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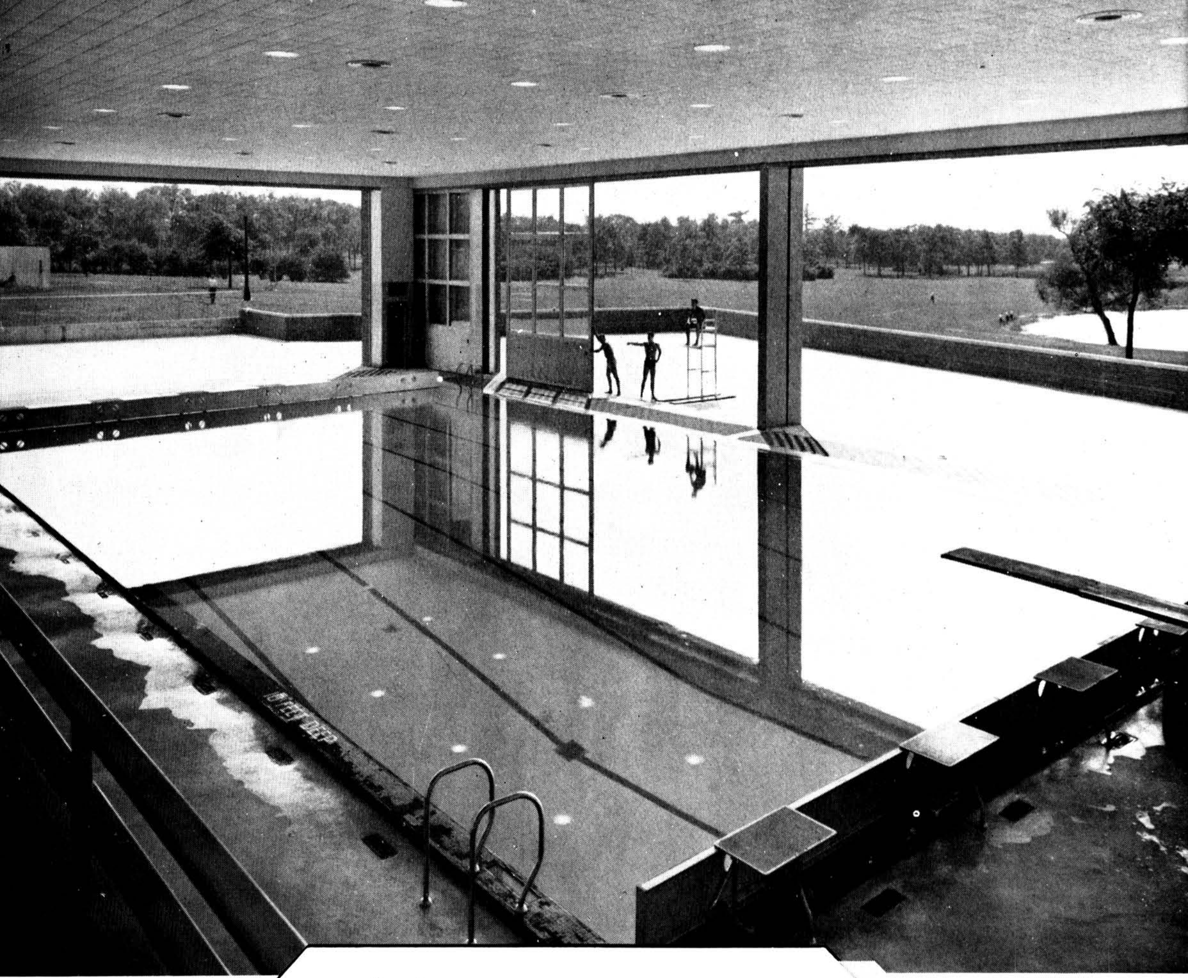
ELECTROCHEMICAL INDUSTRY

Canada



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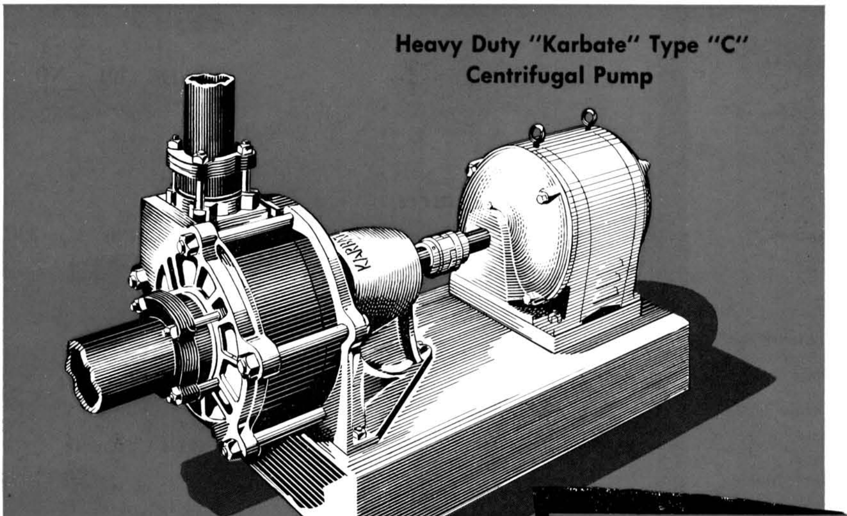

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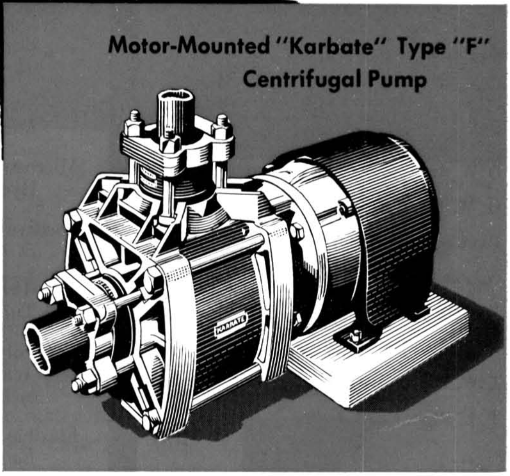

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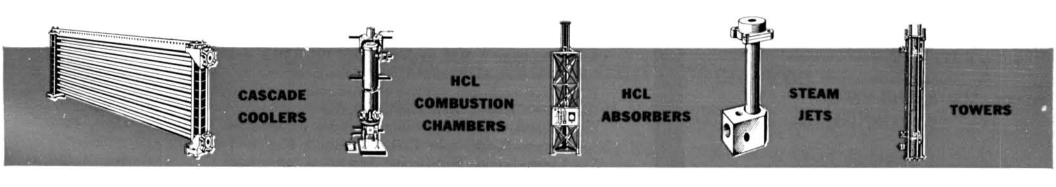

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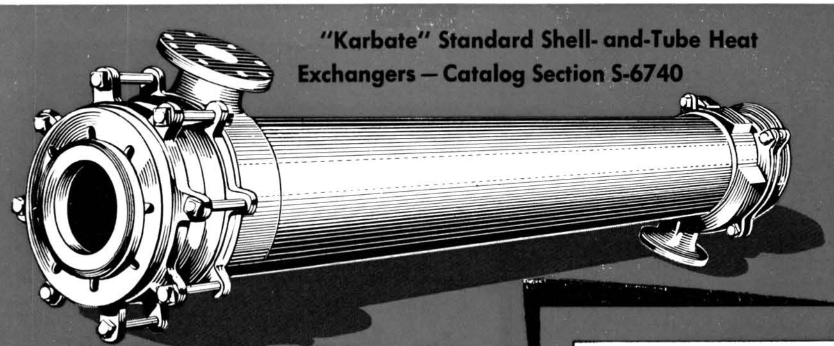

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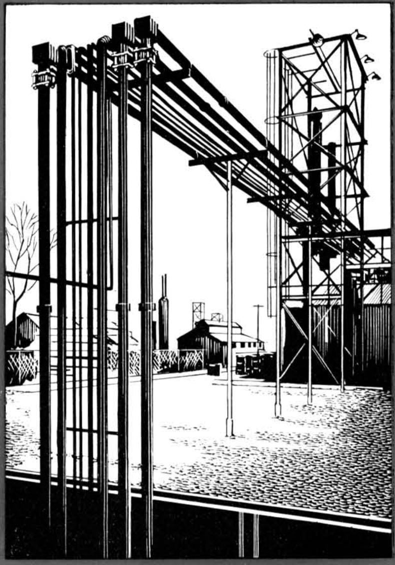

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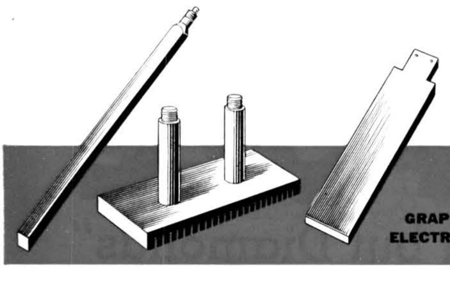

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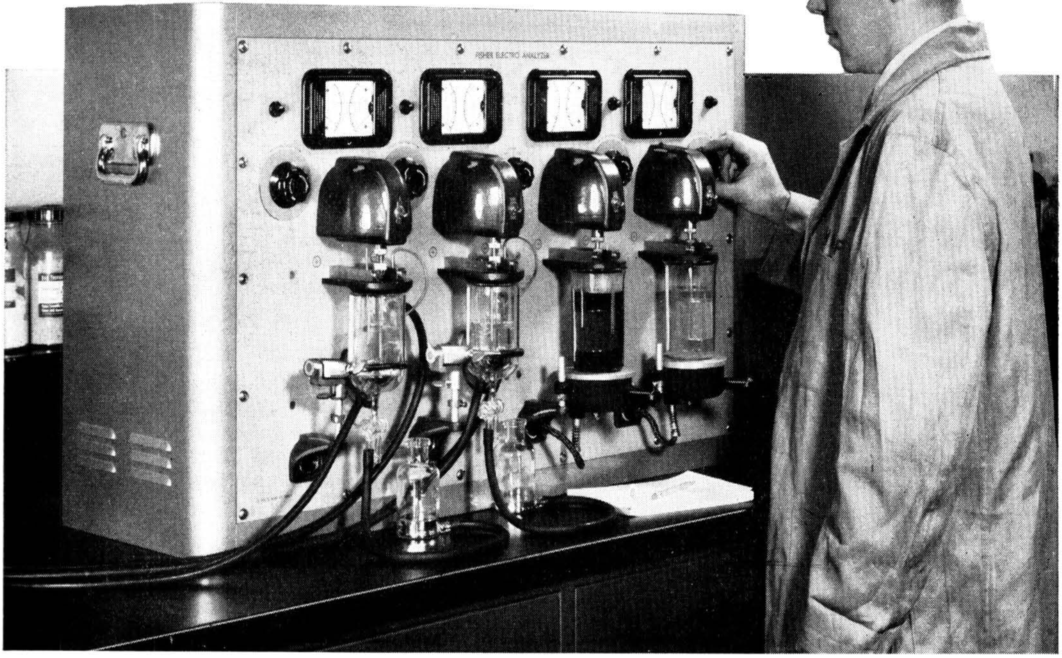

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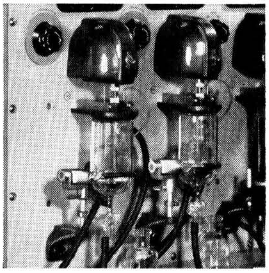

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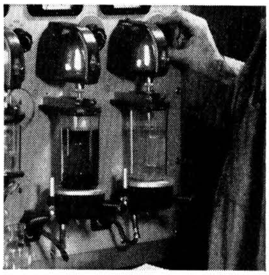

