1—0 Co; curve 2—10^{-6} Co; curve 3—10^{-5} Co; curve 4—10^{-4} Co.

Both killers produce new absorption bands at the long-wave side of the lattice absorption (Fig. 13 and 14). These are probably related to a direct filling of the Co^{+} and Ni^{+} levels with electrons from the filled band (transition [1] of Fig. 9). The absorption caused by nickel extends further into the visible due to its greater trap depth. Both ions show also characteristic absorption in the red region.

According to the well-known Mott-Seitz theory, radiationless transitions from an excited state to a lower state may occur at relatively low temperatures when the potential energy curves for the two states plotted against a generalized configurational coordinate cross at a point not too far above the minimum of the curve of the higher state. This is the more likely to occur the smaller the energy difference between the two states. Both the Ni^{2+} and the Co^{2+} ions have a partially filled third shell. Many combinations of the orbital and spin moments are possible and the energy differences between the various combinations are not great. When, therefore, the energy released by transition [2] ($S^{-} + Ni^{+} \rightarrow S^{2-} + Ni^{2+}$) is transferred to the Ni^{2+} ion itself, bringing it into one of the excited states, it is not surprising that the ion returns to the ground state via a number of radiationless transitions to intermediate states. The killers can thus be considered to be activators with a low quenching temperature. That they are sometimes also capable of emitting light is shown by the fluorescence of MgO — Ni (30) and ZnS — Fe (31).

INTERACTION BETWEEN C- AND T-LEVELS

We have distinguished above between two kinds of impurity levels in zinc sulfide phosphors. The C-levels are normally occupied by electrons and the T-levels are normally empty. In the excited state this situation is partly reversed. Since both types of levels are usually present in zinc sulfide phosphors, several processes indicated by transitions [1 to 9] in Fig. 9 may happen simultaneously. Which process dominates depends on the rates of the various transitions. The temperature which determines the rates of transitions [5] and [7] is an important factor. If [5] or [7] are too fast, the corresponding emissions [2] and [4] do not take place. Interaction between the two centers may occur when electrons are liberated from T-levels and recombine with empty C-levels, or when holes are transferred from empty C-levels and recombine with occupied T-levels.

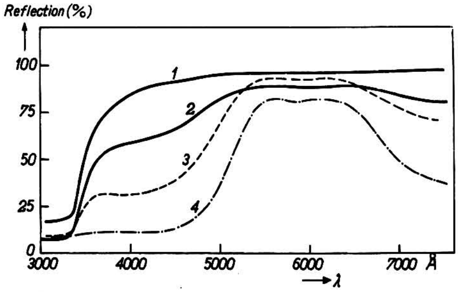

FIG. 14. Reflection spectra of ZnS—Ni. Curve 1—0 Ni; curve 2—10^{-5} Ni; curve 3—10^{-4} Ni; curve 4—10^{-3} Ni.

The rate of process [5] or [7] is determined by a temperature-dependent factor $\gamma = s \exp(-E/kT)$, where s is a constant and E the distance between the levels and the nearest band. Whether energy will be transferred from C to T or vice versa is determined mainly by the ratio of the γ factors of processes [5] and [7]. This may be illustrated by a few examples.

ZnS—Cu—Co: The glow curve of this phosphor shows a peak at 380°K which is characteristic for Co (7, 32, 33). At that temperature, electrons are released from the Co traps and recombine with the empty Cu levels.

ZnS—Ag—Co: The distance between C and the occupied band is smaller in Ag activated than in Cu activated sulfides. Now the peak at 380°K is not observed. Instead, the glow at higher temperatures is reduced, because holes move away from the empty Ag levels to recombine without radiation with electrons trapped in the Co traps.

ZnS—Ag—Sc: Scandium gives a characteristic peak in the glow curve. The color of the emission during the thermal glow is blue. Energy is transferred from T to C.

ZnS—Ag—In: The In trap is deeper than the Sc trap. The color of the emission during thermal glow is yellow. Now the energy transfer is from C to T.

Transitions [5] and [7] can also be stimulated optically. Antonov-Romanovskii and Shchukin (34) found new absorption bands with maxima at 13,000, 8000, and 4500 Å in a ZnS—Cu—Co phosphor during excitation. The first two bands are also found in the stimulation spectra of ZnS—Cu—Pb and ZnS—Cu—Mn (13, 35) and in the quenching spectrum of ZnS—Cu—Co (36). They are a property of the excited Cu center and probably correspond to transition [7]. The fact that two bands are observed indicates an intermediate level between C and the full band. Thermal energy is required to bring the hole from this band to the full band. Fonda (35), indeed, observed that at 77°K stimulation only occurs in the 8000 Å band.

The release of electrons from traps may also be produced optically. Infrared radiation causes stimulation in most Cu activated sulfides at low temperatures where transition [7] is sufficiently reduced. Even the exciting radiation may liberate trapped electrons. This is shown by the results of Smith and Turkevich (38) who found a marked effect of the wavelength of excitation on the thermal glow curve, while Hoogenstraaten and Klasens (32) have deduced from the properties of ZnS—Cu—Co phosphors that electrons trapped by the Co traps are ejected again by 3650 Å radiation.

Infrared radiation and increase of temperature often show the opposite effects. In ZnS—Cu—In the afterglow is green and increases in intensity when the temperature is raised. The electrons go from the In traps through the conduction band to the empty C-levels due to Cu. If, however, during the afterglow the phosphor is exposed to infrared radiation, the green emission is quenched while the yellow indium emission is stimulated. Now the holes go from the empty C-levels through the occupied band to recombine with the electrons in In traps. A similar mechanism has been proposed for SrS—Ce—Sm by Kröger (39), Urbach (40), and Brauer (41). In this phosphor, heating after excitation produces the Sm-emission, while with infrared radiation the Ce-emission is stimulated.

In phosphors emitting two bands, one belonging to a level C and another to a level T, quenching of one emission will generally stimulate the other. Such phenomena were already observed by Lenard (42) with CaS—Bi phosphors. The maxima in the stimulation spectrum of the β emission (5030 Å) were found to coincide with the maxima in the quenching spectrum of the α band (4740 Å). Many more examples may be given to illustrate the above theory of energy levels and energy transfer in zinc sulfide phosphors. On the other hand, no doubt other cases may be brought forward, for example the fact that zinc sulfoselenides activated by Cu behave differently from zinc sulfoselenides activated by Ag, where this simple theory seems to fail.

It is firmly believed, however, that such apparent exceptions, when better understood after further research, will call for modification or refinement rather than for a total rejection of the present theory.

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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Optical Measurements on Electroluminescent Zinc Sulfide[1]

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ABSTRACT

Absorption and emission spectra of electroluminescent ZnS phosphors, activated by Cu and Pb, are reported. Three absorption bands are observed, at 3.18 electron volts (ev), at about 2.7 ev, and somewhere below one ev. The infrared absorption band is associated with the Pb activator but its exact location is uncertain. The emission spectra of both blue and green phosphors may be resolved into the same emission bands, at 2.15, 2.4, and 2.7 ev, respectively. The primary difference between the spectra of blue phosphors and green phosphors lies in the ratio of the amplitudes of the green and blue bands. This ratio is also shown to be a function of the frequency of the applied alternating field, but is independent of the magnitude of the field.

INTRODUCTION

The measurements described in this report were made primarily to furnish information which would be helpful in developing a theory of the mechanism of electroluminescence (1, 2). They were made on zinc sulfide phosphors, activated with about 10^{-3} moles Cu and 10^{-5} moles Pb per mole of ZnS. $ZnCl_2$ was used as the fluxing agent in these phosphors. The percentage of ZnO in the finished phosphors is believed to be extremely small. The measurements may be divided into two categories: measurements of the optical absorption of the phosphors, and measurements of the energy distribution of the radiation emitted from the phosphors when excited by electroluminescence.

OPTICAL ABSORPTION

Since these phosphors are in the form of fine powders, the measurements of the optical absorption were performed using a diffuse reflection technique. This was done with the diffuse reflection apparatus which may be purchased for use with the Beckman Model DU spectrophotometer. With this apparatus, the reflectance of a powder sample is measured by comparing the amount of light diffusely reflected from its surface with that reflected from the surface of a "standard white" powder, which was in this case basic magnesium carbonate. Measurements of reflectance of the phosphors were made in this way between 10,000 and 3500 Å.

Since these phosphors fluoresce under excitation by radiation in the far blue and near ultraviolet, a filter with a cutoff at 4100 Å was used to separate fluorescent emission from the reflected light for wavelengths of the incident radiation less than 4250 Å. In this way, curves of true reflectance could be obtained as a function of wavelength.

Fig. 1 illustrates the type of curves which are obtained. The upper of the two curves is for ZnS, while the lower is for a typical green phosphor. Obviously, the phosphor shows the presence of additional absorption bands which must be due to the presence of activators. To show up the location of these bands more definitely, the analysis shown below is employed.

The basic assumption is that the reflected light has travelled on the average a distance, D, through the powder; its reflection coefficient will therefore be given by:

$$R_p \alpha \exp(-[\sigma_A + \sigma_M]D), \tag{I}$$

where σ_A is the absorption coefficient due to the activators and σ_M is the absorption coefficient due to the matrix. Similarly the reflection coefficient of ZnS will be given by:

$$R_Z \alpha \exp(-\sigma_M D). \tag{II}$$

By a separate measurement of the reflectance of ZnS, $\exp(-\sigma_M D)$ can be determined; thus, by division of phosphor reflectance by ZnS reflectance and subtraction of the quotient from unity the following expression is obtained,

$$A = 1 - R_p/R_Z = 1 - \exp(-\sigma_A D), \tag{III}$$

which is then called "the absorption due to the activators."

Fig. 2 shows typical curves of absorption due to activators plotted as a function of photon energy for a typical green phosphor. There appears to be a major absorption band centering at 3.18 ev (3900 Å), a minor absorption band in the neighborhood of 2.7 ev (4600 Å), and a third absorption band centering somewhere below 1 ev. The location of the infrared band is uncertain, since the monochromator could not be used beyond 12,000 Å (1.03 ev), but it is estimated as lying in the neighborhood of 0.8 ev. Absorption curves for blue phosphors are very simi-

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[1] Manuscript received June 2, 1952. This paper was prepared for delivery before the Philadelphia Meeting, May 4 to 8, 1952.

lar to those shown for the green; the same three absorption bands are present in both. The 3.18 ev band is much weaker in blue phosphors than in green phosphors; this observation is valid enough so that blue phosphors may be identified by their absorption curves.

The infrared absorption band which is found in the absorption spectrum has been assigned to the Pb activator, as is shown in Fig. 3. In this figure, the absorption at 1.03 ev is plotted against the logarithm of the concentration of Pb found by chemical analysis in the phosphor. For concentrations less than 4 × 10^{-3} per cent Pb by weight, the absorption and Pb concentration are well correlated. At higher concentrations than 4 × 10^{-3} per cent, there is no correlation. It has been suggested that at higher concentrations of Pb, crystals of galena (PbS) form, and that these rob the ZnS lattice of dissolved Pb. Some evidence has been found by x-ray analysis for the presence of PbS in some of these high-Pb phosphors, but it is as yet inconclusive.

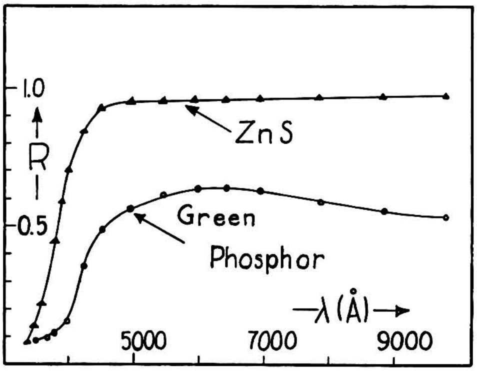

FIG. 1. Reflectance vs. wavelength

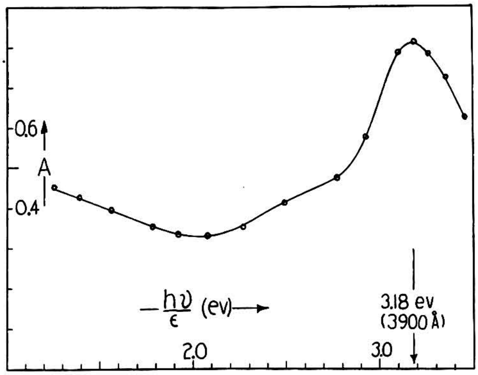

FIG. 2. Absorption due to activators vs. energy of photons (green phosphor).

SPECTRAL ENERGY DISTRIBUTION

The energy distribution of the radiation emitted from a number of phosphors has been measured, as an alternative means of gaining information about the energy level scheme of the phosphor. This measurement was made using a Beckman monochromator with a 1P21 photomultiplier as a detector. The system was calibrated using a fluorescent lamp of known spectral energy distribution as a secondary standard. Care was taken to exclude stray radiation of shorter wavelength than the monochromator setting from the beam emergent from the exit slit by means of a series of sharp cutoff filters.

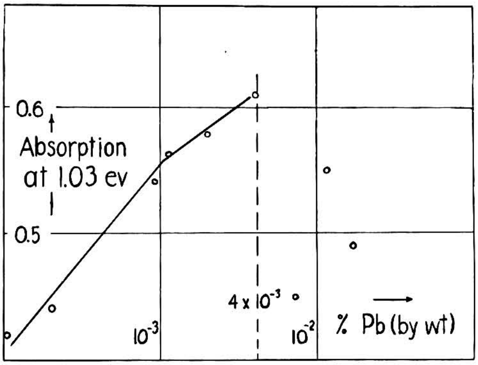

FIG. 3. Infrared absorption vs. Pb concentration

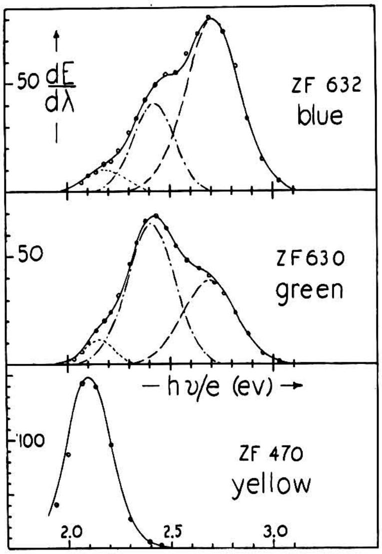

FIG. 4. Spectral energy distribution as a function of photon energy (blue, green, and yellow phosphors).