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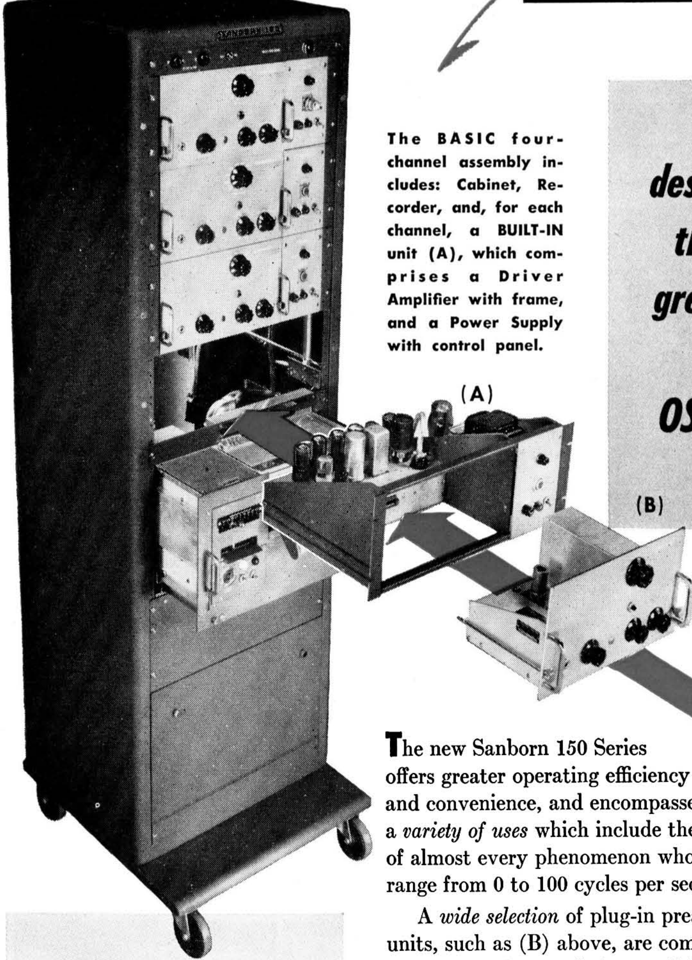

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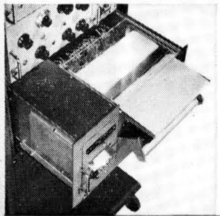

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Editorial

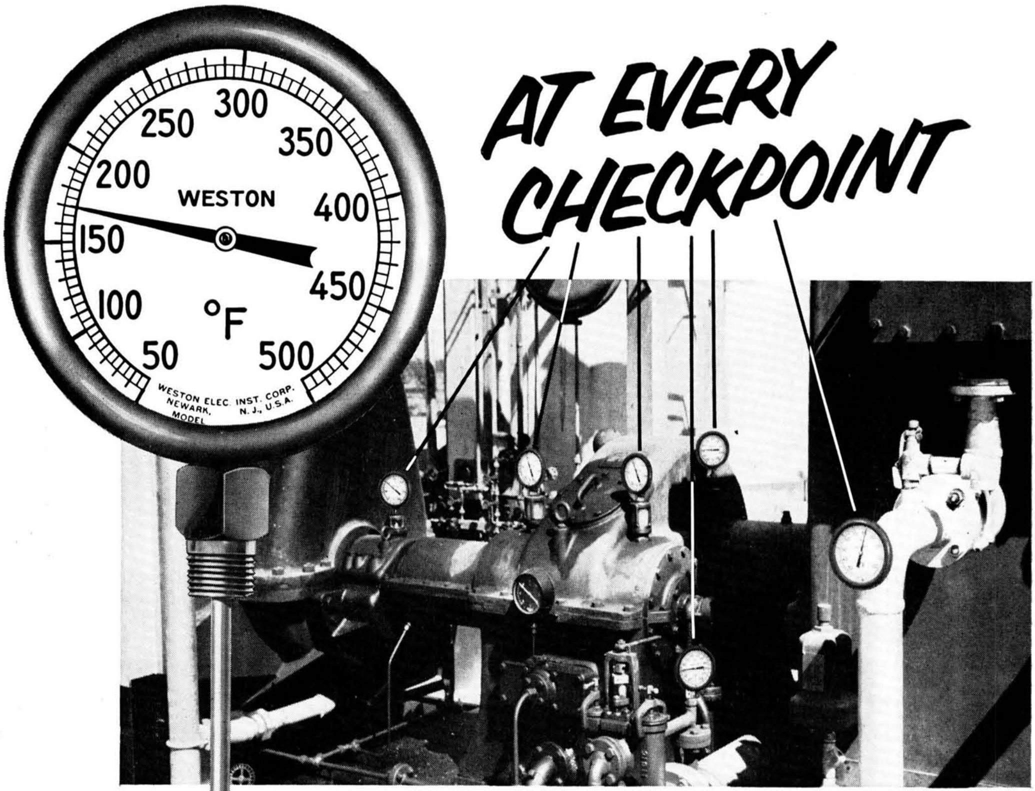
Canada, Country with a Future

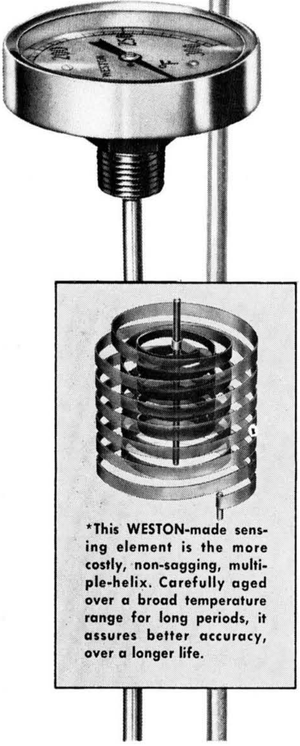
THIS issue presents the third article on the electrochemical and electrometallurgical industries of Canada. The fascinating account of the remarkable expansion of these industries and the great hydroelectric developments upon which they depend will be widely appreciated. It is clear that these developments have contributed in great measure to the extraordinary industrial growth of Canada that has taken place in recent years. With less than ten per cent of the population of the United States, Canada has become the sixth ranking industrial power and the third greatest trading nation in the world. The leading exporter of nonferrous metals, Canada supplied nearly 40% of the Allied requirements of aluminum in World War II.

These exciting achievements have grown out of the pioneering electrochemical work of ingenious scientists and engineers on both sides of the border. Among them over the years were such men as E. G. Acheson, Charles M. Hall, F. J. Tone, T. L. Willson, H. Y. Castner, Herbert Dow, L. D. Vorce, Lawrence Addicks, F. M. Beckett, R. A. Witherspoon, F. A. Lidbury, A. F. G. Cadenhead, and R. R. Ridgeway. These and many others deserve acclaim.

Natural resources of Canada are plentiful, widely distributed, and varied in character. Profiting by the unfortunate experiences of countries like the United States that have wasted a considerable proportion of their natural resources, the Canadian Government has wisely insisted upon conservation and care in the use of these resources. For example, timber lands must be reforested at the same rate that timber is removed. Modern methods of mining and extractive metallurgy are encouraged.

Favored with abundant water power, tremendous natural resources, and a people of great enterprise, it is evident that the present rapidly expanding industrial activity will continue at an accelerated pace. Truly the twentieth century belongs to Canada! —RMB





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ELECTROCHEMICAL AND ELECTROMETALLURGICAL INDUSTRIES OF CANADA

Part III. Ontario and Manitoba[1]

A. C. Holm[2]

Introduction

In this, the third of a series of four articles describing the electrochemical and electrometallurgical industries of Canada, together with that nation's major power developments, our tour will start in the Province of Ontario and proceed westward through Manitoba; Saskatchewan, Alberta, British Columbia, the Yukon Territory and the Northwest Territories will be discussed in the March issue.

Across the immense part of Canada from the Ottawa River and James Bay to the Pacific, and from the Great Lakes north to the Arctic, there are vast resources not only of raw materials but also of power to process them.

Not the least of the resources, of course, is uranium, and studies are now going forward toward the production of electric power by atomic-driven generators. But there are tremendous stores of natural gas and of coal which have hardly been tapped yet. And there is a wealth of water power still to be harnessed, particularly on the fringes north of the present industrial areas.

Here, estimated at December 31, 1953, for the five westerly provinces and the Territories, are the hydroelectric developments, the water power remaining to be developed, and the year's production of electricity from all sources:

Province	*Water resources (Thousand hp)*		*Production 1953 (Million kwh)*
	developed	*undeveloped*	
Ontario	3981	5458	21,700
Manitoba	717	6513	3008
Saskatchewan	112	1343	1173
Alberta	208	1422	1362
British Columbia	1768	12,532	7650
Yukon & N.W.T.	33	1028	64

The Province of Ontario

Canada's second largest province in physical area (412,582 square miles) and largest in population (4,897,000), Ontario has the distinction of being the most highly industrialized province in the nation, a position it has maintained for over 70 years. Favored in its southern portion by a mild climate (Canada's southernmost projection in Ontario lies farther south than a large sector of the United States) and fertile soil, Ontario early attracted large numbers of settlers. The steadily growing population spurred on local manufacturing, and these two have since advanced vigorously hand in hand so that Ontario now accounts for one-third of Canada's population and about one-half of her manufactured goods.

Important factors in the industrial growth of Ontario have been the development of its great resources of minerals, water powers, and forests, as well as its location on the Great-Lakes—St. Lawrence shipping channels. For half a century Ontario has led all of Canada in mineral production, with some 35% in value of the nation's mineral output originating in this province. Ontario took an early lead in developing hydroelectric power, and while it gradually surrendered first place to Quebec in the nineteen-twenties it still produces some 30% of Canada's total power and more kwh per capita than any whole nation in the world except Norway. Its forests turn out about 27% in value of the nation's pulp and paper and some 16% of its sawmill products. And Ontario's location on the shores of the Great Lakes and the St. Lawrence River (the province has a fresh-water shoreline of 2362 miles) has permitted cheap transportation of raw materials and products. Of special importance has been the relatively easy access to the coal and iron ore of the neighboring states, for Ontario has no coal, and until recent years produced no iron ore in quantity. Not to be overlooked also is the fact that Ontario's varied farm crops can support a large industrial population; the total cash return from farm crops is greater than in any other province.

The varied and numerous manufacturing industries of Ontario are the mainstay of its production, accounting for some two-thirds of the total dollar value of the province's output. These manufacturing industries represent the following percentages of total Canadian manufacture: automotive 96, agricultural implements 96, heavy electrical machinery 95, rubber goods 81, primary iron and steel 74—and many others in this same range; in all, about 50% of total Canadian manufacture. Volume of manufactured products from Ontario has doubled from 1942 to 1952 and is still expanding rapidly.

So vast has become the output of Ontario's factories that its electroproducts industry, large and vigorous though it be, is finding itself gradually receding in relative importance in the province's economy. For a decade or two after the harnessing of Niagara, Ontario led all of Canada in electrometallurgical and electrochemical production. But this supremacy was gradually relinquished to the Province of Quebec as the latter developed its own larger hydroelectric resources and began to outstrip Ontario in the production of low-cost hydro power. The tremendous upsurge of manufacturing in Ontario has actually had the effect of impeding the normal expansion of Ontario's electroproducts industries by avidly outbidding the latter for any new or surplus power and, in fact, at times creating serious power shortages. Ontario is rapidly approaching full development of all its economic hydroelectric power resources and has already been forced to resort to steam power in large quantity, although

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[1] This is the third in a series of articles on Canada provided by A. C. Holm, Canadian Regional Editor.

[2] Shawinigan Chemicals Limited, Shawinigan Falls, Quebec, Canada.

it lacks any cheap indigenous fuel for this purpose. The eagerly awaited development of the St. Lawrence Waterway, which now appears imminent, would provide Ontario with an additional 1,100,000 hp. This, together with other hydro developments now under way, would probably take care of the province's growth in power demand for about the next ten years. The probability is, however, that the major share of this additional power will be snapped up by Ontario's new and expanding factories, leaving relatively little for the electroproducts industries. However, despite these difficulties of rising costs and decreasing availability of power, Ontario's electrometallurgical and electrochemical industries are still maintaining a high rate of production and a healthy growth. Of particular importance is the output of calcium cyanamide, ferroalloys, artificial abrasives, graphite, electrolytic nickel and copper, magnesium, and chlorine.

Raw Materials

Of the indigenous minerals, Ontario's electroproducts industries have made use mainly of salt, limestone, sand and quartz, dolomite, shale (for rock wool), and ores of nickel, copper, and cobalt. Imported from other provinces, from the U. S., or abroad are such raw materials as coal, manganese and chrome ore, bauxite, and a certain amount of steel scrap. As by-products of the electrolytic refining of its metal ores, Ontario also recovers gold, silver, platinum and other precious metals, selenium, and tellurium. Other important mineral products of Ontario include iron ore, gold and silver, arsenic, lime and cement, clay products and building stone, nepheline syenite, fluorspar, mica, and asbestos. From its smelting operations Ontario also recovers liquid SO_2 and will soon recover elemental sulfur. Ontario also has Canada's only refinery for uranium and radium, supplied with ore from the Northwest Territories. Promising showings of uranium ore are now being investigated in the Haliburton and Algoma areas of Ontario. Of interest also is a recent find of columbium-tantalum ore under Lake Nipissing near North Bay. The mineral-rich Canadian Shield traverses Northern Ontario, and year after year, as exploration proceeds, new indications of mineral wealth are unearthed.

Electric Power

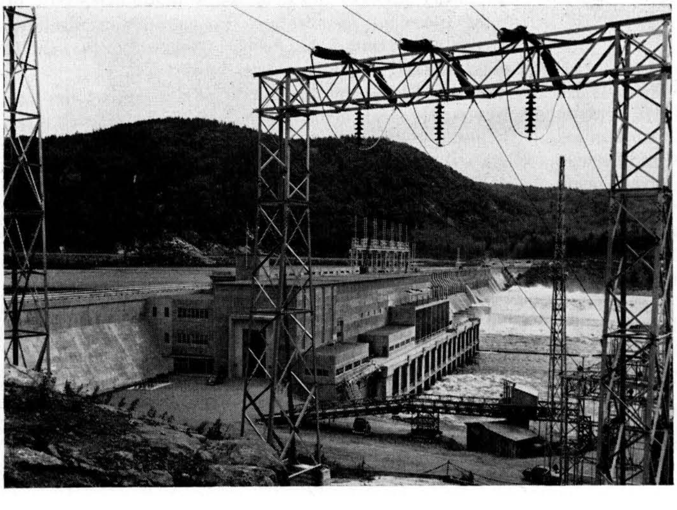
For the further production of electricity to power its rapid industrial and commercial expansion, the Province of Ontario is at the point of proceeding with two developments which have had international attention. First, Ontario has laid plans for the harnessing of atomic reactors to drive generators. And second, it is about to start work on the Canadian half of the St. Lawrence Waterway development, to produce more than a million horsepower. The Ontario Hydro-Electric Commission, the government-sponsored body which is Canada's largest single public utility, with a peak capacity at present of about 4 million hp, is working hand-in-hand with Canada's federal government in both those projects.

In the plan for atomic-generated electricity, the Commission is working jointly with a federally-owned corporation, Atomic Energy of Canada Limited, in a "feasibility study" being carried on at Chalk River, Ontario, where Canada's work in atomic energy has been concentrated since World War II days. No target-date has been set yet for the first production of atomic-generated power, but it's believed that Canada is probably farther ahead than any other country in harnessing the atom for peace-time uses.

In the development of hydroelectric power from the International Rapids section of the St. Lawrence River, Ontario is acting as the agency appointed by the federal government, just as New York State has been designated by the United States Government to harness the American share of the riverflow. No schedule has been set for completion of that job, either, but it is expected that, despite delays through actions in American courts, work will start during the coming spring. The seaway, an accompaniment to the power project, is expected to be built by the Canadian government itself.

Since the end of World War II, Ontario Hydro has completed 13 new power developments, all but two of them hydroelectric. Another, the largest of all, is now approaching completion. Named Sir Adam Beck No. 2, it is a 1,260-000-hp development on the Niagara River, adjoining the 560,000-hp plant—Sir Adam Beck No. 1—at Queenston, and like the older one will use water drawn from the river above the cataract and carried, in this case by giant twin tunnels, 5½ miles to the penstocks which drop it about 300 feet to the turbines. The first units are to be in operation this year, and all of them by mid-1956.

With the half-dozen other plants which it operates on the Niagara and Welland Canal by using the Canadian share of Lake Erie's outflow, Ontario Hydro will then be developing



Last of Ontario Hydro's three postwar Ottawa River plants which harness a total of 942,000 hp on a 174-mile stretch of the river, is the Otto Holden generating station. This giant, named after Hydro's assistant general manager-engineering, Dr. Otto Holden, has a dependable peak capacity of 273,000 hp following completion early in 1953 with eight units in service. The station went into operation initially in June 1952.

more than 2,500,000 hp within that area of a few square miles. And including the nearly 60 plants which it operates in other parts of the province, and the power it buys under long-term contract, principally from Quebec, the capacity of the Commission will exceed 5,800,000 hp. All of its plants, except one at Toronto and another at Windsor, with a combined capacity of about 900,000 hp, are hydroelectric.

Ontario's fully-developed share of the Ottawa River (the rest being under Quebec's control) yields more than 1,100,000 hp. The largest of those Ontario Hydro plants on the Ottawa are Des Joachims, of 496,000 hp, and Otto Holden, of 264,000.

In all, there are 99 hydroelectric plants in the province, with a total generating capacity of about 4,000,000 hp. Most of the plants not owned or operated by the provincial commission are devoted largely to the production of power for individual industries.

By the end of 1953, Ontario Hydro had completed more than one-third of its gigantic project to convert to 60-cycle circuits the frequency in about 12,000 square miles of southwestern Ontario, with nearly one million household, farm, commercial, and industrial customers. In the past, that area has constituted a 25-cycle "island" surrounded by the standard 60-cycle service. Cost of the complete conversion operation, which was started in 1949, is estimated now at about $400,000,000; approximately 5,000,000 pieces of frequency-sensitive electrical equipment are being changed over for 60-cycle operation, or replaced entirely, at the Commission's expense. Newer generating stations have been designed for 60 cycles, and in older ones the frequency is being altered.

Last year saw, too, completion of an agreement for an international exchange of emergency power. Transmission lines crossed the Detroit and St. Clair Rivers to permit Ontario Hydro and the Detroit Edison Company to send one another power, as required, on the two systems—between Windsor, Ontario, and Detroit, and between Sarnia, Ontario, and Marysville, near Port Huron, Mich.

Nickel and Copper

Nickel is one of Ontario's most important products, representing as it does over 85% of the free world's output of this metal. In 1952 this province produced some 140,000 tons of nickel in all forms. In Canada up until now Ontario has been the only producer of nickel; a nickel-copper ore is just coming into production in Manitoba. After gold, nickel has contributed the most to Ontario's total output value of minerals since 1900, and it is followed by copper. Practically all of Ontario's nickel and copper is derived from the immense sulfide ore-bodies of the Sudbury area. These Sudbury mines also produce about 48% of Canada's copper.

There are two large operators in the Sudbury area, the International Nickel Company of Canada Limited and the Falconbridge Nickel Mines Limited. The latter company, holding contracts with the U. S. Government for nickel, copper, and cobalt, has a capacity for some 30 million lb of nickel a year and has embarked on a program designed to double its capacity. Falconbridge operates a smelter in Ontario, but ships all of its nickel and copper as a matte to its Norwegian plant for refining. The International Nickel Company of Canada operates a smelter at Copper Cliff and Coniston and a nickel refinery at Port Colborne, Ontario. Some of its nickel is exported as nickel oxide or as matte, but about 60% is in the form of refined electrolytic nickel. In 1952, about 249,000,000 lb of nickel in all forms, i.e., over 75% of the nickel used by the free world, was produced by "Inco." Inco's copper is refined electrolytically at Copper Cliff; output in 1952 was about 234,000,000 lb. A minor portion of nickel and copper is shipped as a matte to the International Nickel Company's plant at Huntington, West Virginia, for the production of Monel metal.

The earliest corporate unit of what is now the International Nickel Company of Canada Limited was the Canadian Copper Company, formed in 1886, which built a smelter at Copper Cliff in 1887 to roast sulfide ores and later produced a copper-nickel matte. This company also experimented for several years with an electrolytic nickel refining process. At first the matte was shipped directly to the Orford Company at Bayonne, New Jersey, for refining; after 1899 it was given a further smelting treatment at the Ontario Smelting Works of the Orford Company at Copper Cliff, before refining at Bayonne. When the Orford Company adopted the electrolytic refining process of the Canadian Copper Company, the two firms amalgamated as the International Nickel Company in 1902. After the formation of the International Nickel Company of Canada Limited (in 1916) a modern refinery was opened at Port Colborne, Ontario, in 1918 and all the refining operations transferred to it from the Bayonne refinery, which closed down in 1922. In 1929, a merger was effected with the Mond Nickel Company to simplify development of adjoining mining properties, and this amalgamation gave Inco another smelter at Coniston, Ontario, a nickel refinery at Clydach, Wales, and a precious metals refinery at Acton, England.

Up to about 1930 the Port Colborne refinery received a high grade Bessemer matte from Copper Cliff, separated nickel and copper sulfides by the Orford process, produced nickel oxide and electrolytic nickel, and shipped blister copper to U. S. custom electrolytic refineries. With the advent of selective flotation of nickel and copper sulfides at Copper Cliff, it became possible in 1930 to transfer the Orford process to this smelter, carry on only electrolytic refining of nickel at Port Colborne, and to undertake electrolytic refining of blister copper right at Copper Cliff. The latter was first done by the Ontario Refining Company, a partly owned subsidiary. In 1935 this company was also absorbed by the International Nickel Company as the wholly owned "Copper Division" of Inco.

Late in 1948 Inco started to replace the Orford process, which had been used for nearly 60 years, by the matte separation process. In these operations, which have the object of separating copper, nickel, and platinum metals in nickel matte, the matte is subjected to controlled cooling, grinding, and flotation. The entire output of nickel at Copper Cliff is now handled by this new process. The nickel oxide sinter produced contains about 75% nickel, and is shipped to the company's refineries at Port Colborne, Ontario, and Clydach, Wales, as well as to market and to the U. S. subsidiary's plant at Huntington, West Virginia.

As another trail-blazing innovation, Inco has adopted in the past two years the flash smelting with oxygen of its copper sulfide concentrates, replacing costly powdered coal, and permitting greater utilization of sulfur in the smelter gas, e.g., as liquid sulfur dioxide. It has recently also announced a $16 million program to supplement its present 250 million lb a year nickel production by the new treatment of low-grade nickel-bearing pyrrhotite ores previously considered uneconomic. This process will produce as a by-product high-grade iron ore containing some 65% iron, and may permit further recovery of sulfur. And finally, as another part of an expansion and conversion program undertaken since the war which has already cost over $150 millions, Inco has been revamping underground mining operations to permit it to hoist 13,000,000 tons of ore per year (67% more than in 1951), the largest nonferrous underground operation in the world.

Electrolytic nickel is produced at the Port Colborne refinery of the International Nickel Company of Canada by the electrolysis of a sulfate-chloride electrolyte, with direct current supplied by rotary converters. Raw material is nickel oxide produced at Copper Cliff. Production is in the order of 75,000 tons per year.

Here there are also two small electric furnace operations. In a submerged-arc type of furnace, backed by a 1000-kva transformer, slag recovered from the nickel anode melting furnaces is treated to reclaim metal, which is recycled to the anode furnaces. In a smaller furnace, energized by a 500-kva transformer, electrolytic cell residues are melted and reduced to place the material in a form suitable for subsequent extraction of the precious metals. A large number of valuable metals are recovered in impure form as by-products of the nickel refining operation, e.g., gold, silver, platinum, and cobalt. These crude metal compounds are shipped back to Copper Cliff for further processing; cobalt oxide goes to the refinery at Clydach, Wales.

Power is supplied to the Port Colborne refinery from the Niagara River developments of the Ontario Hydro-Electric Power Commission, as 25 cycle power.

Electrolytic copper is produced at Inco's Copper Cliff refinery, which has a capacity of 168,000 tons of refined copper per year. The plant contains some 1350 deposition tanks, and d-c power is supplied by six motor generator sets of 6000 amp, 80–160 volt rating. The raw material is blister copper produced at the Copper Cliff smelter by oxygen flash smelting of copper sulfide concentrates.

Insoluble portions of the crude copper anodes collect in the bottom of the electrolytic cells as a sludge, which contains gold, silver, and platinum metals, selenium and tellurium, and minor amounts of other metals. Treatment of this sludge, together with the residues from the electrolytic nickel cells at Port Colborne, is carried on at Copper Cliff to produce refined gold, silver, selenium, and tellurium. Preliminary refining of the platinum group metals is done at Copper Cliff, but the concentrates are shipped to the company's precious metal refinery at Acton (near London) England, which produces pure platinum, palladium, rhodium, iridium, and ruthenium from these concentrates.