Fig. 4 shows curves of the energy distribution of the radiation emitted from three different phosphors plotted as a function of photon energy. In these curves, therefore, blue is at the right hand side of the diagram and red is at the left. The ordinate is in arbitrary units. These curves are not necessarily typical; this green phosphor has a good deal more blue than is normal. It was chosen for the purpose of illustration here for that very reason, so as to emphasize the presence of the blue band in the emission spectrum of green phosphors. The solid curve is in each case the sum of the Gaussian bands, which are shown as dotted and dashed lines. The circles are the experimental points. It is evident that the points are well represented by the synthesized solid curves.

The emission spectra of both green and blue phosphors are composed of the same three bands, at about 2.7, 2.4, and 2.15 ev, respectively. The primary difference is in the ratio of amplitudes of green and blue bands. It is interesting to note that the curves of spectral energy distribution of green and blue phosphors excited by 3650 Å ultraviolet radiation are composed of the same emission bands as when the phosphors are excited by electroluminescence. The ratio of green to blue is always smaller when the phosphor is excited by ultraviolet. In the curve for the yellow phosphor which is plotted here, only a single band, centering at 2.10 ev (5900 Å), is observed.

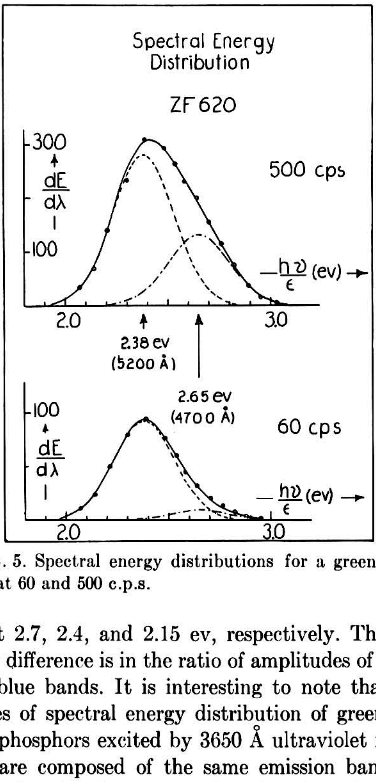

FIG. 5. Spectral energy distributions for a green phosphor at 60 and 500 c.p.s.

Fig. 5 shows the result of measurements of spectral energy distribution of a typical green phosphor at two different frequencies of exciting alternating field. The ratio of amplitudes of the green and blue bands is about 10:1 at 60 c.p.s., while at 500 c.p.s. it is about 2:1. Since the bands are quite broad, the change in the over-all distribution appears at first glance to be merely a shift of modal energy. Fig. 6 shows the variation of the amplitudes of the green and the blue bands with frequency of exciting alternating field.

The amplitude of the blue band increases almost linearly with frequency, while that of the green band saturates at about 1000 c.p.s. This can only be the case if the time required to "activate" blue centers is very much shorter than the shortest period encountered (5×10^{-4} sec), so that the same number of blue centers are active each cycle, and the total emission from them is proportional to the number of cycles per second. By similar reasoning, it is concluded that the time required to activate green centers is comparable with 5×10^{-4} sec.

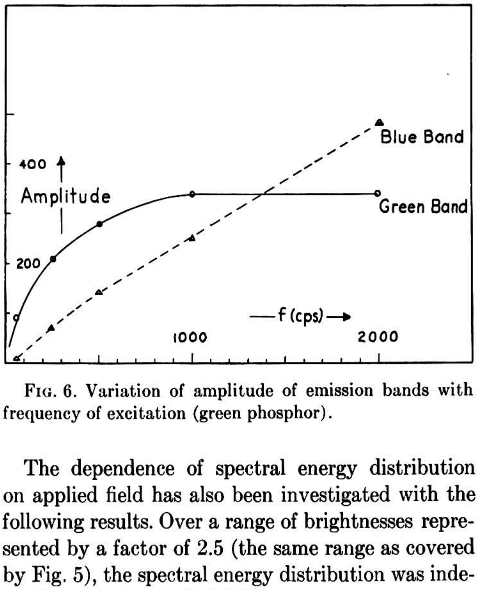

FIG. 6. Variation of amplitude of emission bands with frequency of excitation (green phosphor).

The dependence of spectral energy distribution on applied field has also been investigated with the following results. Over a range of brightnesses represented by a factor of 2.5 (the same range as covered by Fig. 5), the spectral energy distribution was independent of the applied field.

SUMMARY

1. Green and blue electroluminescent zinc sulfides show substantially the same absorption bands, e.g., 3.18 ev, about 2.7 ev, and about 0.8 ev or less.

2. The 0.8 ev absorption band is associated with the Pb activator.

3. Blue and green phosphors show the same major emission bands, e.g., 2.70 ev, 2.40 ev.

4. Increased emission in the higher energy emission band (2.70 ev) is paralleled by decreased absorption in the higher energy absorption band (3.18 ev). This correlation is good enough so that blue phos-

phors may be readily identified from their absorption curves.

5. The ratio of the amplitude of the green band to that of the blue band is a function of frequency.

ACKNOWLEDGMENTS

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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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Acid Dissociation of the Aquoscandium Ions[1]

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ABSTRACT

A study of the hydrogen ion concentrations of scandium perchlorate solutions to which sodium hydroxide has been added reveals that the data cannot be explained by assuming a single acid dissociation step. The data can be interpreted in terms of a single acid dissociation followed by dimerization of the base conjugate to the hexaquo ion. In the solvent salt sodium perchlorate at a concentration of one molar, *K* for the first step is equal to 1.17×10^{-5}, with the *K* for the dimerization equal to 7.38×10^{3}. The literature indicates that this may be a general phenomenon.

INTRODUCTION

As early as 1907, studies of the structure of metal hydroxides, hydrous oxides, and basic salts led to the conclusion that these species may be polymeric (1). Thomas has explained the properties of the hydrous oxides in colloidal systems in terms of polynuclear metal ions, using the idea of dihydroxy or diol bridges employed earlier by Werner and Pfeiffer (2). While most chemists today recognize the complications in aqueous chemistry due to formation of various types of complexes and of ion pairs, metallic cations are usually assumed to be monomeric (3, 4). However, examination of the precipitated basic salts or hydrous oxides on addition of sodium hydroxide has demonstrated that there are usually dimers or higher polymers in the solid phase. It is one of the purposes of this paper to demonstrate that the hydrated scandium ion also forms dimers and polymers in solution as has been shown recently by Pedersen (5) for copper nitrate, by Graner and Sillén (6) for bismuth perchlorate systems, and by Ahrland (7) for uranyl ion in aqueous perchlorate systems; and further that no mass law expression which does not include the formation of polymers can successfully describe the systems studied.

EXPERIMENTAL METHOD

The system chosen for study was aqueous scandium perchlorate where the hexa-aquoscandium ion is partly reacted with hydroxyl ion. The coordination number of six is assumed for the scandium aquo ion. It will be shown that the experimental results cannot be explained on the basis of the equilibrium

$$\underset{Sc_3}{[Sc(H_2O)_6]^{3+}} + H_2O \rightleftarrows \underset{Sc_2}{[Sc(H_2O)_5OH]^{2+}} + H_3O^+ \qquad \text{(I)}$$

nor

$$\underset{Sc_2}{[Sc(H_2O)_5OH]^{2+}} + H_2O \rightleftarrows \underset{Sc_1}{[Sc(H_2O)_4(OH)_2]^{+}} + H_3O^+ \qquad \text{(II)}$$

or a combination of the above equilibria. However, the experimental data appear to be consistent with a combination of (I) and (III)

$$2\underset{Sc_2}{[Sc(H_2O)_5OH]^{2+}} \rightleftarrows \underset{Sc_{2,4}}{[Sc(H_2O)_5OH]_2^{4+}} \qquad \text{(III)}$$

The experimental method was the determination of hydrogen ion concentration in buffers of known stoichiometric composition in the solvent salt sodium perchlorate in swamping concentrations.

The hydrogen ion concentrations were determined by a modification of the method used by Kilpatrick and coworkers (8), with the additional assumptions that the scandium ion does not complex with perchlorate nor with quinhydrone. The second assumption seemed justified by the fact that absorption patterns for the scandium-quinhydrone systems showed no bands indicating complexes.

The emf of the cell

$$\mathrm{Au}\ \left|\ \begin{array}{l} HClO_4 \\ NaClO_4 \\ \text{Quinhydrone} \end{array}\ \right\|\ NaClO_4\ \left\|\ \begin{array}{l} Sc(ClO_4)_3 \text{ buffer} \\ NaClO_4 \\ \text{Quinhydrone} \end{array}\ \right|\ \mathrm{Au}$$

was measured using a Type K-2 potentiometer with suitable galvanometer.

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[2] This paper was abstracted from a part of the dissertation presented by Lewis Pokras to the Faculty of the Graduate School of the Illinois Institute of Technology in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Chemicals

Sodium perchlorate was prepared from primary standard grade sodium carbonate and vacuum-distilled 70–72 per cent perchloric acid in approximately stoichiometric proportions. The product was recrystallized at least three times from distilled water. Concentrated stock solutions (ca $4M$) were prepared as needed and standardized by precipitation of the perchlorate as tetraphenyl arsonium perchlorate salt. The analytical method is a variation of the tetraphenyl phosphonium perchlorate procedure of Willard, as modified by Hunt (9).

Scandium perchlorate hydrate was prepared by dissolving the purified oxide in excess perchloric acid and recrystallizing from perchloric acid and water (10). Microscopic examination of the product indicated it to be crystalline. The product was highly hygroscopic, having a vapor pressure of 2 to 3 mm at 25°C. Spectrographic examination indicated only traces of various impurities including the rare earths, with approximately 0.06 per cent yttrium. The sample was analyzed for scandium by the oxine method (11) and for perchlorate. All determinations were carried out in triplicate, the average deviation from the mean being ±0.4 per cent for scandium and ±0.3 per cent for perchlorate.

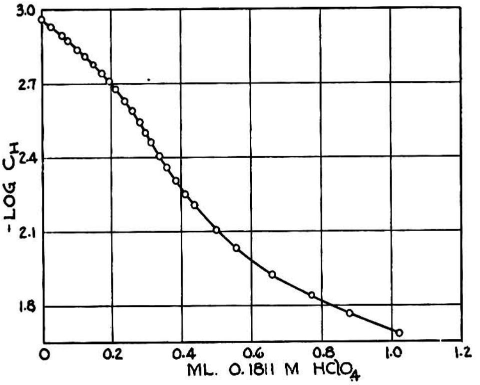


FIG. 1. Titration of 0.100_0M $Sc(ClO_4)_3$

During the course of the work, four lots of scandium perchlorate were prepared with ratios of perchlorate to scandium, a, of 2.933, 2.059, 2.026, and 2.906 ± 0.5 per cent. Three recrystallizations of a portion of lot 4 from water gave a product which showed a ratio of 2.738. Apparently the solid product is not necessarily the pure hexahydrate, Sc_3, but may be a mixture of Sc_3 and Sc_2 perchlorates where the ratio a is 2. These results are entirely consistent with the observations of Sterba-Böhm and Melichar (12) that basic formates can be obtained by repeated slow recrystallization of the normal salt from aqueous solutions.

A stock solution of lot 4 was prepared and the base, Sc_2, titrated with perchloric acid using a microburette. All reagent solutions involved were made up to an ionic strength of 1 with $NaClO_4$. Fig. 1 presents the titration curve and Fig. 2 gives the end point by the method of MacInnes (13). This end point yields a calculated a value of 2.973; and for lots 1, 2, and 3, values of 2.978, 2.066, and 2.051, respectively.

Preparation of Buffer Solutions

The solutions were prepared by mixing measured volumes of standardized stock solutions of scandium perchlorate, carbonate-free sodium hydroxide, perchloric acid, sodium perchlorate, and distilled water.

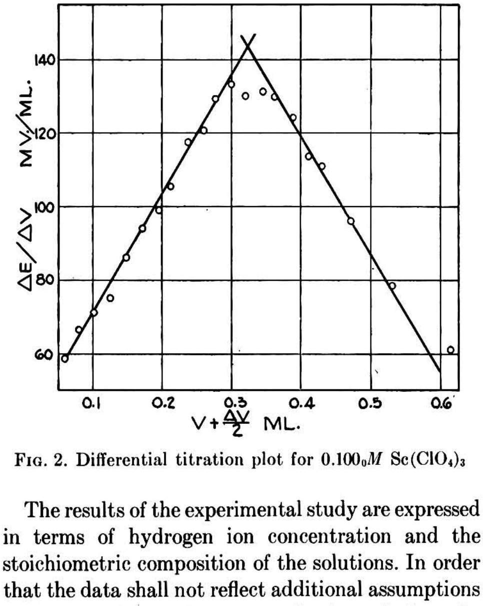


FIG. 2. Differential titration plot for 0.100_0M $Sc(ClO_4)_3$

The results of the experimental study are expressed in terms of hydrogen ion concentration and the stoichiometric composition of the solutions. In order that the data shall not reflect additional assumptions concerning the species present in the solution, the compositions of the buffers have been expressed in terms of C, the stoichiometric scandium concentration in moles per liter, and the parameter n. This parameter is the hydroxyl number, the stoichiometric ratio of moles OH^- per gram atom of scandium

$$n \equiv (3 - a) + \frac{C_{NaOH} - C_{HClO_4}}{C} \qquad \text{(IV)}$$

where a is the ratio of perchlorate to scandium in the solid scandium perchlorate sample employed to prepare the stock solution.

Table I gives a typical experiment which shows the reproducibility of the results, and Fig. 3 shows the logarithm of the hydrogen ion concentration as a function of n for different stoichiometric concentrations of scandium. For values of n between 0.3 and 1.0 there is essentially a linear relationship and the results can be represented by equations of the form

$$-\log C_H = A + Bn. \qquad \text{(V)}$$

The values of A and B are given in Table II.

The linear relationship noted here is in itself only a convenient empirical means of calculating $-\log C_H$ values for scandium perchlorate solutions of known stoichiometric composition. However, in conjunction with the observed dependence of C_H on C, the linearity demonstrates that the acid involved does not obey monoprotic, diprotic, or triprotic acid mass-law relationships.