Certain electrothermic operations are also of interest at Copper Cliff. Copper sulfide concentrates obtained by the matte flotation separation process (from high-nickel matte) are melted in an electric arc furnace. Power is supplied to this furnace by a 6000-kva transformer at 80–100 volts and up to 30,000 amp per phase. In melting down refined copper cathodes, two 3-phase direct-arc type furnaces are used, each 15 ft in diameter with a holding capacity of 30 tons. These furnaces are supplied by a 4000-kva transformer at 46–120 volts, and run at about 21,000 amp per phase. This operation was pioneered by Inco.

Power for Inco's Copper Cliff operations comes from the Ontario Hydro's Abitibi Canyon development and from generating stations of the Huronian Company, a subsidiary, on the Spanish and Vermillion Rivers.

Gold and silver are recovered by electrolytic means from the International Nickel Company's cell residues. At Copper Cliff, gold is electrolyzed in Wohlwill cells and silver in Balbach-Thum cells.

Selenium and tellurium are produced at Copper Cliff from recovered residues of the copper cells. Production of selenium in 1952 was about 88,600 lb, of tellurium about 5,700 lb. Capacity of the plant is believed to be much higher for both metals.

Cobalt

Ontario has for many years been Canada's leading producer of cobalt, formerly from ores worked mainly for their silver content. Since 1950, with demand for the metal pyramiding due to its use in high-temperature alloys, permanent magnets, stellite alloys, etc., ores of lower silver content are being exploited. These come mainly from the Cobalt and Gowganda areas of Northern Ontario, and are being treated at Canada's one operating cobalt smelter, the Deloro Smelting and Refining Company Limited at Deloro, Ontario, near Belleville.

As a sign of the recent activity in cobalt, a second smelter is being erected in Ontario by Cobalt Chemicals Limited, and in Alberta the Sherritt Gordon Mines Limited is completing a refinery at Fort Saskatchewan which will produce cobalt as well as nickel and copper.

The total cobalt produced in Canada (mainly in Ontario) in the form of metal, oxides and other salts, and exported ores, has grown as follows:

1950— 583,806 lb
1951— 951,607 lb
1952—1,421,923 lb

The Deloro Smelting and Refining Company, Limited at Deloro, Ontario, makes use of electric furnaces in some of its smelting, melting, and refining operations. In a Pittsburgh Lectromelt 150-kva, 3-phase smelting furnace with 4-in. diameter electrodes some 3–5 tons of cobalt-silver ore is smelted per day to yield a bullion containing about 75–87% of the silver, a speiss with about 98–99.5% of the cobalt and 25–13% of the silver, and a slag. The ore, which may run 2000–5000 oz Ag per ton, 5–7% Co, 25–30% As, 5–10% Fe, 25–30% gangue, is fluxed with iron ore, silica, or lime, and coke for reduction. The power consumption averages 800 kwh per ton of charge, and the electrode consumption 3–4 lb per ton.

The melting and refining of cobalt metal or of cobalt-chrome-tungsten alloys is carried out in two Moore Rapid Lectromelt furnaces, single-phase, 100 kva, with 2½ in.-diameter graphite electrodes. The rated capacity is 125 lb/hr.

High cobalt-base alloys are melted and deoxidized in three 75-kw Detroit indirect-arc rocking-type furnaces lined with magnesite refractory. The melt, made without slags, comprises prime pig metal, revert and prime metals to balance out the charge.

Magnesium and Calcium

One of Canada's two producers of magnesium, and its only producer of metallic calcium, is located in Ontario, Dominion Magnesium Limited, at Haley (near Renfrew). This plant came into operation in 1942 to produce high purity magnesium by the Pidgeon process. Named after its Canadian inventor, this process involves the reduction of calcined magnesite or dolomite by the use of ferrosilicon. At Haley, a briquetted charge of calcined dolomite and finely ground ferrosilicon is heated in highly evacuated, cylindrical retorts of heat-resisting steel to about 1150°C in electrically heated furnaces. The reduced volatilized magnesium condenses in the cool head of the retort as large crystals. The metal is of exceptionally high purity, particularly as regards iron. Rated capacity when operated entirely on magnesium is about 12,000,000 lb per year.

Since 1947 this plant also produces high purity calcium metal by a similar process in the same equipment. It is reported that aluminum is used to reduce calcium oxide in this case. Currently, part of the retorts are operating on calcium production, part on magnesium.

This plant is also equipped to produce extrusions in magnesium or aluminum metals, using for this purpose a 2400 ton Loewry press, which has a yearly capacity of 1800 tons of magnesium extrusions.

Dominion Magnesium Limited has also experimented with production of titanium metal on a pilot-plant scale.

Caustic Soda and Chlorine

Ontario produces the major share of Canada's chlorine and caustic soda, seven of the ten present producers being located in this province. The earliest commercial production of chlorine in Canada took place at Kincardine, Ontario, where the Ontario Peoples' Salt & Soda Company operated a diaphragm cell in the 1890's and at Sault-Ste-Marie, Ontario, where some 120 Rhodin mercury cells were operated in 1901 by the Canadian Electro-Chemical Company Ltd. These enterprises did not continue long in operation, however, and the oldest existing chlorine plant in Canada is the one now operated at Windsor by Canadian Industries Limited.

Canadian Industries Limited plant at Windsor, Ontario, (at that time the Canadian Salt Company), installed the vertical diaphragm type of cell known as the Gibbs cell in 1910, and this type of cell is still used at Windsor. The plant has been expanded over tenfold since then and today covers a site of some 50 acres on top of the salt beds some 1600 ft below, from which the salt is pumped as a brine. The Windsor Works employs 314, and its chief products are liquid chlorine, caustic soda, ammonia, and ferric chloride. The chlorine is sold chiefly to pulp and paper companies; half of the caustic is sold as a liquid to soap companies, etc., while the remainder is sold as solid or flake caustic. Ammonia made from cell hydrogen goes to C.I.L.'s fertilizer plants, chiefly, while residual chlorine is used to produce ferric chloride, sold for water and sewage treatment. Power for this plant comes from the Ontario Hydro. Cell current is 1000 amp, and a cell line is operated at 250 volts.

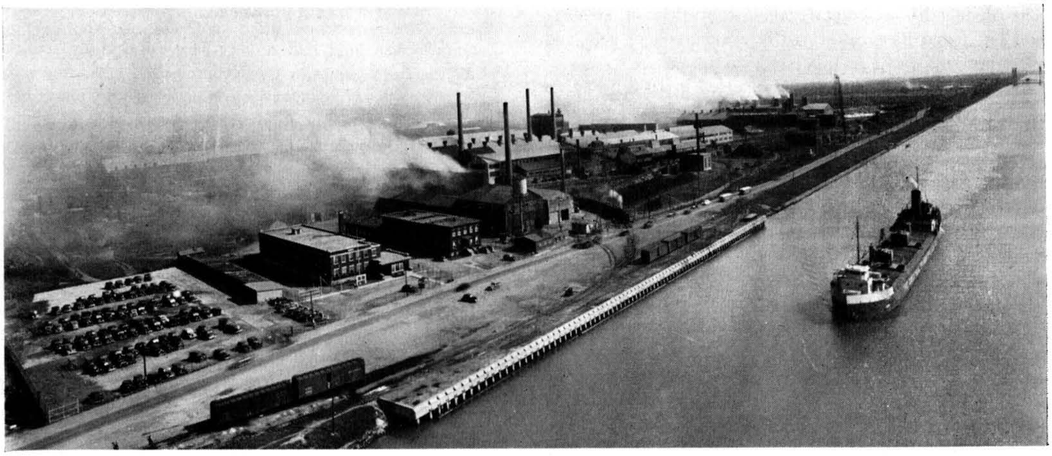
A second C.I.L. plant at Cornwall, Ontario, was started in 1935. This plant employs the mercury cell, and has about 135 employees. Chlorine and caustic are sold mainly to pulp and paper mills, and hydrogen to a neighboring chemical plant.

Chlorine plants are operated also by the following pulp and paper mills in Ontario, for their own use: Howard Smith Paper Mills Limited, Cornwall; The K V P Company Limited, Espanola; Canadian International Paper Company, Temiskaming; and Marathon Paper Mills of Canada Ltd., Marathon. These plants are of a conventional design, except for the one at Marathon. The Marathon unit, brought into operation in 1952, employs De Nora mercury cells with the Achille modification for the simultaneous production of sodium sulfide. The sodium amalgam in this operation is in part decomposed to caustic, and partly reacted with a polysulfide solution to form sodium sulfide, the latter being used for pulp cooking. Chlorine and caustic soda are used for bleach purposes, while part of the hydrogen is combined with a little chlorine to make hydrochloric acid, used for *p*H adjustments of the brine. The installation consists of 30 De Nora mercury cells, fed by 3 mechanical rectifiers of 10,000 amp each. A.C. power is supplied to the rectifiers from the mill's turbogenerators through step-down transformers.

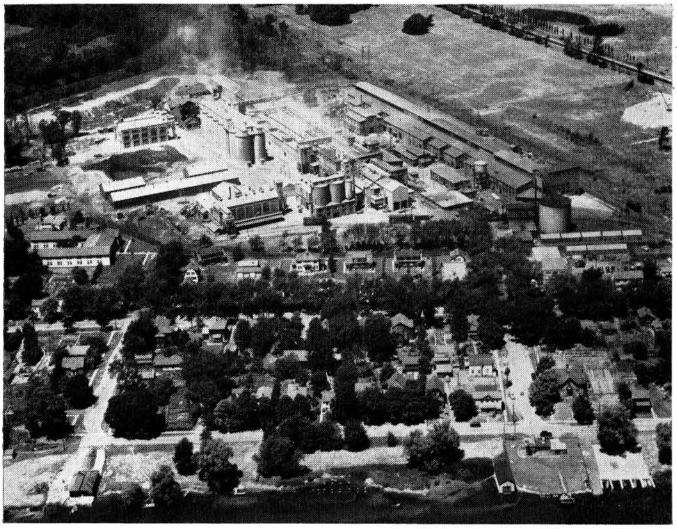
Dow Chemical of Canada Limited, at Sarnia, Ontario, also operates a mercury cell chlorine plant. Most of the output is used in the company's other operations, viz., production of ethylene glycol, hydrochloric acid, chlorinated solvents, ammonia, styrene, etc. This company came into being in 1942 as part of a team organized to produce synthetic rubber at Sarnia during World War II; the chlorine plant is a postwar addition, enlarged in 1952.

Calcium Cyanamide, Cyanide, and Related Products

The plant of North American Cyanamid Limited at Niagara Falls, Ontario, is the only cyanamid plant in the western hemisphere and the largest of its kind in the world. A wholly owned subsidiary of the American Cyanamid Company, it started producing calcium cyanamide in 1909 at a rate of about 5000 tons a year. Today it has a capacity of about 270,000 tons of cyanamid per year, and produces



Ferroalloys plant of the Electro Metallurgical Company of Canada, Limited, located on Welland Canal at Welland, Ontario.



Norton Company's artificial abrasives plant at Chippawa, Ontario

many other products as well. These include dicyandiamide, melamine and melamine resins, urea and urea resins, and calcium cyanide. During the war, nitroguanidine was also made from dicyandiamide. Much of the cyanamide and cyanide is exported to the United States.

The intermediate in the manufacture of cyanamid is calcium carbide, and NACL operates five carbide furnaces to produce it, three of 20,000 kw or better and two of 10,000 kw. They are charged with lime (burned in rotary kilns) and coke, and are tapped continuously onto a special cooling conveyor. Cooled carbide is crushed and milled and charged to one of a multitude of batch ovens where it is reacted with nitrogen under controlled conditions to form crude cyanamid. To start the furnace a zone of local high temperature is created within the charge by means of a carbon electrode; about three hours is sufficient heating to start the reaction. Since this is an exothermic reaction, no additional heat is required for its completion. The whole nitrification cycle, including cooling, requires about seven days for a four-ton charge of carbide.

Crude calcium cyanide (Black cyanide) is made from cyanamid and salt by fusion in a three-phase electric furnace. The product has a sodium cyanide equivalent of 48–50%, and has found its greatest use in cyanidation of gold and silver ores.

Sodium silicate production was started in 1933, using an electric resistor furnace to fuse soda ash and sand together in a continuously operated unit.

A $4 million expansion program was completed at the Niagara Falls plant in 1952, involving an additional carbide furnace (the fifth) and other new production facilities. This latest furnace is equipped with hydraulically controlled Soederberg electrodes of a rectangular shape and has one three-phase transformer.

Power is supplied to North American Cyanamid Limited from the Niagara River developments of the Ontario Hydro.

Ferroalloys

There are two producers of ferroalloys in Ontario, both operating to a large extent on imported ores. Four producers of artificial abrasives (listed later) recover a small quantity of ferrosilicon as a by-product of their operations.

The Electro Metallurgical Company of Canada, Limited, plant at Welland, Ontario, was established in 1907, the first ferroalloys plant in Canada. Production facilities are available for ferromanganese, ferrosilicon, silico manganese, ferrochrome—both high and low carbon grades, and special briquetted ferroalloys for the iron foundry industry. Capacity is well in excess of domestic requirements and an extensive export business is enjoyed.

Located in close proximity to Niagara Falls, and possessing dock facilities on the Welland Ship Canal, this plant is well situated to receive large blocks of power (from the Ontario Hydro) and to move large tonnages of raw materials and products.

The Chromium Mining and Smelting Corporation at Sault-Ste-Marie, Ontario, began operations in 1935, having taken over the idle plant of Superior Alloys Limited which started up in 1929 to make ferroalloys. Products are ferrosilicon and ferrochrome and the exothermic alloys Chrom-X, Sil-X, and Chrom-Sil-X. This company has done considerable development work on the use of domestic low-grade chrome ores and on the production of exothermic ferroalloys.

Artificial Abrasives and Refractories

Ontario has long had a very large output of artificial abrasives from plants in the Niagara Falls area, where the great quantities of low-cost electric power required have been available. These plants supply a major share of U. S. requirements for crude abrasives, and export to other countries as well.

The Canadian Carborundum Company Limited has produced fused alumina (Aloxite) at Niagara Falls, Ontario, since 1916.

Norton Company, at Chippawa, Ontario, has operated since 1910 and now produces such materials as fused alumina (Alundum), silicon carbide (Crystolon), fused magnesia (Magnorite), and boron carbide (Norbide) as well as zirconia. The Chippawa plant has nearly 800 employees.

Exolon Company established its plant at Thorold, Ontario, in 1914 to produce silicon carbide and fused alumina.

Lionite Abrasives Limited, at Stamford, Ontario, started in 1950 to produce silicon carbide and fused alumina.

[A more detailed discussion of these operations may be found in the JOURNAL Vol. 100, No: 3 (March 1953) pp. 61C–64C, in an article by G. R. Finlay and J. A. Upper entitled "Developments in the Abrasives Industry in the Niagara Area, 1945–1953."]

Artificial graphite products.—National Carbon Limited, at Welland, Ontario, manufactures carbon and graphite refractories, electrodes, and electrolytic anodes. A recently completed expansion was purposely designed to afford production capacity considerably in excess of the domestic and export demands experienced to date, in that a major future growth is anticipated in the use of these products, with Canada's vast potential in hydroelectric power. National Carbon Limited is the only producer of artificial graphite in Canada at the present time.

Mineral Wool

An electric furnace process for producing mineral wool has been operated by Spun Rock Wools Limited, at Thorold, Ontario, since 1934, the only operation of its kind in Canada. The raw material, quarried locally, is Rochester dolomitic shale; this is melted in electric furnaces at about 2800°F and poured onto a rotating disk in a thin stream. The centrifugal action of the disk revolving at high speed, combined with the special characteristics of the melt, produces a very long-fibered wool (Spun Rock Wool). By blowing the molten stream with an air-jet a short-fibered material can also be produced. This rock wool is used in thermal insulation applications.

For the melting operation, three 200-kw, 3-phase electric furnaces are used, operated at about 130 volts and 1000 amp per phase. These furnaces are about 5½ ft in diameter and are quite similar in design to the conventional 1-ton steel furnace, except that the furnace pivots on the pouring spout. The furnaces were built by the Volta Manufacturing Company of Welland, Ontario. Operation is more or less continuous and each furnace can produce about 2 tons of rock wool in 24 hours.

Electric Furnace Steel

In keeping with Ontario's leading position in the primary iron and steel and heavy manufacturing industries of Canada, the province has the largest number of electric steel melting furnaces in the country. The total, believed to number 44, is about one-half of the total for all Canada, and the aggregate rated capacity is nearly 650,000 net tons annually, or about 65% of the Canadian total. Some 11 firms operate electric steel furnaces in Ontario.

Atlas Steels Limited, at Welland, Ontario, produces all its steel in six Heroult-type furnaces ranging in size from 5–50 tons capacity. Peak power demand for these furnaces is 35,000 kw, and annual melting capacity is rated at about 200,000 ingot tons per year. Production includes carbon, tool and alloy steels, and a full line of stainless steel sheet, strip, bar, wire, and special forged sections. In recent years, Atlas has installed hot and cold mills for stainless strip, equipment for welded stainless tubing, an automatic powder scarfing machine, and Canada's first continuous commercial casting machine for steel. Power is supplied by Ontario Hydro.

Dominion Foundries and Steel Limited, Hamilton, Ontario, operates five steel-making furnaces, in addition to four open hearths. Two are of 50–60 ton capacity, two about 10 ton, and one about 2½ ton size. Peak power load is about 43,000 kw; annual capacity is reported to be 175,000 tons in the electric furnaces. Equipment for continuous strip annealing has a peak load of 1400 kw and for electrolytic tinning about 2000 kw. The plant has a turbo generator of 1500 kva rating, and Ontario Hydro supplies the balance of power needs.

The Steel Company of Canada, Limited, at Hamilton, Ontario, operates one Heroult-type electric steel furnace with a 20,000 kva transformer, and an average capacity per heat of about 92 tons. This furnace produced about 110,000 net tons in 1952, with an average energy consumption of about 475 kwh per ton. This production is only a small fraction of Stelco's open-hearth steel output.

Ford Motor Company of Canada Limited, at Windsor, Ontario, has 18 electric steel furnaces ranging in size from ¼ to 5 tons, with an annual capacity of about 100,000 net tons.

Of the smaller producers of electric steel in Ontario, Burlington Steel Co. Limited, Hamilton, has one 7 ton furnace; Canada Electric Castings Limited, Orillia, has two 2 ton furnaces; Fahralloy Canada Limited, Orillia, has 3 furnaces ranging from ½ to 2 tons; William Kennedy And Sons Limited, Owen Sound, have 2 electric furnaces, 4 ton and 1-¼ ton; Welland Electric Steel Foundry, Limited, Welland, has 3 furnaces, ranging from ¼ to 1-½ ton size.

Data on the last six firms above were taken from the Dominion Bureau of Statistics publication, "The Primary Iron and Steel Industry 1951," which was issued in June 1953. Some changes may have occurred since then, e.g., two additions may be noted: Sheepbridge Engineering (Canada) Limited has set up an alloy steel plant at Guelph, Ontario, and employs high-frequency induction melting furnaces, with a labor force of 40. Hayward-Tyler of Canada, Limited (formerly of Luton, England) has opened a new stainless steel foundry at Kitchener, Ontario, employing 25.

The above list of direct electroproducts manufactured in the Province of Ontario is believed to be reasonably complete. No attempt has been made to include derivatives of these electroproducts, which are quite numerous, nor to cover applications of electrical energy for straight heating purposes, as in electric steam boilers, or for mechanical operations such as crushing and grinding. Ontario's many mines and paper mills consume a very large amount of power for these purposes.

The Prairie Provinces

Moving westward from Ontario, we cross in succession the three "Prairie Provinces" of Manitoba, Saskatchewan, and Alberta. Together their great plains account for some 95% of the total acreage in wheat, barley, and flax, and about 71% of the occupied farm land of all Canada. These statistics, indicating an essentially agricultural economy, might appear to proffer little of interest in this region for the electrochemist; such is not the case, however. One of Canada's two electrolytic zinc refineries is located here, five electric steel furnaces are in operation, and a chlorine-caustic soda plant is now being built. Hydroelectric resources are ample, and exploitation of tremendous reserves of petroleum, natural gas, lignite, and coal has barely begun. Manufacturing production has increased fourfold in value over the past ten years. It may be surprising to learn that from one-third to one-half of the area of these provinces is covered by forest, and that the often mineral-rich rocks of the Precambrian Canadian Shield, which are so prominent a feature in Northern Ontario and Quebec, also carry through into the northern parts of the Prairie Provinces, underlying almost 60% of the area of Manitoba, 45% of Saskatchewan, and about 5% of Alberta. Mineral exploration is proceeding at a brisk pace and there seems to be a good chance that mineral exploitation and power production will create further electrochemical and electrometallurgical enterprises in these provinces in the future.

Province of Manitoba

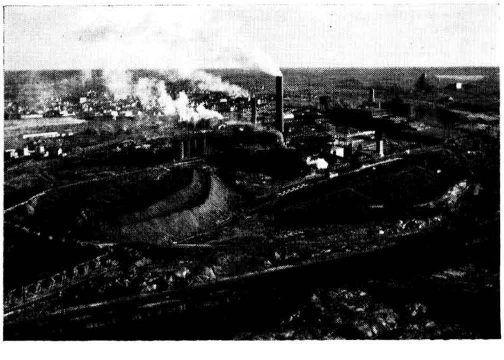
Manitoba has an area of 246,512 square miles and a population of 809,000. Over 95% of its people inhabit the southern, prairie-land half of the province, with Winnipeg, Canada's fourth-largest city, accounting for some 354,000 alone. Manitoba is Canada's fourth-largest manufacturing province and accounts for some 50% of the manufactures of the Prairie Provinces. In 1952, manufacturing output at $630 millions was about double that of primary agriculture; far behind was mineral production at $25 millions, forest products (lumber, pulp, and paper) at $19 millions, and fresh-water fisheries at $7.5 millions.

Minerals

In the way of minerals (2.4% of the Canadian total output), copper and zinc predominate, with gold next and silver, cadmium, selenium, and tellurium, as by-products of copper and zinc smelting, ranking among the metals. This output is largely due to the operation, by the Hudson Bay Mining and Smelting Company Ltd., of the Flin Flon mine, which straddles the Saskatchewan-Manitoba border. Sherritt Gordon Mines Ltd., until September 1951 a large base-metals ore producer at Sherridon, Manitoba, is just now resuming operation at a newly-developed 14 million ton copper-nickel-cobalt ore body some 145 miles to the north at Lynn Lake, Manitoba. The Lynn Lake ore will be shipped to Alberta for treatment, while the Flin Flon ore is smelted in Manitoba. There is also active gold mining carried on, while indications have been found of ores of chromium, lithium, beryllium, and molybdenum, without, however, any exploitation of these taking place as yet. Of interest also is the output of salt, gypsum, lime, cement, clay products, and a little petroleum.

Electric Power

Of Manitoba's power supply of about 870,000 hp, all but 56,000 hp is hydroelectric. That hydro total includes the 108,500-hp capacity of a site which lies just over the provincial border in Saskatchewan and which, owned by a subsidiary of Hudson Bay Mining and Smelting Company, supplies the Flin Flon mining and metallurgical area. About 9000 hp of the capacity within Manitoba itself is owned by mining companies; all the rest is owned by the provincial or municipal governments. Public ownership of the public supply of power became complete last year when the provincial government bought out the plants of the Winnipeg Electric Company, which previously divided with the City of Winnipeg the generation and distribution of power in that metropolis.



The Hudson Bay Mining and Smelting Company Limited plant at Flin Flon, Manitoba, Canada's northernmost electroproducts plant, comprising a copper smelter and electrolytic zinc refinery.

Thus the provincial government, through its power commission, now owns and operates the three largest plants on the Winnipeg River: Seven Sisters, of 225,500 hp; Great Falls, of 168,000; and Pine Falls, of 114,000. In addition, it is now building, for operation in 1955, the 80,000-hp McArthur Falls plant at the last undeveloped site on that river. Also on the same river are the two plants owned by the City of Winnipeg: Pointe du Bois, of 105,000 hp, and Slave Falls, of 96,000. Because remaining water power lies almost entirely in the northern part of the province, authorities are now studying the cost of its development and transmission compared to the thermal production of power in the populated southern sections.