TABLE I. *Measurements with scandium perchlorate buffers at 25°C*

Composition of scandium solution:

Ionic strength, μ 1.000	Stoichimetric molarity: Total Sc 2.000×10^{-2}
Ratio ClO_4/Sc, a 2.973	NaOH 1.000×10^{-2}
Hydroxyl No., n 0.527	$NaClO_4$ 0.915

Cell:

Au	9.061×10^{-3} M $HClO_4$ 0.991 M $NaClO_4$ Quinhydrone	4.12_5 M $NaClO_4$	9.46×10^{-3} M Sc_3 1.054×10^{-2} M Sc_2 0.915 M $NaClO_4$ Quinhydrone	Au

Trial	Time min	Electrode pair	EMF		a.d.
			mv	avg	
1	11	1-4	108.23		
		2-4	108.23		
		2-3	108.25		
		1-3	108.25		
		1-2	0.00		
	13	3-4	−0.01	108.24	0.01
2	20	1-4	108.27		
		2-4	108.28		
		2-3	108.29		
		1-3	108.29		
		1-2	0.00		
	23	3-4	0.00	108.28	0.01
3	30	1-4	108.33		
		2-4	108.33		
		2-3	108.34		
		1-3	108.34		
		1-2	0.00		
	33	3-4	−0.01	108.33	0.00_5
		1-3		108.28	0.03

$RT/F \ln$ (avg emf) = 1.8310, $-\log [H_3O^+] = 3.8738$

THE MONOPROTIC TREATMENT

If one assumes that the aquoscandium ion Sc_3 acts as a monoprotic acid as given in equation (I), the equilibrium constant formulated in terms of measured parameters may be written as

$$K_1 = \frac{C_H(Cn + C_H)}{C(1-n) - C_H}. \qquad \text{(VI)}$$

The calculated values of K_1 for a portion of the data are given in column 4 of Table III.

If in addition to the equilibrium of equation (I) that of equation (II) is involved, the equilibrium constants K_1 and K_2 can be calculated from the relationship

$$\frac{C_H(Cn + C_H)}{C(1-n) - C_H} = K_1 + \frac{C(n-2) + C_H}{C_H[C(1-n) - C_H]} K_1 K_2. \qquad \text{(VII)}$$

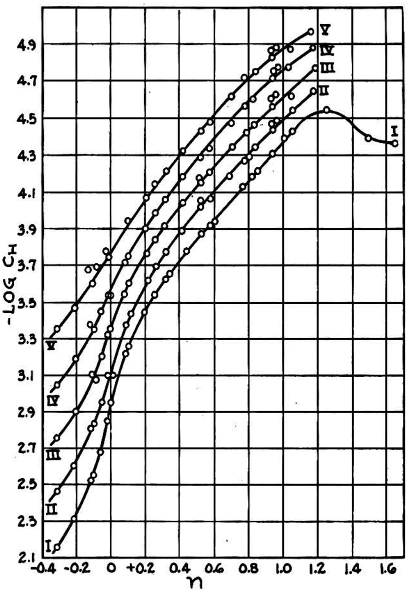


FIG. 3. Acidity of scandium perchlorate solutions at t = 25.0°C, $\mu = 1.00_0$. 10^3C = curve I—20.0_0; curve II—10.0_0; curve III—5.0_0; curve IV—2.50_0; and curve V—1.25_0.

TABLE II. *Coefficients for equation (V)*

Temp °C	Total conc. Sc	A	B	Mean dev. in $-\log C_H$
	moles/liter			
25	2.00×10^{-2}	3.262	1.131	0.0066
	1.00×10^{-2}	3.425	1.098	0.0060
	5.00×10^{-3}	3.582	1.078	0.0065
	2.50×10^{-3}	3.711	1.088	0.0076
	1.25×10^{-3}	3.875	1.052	0.0115
40	1.00×10^{-2}	3.179	1.069	0.002
	1.25×10^{-3}	3.648	0.968	0.014
10	1.00×10^{-2}	3.745	1.050	0.005
	1.25×10^{-3}	4.187	1.022	0.012

Best values of K_1 and K_2 were calculated by linear regression methods yielding values of 4.39×10^{-4} and -3.19×10^{-6}. Substitution of K_2 back in equation (VII) yields the numbers given in column 5 of Table III. The values in columns 4 and 5 are not constant, indicating that neither treatment is satisfactory. The same statement can be made in regard to a triprotic treatment.

DIMER TREATMENT

On the assumption that equations (I) and (III) represent the equilibrium, one has the following mathematical relationships relating concentration of species

TABLE III. *Test of the monoprotic and diprotic acid postulates*

Total conc. Sc 10^3C	n	$-\log C_H$ exp	10^4K_1	10^4K_2
20.00	−0.307	2.152	3.347	3.351
	+0.093	3.256	0.761	0.815
	0.327	3.620	1.230	1.377
	0.527	3.874	1.530	1.860
	0.827	4.187	3.180	4.666
	0.993	4.394	80.64	69.5
10.00	−0.213	2.603	0.945	0.956
	+0.260	3.694	0.788	0.954
	0.527	4.008	1.138	1.589
	0.787	4.285	1.978	3.548
5.00	−0.107	3.087	0.492	0.527
	+0.527	4.156	0.823	1.461
	0.780	4.425	1.393	3.523
	0.934	4.591	3.956	13.48
2.50	−0.0100	3.544	0.332	0.435
	+0.260	3.991	0.439	0.775
	0.527	4.293	0.616	1.499
	0.933	4.711	3.090	15.99
1.250	−0.307	3.351	0.232	0.297
	+0.260	4.134	0.344	0.815
	0.527	4.435	0.461	1.703
	0.827	4.739	0.969	6.59
	0.949	4.878	3.145	30.41

$$C = C_3 + C_2 + 2C_{2,4} = \frac{1}{a} C_{ClO_4^-} \qquad \text{(VIII)}$$

where C_3, C_2, and $C_{2,4}$ represent the concentrations of Sc_3, Sc_2, and $Sc_{2,4}$ and

$$3C_3 + 2C_2 + 4C_{2,4} + C_{NaOH} + C_H = aC + C_{HClO_4} \qquad \text{(VIIIa)}$$

and

$$K_0 = C_H^2 C_{2,4}/C_3^2 = K_1^2 K_D \qquad \text{(IX)}$$

where K_D is the equilibrium constant for equation (III) and K_0 is an over-all constant for the equilibria of (I) and (III). From the above, introducing equation (IV), one may derive the expression

$$\frac{C_H(Cn + C_H)}{C(1-n) - C_H} = K_1 + \frac{2[C(1-n) - C_H]}{C_H} K_0 \qquad \text{(X)}$$

and this equation may be written in the form

$$C_H^3 + C_H^2 (Cn + K_1 - 2K_0) + C_H[C(1-n)(4K_0 - K_1)] - 2K_0[C(1-n)]^2 = 0. \qquad \text{(XI)}$$

On substituting measured values of C, C_H, and n into equation (X) one derives equations of the form $A = K_1 + BK_0$, where A and B are pure numbers. While such an equation can be derived from the data for each individual buffer studied, it is obviously necessary to group the data at least into pairs of equations in order to evaluate K_1 and K_0. We have felt it preferable to group the equations into sets of five, each such data group consisting of the equations derived from buffers at essentially the same values of n, but for each of the five scandium concentrations studied. The resulting groups of five equations when solved simultaneously by linear regression methods, lead to the values of K_1 and K_0, and thence to K_D by equation (IX), which are summarized in Table IV. The resulting sets of constants should be identical and independent of the method of grouping data. Table IV shows that this is not the case and, furthermore, combinations of the various groups of data do not yield average values.

TABLE IV. *Test of the dimer postulate*

Data at $t = 25°C$, $\mu = 1.00_0$, primarily $NaClO_4$

Data group	Approx. values of n	Best values of the constants			
		10^5K_1	10^6K_0	$10^{-3}K_D$	$10^{11}K_1K_0$
1	−0.0100	0.842	1.683	13.80	1.420
2	+0.103	1.172	1.016	7.38	1.190
3	0.209	1.383	0.916	4.78	1.266
4	0.527	1.685	0.978_5	3.45	1.648
1 and 2		2.035	0.901	2.17_6	1.825
1, 2, and 3		1.865	0.957	2.75_2	1.785

Nevertheless, a further examination of the postulate was made by choosing a value of K_1 and K_0 from Table IV, substituting this value in equation (XI) and comparing the calculated values of hydrogen ion concentration with those determined experimentally. Table V presents the comparison for $K_1 = 1.17_2 \times 10^{-5}$ and $K_0 = 1.01_6 \times 10^{-6}$ for stoichiometric concentrations of scandium from 2×10^{-2} to 1.25×10^{-3}, and at $t = 25°C$, $\mu = 1.00_0$. Comparison of experimental and calculated values indicates good agreement up to $n = 0.5$; the mean deviation for $n < 0.5$ is 0.026 log units. The results for one set of buffers are shown graphically in Fig. 4, which is typical for all graphs of the data. Fig. 5

shows a comparison between the titration data employed to establish *a* values, and the curve calculated from equation (XI). It appears that the postulated equilibria of equations (I) and (III) enable one to predict the values of the hydrogen ion concentration over the range of *n* values indicated.

Continuous Polymerization

Returning to the linear relationship between $-\log C_H$ and n in the region $n = 0.3$ to 1.0, it should be noted that the dependence of C_H on n can be expressed only by an exponential function and no simple power series of the type employed above can explain the data over the entire range of *n* values. However, by employing the first few terms of such a series, we have been able to reproduce the experimental values of hydrogen ion concentration over a limited range of *n* values.

TABLE V.

$-\log C_H$ for Sc buffers at $t = 25.0°C$, $\mu = 1.00_0$

C	$2.00_0 \times 10^{-2}$		$1.00_0 \times 10^{-2}$		5.00×10^{-3}		2.50×10^{-3}		1.25×10^{-3}	
n	exp	calc	exp	calc	exp	calc	exp	calc	exp	calc
−0.307	2.152	2.208	2.460	2.505	2.752	2.797	3.054	3.086	3.351	3.365
−0.207	2.312	2.373	2.604	2.665	2.901	2.949	3.192	3.223	3.466	3.484
−0.107	2.530	2.624	2.818	2.893	3.087	3.149	3.358	3.393	3.600	3.624
−0.067	2.675	2.761	2.942	3.028	3.196	3.242	3.463	3.466	3.697	3.684
-0.010_0	2.933	2.972	3.105	3.175	3.343	3.375	3.544	3.572	3.747	3.768
+0.083	3.218	3.235	3.387	3.397	3.555	3.562	3.731	3.731	—	—
+0.103	—	—	—	—	—	—	—	—	3.934	3.928
0.193	3.451	3.434	—	—	—	—	—	—	—	—
0.209	—	—	3.618	3.609	3.769	3.758	3.905	3.912	4.083	4.066
0.260	3.559	3.531	3.694	3.680	3.846	3.829	3.991	3.979	4.134	4.128
0.327	3.620	3.619	3.777	3.768	3.919	3.915	4.055	4.062	4.202	4.209
0.419	—	—	3.890	3.883	4.033	4.029	4.171	4.175	4.319	4.319
0.456	3.785	3.782	—	—	—	—	—	—	—	—
0.527	3.874	3.873	4.011	4.021	4.161	4.167	4.291	4.311	4.435	4.455
0.577	3.911	3.941	4.047	4.089	4.201	4.239	4.330	4.379	4.473	4.522
0.696	—	—	4.187	4.368	4.339	4.418	4.478	4.562	4.627	4.705
0.761	4.130	4.250	—	—	—	—	—	—	—	—
0.827	4.187	4.408	4.339	4.555	4.470	4.701	4.602	4.845	4.739	4.987
0.934	4.316	4.853	4.452	5.000	4.591	5.146	4.735	5.290	4.861	5.432
1.033	—	—	4.524	5.347	4.628	5.502	4.774	5.660	4.866	5.820
1.043	4.428	5.080	—	—	—	—	—	—	—	—
1.181	—	—	4.660	4.636	4.766	4.791	4.880	4.949	4.968	5.104
1.243*	4.542	4.365	—	—	—	—	—	—	—	—
1.493	4.389	4.097	—	—	—	—	—	—	—	—
1.642	4.372	4.003	—	—	—	—	—	—	—	—

* Precipitation of scandium occurred at this and higher values of *n*.

From the standpoint of the structural chemistry involved, it follows that the degree of aggregation of the scandium species in solution must increase as *n* increases, passing through dimer, trimer, tetramer, and higher stages of aggregation. This concept has been applied with considerable success by Graner and Sillén (6) in their study of bismuth perchlorate systems. Calculations based on various postulates of polymerization involving oxygen or hydroxy bridges indicate that the data at high values of *n* are consistent with the idea of continuous polymerization, but no definite quantitative conclusions can be drawn.

Accepting the concept of continuous polymerization, values of K_1 and K_0 calculated as above must depend on *n* since other equilibria beyond those of equations (I) and (III) become increasingly important as *n* increases. On this basis, values of the constants should be calculated at the lowest values of *n* studied. Analysis of the derivatives dC_H/dn, dC_H/dK_1, dC_H/dK_0, as well as the second derivatives, indicates that the calculated values of C_H are most sensitive to changes in K_1 and K_0 at $n = 0$. However, at $n = 0$, experimental uncertainties in C and n are at a maximum. As a compromise, we have employed constants calculated at $n = 0.1$ in examining the equilibria proposed above.

Considerable data were also obtained at $t = 10°C$

and 40°C, and at ionic strengths of 0.500, 0.100_0, and 0.0100_0. These data, treated in the manner discussed above, led to dissociation and dimerization constants under the conditions indicated, the resulting calculated values of $-\log C_H$ agreed as well with experimental values as above. These data plus the associated values of ΔH, ΔS, and ΔCp for the processes involved will be the subject of a later paper.

SIGNIFICANCE OF THE RESULTS

It has been shown that the hydrogen ion concentrations of scandium perchlorate systems cannot be represented by equilibria involving simple proton dissociations as the systems are complicated by the formation of polymeric species. However, the hydrogen ion concentrations of these solutions can be represented over a broad range of concentrations and buffer ratios by assuming only two equilibria to be of importance. These are the acid dissociation of the aquoscandium ion and a dimerization of the conjugate base of the aquo acid. The assumed equilibria are consistent with data obtained at 10°, 25°, and 40°C at ionic strengths 1.00, 0.500, 0.100, and 0.0100 where the solvent salt is sodium perchlorate in swamping concentration.

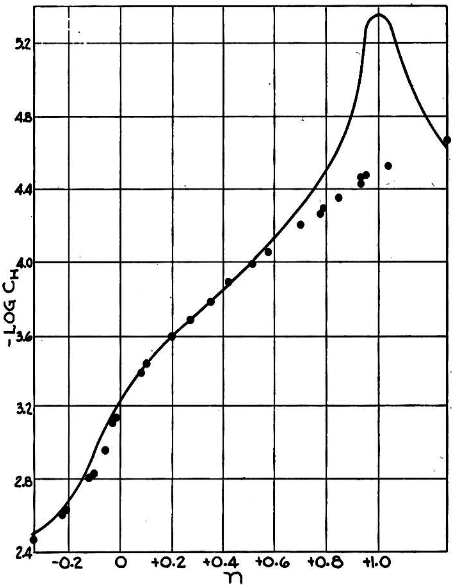


FIG. 4. Acidity of scandium buffers at $C = 1.00_0 \times 10^{-2}$ M, $t = 25.0$°C, $\mu = 1.00_0$. Solid curve calculated from dimerization equilibrium constants; closed circles are experimental points.