The abundant, although undeveloped, hydroelectric resources of Manitoba's northland, particularly along the Nelson and Churchill Rivers, and the probability of important ore deposits being located in the Precambrian rocks of this northern area, offer the possibility that in future years a large electrometallurgical enterprise might spring up here. Added to this are the existing facilities for deep-water shipping from the Hudson Bay port of Churchill, Manitoba. The sea route through Hudson Strait to Liverpool, England, from Churchill is only 175 miles longer than the shortest route from Montreal to Liverpool; it is navigable for 98 days of the year. From Churchill also a 510-mile railway line leads to the south and west to The Pas, Manitoba, whence good transportation facilities exist tying in with transcontinental rail lines.

The following electrometallurgical establishments are now to be found in Manitoba.

Electrolytic Zinc

The Hudson Bay Mining and Smelting Company Ltd. operates a mine, smelter, and zinc refinery at Flin Flon, Manitoba. This is located on the Manitoba-Saskatchewan border just south of the 55th parallel, and is Canada's most northerly electroproducts industry. The plant went into operation in 1930. Ore is treated by differential flotation to produce a zinc concentrate and a copper concentrate; the flotation tailings contain some gold and silver which are recovered by cyanidation. The copper concentrates are roasted, smelted to a matte, and blown to blister copper in a converter; this copper is shipped to the electrolytic refinery at Montreal East, Quebec (Canadian Copper Refiners Ltd.), where pure copper is produced and the selenium, tellurium, and gold and silver content is recovered.

The zinc concentrates are roasted and leached, and pure zinc is recovered from the purified leach solution at Flin Flon by electrolysis. Cadmium is a by-product. The zinc cell room has 1180 cells arranged in seven series circuits comprising 160 operating cells each, with 60 standby cells. Each circuit has a nominal rating of 6,000 d-c amp at 600 volts. Each cell has 17 aluminum sheet cathodes and 18 lead-silver anodes. Direct current is supplied by seven motor-generator sets and two mercury-arc rectifiers. Each M.G. set has one 5,000-hp motor driving two motor-generators, each rated at 3,000 amp at 575 volts. The rectifiers are rated at 8,000 amp d-c at 600 volts.

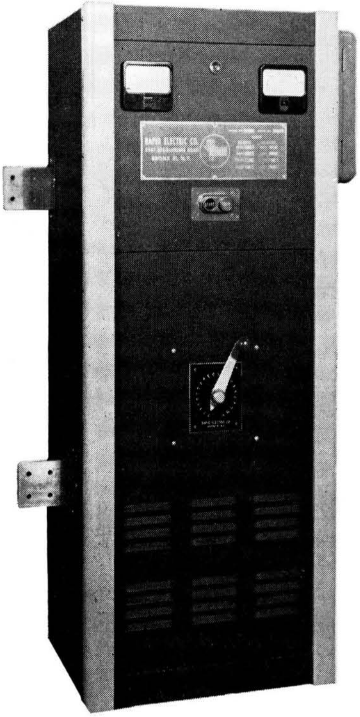
Output from Flin Flon is about 40,000 tons per year of blister copper and 65,000 tons of electrolytic zinc, as well as 60 tons annually of high-purity cadmium, 50–60 tons selenium, and over a ton of tellurium as by-products. In 1952 a slag fuming plant was installed to permit recovery of zinc from residues.

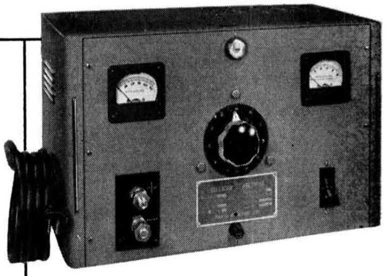
Electric power for the plant is obtained from the Island Falls hydroelectric plant in Saskatchewan. This development, located on the Churchill River about 60 miles northwest of Flin Flon, is operated by the Churchill River Power Company, a wholly owned subsidiary of the H.B.M. & S. Co. Ltd., and has an installed capacity of nearly 110,000 hp. It was this power that made possible the economic exploitation of the Flin Flon ore body and the production of electrolytic zinc at this site.

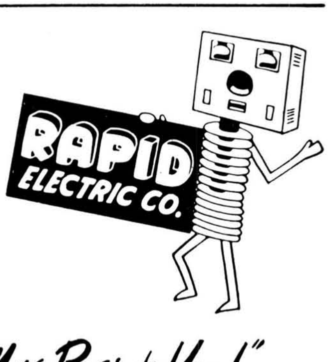
Electric Furnace Steel

Steel for ingots or castings is melted in electric furnaces by the following firms in Manitoba: Manitoba Rolling Mill Co. Ltd., at Selkirk, operates a 6-ton electric furnace as well as open hearths; Manitoba Steel Foundries, Ltd., at Selkirk, operates one 5-ton electric furnace; Vulcan Iron Works Ltd., at Winnipeg, has a 3-ton electric furnace in service.

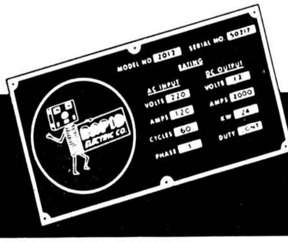
Note: The final part of this series will appear in the March issue of the JOURNAL.







RAPID
ELECTRIC CO.



MODEL NO 2012
SERIAL NO. 50217
RATING
AC INPUT
VOLTS 220
AMPS 120
CYCLES 60
PHASE 3
DC OUTPUT
VOLTS 12
AMPS 2000
KW 24
DUTY CNT
RAPID ELECTRIC CO.

Anodic Behavior of Aluminum and Its Alloys in Sulfuric Acid Electrolytes[1]

RALPH B. MASON AND PHYLLIS E. FOWLE

Aluminum Research Laboratories, New Kensington, Pennsylvania

ABSTRACT

This paper deals with the main factors affecting the rate of solution of anodic oxide coatings on aluminum as they are being formed in sulfuric acid electrolytes. Conditions favoring high coating ratios or thick, hard abrasion-resistant coatings have been investigated. Low temperatures, high current densities, which permit a shorter time of immersion in the electrolyte, and the addition of substances such as oxalic acid to the electrolyte, favor the formation of such coatings. This has been mainly an investigation of the competition between the rate of formation and the rate of solution of the coatings.

INTRODUCTION

The physical characteristics of the thick commercial anodic coatings on aluminum are markedly affected by the rate at which the coatings dissolve during formation. Some of the factors affecting the efficiency of anodic coating formation in sulfuric acid electrolytes have been discussed in several papers (1–3). The present paper extends previous work (3) to include conditions favoring higher coating efficiencies which result in improved physical properties.

It has been shown (4) that a high purity aluminum (99.95%) anode in a coulometer reacts electrochemically in a sulfuric acid electrolyte with an efficiency of 100% even though the operating conditions are varied over a wide range. On the other hand, the anodic oxide coating is slowly attacked by the sulfuric acid electrolyte and the efficiency of coating formation decreases as those factors which favor chemical solution of the coating predominate. There is always competition between the rate of formation and the rate of solution of the coating and, if the coating is not formed rapidly enough, little or no oxide coating remains on the surface under unfavorable conditions.

As a measure of the efficiency of oxide coating formation, some investigators (1, 2, 5) used the ratio of the weight of coating to the theoretical weight of aluminum oxide that should be formed from the weight of aluminum reacting. In the case of oxide coatings formed in sulfuric acid electrolytes, however, the coating ratio or the weight of coating divided by the weight of aluminum reacting appears to be a more practical figure to use for the evaluation of the efficiency of coating formation (6), since coatings formed in sulfuric acid electrolytes are known to contain an appreciable percentage of sulfate (7–9). Oxide coatings formed on 99.95% aluminum in a 15% (by weight) sulfuric acid electrolyte under certain standard conditions of operation contain about 12–14% SO_3 (calculated from the sulfate determination), some water, and the remainder alumina. In addition, oxide coatings formed on aluminum alloys may contain other substances derived from the alloying elements.

It has been demonstrated, within certain limits, that the coating ratio (weight of coating divided by the weight of aluminum reacting) is increased by decreasing the concentration of the electrolyte or the temperature, or by increasing the current density (3). These factors have an appreciable effect on the amount of coating dissolved by the electrolyte during formation. Lowering the temperature of the electrolyte is especially effective in reducing the solution of the anodic oxide coating during formation (3, 10, 11). Thus, by changing the conditions of treatment so as to decrease the rate of solution of the oxide coating, the coating ratio is increased. If all the aluminum reacting were converted to aluminum oxide and none of the oxide were dissolved by the electrolyte, the coating ratio would be 1.89 (6). When the coating contains 14% SO_3, the theoretical coating ratio would be about 2.2. Because of the solvent action of the sulfuric acid electrolyte on the coating, however, a coating ratio of 2.2 has not been observed as yet. In these experiments, it is shown that, by selecting suitable conditions for forming the coating, it is possible to approach, but not actually reach, a coating ratio of 2.2.

While it is possible to reduce the rate of attack of the oxide coating during treatment by lowering the concentration of the electrolyte, it is not always

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practical to do so, especially at lower operating temperatures. In the present experiments, the electrolytes which were used contained from 12% to 25% (by weight) sulfuric acid; the one used in the majority of cases contained 15% (by weight) of sulfuric acid.

PROCEDURE

Specimens of 0.064-in. (1.63 mm) aluminum sheet were cut to size, cleaned, weighed, and anodically treated in 12–15% (by weight) sulfuric acid electrolyte for 10, 20, and 30 min, or other convenient times, at temperatures of 34°, 50°, 60°, and 70°F (1.1°, 10.0°, 15.6°, and 21.1°C). After washing and drying, the specimens were weighed. The coatings were then stripped in a phosphoric-chromic acid solution, according to a suggestion of Mason (12), and they were washed, dried, and weighed again. From these measurements, the weight of aluminum reacting and the weight of the coating was calculated.

The specimen dimensions were so chosen that, with 1 amp of current flowing, the desired current density could be obtained. For example, the area of the surface for the specimen used at 12 amp/ft^2 (1.3 amp/dm^2) was 12 in.^{2} (77.4 cm^2), for the specimen used at 48 amp/ft^2 (5.2 amp/dm^2) the area was 3 in.^{2} (19.4 cm^2). In all cases, the area of the cut edges of the specimens was included in the total area.

The specimens were suspended in the electrolyte by means of a tantalum clip between two pure lead cathodes. Suitable agitation of the electrolyte was obtained by means of an electrically driven glass stirrer. When a high current density is used, a higher voltage is necessary, and this results in considerable heat which must be removed rapidly in order to minimize attack of the coating or burning. The electrolyte for the experiments at all but the lowest temperature was held in a rectangular Lucite tank 4 in. x 8 in. x 8 in. (10.2, 20.3, and 20.3 cm), and was cooled by passing ice water through a lead coil immersed in one end of the tank. A sensitive mercury thermoregulator in conjunction with a delayed-action vacuum tube relay was used to control the centrifugal type pump which circulated the ice water. It was possible to hold the temperature of the electrolyte constant to about 0.1°F (0.06°C).

For the experiments at 34°F (1.1°C), a rectangular lead tank holding about 9 liters of electrolyte was placed within a larger iron tank and surrounded with cracked ice. An electrically driven glass stirrer was used for agitation. Since the maximum current used was only 1 amp and the volume of the electrolyte was relatively large, it was possible to hold the temperature of the electrolyte constant.

EXPERIMENTAL WORK

All results obtained in the experiments on coating ratios are shown in graphical form. Coating ratios have been plotted against the weight of metal removed by electrochemical action or the approximate time of treatment.

High purity aluminum (99.95%) was anodically treated in a 15% sulfuric acid electrolyte at 70°F (21.1°C) using various current densities and times of treatment. The family of curves in Fig. 1 shows the effect on the coating ratio of varying the current density from 6 to 72 amp/ft^2 (0.65 to 7.8 amp/dm^2) for coating periods up to about 40 min. As the time of treatment increases, the coating ratio decreases. This indicates that for a given current density there is more chemical solution of the coating as the thickness or time of treatment increases. This solution takes place on the outer surface and on the pore walls. All the curves at 70°F (21.1°C) have about the same slope. As the current density is increased beyond 12 amp/ft^2 (1.3 amp/dm^2), it is more difficult to obtain consistent coating ratio values, and it is usually necessary to make several check determinations.