The results of the study provide a physical picture of the processes which occur in solution as hydroxide is added to aqueous solutions of aquo ions.

It is proposed that the scandium species present in largest concentration in scandium perchlorate solutions is the Sc_3 species. Complexes with perchlorate are presumed not to exist nor are complexes other than hydroxy complexes possible in the systems containing only $Sc(ClO_4)_3$, NaOH, $HClO_4$, and $NaClO_4$. The Sc_3 ion, by interaction with the solvent in the Brönsted sense, undergoes acidic dissociation to produce the Sc_2 species, as in equation (I).

$$Sc_3 + H_2O \rightleftarrows Sc_2 + H_3O^+ \qquad \text{(I)}$$

Under ordinary conditions, that is, in solutions of the normal perchlorate which do not contain added base, reaction (I) would not proceed very far to the right if only equilibrium (I) occurred in the solution. This statement follows from the low values of K_1, found in this study to be of the order of 10^{-5}. However, a second reaction occurs; the Sc_2 species formed in equation (I) dimerizing as indicated in equation (III)

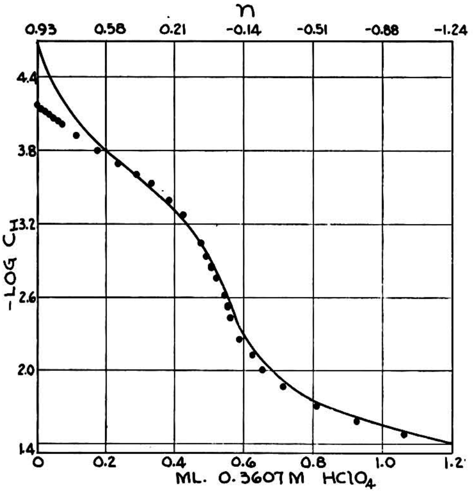
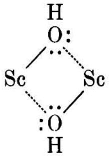


FIG. 5. Titration of $0.0400M$ $Sc(ClO_4)_3$. Solid curve calculated from dimerization equilibrium constants; closed circles are experimental points.

$$2Sc_2 \rightleftarrows Sc_{2,4} \qquad \text{(III)}$$

Since the dimerization constant for this reaction is quite large—of the order of 5000 to 10,000—it follows that most of the Sc_2 species is effectively removed from the solutions by the dimerization reaction. Consequently, reaction (I) is shifted to the right much more than would be the case if no dimerization occurred. It would appear that the dimerization process is strongly temperature-dependent, and may be accompanied by large positive entropy changes.

From the standpoint of the structural chemistry involved, the structure of the dimer is probably



where the groups other than hydroxyl in the coordination sphere of the scandium are omitted for the sake of simplicity.

The presence of two hydroxyl groups in the bridge, while perhaps not necessary for the formation of a dimer, seems nevertheless to be necessary for the formation of a dimeric species of sufficient stability to be of importance in the equilibria. This statement follows from the fact that the dimerization postulate employed here is successful in reproducing the C_H values of the solutions studied. If the intermediate species $Sc_{2,5}$ were present in the solutions in concentrations of the same magnitude as Sc_2 or $Sc_{2,4}$ it seems very unlikely that the calculations could have been successful.

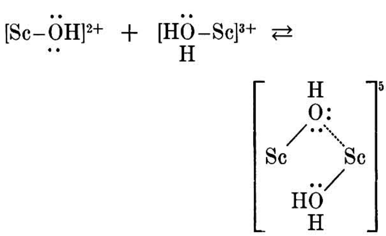
On the other hand, it must not be supposed that the monohydroxy discandium species is completely insignificant in these postulates. Thus, if a mechanism were to be proposed for the dimerization, it might be in terms of the following series of reactions:

$$Sc_3 + H_2O \rightleftarrows Sc_2 + H_3O^+ \qquad \text{(I)}$$

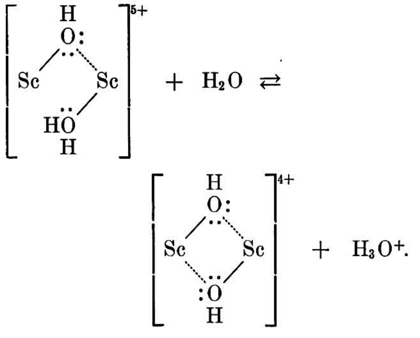
$$Sc_3 + Sc_2 \rightleftarrows Sc_{2,5} \qquad \text{(XII)}$$

$$Sc_{2,5} + H_2O \rightleftarrows Sc_{2,4} + H_3O^+ \qquad \text{(XIII)}$$

or, rewriting (XII) and (XIII) structurally:



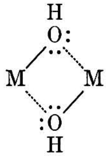
(XIV)



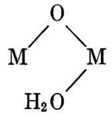
(XV)

The greater stability of the dihydroxy dimer as compared with the monohydroxy species, proposed here, could be explained readily on the basis of the great increase in resonance energy which must accompany formation of the dihydroxy bridge as a consequence of the equivalent structures of the hybridized forms in the latter case only.

The proposals above differ from those of Graner and Sillén (6) primarily in that hydroxy rather than oxo bridging is proposed here. It is not possible by experimental techniques available at present to distinguish between the two types of ions proposed in the dispersed phase, namely,



[I]



[II]

Since species [I] is undoubtedly readily converted to [II] and vice versa, by general acid-base reaction with the solvent water, there is no major difference between the two proposals, as far as the dispersed phase is concerned. However, it is felt that the proposal of dihydroxy bridges better reflects the steps by which the polymerization occurs initially. The distinction between oxy and diol links, if real, is probably unimportant until the degree of polymerization approaches that of the insoluble species.

Finally, by extending the ideas proposed here, we may explain the eventual formation and precipitation of solid polymers from the scandium systems. We propose that the $Sc_{2,4}$ species can go on to form higher molecular weight polymers by an almost infinite number of different mechanisms involving, at least initially, formation of additional dihydroxy bridges. Thus one may write the sequence of steps:

$$Sc_{2,4} + H_2O \rightleftarrows Sc_{2,3} + H_3O^+ \qquad \text{(XVI)}$$

followed either by

$$2Sc_{2,3} \rightleftarrows Sc_{4,6} \qquad \text{(XVII)}$$

or by

$$Sc_{2,3} + Sc_2 \rightleftarrows Sc_{3,5}, \text{ etc.} \qquad \text{(XVIII)}$$

The addition of base to the scandium solutions would be expected to result in increasing the average number of coordinated OH^- groups per scandium, which in turn determines the extent of the polymerization. The process is terminated with formation of species whose solubility is so low that precipitation occurs.

The entire situation is very much more complex in the presence of anions, other than perchlorate, which may form complexes with the metal ions since under these conditions there must be a competition between the anions, water, and OH^- for the available positions in the coordination sphere of the metal ion. The insoluble species formed on the addition of base will, in these cases, depend on the stability of the coordinate bond between metal ion and complexing anion. Considerable experimental data concerning this phenomenon in hydrous alumina systems may be found in the paper by Clay and Thomas (2).

ACKNOWLEDGMENT

The aid of a Frederick Gardner Cottrell grant from the Research Corporation is gratefully acknowledged.

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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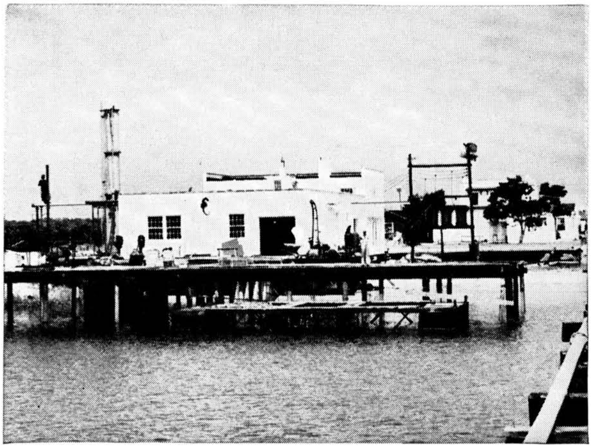
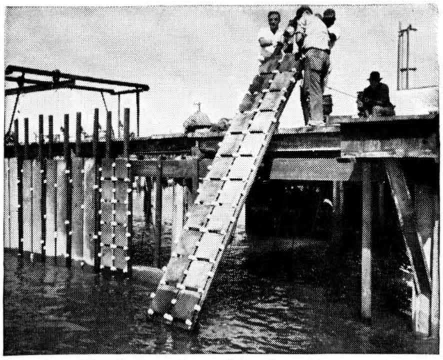


View of Harbor Island Laboratory and Testing Station.



Lowering piling test specimens into place. Sea water is something more than a mixture of chemicals; its corrosive action over an extended period can be studied properly only by exposure of specimens to attack under natural conditions.

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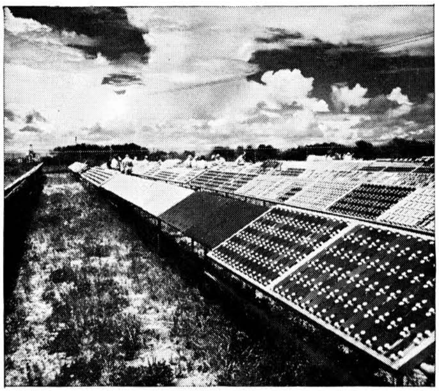
Running water troughs. For studying the action of sea water flowing at moderate velocities, specimens are immersed in the troughs, shown above. The total length of trough used for this purpose now amounts to about 600 feet.



Atmospheric and spray test lot. Shown above is part of the atmospheric test lot at Kure Beach in which over 20,000 specimens have been exposed, some for over nine years. The racks face south, and the specimens, supported on porcelain insulators, are all set at a slope of 30 degrees.

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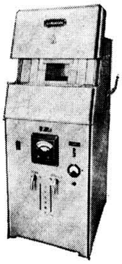

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The Development of Rare Metals[1]

J. W. Marden[2]

Introduction

On an occasion of this kind one is at a loss for words to express to the Society, and to friends, his thanks for the great honor that they have awarded him. One feels as though he had been given more than he deserves, since the accomplishments of research are in modern days rarely the accomplishments of one alone, but rather those of many; some have laid the foundation for the work and others have carried or supplied the materials and read the measuring instruments. I not only owe you, tonight, a debt of gratitude for this great honor but I owe much to the Society, and in particular to those who have gone many years before us, who have, by their counsel and advice, guided my course and helped me to make a small measure of success.

In return, it is a pleasure to hand back to the Society the $1,000 which accompanies the Acheson Award. This money may be used by the Board either for augmenting the scholarship or award funds of the Society, or it may be used by the Board in any way considered to be to the best interests of the Society.

The Less Common Metals

The Electrochemical Society has, in its half century of existence, always fostered and encouraged work on the less common elements. Of course, such work is only one portion of the field covered by our Society but since some of these rare metals have now become of extreme importance, a brief discussion of their development with some indication of how the Society has aided may be of general interest.

At the beginning of the century, elements like uranium, thorium, vanadium, zirconium, or titanium were, to many chemists, only names in the periodic table. There seems to be no generic name for these metals. Perhaps they might be called "rare refractory metals" if the term "rare refractory" is defined to mean difficult to produce in pure metallic form freed of oxides, nitrides, or carbides.

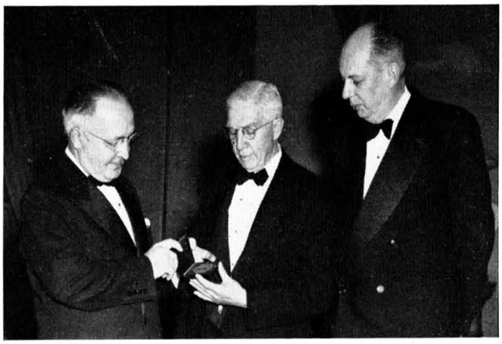
Metals like gold are rare to some of us but they are precious metals. No matter how difficult gold is to obtain, it may be easily freed from oxygen impurities by simply heating. It is a noble metal. Metals like iron are readily obtained by reducing the oxides with carbon or hydrogen.

The group of metals under discussion cannot be electroplated from aqueous solution, nor can their compounds be reduced with hydrogen or carbon. They retain their last traces of oxygen and nitrogen impurities with great tenacity and these must be removed if the metals are to be ductile and pliable at room temperature.

These metals have been known as impure powders for over one hundred years but it is only within recent times that methods have been refined sufficiently so that good fabricated sheet and wire may be produced.

Early experimenters used the same compounds and the same reducing methods that are used today. Broadly, four such methods have been employed with some degree of success:

1. The deposition of metals from volatile compounds was used to a limited extent by the carbon and tungsten lamp filament industry. The small quantity produced and equipment difficulties have prevented extensive commercial developments.
2. The reduction of oxides with aluminum or calcium is similar to the well-known thermite process. Unfortunately, in most cases, the heats developed during the reductions are insufficient to melt the metals or slags covering the charge.
3. Early experimenters attempting the reduction of chlorides with sodium, potassium, or magnesium experienced difficulty because of the extreme chemical activity of the halides.
4. Electrolysis of fused baths has always offered possibilities but in general only powders have been produced.



Dr. John W. Marden receives the Acheson Medal from President J. C. Warner at the Montreal Meeting while Dr. C. M. Slack looks on. Dr. Slack introduced Dr. Marden at the banquet, outlining some of his many achievements; his talk appears immediately after this article.

With the last three methods even if reductions could be made complete, the metals in fine powder form were, in the early days at least, partially reoxidized in subsequent handling.

During the first few years of the present century experimenters began to work with tightly sealed containers, but it was not until good vacuum pumps were in the hands of the chemist that a purer product could be made. A good vacuum, however, was not enough since some of these metals needed to be melted and cast prior to fabrication. At about the time of World War I high-frequency induction furnaces were developed and these were a great help in making pure metals.

It was possible, however, at the time of World War I, to

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[1] Acheson Medal Address delivered at the Montreal Meeting, October 28, 1952.

[2] Consultant, Westinghouse Electric Corporation, Bloomfield, New Jersey.

press powder, reduced in sealed containers, into bars or rods and pass current through them to metalize. It might be stated in passing that some of the work on rare metals was stimulated and fostered by the U. S. Government during World War I when a rumor came to this country that the Big Bertha, which bombarded Paris from great distances, was lined with either zirconium or zirconium steel. As it turned out, the rumor was false but much work was done to investigate the properties of such metals as zirconium and titanium. Work continued in the U. S. Bureau of Mines has resulted in methods now used for their commercial manufacture.

It is also interesting to those working on this subject to know that wires of sorts of zirconium, titanium, thorium, and uranium were made, sealed into lamp bulbs, and operated for tests as lamp filaments in the early 1920's. These filamentary wires were made by a method suggested by Von Bolton. Powders produced by reduction of oxides with calcium in sealed iron "bombs" were tightly packed into copper tubes and rolled down to small size. The thread of rare metal powder sheathed in the copper was fastened to lead in wires, mounted in glass bulbs, and attached to vacuum pumps. With this arrangement dilute acid could be drawn into the bulb to dissolve the copper and the filament could be washed with water. After drying, current was passed through the wire and the filaments were operated. At that time, interest centered in making lamp filaments, and since these metals did not appear to be satisfactory for such a purpose, a description of this was never published.

The metal produced in the early 1920's by passing current through pressed powder bars was not of sufficient quality to be entirely satisfactory. Zirconium and titanium so made could be hot-rolled or forged but were brittle at room temperature. Small amounts of thorium and uranium that could be fabricated into fine wire and sheet were, however, made at the time. There were, of course, no commercial applications and hence no reason to stimulate further improvement on methods of production.

In the early 1920's uranium and vanadium salts were drugs on the market. Howard Barker and Dr. Victor Hess, then employed by the U. S. Radium Company, strove vainly to find some outlet where they could sell these salts. They were having difficulty with the Department of Sewers in Orange, New Jersey, because they were contaminating the sewers and were even having trouble throwing the uranium away. This is certainly in sharp contrast to the demand for uranium today.

It should be pointed out that early experimenters and those of today are still having difficulties in finding suitable refractories in which to melt these metals and this problem is one of vital interest to some of our members.

In the latter 1920's, the scientists of the Philips Lamp Company in Holland greatly improved the vapor deposition method for producing very pure, ductile zirconium under good oxygen-, nitrogen-, and carbon-free conditions. This method is now employed to manufacture a very fine grade of zirconium used, in part at least, for medical purposes.

Within the last several years experimenters in the U. S. Bureau of Mines have developed their excellent processes for producing titanium. They reduce the chloride with magnesium, carefully excluding gaseous and other impurities. It is said that attempts are now being made to produce about 30 tons a day of this metal, which a very few years ago was only a laboratory curiosity. This is practically all absorbed for military purposes. Titanium is a particularly interesting metal since, volume for volume, it weighs only a little over half as much as iron or steel, and when alloyed can be given good room temperature hardness and strength. Some of you may have had the problem of studying the corrosion resistance of titanium.

Quantity production of uranium came during World War II and relatively large amounts of uranium are now manufactured for military purposes. When uranium and thorium were first produced in our laboratories it was assumed, since uranium was below tungsten in the sixth group of the periodic table, that it might have a higher melting point than tungsten, and that both uranium and thorium, since they had very high atomic weights, might be satisfactory metals to use as x-ray targets for deep therapy work. These assumptions have proved to be erroneous but the metals have found other and extremely important uses.

It has been stated that a knowledge of, and experience with, uranium greatly hastened work on atomic weapons, resulting in a shortening of World War II with a saving of many American lives.

The other less common metals are developing more slowly, but in like manner, and no doubt the day will soon come when some of them will be classed as useful household articles. There will always be much to be done. Chromium as electroplate is used everywhere but we still have the problem of making pure, ductile chromium metal in useful wire and sheet form, just as we have of many of the other less common metals. Judging from the literature, methods for producing rare metals by electrolysis of fused baths have not been fully developed and this problem belongs to members of this Society.

Contribution of the Society

Rare metals are being developed with increasing rapidity and as new and better equipment, such as vacuum pumps, furnaces, and handling techniques, become available, larger quantities of purer metals will be produced. One can scarcely prophesy the uses to which they will be put. If the past is an indication of the future, there should be many new and unexpected applications. The Society has done much to bring about these changes. It has offered a place in the JOURNAL for publication of new processes and discoveries and it has opened its doors to symposia and discussions on the subject of the less common elements. It has afforded a place where those employed in industry, the student, and the teacher may see and hear the leaders in their respective fields and from these contacts obtain the inspiration to continue.

According to Martin F. Quaely, the Society has published approximately 330 papers relating to the rare metals. To mention only a few, there have been 26 contributions on zirconium, 23 on titanium, 21 on chromium, and eight on uranium. This small number of papers on uranium has, of course, been due to the restrictions of security regulations.

Many owe much to the examples and words of wisdom of some of the great leaders of our Society. The speaker has been particularly influenced by the work of such men as W. D. Bancroft, one of our founders; W. Lash Miller, a great Canadian; Herman Schlundt, who did much to foster work on less common elements; H. S. Miner and C. James, of rare earth fame; Louis Kahlenberg and Colin Fink, to mention only a few. From my point of view, these men long ago reached the pinnacle of success.

Since some of you have been students of Kahlenberg, and since the story illustrates how the older members of the Society may be of real help to the younger ones, it should be of interest to recount a personal contact with this great leader.

It happened during an extended plant inspection trip at an Annual Meeting, approximately 35 years ago. Perhaps by previous arrangements of others, a young college teacher, who was trying to do some independent research, was introduced to Dr. Kahlenberg. The young man was thrilled and intrigued by the great teacher's attention and he was content for the most part to listen during the whole time of the trip. Many things were discussed in this long lecture not included in college courses of chemistry and physics. It can now be reported that the same things are the matter with the young research workers of today that were wrong with us 35 or 40 years ago. Of course, the old timers would frown upon the present day regimentation and the establishment of fixed hours of work. During the discourse, one gathered that young men were not as careful in their thinking as those who went before. When it was suggested that this might be a matter of viewpoint, it was soon found from the answers that such an argument was considered immature and immaterial. It might be said, however, it became very clear that there were rewards to research which are not necessarily monetary.

In conclusion, let me state that the young men of today have far better working conditions, better equipment, and better financial support, than those who preceded them. A research engineer is like a skilled mason working side by side with other masons. He lays his stone upon a scientific foundation built by others who preceded him, and he expects those who follow to lay their stones upon the ones he has so carefully placed on the wall. There are many more masons now than there were when the Society was organized. Before the days of scientific societies, technical skill was handed down by word of mouth from father to son. Today, we hand it down through our publications. There are still, however, many technical details which are only obtained by personal contact. It is hoped that the older and more mature members of our Society will always continue to encourage and help those who are to follow in their footsteps.

An Introduction with Comments on the Medalist's Achievements

C. M. Slack[1]

May I express my appreciation for the honor of participating in the presentation of the Acheson Medal to Dr. Marden. I would also like to commend this Society on the indomitable courage which it has shown in asking a physicist to sing the praises of a chemist. Somehow, it makes the prospects for international peace seem brighter.

At my first meeting with Dr. Marden back in 1927, he told me he was looking for a chemist. Being a physicist, I could offer him little in the way of advice, but I had thought that chemists were a pretty plentiful lot. It soon became apparent that Dr. Marden was not looking for an ordinary chemist; the word "electrochemist" had little meaning to me at that time. He wanted one who understood chemical reactions at high temperatures in a vacuum, and one who understood chemistry in the presence of electrical discharges. This was my first real impact with the degree of specialization required by industry for a scientist to fit into the complex team work needed to attack even a small segment of an industrial endeavor. It impressed me greatly. Dr. Marden realized fully the trend which industrial research was taking and had a clear view of what was required in the way of men and materials to accomplish it. Incidentally, he found such a man, who worked with him for many years, and who is now a vice-president in charge of development work for a large company.

Dr. Marden was trained in both chemistry and metallurgy, and I think he was the most versatile individual with whom I have ever been associated. He willingly tackled problems as they presented themselves to the Lamp Division, no matter into what branch of science they would normally fall; he concentrated on them with a singleness of purpose and a vigor which usually brought results in a minimum of time.

Dr. Marden has many outside interests. Perhaps, his chief one is farming in the country gentleman style. He is a collector of guns and an expert in their use. It is reported that his farm is freer of rabbits and groundhogs than any other in Morris County.

Dr. Marden was born in Saginaw, Michigan, on May 11, 1887. He obtained his B.S. degree from Illinois Wesleyan University in 1909; he was a fellow at the University of Illinois in 1909 and 1910, received his M.S. degree from the New York University in 1911, and his D.Sc. in 1912. From then until he came to Westinghouse, he held such positions as soil analytical chemist at the University of Minnesota, assistant professor of chemistry at the University of Missouri, and metallurgist at the U. S. Bureau of Mines. He became assistant Director of Research of the Westinghouse Lamp Division in 1925, and held this position until 1947, when he was appointed Manager of the Molybdenum Development Department. Although retired in June of this year, he is still a consultant for the company in regard to metals and electrochemistry.

Dr. Marden's major researches have been in the field of extractive metallurgy of the rare metals and their application to lamps, electronic devices, and nuclear reactors.

At the outbreak of World War I, he volunteered his services to the Bureau of Mines and was assigned the preparation of zirconium metal. This formally started a long career in rare metal technology lasting more than thirty years. While at the Bureau of Mines, he was co-author of several very important monographs on rare metals.

His work includes many papers and patents related to methods of preparation, properties, and industrial applications of the rare metals. Early investigations on the preparation of thorium, uranium, vanadium, chromium, and zirconium in the late twenties secure him a place among the few remaining pioneers in this field. The commercialization of thorium of high purity by Marden and Rentschler represented an outstanding accomplishment. He demonstrated the possibility of producing ductile vanadium by calcium reduction of the oxide in the twenties. This process with some improvements has become standard procedure for the production of this metal.

It would obviously be impossible to recall even briefly in any significant detail such a ramified career, so I have decided

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[1] Westinghouse Electric Corporation, Atomic Power Division, Pittsburgh, Pennsylvania.

to select one phase of his work which perhaps has more glamour to it than others, and which I believe would be understood as to its import by everyone here.

Dr. Marden's early work on the production of uranium by calcium reduction of the oxide and magnesium reduction of the fluoride and his extensive knowledge of rare metal chemistry stimulated important new developments in uranium technology by associates in the Westinghouse Research Laboratories at Bloomfield.

He, together with Dr. Rentschler, had refined uranium metal in the very early days in the vain hope that its melting point might be high enough for use as lamp filaments, and so serve as a substitute for tungsten. For the first time, uranium was produced in a relatively pure form. As a consequence of this work the Lamp Division went into the production of uranium in the early twenties, supplying laboratories all over the world with experimental quantities of this interesting but relatively useless material. This work continued, and in the early thirties, under Dr. Marden's supervision a method was perfected for the production of uranium by the electrolysis of the fused salt.

In 1940, Dr. Marden and coworkers undertook the commercialization of the electrolytic process for the production of uranium metal under the Manhattan Project at Westinghouse. This development supplied most of the uranium metal for the first atomic pile at the University of Chicago.

Much of the success of this large-scale development may be attributed to the resourcefulness of Dr. Marden. The story goes that Bloomfield smelled to high heaven that summer because Dr. Marden had cornered the market on garbage cans for conversion into electrolytic tanks. Also, many a dirty shirt was being worn after he bought up all the wash tubs available. These he set out on the roof of the plant in order to carry on the production of potassium uranium fluoride by the photochemical action of sunlight. Unfortunately, it was rainy that spring and summer, and all hands had to be ready on a moment's notice to rush to the roof to cover the precious chemicals. Eventually, special arrangements were made for advanced weather information.

This work on uranium is classified information at the present time in an extensive report. Its import is best evaluated by reference to a letter to the Westinghouse Electric Corp. from Dr. Arthur E. Compton, Project Director, quoted below:

> October 6, 1945
>
> Mr. A. Frankel,
> Westinghouse Electric Corporation,
> Bloomfield, New Jersey.
>
> Dear Mr. Frankel:[2]
>
> Now that the war has been successfully completed, the "Atomic Power Project" is undergoing complete reorganization in an attempt to place its activities on a long time basis. As a result of this change, the Metallurgical Project Office, through which I have discharged my responsibilities, is being closed out.
>
> Before relinquishing my active responsibilities, I wish to express to you my deep appreciation of the help which Westinghouse Electric Corporation, in making available the services of J. W. Marden, rendered. While at a later date other methods supplanted those developed at Westinghouse, our initial supply of metal was dependent upon your efforts, and the initial success of our work was determined by the Westinghouse production.
>
> I am writing Dr. Marden directly, but I would appreciate your expressing my thanks and those of the project to all the members of your staff whose cooperation made Dr. Marden's work effective.
>
> Sincerely,
> Arthur E. Compton
> Project Director

As Manager of Molybdenum Development since 1947, Dr. Marden has been engaged in diverse projects under government sponsorship. Outstanding developments include the fabrication of very large pieces of molybdenum and extensive studies on the effects of heat treating and fabrication on the physical properties of the metal.

Over a long period of years, Dr. Marden has made many important contributions in the fields of gaseous discharge devices, lamps, and electronic tubes. Specific examples are his work on the Cesium Amplifier Tube, the G-5 Ultraviolet and Germicidal Lamp (this was one of the earlier types of sun lamps), and the sodium, cadmium, zinc, tellurium, and arsenic lamps.

He did extensive work on the high pressure mercury vapor lamp, which included initial experimentation in the company on mercury pressures up to 30 atmospheres.

Other investigations included those on the low pressure mercury vapor fluorescent lamp, the effects of trace impurities in phosphors on light output during the early stages of fluorescent lamp technology.

During his long career, Dr. Marden has had 71 patents issued, covering a wide field from basic metallurgy to lamps and x-ray tubes.

I do not feel qualified to relate his experiences with the Society. Dr. Marden, however, has told me how much the Society has meant to him, and others have described how much he has meant to the Society, particularly in its struggle for existence during the early thirties.

This honor being conferred upon Dr. Marden by The Electrochemical Society is one of which any man would be proud, and it comes to Dr. Marden after a long and illustrious career as a scientist. In turn, The Electrochemical Society has every reason to feel proud that they have such a worthy member of their organization as a recipient of this honor. The many friends that Dr. Marden has both inside and outside of scientific circles are equally proud of his accomplishments and of this honor which he is receiving here tonight.

I am sure that I express the feeling of the members of the Society and of his colleagues in Westinghouse and elsewhere in wishing him many more years of a fruitful and interesting life, with more leisure to concentrate upon those accumulated personal wishes than are allowed in the hectic life of industry.

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[2] Mr. Frankel was in charge of contract arrangements between the Project and Westinghouse.

Early Plans for the New York Meeting—April 1953

Interest in the forthcoming spring meeting of the Society in New York City has been greatly stimulated by the development of plans for a program which offers a number of exceptional features, in addition to a fine technical schedule. A visit to New York is in itself an incentive, and a few of its attractions are touched on in the columns below. The meeting will take place at the Hotel Statler, New York, from April 12 through April 16, 1953. Completed and tentative plans, as of this writing, are outlined below.