Effect of Lowering Temperature

When the temperature of the sulfuric acid electrolyte is reduced to 50°F (10°C), the rate of solution of the coating is decreased (see Fig. 2). The slope of the curves for 6, 12, and 24 amp/ft^2 (0.65, 1.3, and 2.6 amp/dm^2) is less steep than at 70°F (21.1°C), indicating less over-all solution of the coating. The curves for 36 and 48 amp/ft^2 (3.9 and 5.2 amp/dm^2) are approximately parallel to the X axis and show that, under these conditions, there is no decrease in the coating ratio with increasing times of treatment. However, at 72 amp/ft^2 (7.8 amp/dm^2) the coating ratio increases with time of treatment. This higher coating ratio may be explained by a continued decrease in the rate of solution of the coating at the bottom or base of the pores because of a build up of solution products within the pore channels. This effect becomes more pronounced as the length of the pore or the path of travel for the dissolved aluminum increases.

Coating ratio curves for 99.95% aluminum anodically treated in 15% sulfuric acid at 34°F (1.1°C) are shown in Fig. 3. At this low temperature, even the coating ratio curve for 6 amp/ft^2 (0.65 amp/dm^2) is very nearly parallel to the X axis, indicating no substantial increase in rate of solution of coating with time of treatment. The curve for 48 amp/ft^2 (5.2 amp/dm^2) starts to turn up at 30 min. At 72 amp/ft^2 (7.8 amp/dm^2) the coating ratio rises rapidly to a value of 1.90 at 43 min.

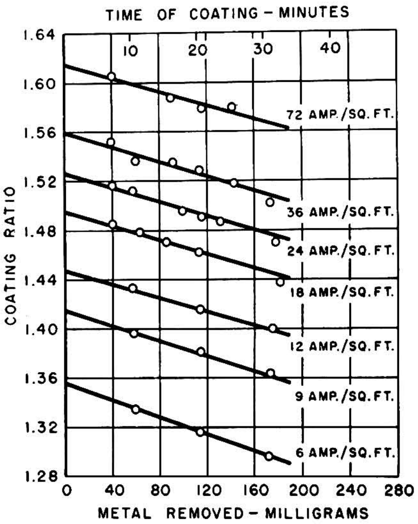

FIG. 1. Effect of current density on coating ratio for 99.95 aluminum treated anodically in 15% H_2SO_4 at 70°F (21.1°C).

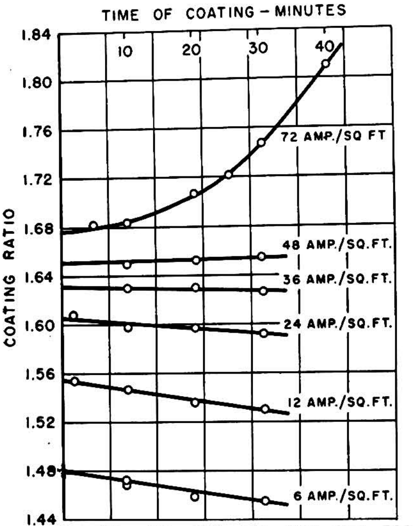

FIG. 2. Effect of current density on coating ratio for 99.95 aluminum treated anodically in 15% H_2SO_4 at 50°F (10°C).

Effect of Time and Current Density

The coating ratios obtained by extending the curves to cut the Y axis at zero time should be the maximum for a given pore size since there should be the minimum chemical attack of the coating already formed. In Fig. 4, the coating ratios at one minute (from Fig. 1–3) are plotted against current density. Judging from these curves, increasing the current density from 36 to 72 amp/ft^2 (3.9 to 7.8 amp/dm^2) at 70°F (21.1°C) would have slightly less effect on increasing the coating ratio than lowering the temperature 20°F (11°C), while increasing the current density from 12 to 24 amp/ft^2 (1.3 to 2.6 amp/dm^2)

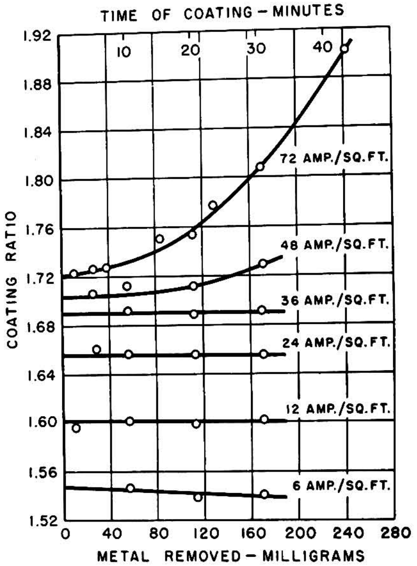

FIG. 3. Effect of current density on coating ratio for 99.95 aluminum treated anodically in 15% H_2SO_4 at 34°F (1.1°C).

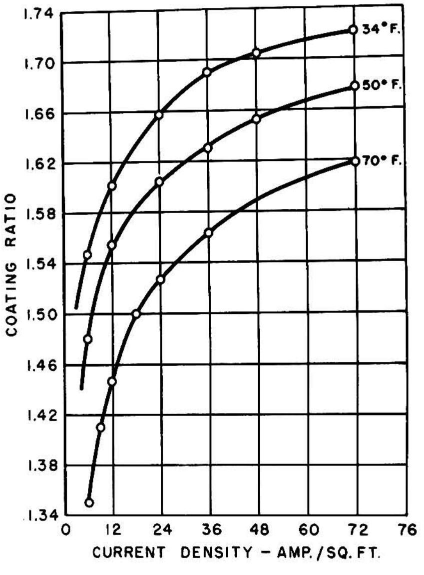

FIG. 4. Effect of current density on coating ratio at 1 min for 99.95 aluminum treated anodically in 15% H_2SO_4.

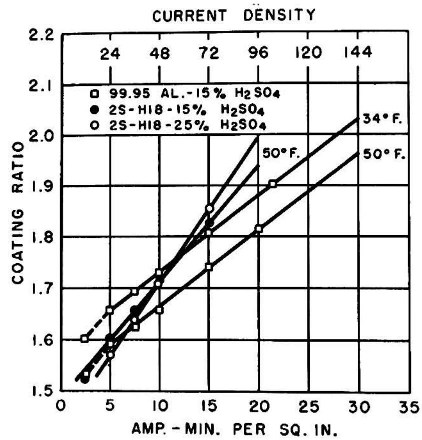

FIG. 5. Effect of current density and temperature on the coating ratio.

at 50°F (10°C) would have slightly more effect on increasing the coating ratio than decreasing the temperature about 16°F (9°C).

The family of curves of Fig. 4 indicates that, depending on high current densities and low temperatures alone, it is exceedingly difficult to obtain a coating ratio greater than about 1.80. In order to take advantage of the rapid increase in coating ratio values with time or thickness of coating when formed at low temperatures and high current densities, the coating ratios for 30 or 40 min coatings taken from Fig. 1, 2, and 3 are plotted against ampere minutes per square inch (or equivalent current densities) in Fig. 5. The total time that each specimen remained in the electrolyte was approximately the same, so the amount of oxide dissolved per square inch from the outer surface should be about the same. As the ampere minutes per square inch are increased beyond 5, the curves appear to be straight lines which, if extended far enough, would give the postulated theoretical coating ratio at some current density higher than 144 amp/ft^2 (15.6 amp/dm^2) or 30 amp min/in.^{2} (4.65 amp min/cm^2). Because of experimental difficulties, no coating ratio higher than 1.90 was obtained at this time. This is perhaps about the highest value that can be obtained experimentally, since the solution of the outer surface cannot be prevented entirely and the pores which are necessary for continued growth are equivalent in volume to the oxide coating which has been dissolved.

In Fig. 5, the curves for 99.95% aluminum at 34°F (1.1°C) and 50°F (10°C) are parallel and indicate that the oxide surface dissolved more rapidly at 50°F (10°C) than at 34°F (1.1°C). The rate of solution of the oxide coating decreased as the concentration of dissolved aluminum in the pores increased with current density.

Behavior of Aluminum Alloys

The coating ratio curves for the common aluminum alloys differ somewhat from those for high purity metal. Coating ratio curves for 2S-H18 anodically treated in 15% sulfuric acid at 50°F (10°C) are shown in Fig. 6. The curve for 24 amp/ft^2 (2.6 amp/dm^2) is parallel to the X axis. Several of the curves for the higher current densities turn upward, indicating a decrease in the rate of solution of the coating at the bottom or base of the pores. This effect takes place at a lower current density

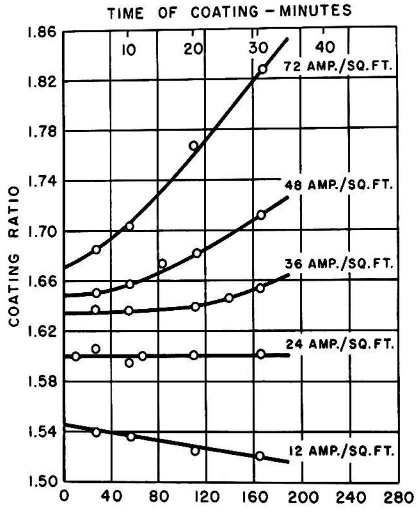

FIG. 6. Effect of current density on coating ratio for 2S-H18 alloy treated anodically in 15% H_2SO_4 at 50°F (10°C).

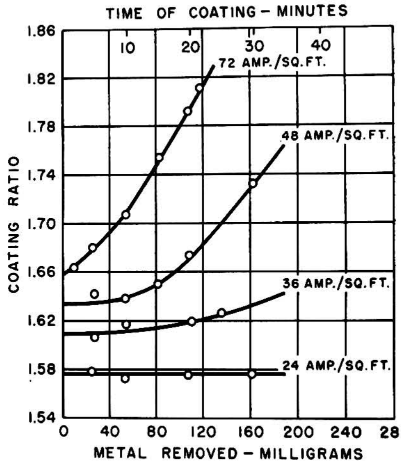

FIG. 7. Effect of current density on coating ratio for 61S-T6 alloy treated anodically in 15% H_2SO_4 at 50°F (10°C).

with 2S than with high purity metal (see Fig. 2). Increasing the acid concentration from 15 to 25% at 50°F (10°C) has only a slight effect on the coating ratio curves. Although the values are slightly lower in the 25% sulfuric acid for normal current densities, increasing the concentration of the acid by 10% has less effect than raising the temperature 10° or 20°F (5.5° or 11°C).

Referring again to Fig. 5, where the 30-min coatings on 2S have also been plotted, it will be noted that the curve for 2S is steeper than the corresponding curve for 99.95% aluminum. Either the pore walls of the coating on 2S are less soluble than the pore walls of the pure aluminum (99.95%) because of the impurities, or the pores are fewer in number because of a higher voltage across the primary or barrier layer (13). At current densities greater than 48 amp/ft² (5.2 amp/dm²), the solvent action of 25% sulfuric acid on the pore walls appears to be less than 15% sulfuric acid.

Since the rapid increase in coating ratio values with time is always accompanied by an abnormal increase in voltage, an investigation of the higher coating ratio values is mainly of theoretical interest. To produce hard abrasion-resistant coatings in the sulfuric acid electrolyte, conditions should be chosen that will give a coating ratio curve parallel to the *X* axis (or time of coating).

Although coating ratio curves for 52S-H34, 61S-T6, and 75S-T6 were determined, only the values for 61S-T6 have been plotted in Fig. 7. The curves for 52S and 61S are very similar to those for 2S (Fig. 6), but have somewhat lower coating ratio values at the lower current densities, as might be expected. In the case of 61S-T6, the curves for 48 and 72 amp/ft² (5.2 and 7.8 amp/dm²) turn up more rapidly than the corresponding 2S and 52S curves, and actually higher coating ratio values are obtained at 20 or 30 min.