New York Convention and Visitors Bureau

The United Nations Building shown from the side facing the East River

Visiting New York for the Spring Meeting

New York, with its myriad attractions, offers much to visitors and residents alike. There is something to see and do anytime, any day, uptown, midtown, or downtown.

If you arrive in the city at Grand Central Terminal, you will see the largest and most costly terminal in the world. Across from it is the Chrysler Building which towers 1045 feet into the air. This is the midtown area in which are located the Public Library, Metropolitan Opera House, Madison Square Garden, Rockefeller Center, St. Patrick's Cathedral, the United Nations, theaters, the smart shops, and many other points of interest.

Visitors can take a subway ride and travel 32 miles for a dime. Located downtown are the Bowery, Bowling Green, and Brooklyn Bridge, and a visit may be paid to the Stock Exchange. Also in this section are Chinatown, the Custom House, Ellis Island, Fraunces Tavern, Holland Tunnel, Manhattan Bridge, Police Headquarters, Seamen's Church Institute of New York, Old John Street Church and St. Paul's Chapel, and the Statue of Liberty.

Upper New York has further points of interest. Places to visit include the American Numismatic Society, Bronx Park and Zoological Gardens, Cathedral of St. John the Divine, Central Park, Columbia University, George Washington Bridge, Grant's Tomb, Jumel Mansion, Medical Center, New York University, Poe Cottage, Riverside Church, Van Cortlandt Mansion, Hayden Planetarium, Metropolitan Museum of Art, American Museum of Natural History, Polo Grounds, and Yankee Stadium.

The Technical Program

Arrangements for an extensive technical program are underway, with simultaneous sessions to be held Monday through Thursday. These sessions are being scheduled for the Sky Top, the Penn Top, and the Keystone Rooms at the Hotel, all of which are of ample size.

A special feature of the program will be a Symposium on the Application of Electrochemistry to Biology and Medicine, which is being sponsored by the Theoretical Electrochemistry Division; it is expected to run for three days, or six sessions. In connection with this, there will be a Symposium Dinner on Monday evening with a talk relating to the symposium.

The Theoretical Division plans to present additional papers, and may have a joint session with the Electronics Division on semiconductors.

The Electronics Division has a full program including a symposium on Luminescence (probably two days), one on Screen Application (one day), and another based on Semiconductors (at least one and possibly two days). "Extended Abstracts" booklets of these papers will be on sale at the meeting.

Another feature of the program will be the Richards Memorial Lecture on "Transistor Physics." This is described in detail below, and will be of special interest in connection with the technical program on semiconductors.

The Electrothermic Division will present a series of papers by the authors of the monograph entitled "High Temperature Materials, Methods and Measurements." A number of the contributors to this monograph have completed their assignments, and they will be asked to review their contributions at the meeting. In addition, there will be general papers concerned with electrothermics.

The Electric Insulation Division is planning four sessions treating on

Electrophysics, Applied Dielectrics, Capacitors, and Electric Insulation; also, a luncheon honoring Peter Debye is being arranged by this Division.

Luncheons, Dinners and Committee Meetings

Meetings will be held by the Ways and Means Committee and by the Board of Directors on Sunday, April 12. Other committee meetings to be held will be announced later.

The Society Luncheon will be held on Monday noon, and will be followed by a nontechnical talk. On Monday evening there will be a reception and dinner in connection with the Symposium on the Application of Electrochemistry to Biology and Medicine.

The Reception and Banquet of the Society will be held on Tuesday evening, April 14, and this will be the occasion of the Presidential Address by J. C. Warner. Dancing will follow the formalities.

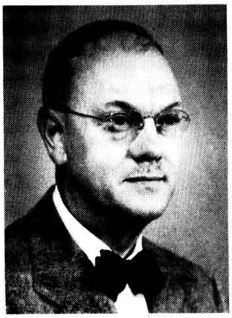
Division Luncheons are planned by the Electronics, Electric Insulation, Theoretical, and possibly by the Electrothermic Divisions. The luncheon of the Electric Insulation Division will be a special affair in honor of Professor Peter Debye, who will speak on the subject, "The Electrical Interpretation of Molecular Forces." Professor Debye is the Nobel Laureate whose name is associated with dipole molecules, X-ray patterns, paramagnetic cryogenics, ionic conductivity, and, recently, light scattering of polymer sols. Time and place for these luncheons will be announced in the Program Booklet.

Richards Memorial Lecture

The Richards Memorial Lecture will be given on the afternoon of Wednesday, April 15, by Dr. William Shockley of the Bell Telephone Laboratories. In his lecture, titled "Transistor Physics," Dr. Shockley will discuss the fundamental principles on which this new and revolutionary device operates. He will describe the more recent developments and improvements, indicating some of the applications being considered. The point-contact transistor, announced in 1948, was invented by J. Bardeen and W. H. Brattain while working under Dr. Shockley's supervision. Dr. Shockley holds several transistor patents, in particular that of the "junction transistor."

Born in London in 1910 of American parents, he attended schools in California and, in 1932, received a B.Sc. degree with physics major from the California Institute of Technology. He was a teaching fellow at the Massachusetts Institute of Technology from 1932 to 1936, when he received the Ph.D. degree. His thesis was on wave functions of electrons in crystals.

Upon leaving M.I.T., Dr. Shockley joined the staff of Bell Telephone Laboratories, and for about one year worked upon electronic devices before returning to solid state physics, particularly theories of the order-disorder transformation of alloys. From 1940–42, he worked on radar design and developed several circuits that found general use in radars manufactured by the Western Electric Company. During the remainder of the war years, he was engaged on Operations Research with the Navy and Air Force, following which he returned to Bell Laboratories and continued his activities in solid state physics in part in a supervisory capacity.



L. I. GILBERTSON
Chairman, Registration Committee

Dr. Shockley is a member of Tau Beta Pi, Sigma Xi, a Fellow of the American Physical Society, a Senior Member of the Institute of Radio Engineers, and a member of the National Academy of Sciences.

Plant Trips

After careful consideration of the transportation problems in taking registrants to and from plants in the New York City area, and because of restrictions on visitors at many of the plants engaged in government work, the Plant Trip Committee decided not to offer any organized plant trips at this meeting. However, if individuals or small groups desire to visit a specific plant in the Metropolitan New York area, G. A. Lux, Chairman of the Plant Trip Committee, should be consulted at the registration desk and every effort will be made to make arrangements for such visits.

It should be remembered that there are but few plants on Manhattan Island of interest to the members of the Divisions attending this meeting. Therefore, a considerable portion of the day would be required to reach, and return from, points in the outlying area because of extreme traffic congestion during morning and late afternoon rush hours. Thus, a plant trip would conflict with attendance at technical sessions and might interfere with evening plans.

G. A. LUX
Chairman, Plant Trips Committee

Ladies' Program

A Ladies' Headquarters Room has been set aside in the hotel for the duration of the convention. This will be on the mezzanine floor in the vicinity of the registration area, and will give the ladies a chance to gather, and discuss their plans. An Information Desk will be set up in the registration area where advice can be obtained about entertainment, restaurants, theaters, night clubs, and other activities in New York City. It is planned to have tickets available for TV and radio broadcasting studios on Sunday evening and perhaps on other evenings during the convention.

F. A. LOWENHEIM
Chairman, Finance Committee

The first scheduled event for the ladies will be the Society Luncheon on Monday in the Keystone Room to which all members and guests are invited. Following the luncheon there will be a brief business meeting, followed by a talk of general interest by a popular speaker. Immediately afterwards there will be a Ladies-Get-Together in the Keystone Foyer.

Tuesday has a full schedule for the ladies. During the morning there will be a bus tour of up-town New York; at noon Tuesday, a luncheon in the Washington Square Room of the Fifth Avenue Hotel; and during the afternoon a bus tour of down-town New York, all of which will be complimentary. In the evening there will be the Reception and Banquet of the Society, followed by dancing.

During the remainder of the Convention the Ladies' Committee will conduct escorted trips for small groups. Some of the more popular trips will be planned in detail and tickets will be required in advance. These will probably include the United Nations, Radio City, the Metropolitan Museum, Hayden Planetarium, the Empire State Building, and a luncheon and fashion show. Full use should be made of the Ladies' Headquarters Room in arranging these activities.

Heading the Ladies' Committee are Mrs. C. G. Fink, *Honorary Chairman*, and Mrs. A. C. Loonam, *Chairman*. Other members include Mrs. H. Bandes, Mrs. H. R. Copson, Mrs. L. I. Gilbertson, Mrs. C. J. Lang, Mrs. H. B. Linford, Mrs. F. A. Lowenheim, Mrs. F. P. Peters, and Mrs. D. Wood.

Local Committees

The local Committee is composed of Colin G. Fink, *Honorary Chairman*; H. R Copson, *General Chairman*; K. G. Compton, *Chairman of Advisory Committee*; L. I. Gilbertson, *Registration*; H. Bandes, *Entertainment*; F. A. Lowenheim, *Finance*; G. A. Lux, *Plant Trips*; F. P. Peters, *Publicity*, A. C. Loonam, *Arrangements*; and Mrs. A. C. Loonam, *Ladies'Program.*

Corrosion Prevention Seminar at Stevens

A series of ten lectures on corrosion prevention will be given at Stevens Institute of Technology in Hoboken, New Jersey, on Thursday evenings starting February 12, 1953. The speakers are: T. P. May, International Nickel Company; F. L. LaQue, International Nickel Company; C. L. Bulow, Bridgeport Brass Company; H. W. Fritts, Aluminum Company of America; E. A. Tice, International Nickel Company; L. P. Sudrabin, Electro Rust-Proofing Corporation; A. Black, Shell Oil Company; A. G. Gray, *Steel* magazine; G. W. Oxley, Standard Oil Development Company; and K. Tator, Consultant.

This series of lectures is given in cooperation with the National Association of Corrosion Engineers and is available to the general public. Further information regarding admission may be obtained from the Admissions Office, Stevens Institute of Technology, Hoboken, New Jersey.

Pictorial Glimpses at the Montreal Meeting

Top row, left to right: Dr. J. W. Marden receives the Acheson Medal from President J. C. Warner with the approval of Dr. C. M. Slack, Dr. William Blum, and Dr. G. W. Vinal; familiar faces at the get-together in the Cartier Room before dinner Monday evening; President Warner, Mayor Camillien Houde, George Hogaboom, and Mrs. Blum flank General Chairman A. W. Whitaker, Jr., as he welcomes members and guests to the meeting at luncheon on Monday.

Center row, left to right: members of the Ladies' Entertainment Committee who helped make the Montreal Meeting such a success; George Hogaboom looks at Dr. Blum's Honorary Membership scroll with Dr. Blum and President Warner; General Chairman Whitaker, President Warner, and Dr. Martin at the cocktail party Monday preceding the dinner at which Dr. Martin was speaker.

Bottom row: informal shots at Monday and Tuesday dinners.

Highlights of Board of Directors' Meeting

(Held October 26, 1952, Mt. Royal Hotel, Montreal, Canada)

The financial structure of the Society was discussed. The budget for the year 1952 predicted a deficit of $1,130. As of the end of September, the principal items of income were holding up in such a manner as to indicate rather clearly that our total of $63,600 income would be met. However, items of expenditures, with respect to advertising agents' commission, were completely upset due to the resignation of Mr. Richard Rimbach as our advertising representative. The mode of operation with Mr. Rimbach was to pay him his commission for the preceding year during the month of January. This amounted to $730. However, since he resigned effective August 31, 1952, his commission will have to be paid on the 1952 advertising before the end of the year. In addition, it was necessary to give Mr. Jack Bain, our new advertising representative, a guaranteed minimum of $100 a week for expenses, beginning September 1. This combination of expenditures in connection with our advertising will most certainly result in a deficit of $2,000 in excess of that estimated.

The activities of our new advertising representative have been very encouraging. It is the opinion of the Secretary that advertising during the year 1953 will be sufficient to balance the budget and allow both the building up of our reserve funds and expansion of our JOURNAL. Since actual contracts are not expected until December, it is impossible at this time to give any concrete figures to support this belief. However, it is definitely expected that at the next Board meeting a completely altered financial picture may be presented.

Dr. William Blum was appointed to act as the official representative of The Electrochemical Society on his forthcoming tour through Australia.

Winners of the Prize Essay Contest were announced as follows: first prize winner, Gordon Gemmell, Massachusetts Institute of Technology, Cambridge, Mass.; second prize winner, Donald W. Hutchings, Oberlin, Ohio; honorable mention, Robert Auerbach, New York City. Mr. Heise reported that the Cleveland Section is planning to honor Donald Hutchings at a forthcoming sectional meeting. It was also agreed that these Prize Essay Contests should be continued.

The Secretary was granted permission to reprint 1000 copies of our "Aims and Activities" booklet.

The detailed report of the JOURNAL activities was presented by the Editor, and is summarized in part below.

Technical papers published in the Journal:

1948	*1949*	*1950*	*1951*	*1952*
63	68	65	79	85

Divisional contributions to Technical Section in 1952:

Division	*No. of papers received*	*% of total*	*Papers rejected*
Battery	16	8.69	0
Corrosion	32	17.39	5
Electric Insulation	8	4.34	0
Electrodeposition	26	14.13	1
Electronics	34	18.47	2
Electro-Organics	7	3.80	1
Electrothermics	4	2.17	0
Industrial Electrolytic	7	3.80	1
Theoretical Electrochemistry	40	21.73	8
Miscellaneous	10	5.43	3
Total	184	99.95	21

Comparative printing costs of 1951 and 1952 Journals

	1951		*1952*	
January	(60)	$1461.43	(68)	$1566.26
February	(60)	1408.07	(72)	1557.76
March	(68)	1641.80	(76)	1805.44
April	(60)	1431.50	(84)	2079.14
May	(56)	1291.58	(60)	1389.14
June	(68)	1544.24	(84)	2040.28
July	(64)	1488.09	(64)	1606.51
August	(56)	1328.25	(88)	2369.72
September	(56)	1331.96	(76)	2012.81
October	(56)	1361.92	(92)	2282.14
November	(68)	1540.83	(80)	—
December	(92)	2041.15	(132)*	—
	(764)	$17,870.82	(976)*	$18,709.20†

* Estimated

† 1952 budget is $24,000.

Dr. Harry Copson, General Chairman of the New York Meeting, reported the dates April 12–16 set for the 1953 Spring Meeting at the Statler Hotel. Registration is expected to be approximately the same as at former spring meetings. It was agreed that symposia chairmen and speakers at the Symposium on the Application of Electrochemistry to Biology and Medicine be charged member registration fees.

The report of the Membership Committee indicates that the Committee is very active in building up the membership of the organization.

The Sustaining Membership Committee reports that the following companies have enrolled since the last meeting held in Philadelphia: Auto-City Plating Company; Eaton Manufacturing Company; Ford Motor Corporation; General Motors Corporation; Merck and Company; National Research Corporation; Poor and Company; Wagner Brothers, Inc.; Yardney Electric Company.

The Ways and Means Committee requested that the Secretary circularize the membership, informing them that the preparation of a Ten-Year Index will be undertaken as soon as 400 prepayments of $10 each have been received, and that a publication date will be announced in the JOURNAL. After that date, the price will be $15. This recommendation was approved by the Board.

The Board also approved a further recommendation in which the Society was to invest $5,200 of the Roeber Research Fund, $2,000 of the earnings of the Acheson Fund, $2,800 of the earnings of the Weston Fund, $1,000 that will be returned by Dr. Marden from the Acheson Award, along with $3,000 of the Richards Memorial Fund, income from the last item to be kept separate from the remainder. The remainder is to be used for a consolidated fellowship at such time as the income is sufficient to insure fairly continuous operation of that fellowship. The investments were to be in two funds, one of the type of the Wellington Fund, and the other of the type of the Fundamental Investors.

The Ways and Means Committee further recommended that the Nominating Committee be appointed at the spring meeting and instructed to report by June 15. The Secretary is to furnish them with the list of names of all past Board members and chairmen of sections and committees for the last ten years. Sections and Divisions are also to be reminded of their privilege of suggesting to the Nominating Committee the names of eligible candidates. This recommendation was approved.

The Palladium Medal Committee was reappointed to serve without precedent. This committee is composed of J. C. Warner, R. M. Burns, Harry Copson, and H. H. Uhlig.

The next meeting of the Board of Directors was set for 10:00 A.M., January 30, 1953, at the Society's Office.

HENRY B. LINFORD, *Secretary*

NACE Conference in Chicago, March 16–20

The 1953 Annual Conference and Exhibition of the National Association of Corrosion Engineers will be held on March 16–20, at the Hotel Sherman, Chicago.

Included in the program will be a symposium on Protective Coatings in which five papers are scheduled; the Corrosion Principles Symposium with four papers; the Chemical Industry Symposium presenting eight papers; the Oil and Gas Industry Symposium with three papers; the Electrical and Communications Symposium with four papers; and others to be announced later. There will also be a round-table discussion on refinery corrosion problems.

Central Electrochemical Research Institute, India

The Central Electrochemical Research Institute at Karaikudi, South India, is one of the National Laboratories planned by the Council of Scientific and Industrial Research, India. The construction of the building for the Institute is nearing completion and it is expected to be in full operation in the early part of 1953. An article describing the Institute has appeared in the *Bulletin of the India Section of The Electrochemical Society,* Volume 1, pages 4–5, 1952.

T. L. R. C.

Spectrographers Symposium in May

The American Association of Spectrographers is planning a symposium on "Emission Spectroscopic Determination of Metals in Non-Metallic Samples." The symposium will be held in Chicago on May 1, 1953. Contributed papers in the fields of petroleum, geology, agriculture, pharmacy, biology, ceramics, etc., are welcome. Please address all inquiries to: J. P. Pagliassotti, Chairman, Symposium Committee, % Standard Oil Company (Indiana), Box 431, Whiting, Indiana.

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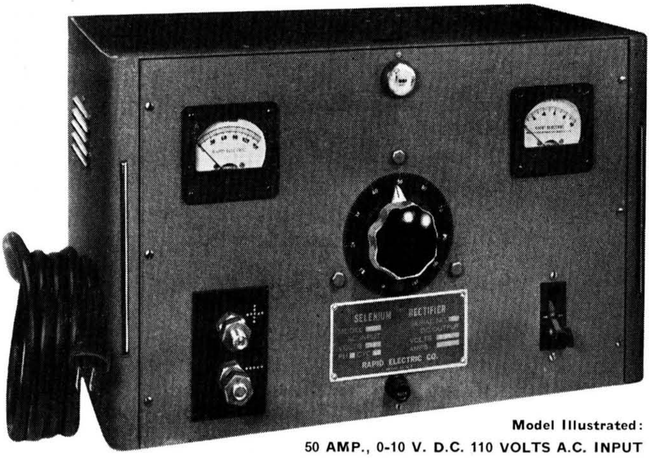

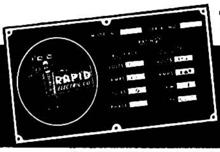

SECTION NEWS

Cleveland Section

The Cleveland Section was honored to have Society President Dr. J. C. Warner as its guest speaker at its December 9th meeting, held at the Cleveland Engineering Society Building.

Dr. Warner spoke on the "History of Theories of Electrochemistry." He told of the early contributions made by Faraday, Clausius, and Van't Hoff. He pointed out that the Arrhenius theory held sway, with various modifications until about 1923 when the Debye-Hückel theory was developed. Dr. Warner then discussed at length the basis and the significance of this theory and of some of the modifications of it, particularly those by Onsager.

The talk was received with keen interest by all.

J. M. MARGOLIS, *Secretary*

Detroit Section

Richard S. Atwood, Research Chemist at the Bersworth Chemical Company, Framingham, Massachusetts, was the guest speaker at the November 21 meeting of the Detroit Section, held at Wayne University. A filet mignon dinner and social hour preceded the technical meeting.

Mr. Atwood's subject was "Chelating Agents and Their Practical Applications in Cleaning, Electroplating, and Allied Industries." The speaker demonstrated the ability of chelating agents to form complexes with various metals, thereby reducing the metal ion concentrations to values where interference with desired reactions does not occur.

One specific example discussed by Mr. Atwood was the complexing of copper present in bright nickel baths. Studies of the effect of chelating agents on bond strength, and corrosion resistance of the electrodeposited coatings have not yet been completed.

The lively discussion period which followed Mr. Atwood's talk was a tribute to its stimulating qualities, and reflected the interest of the Detroit Section and its guests in subjects relating to technical progress in the field of electrodeposition.

G. V. KINGSLEY, *Secretary-Treasurer*

Niagara Falls Section

A joint meeting of the Niagara Falls Section with the National Association of Corrosion Engineers and the American Institute of Chemical Engineers took place at the Red Coach Inn, Niagara Falls, on November 12. This joint meeting was suggested by, and arrangements for the speaker were made by, NACE. The attendance was excellent, with 94 members and guests of the three societies present for dinner, and a total of 120 for the talk following.

The speaker, Thomas P. May, of the Corrosion Engineering Section of the International Nickel Company of New York, talked on the subject "Choosing a Metal." Dr. May has concentrated on marine corrosion since 1939. From 1939 to 1947 he was a member of the Research Staff of the Chemistry Division, Naval Research Laboratory, Washington, D. C., and was head of the Corrosion Section there from 1943 to 1947. He joined the International Nickel Company in 1947.

THOMAS P. MAY

Dr. May described some of the fundamental principles that should be considered by an engineer in selecting metals for equipment or structures. His presentation included a discussion of electrode potentials and their relation to corrosion rates, both in the corrosion of base metals and of galvanic couples. He then discussed several forms of corrosion attack that are commonly encountered in process equipment.

M. JANES, *Secretary-Treasurer*

Midland Section

At its November 28 meeting, the Midland Section of the Society heard an address by R. F. Humphries, Chairman, Physical Research Department of Armour Research Foundation, Chicago; his topic was "Nuclear Tracers in Chemical Processes."

Dr. Humphries outlined the principles of the tracer work including the α, β, and γ particles, and also showed slides of the various instruments useful for measurement.

* * *

The executive committee of the Detroit Section, including H. H. Roth, Chairman, W. R. Perry, Vice-Chairman, and F. N. Alquist, recently named committees to serve for 1952–53. They include:

Program—W. R. Perry, R. D. Blue, and R. C. Kirk
Membership—P. F. George, M. P. Neipert, and R. E. Friedrich
Nominating—H. A. Robinson, H. E. Houser, and W. S. Loose
Publicity—R. S. Karpiuk and R. I. Thrune

W. R. PERRY, *Secretary-Treasurer*

New York Metropolitan Section

The New York Metropolitan Section held a meeting on December 10, at which Moses D. Heyman, Integrated Mica Corporation, Woodmere, New York, spoke on the subject "Integrated Mica."

Dr. Heyman is a pioneer in developing this new material and is a member of the Reconstituted Mica Committee under the auspices of the National Research Council.

He displayed a thorough grasp of a subject which turned out to be of considerable interest and fascination, and he illustrated his talk with many samples of mica sheets which had been fabricated from scrap. It is not generally realized that mica in the form of large sheets is an extremely strategic material and that the ability to closely duplicate properties of natural sheet mica by "integrating" the much cheaper and more available small flakes, which are normally considered practically a waste product, can go far to eliminate our reliance on foreign sources.

Presumably because of the nearness to the Christmas season, the audience was of relatively smaller size than usual, but there was no lack of interest and discussion.

F. A. LOWENHEIM, *Secretary*

India Section

The Fourth Technical Meeting of the Section for 1952 was held on November 29 at the Central Electrochemical Research Institute (C.E.C.R.I.), Karaikudi, with Dr. A. Joga Rao in the chair in the absence of the chairman and vice-chairman. Three speakers addressed the gathering on the subjects outlined below.

Dr. T. L. Rama Char of the Indian Institute of Science, Bangalore, delivered a lecture on "Some Aspects of the Electrodeposition of Cadmium." The speaker first stated the importance of cadmium plating and then gave an account of the work carried out in his laboratory on the electrodeposition of cadmium and cadmium-zinc alloys from the sulfamate bath.

The bath was found to compare well with the cyanide bath in respect to current-density range and current efficiencies. The advantages of this bath over the cyanide bath were: simplicity of composition, stability; nonpoisonous nature, rate of control, and maintenance and production of bright plates without the use of addition agents. The cyanide bath gave finer-grained deposits and possessed better throwing power.

The electrochemistry of the cadmium sulfamate solutions was then touched upon with specific reference to the experimental results of the effect of the common variables on plating and the significance of polarization data. Measurements of the cathode potentials of cadmium and zinc indicated that it was possible to co-deposit the two metals from these solutions. Alloy deposits with a wide range of composition could be obtained by varying the operating conditions.

J. Balachandra, Department of Metallurgy, Indian Institute of Science, then gave a brief report of his work on the use of the fluoborate bath for cadmium plating. He stated that the performance of the fluoborate bath was quite comparable to that of the cyanide bath and that it offered interesting possibilities in the field of commercial plating.

V. Aravamuthan, Central Electrochemical Research Institute, Karaikudi, delivered a lecture on "The Industrial Applications of Electrolysis of Water." The lecturer pointed out the best methods for utilizing the products of electrolysis of water in industries that could be started at or near the electrolysis plants, and also mentioned the industries that could benefit from the products of electrolysis in spite of the distance from the plants. According to him, the production of synthetic ammonia, urea, nitric acid, ammonium nitrate, methane, ethylene, acetylene, benzene, toluene, and products that could be catalytically obtained from the above, as well as the products that could be obtained from these organic chemicals by reaction with nitric acid and/or by reaction with electrolytic hydrogen, would be commerically very successful. In these processes, besides air and water, only cheap carbon dioxide, by-product of fermentation industries, is employed.

Interesting discussions followed these lectures and the Secretary expressed the thanks of the Section to Dr. A. Joga Rao, and to the staff of the Central Electrochemical Research Institute for giving all facilities in arranging for this meeting, the second one outside Bangalore. With a vote of thanks to the speakers, the technical meeting came to a close. The program was rounded off with tea arranged by the Section for the members and guests, and a visit to the C.E.C.R.I., one of the National Laboratories of India.

* * *

The *Bulletin of the India Section of The Electrochemical Society* has completed one year. It was started in January 1952, and four numbers were issued during the year.

J. Balachandra, *Secretary*

HENRY F. KLEINFELDT

Henry F. Kleinfeldt, vice-president of Abbe Engineering Company, New York City, died at his home in Bloomfield, N. J., on June 6 last.

Mr. Kleinfeldt had been with the Abbe organization for more than 40 years and had been active in the development of many mixing, pulverizing, and blending operations which are standard practice in industry today. He was a longtime member of The Electrochemical Society, which he joined in 1915.

PERSONALS

Laurel E. Putnam of Ft. Belvoir, Virginia, is now employed as chief engineer at Superior Air Products Company, Newark, N. J.

Myron T. Cory, formerly of Great Lakes Carbon Corporation, Niagara Falls, N. Y., has been named president of Graphite Specialties Corporation in Niagara Falls.

Bernard C. Case has left the Hanson-Van Winkle-Munning Company, Matawan, N. J., to accept a position with Sunbeam Corporation, Chicago, Ill.

William F. O'Connor, associate professor of chemistry at Fordham University, New York City, has been named Chairman of the Department of Chemistry, Fordham University.

Harry K. Ihrig, vice-president in charge of research, Allis-Chalmers Manufacturing Company, Milwaukee, has been elected to the Board of Directors of Nuclear Instrument & Chemical Corporation, Chicago. Dr. Ihrig is nationally known for his research in metallurgy and related fields.

Kenneth J. Kelly of Pratt & Whitney Aircraft Division, United Aircraft Corporation, Hartford, has been assigned to work, on loan, in the Materials Chemistry Division of the Oak Ridge National Laboratory, Oak Ridge, Tenn.

Max E. Bretschger, formerly vice-president of Buffalo Electro-Chemical Company Inc., Buffalo, N. Y., has been elected president of the company, filling the vacancy created by the death of the late Charles A. Buerk. **George G. Crewson**, director of engineering, Buffalo Electro-Chemical Company, has been elected to the Board of Directors.

T. L. Rama Char of the Indian Institute of Science, Bangalore, India, has been awarded the Fellowship of the Royal Institute of Chemistry in London.

P. A. Chengappa, D.C.M. Chemical Works, Delhi, India, has left for Germany to work in a caustic soda-chlorine plant under the Indo-German Industrial Cooperation plan.

FREDERICH FICHTER

Professor Frederich Fichter, internationally famous scientist, of Basle, Switzerland, died at Basle on June 6th.

Professor Fichter was one of the eminent scientists of his time and was well known to many members of The Electrochemical Society, which he joined in 1907.

Frederich Fichter was born on July 6, 1869. He attended the University of Basle from 1888–90, and later the University of Strasbourg, where he became assistant to Dr. Rudolf Fittig in 1893 and received the Ph.D. degree in 1894. The following year he returned to the University of Basle as assistant to J. Piccard and continued his work there throughout his life. In 1912 he was appointed full professor and chairman of the Department of Inorganic Chemistry, continuing until his retirement in 1939. During this time 300 papers were published from his laboratory. Many of these appeared in the TRANSACTIONS of this Society.

In 1928 Professor Fichter was guest professor at the University of Birmingham in England. Since its founding in 1918 until 1948, he was editor of the well-known *Helvetica Chimica Acta* and was awarded the Paracelsus Medal in 1947 by that organization. He also served as president of the Union of Swiss Chemical Societies and vice-president of the International Union of Chemistry. His chief fields of interest included oxidation by gaseous fluorine, preparation of molten beryllium, and especially the field of organic electrochemistry.

JOHN M. PEARSON

John M. Pearson, director of production, physical, and development research for Sun Oil Company, died on November 16th at his home in Swarthmore, Pennsylvania. He was 48 years old.

Dr. Pearson joined The Electrochemical Society in 1942 and was active in the Corrosion Division. He was the author of a number of articles on corrosion, and held 15 patents on electrical instruments for measurement and control. In 1948, he received the Frank Newman Speller Award for his work in the corrosion field from the National Association of Corrosion Engineers.

Dr. Pearson was a native of Portland, Oregon. He attended Reed College, later receiving the B.Sc. degree from the University of Chicago, and the Ph.D. degree from the California Institute of Technology.

B. SMITH HOPKINS

B. Smith Hopkins, professor Emeritus of chemistry at the University of Illinois, died at his home in Urbana on August 27th.

Professor Hopkins was born in Owossa, Michigan, in 1873 and received the A.B. and A.M. degrees from Albion College in 1896–97, and his Ph.D. from M.I.T. in 1906. He spent most of his life teaching, with the later years at the University of Illinois where he was Professor of Inorganic Chemistry. He had been a member of The Electrochemical Society since 1922.

JOHN L. BRAY

John L. Bray, 62, professor of metallurgy at Purdue University since 1923, and head of the school of chemical and metallurgical engineering from 1935 to 1947, died at his home in West Lafayette, Indiana, on December 6.

Dr. Bray was born in Millbridge, Massachusetts, in 1890, was graduated from Massachusetts Institute of Technology in 1912, and obtained a doctorate there in 1930. He had eight years' experience with mining companies in Central and South America and British Columbia, and taught for a year at M.I.T. and at Nova Scotia Technical College before coming to Purdue. He was the author of several text books in the field of metallurgy and was a widely recognized authority on this subject. He joined The Electrochemical Society in 1929.

NEW MEMBERS

In December 1952 the following were elected to membership in The Electrochemical Society:

Active Members

Harold Berzof, United States Air Force, mailing add: 476 N. Thomas St., Arlington, Va. (Electric Insulation)

Horace A. Cataldi, Standard Oil Company, 910 S. Michigan Ave., Rm. 200, Chicago, Ill. (Corrosion)

Harry C. Gatos, E. I. duPont deNemours & Co., Experimental Station, Wilmington, Del. (Corrosion, Electrodeposition, and Theoretical Electrochemistry)

John W. Judy, Hooker Electrochemical Company, Tacoma, Wash. (Industrial Electrolytic)

George P. Kirkpatrick, R.C.A. Victor, mailing add: Oyster Pt., R.D. #1, Lancaster, Pa. (Electronics)

Ellwood R. Lanahan, Accurate Electro Plating, Inc., 11th & Westmoreland Sts., Philadelphia, Pa. (Electrodeposition)

Robert A. Lewis, Kaiser Aluminum & Chemical Corp., mailing add: N. 621 Burns Rd., Veradale, Wash. (Industrial Electrolytic)

Charles E. Martens, Glasfloss Division, Tilo Roofing Company, New South Rd., Hicksville, N. Y. (Battery)

Aldo Martone, Elettrografite di Forno Allione S.P.A., mailing add: Via Serbelloni, 8, Milano, Italy (Electrodeposition, Electrothermic, and Industrial Electrolytic)

Paul P. Mozley, Lockheed Aircraft Corp., Dept. 72-25, Bldg. 63-1, Plant A-1, Burbank, Calif. (Corrosion)

Robert C. Pelletier, Canadian Carborundum Company, Ltd., Niagara Falls, Ontario, Canada (Electrothermic)

Robert S. Sheppard, Columbia-Southern Chemical Corp., mailing add: P.O. Box 321, Doylestown, Ohio (Industrial Electrolytic)

Henry J. Wittrock, Kaiser Aluminum & Chemical Corp., mailing add: N. 1404 Boeing Rd., Opportunity, Wash. (Battery, Corrosion, and Electrodeposition)

Associate Members

John C. Clayton, University of Pennsylvania, mailing add: 629 E. Dupont St., Philadelphia, Pa. (Electrodeposition, Electronics, Electro-Organic, and Theoretical Electrochemistry)

Richard L. Nolder, Kaiser Aluminum & Chemical Corp., Box 1451, Spokane, Wash. (Battery, Corrosion, Electrodeposition, Industrial Electrolytic, and Theoretical Electrochemistry)

Edward V. Raymond, General Electric Company, mailing add: 46 John St., Pittsfield, Mass. (Electrodeposition)

George L. Schnable, University of Pennsylvania, mailing add: 36 S. Wyomissing Ave., Shillington, Pa. (Electronics and Theoretical Electrochemistry)

Thomas J. Summerson, Kaiser Aluminum & Chemical Corp., mailing add: S. 402 Freya, Spokane 31, Wash. (Corrosion)

Student Associate Members

Gordon D. Gemmell, Corrosion Laboratory, Rm. 8-204, Massachusetts Institute of Technology, Cambridge, Mass. (Corrosion); Prize Essay Winner

Donald W. Hutchings, Oberlin College, Severance Chemical Laboratory, Oberlin, Ohio (Corrosion); Prize Essay Winner

Robert E. Rowley, State College of Washington, mailing add: Kiona, Wash. (Electronics and Industrial Electrolytic)

LETTER TO THE EDITOR

Regarding Function of Oxygen in Zinc Sulfide Phosphors

Dear Sir:

We desire to make the following comments upon the paper by F. A. Kroeger and J. Dikhoff entitled "The Function of Oxygen in Zinc Sulfide Phosphors."[1]

It is an experimental result, obtained by various authors, that in certain circumstances the ratio of the two kinds of the luminogene centers, respectively responsible for green and blue emission bands, decreases as the copper content of ZnS (Cu) phosphors increases. This result was never questioned and the paper of Kroeger and Dikhoff gives a new detailed confirmation of this influence.

But we have also experimentally ascertained that, with a constant copper concentration of 5.10^{-5} (which, from the work of previous authors, must lead to phosphors containing green centers in important predominance), samples of ZnS (Cu) show either a blue-violet luminescent emission without afterglow, a green luminescent emission with strong afterglow, or an intermediate one.[2] In these various samples characterized by exactly the same concentration of copper, the ratio green/blue centers has a considerable range of variation. We observed that these important differences must be imputed to a variation of the oxidized state of luminogene centers, a center containing oxygen which is green and a center without oxygen which is blue. It seems that Kroeger and Dikhoff have understood that, in our own investigations, we took, as they did, zinc oxide ZnO as oxidizing agent. Actually, our oxidizing agent was oxygen itself, in gaseous state. Under these conditions, very small amounts of O_2, comparable to those of activating copper, were sufficient to obtain a total shift from blue to green.

These results are in good agreement with those of Kroeger and Dikhoff concerning the tendency of oxygen and activating atoms or ions to associate with one another in the lattice. This tendency indicates a kind of chemical affinity, which may alter the energy level of the luminogene centers built with these atoms.

These results also agree with those concerning the influence of the copper content upon the ratio of the green/blue centers, as we shall show with more detail in a later paper which we plan to submit to this Journal. Nevertheless, they indicate that this influence is not a direct one but quite the reverse, an indirect one, through the intermediate oxidization of the activating atoms. The two models Cu^+ and Cu_2^+, respectively proposed for the green and the blue centers, do not seem to fit with the results of our experiments.

Edmond Grillot
and Marguerite Bancie-Grillot
Laboratoire de Luminescence—Faculté des Sciences, P. C. B., Paris, France

RECENT PATENTS

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

September 16, 1952

Wilcock, R. C., and Hastings, P. E., 2,611,008, Circuit Tester for Battery-Energized Circuits

Cade, P. J., and MacDougall, D. J., 2,611,113, Electrolyte Indicating and Control Apparatus

September 23, 1952

Koch, H. E., 2,611,790, Electric Heat Treating Furnace

Brandau, W. E., 2,611,791, Thermocouple Means

André, H. G., 2,611,792, Method of Making Electric Accumulators

Simpson, A. W., 2,611,793, Dry Cell with Improved Thermoplastic Seal

Peterson, J. L., 2,611,794, Terminal Assembly for Electric-Cell Batteries

Kerby, W., 2,611,853, Battery Heater

September 30, 1952

Andrus, O. E., Re. 23,559, Corrosion-Resistant Metallic Structure

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[1] F. A. Kroeger and J. Dikhoff, *J. Electrochem. Soc.*, **99**, 144 (1952).

[2] Edmond Grillot and Marguerite Bancie-Grillot, *Compt. rend. l'acad. sci.*, **231**, 966 (1950); Edmond Grillot, *J. chim. phys.*, **48**, 112 (1951).

Reisinger, F. F., 2,612,469, Rapid Fine-Grained Copper Electrodeposition
Griess, J. C., Jr. and Rogers, L. B., 2,612,470, Selective Electrodeposition of Silver
Standing, S. A., 2,612,476, Luminescent Screen for Image Reproducing Tubes
Heise, G. W., and Schumacher, E. A., 2,612,532, Primary Cell or Battery
Blake, I. C., 2,612,533, Primary Cell; 2,612,534, Primary Cell; 2,612,535, Primary Cell; 2,612,536, Primary Cell; 2,612,537, Primary Cell
Cahoon, N. C., and Heise, G. W., 2,612,538, Primary Galvanic Cell and Battery and Method of Making Same
Dyer, C. A., 2,612,539, Cell and Support

October 7, 1952

Mulford, S. F., 2,612,779, Compensated Thermocouple
Grant, A. W., 2,613,178, Method of Electroforming Seamless Tubes
Wolfson, H., and Thomson, B., 2,613,179, Silver Plating
Eppley, M., 2,613,234, Plug or Septum for Electrolytic Cells
Christie, S. L., 2,613,248, Battery Testing Apparatus and Method

October 14, 1952

Mackey, R. W., and Swalheim, D. A., Application 105,447, Current Reversal Electroplating
Lloyd, R. R., and Rosenbaum, J. B., Application 238,361, Electrolytic Diaphragm Cell
Taylor, H. L., and Hedding, L. K., 2,614,052, Manufacture of Copper Oxide Rectifiers
Smith, A. L. J., 2,614,082, Zinc Sulfide Type Phosphors Containing Magnesium Sulfide
Jacquier, P. A. C., 2,614,138, Sealable Storage Battery Construction

October 21, 1952

Tanczyn, H., 2,614,921, Stainless Steel and Method
Loosjes, R., and v. Genuchten, A. J., 2,614,942, Thermionic Cathode
Proudfoot, C. B., 2,614,946, Granular Silicon Carbide and Method of Making Same
Heyroth, A. H., 2,614,947, Refractory Articles and Method of Making
Chester, A. E., 2,164,975, Electroplating of Zinc and Electrolyte Therefor
Patnode, H. W., and Wyllie, M. R. J., 2,614,976, Electrode for Determining Cationic Activity
Marinace, J. C., and Le Loup, T. E., 2,615,060, Crucible for the Purification of Molten Substances

LITERATURE FROM INDUSTRY

TEMPERATURE RECORDER DATA. New 20-page bulletin just issued by manufacturer of industrial instruments for the measurement and control of process variables, contains complete details of temperature recorder construction, showing how each component part, from bulb to chart, contributes to recorder accuracy. Includes more than 50 photographs, charts, and diagrams. The Foxboro Co. P-105

OIL-FILLED ACCELEROMETER. A new accelerometer, No. 24133, has been announced. Compactly designed to fit in an oil-filled case, it is extremely resistant to vibration and has long life-expectancy. It utilizes a potentiometer resistance with a large output, requiring no amplifying unit in most cases; has low, natural frequency. Designed for applications in computing, telemetering, and aircraft missile control. G. M. Giannini & Co., Inc. P-106

ELECTRODE RAPPING SYSTEM. Booklet with illustrated information on the recently developed M.I. (magnetic impulse) continuous electrode rapping system for electrostatic precipitators has been announced. The M.I. rapping system is a continuous, self-monitoring electrode cleaning system that improves over-all precipitator efficiency and reduces operating costs. Research Corp. P-107

CONTROL CENTER BOOKLET. New 31-page application booklet on control centers stresses the case for centralizing all controls of an entire system in one group of enclosures. Also discussed are characteristics of control centers that make for flexibility of application, ease of servicing, and safety of operating personnel. Three types are described and the various electrical components that make up typical units are illustrated and defined. Westinghouse Electric Corp. P-108

AUTOMATIC VOLTAGE STABILIZERS. New 12-page, two-color booklet on automatic voltage stabilizers ranging from 15 to 5,000 volt amperes is available. Contains photographs and diagrams of the equipment, explains operation principles and construction, and gives complete specifications. General Electric Co. P-109

LABORATORY SUPPLIES. New 4-page, 2-color illustrated folder describes over 15 indispensable laboratory items. Included are bottles and funnels, Kemflex polyethylene tubing, glass tubing gauges, Orlon laboratory jackets, etc. E. Machlett & Son. P-110

To receive further information on any product or process listed here send inquiry, with key number, to JOURNAL of The Electrochemical Society, 235 West 102nd Street, New York 25, N. Y.

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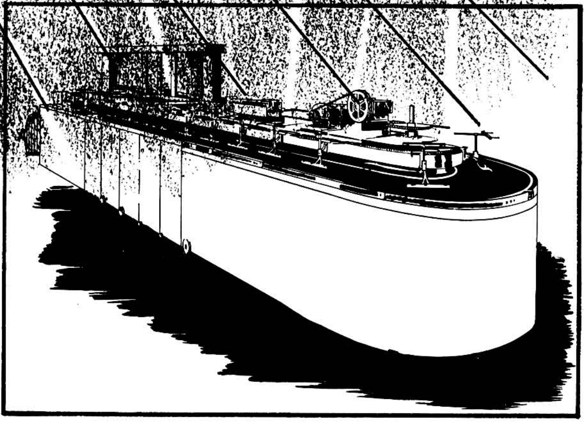

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Watch for further developments. Meanwhile if either we or Ronal can be of help in any research or pilot plant studies you are making, do not hesitate to call on us. If your responsibilities cover plating and finishing—and you're not satisfied with the results—perhaps we can help in this, too.

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