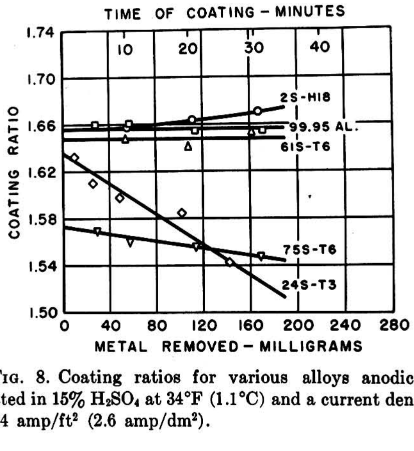

FIG. 8. Coating ratios for various alloys anodically treated in 15% H_2SO_4 at 34°F (1.1°C) and a current density of 24 amp/ft² (2.6 amp/dm²).

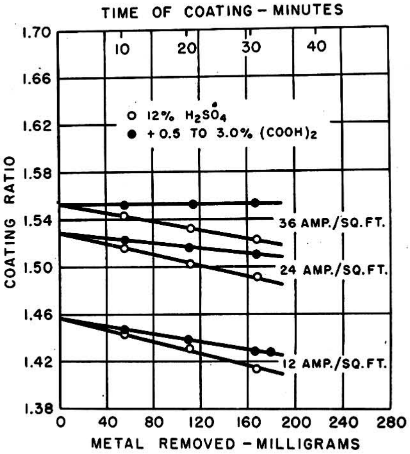

FIG. 9. Effect of addition of oxalic acid to 12% H_2SO_4 electrolyte at 70°F (21.1°C) on coating ratio of 2S-H18. Average results have been plotted for the various additions of oxalic acid.

No values have been shown for the 75S-T6 alloy at 50°F (10°C) since the coatings appear to be appreciably more soluble than those on the other two alloys. The slope of the curve for 36 amp/ft² (3.9 amp/dm²) is still noticeably steep.

In Fig. 8 are shown a few coating ratio curves for some of the alloys anodically coated in 15 % sulfuric acid at 34°F (1.1°C). A single current density of 24 amp/ft² (2.6 amp/dm²) was used for this particular test. The curves are very similar for 99.95% Al, 2S-H18, and 61S-T6. The curve for 2S shows a tendency to turn upward at 30 min, indicating a slight decrease in the rate of solution of the coating. The curve for 75S-T6 is less steep than the corresponding one at 50°F (10°C). The curve for 24S-

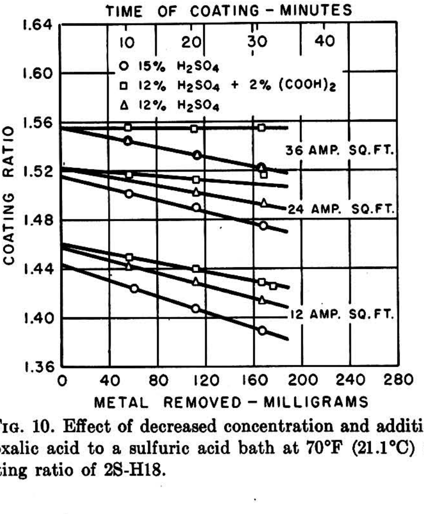

FIG. 10. Effect of decreased concentration and addition of oxalic acid to a sulfuric acid bath at 70°F (21.1°C) on coating ratio of 2S-H18.

T3 is noticeably steep, indicating substantial solution of the coating in the electrolyte as the time of treatment increases. It is very difficult to treat 24S-T3 anodically for 30 min at a current density of 24 amp/ft^2 (2.6 amp/dm^2) and obtain a uniform coating. Several 30-min samples were discarded because of burning.

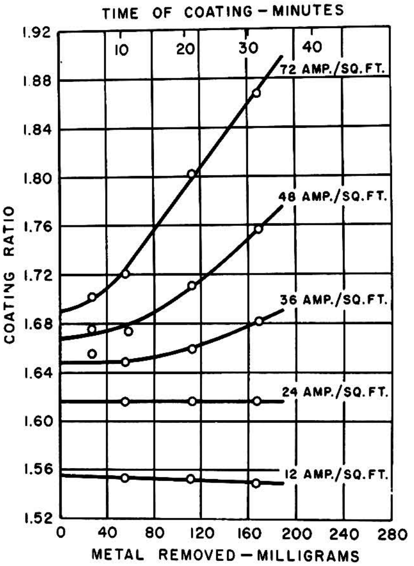

FIG. 11. Effect of current density on coating ratio for 2S-H18 alloy treated anodically in 12% H_2SO_4 + 1% $(COOH)_2$ at 50°F (10°C).

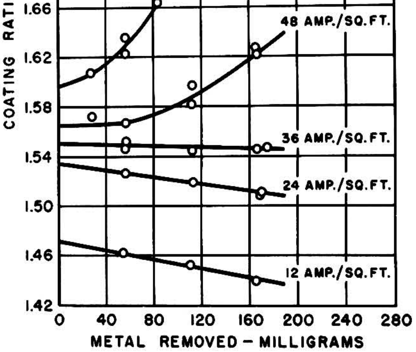

FIG. 12. Effect of current density on coating ratio 75S-T6 alloy treated anodically in 12% H_2SO_4 + 1% $(COOH)_2$ at 50°F (10°C).

Addition of Oxalic Acid

One of the most effective addition agents known for decreasing the solubility of the anodic oxide coating in sulfuric acid is oxalic acid. The coating ratio curves for 2S-H18 in 12% sulfuric at 70°F (21.1°C) plus small amounts of oxalic acid are shown in Fig. 9. It is apparent that small amounts of oxalic acid are effective in reducing the rate of solution of the coating as the time of treatment increases. The smallest addition (0.5%) appeared to be as effective as the addition of 3.0%, and average values have been plotted. Because of the decomposition of oxalic acid in use, it is more practical to use 1 or 2% as the addition agent.

Coating ratio curves for 2S-H18 in 12% sulfuric acid, 15% sulfuric acid, and 12% sulfuric acid plus 2% oxalic acid are compared in Fig. 10. The differences between 12 and 15% sulfuric acid are less pronounced as the current density is increased to 36 amp/ft^2 (3.9 amp/dm^2). The curve for 12% sulfuric acid plus 2% oxalic acid at 36 amp/ft^2 (3.9 amp/dm^2) is parallel to the X axis even though the temperature is 70°F (21.1°C).

Coating ratio curves for 2S-H18 and 75S-T6 anodically coated in 12% sulfuric acid plus 1.0% oxalic acid at 50°F (10°C) have been plotted in Fig. 11 and 12. Here the effect of the oxalic acid addition is about as pronounced as at 60° or 70°F (15.6° or 21.1°C). The presence of 1% oxalic acid in 12% sulfuric acid is especially effective in reducing the solubility of the oxide coating in the case of the 75S-T6 alloy. It is possible that the addition of oxalic acid to the sulfuric acid electrolyte decreases the solution of the pore walls, resulting in a smaller total pore volume than would be obtained normally.

For practical use, the sulfuric-oxalic acid electrolyte at 50°F (10°C) is as good as the plain 15% sulfuric acid at 34°F (1.1°C). A higher operating temperature is permitted since the oxalic acid decreases the rate of solution of the pore walls. A slightly longer time of treatment would be required to obtain the same weight of coating at the higher temperature because of the somewhat greater coating ratios obtained at 34°F (1.1°C).

SUMMARY

Coating ratios have been determined for aluminum and its common wrought alloys in sulfuric acid under various operating conditions. The rate of solution of the oxide coating from the pore walls and the outer surface is a determining factor for the value of the coating ratio. The highest coating ratio values are found where the conditions of coating are adjusted to give the minimum rate of solution of the coating.

For a coating containing 14% SO_3, the postulated theoretical coating ratio would be 2.20 and not 1.89 (Al_2O_3 only) when the efficiency is 100%. It is possible to approach, but never reach, the theoretical value because the volume of the coating represented by the pores has been dissolved as well as some of the outer surfaces.

When high current densities and low temperatures are employed to produce thick oxide coatings, it appears that the rapid formation of solution products in the pores causes a decrease in the rate of solution of the oxide coating, which in turn produces higher coating ratio values.

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

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The Mechanism of the Anodic Formation of Lead Chromate[1]

CARL WAGNER

Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts

ABSTRACT

This paper deals with the interplay of diffusion and convection processes governing the anodic formation of lead chromate during the electrolysis of a solution of sodium chromate and sodium chlorate between lead electrodes. At sufficiently high current densities, the boundary layer contains excess lead ions and flows downward in virtue of its higher density. Lead chromate is formed, in part, at a distance of 0.01 to 0.1 cm from the anode by counterdiffusion of lead ions and chromate ions and, in part, at the lower edge of the anode by mixing of boundary layer and bulk solution.

INTRODUCTION

The electrolysis of a dilute solution of sodium chromate between lead electrodes leads to the formation of a thin adherent layer of lead chromate and lead dioxide at the anode, and subsequently oxygen is evolved. On the other hand, according to a patent by Luckow (1) and a fundamental investigation by Le Blanc and Bindschedler (2), the electrolysis of a solution containing a mixture of sodium chromate and sodium chlorate yields a precipitate of lead chromate appearing at some distance from the surface of the anode and falling down to the bottom of the trough, provided that the excess of sodium chlorate is sufficient and the current density is appropriately chosen. Thus, lead chromate is formed with a current efficiency close to 100% without passivation of the anode. This process is of industrial importance, since the crystals of lead chromate produced in this way have a well-defined size, which is appropriate for use of the product as a pigment. The same principle may be employed for the production of other nearly insoluble lead salts such as lead sulfate and basic lead carbonate, as has been shown by Luckow (1), Isenburg (3), and others.

The striking difference between the electrolysis of a solution containing only sodium chromate and the electrolysis of a solution containing a mixture of sodium chromate and sodium chlorate has been explained by Le Blanc and Bindschedler (2) in the following manner. In a solution of sodium chromate there are only chromate ions as anions, and thus a noticeable concentration of lead ions can nowhere be expected in view of the extremely low solubility of lead chromate. Consequently, formation of lead chromate can take place only at the surface of the anode and, thereby, the anode is passivated after some time. In a solution containing a mixture of sodium chromate and sodium chlorate, however, a thin layer of the solution near the anode may contain lead, sodium, and chlorate ions, but practically no chromate ions. When lead ions migrating away from the anode encounter chromate ions migrating from the bulk solution toward the anode, a precipitate of lead chromate is formed. The local depletion of chromate ions in the vicinity of the anode is due to the fact that in a mixture of sodium chromate and sodium chlorate only a small portion of the electrical current is carried by chromate ions, and the larger portion of chromate ions required for the formation of lead chromate approaches the anode by diffusion rather than by electrolytic migration. The prevalence of lead ions in the solution near the anode has been ascertained with the aid of potential measurements by Just (4).

It remains open to question why the chromate ions reach the vicinity of the anode but not its surface. To find a solution of this paradox, one has to take into account not only diffusion processes, but also convection caused by local concentration and density differences according to Levich (5), Agar (6), Wagner (7), Keulegan (8), and Wilke, Tobias, and Eisenberg (9).

At the beginning of the electrolysis of a solution of sodium chromate and sodium chlorate, chromate ions are, of course, present at the surface of the anode and, therefore, initially lead chromate at the surface of the anode is formed under all conditions. The following events, however, depend on the current density applied and the concentration of chromate.

STRUCTURE OF THE BOUNDARY LAYER IF AN ADHERENT LAYER OF LEAD CHROMATE IS FORMED

When, for a given concentration of chromate, the current density is relatively low, depletion of chromate at the anode will not be complete, for the depleted solution has a lower density and, thus, flows upward. Since the effective thickness and the average flow velocity of the boundary layer increase

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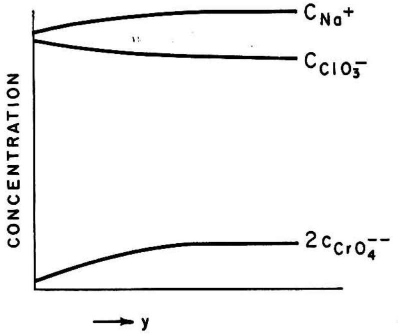

FIG. 1. Concentration distribution in the boundary layer when an adherent layer of lead chromate is formed.

in the flow direction (7), fresh solution flows toward the electrode and supplies chromate ions. Thus lead chromate is formed at the surface of the anode until the anode is passivated by too thick a layer of lead chromate. Conditions in the boundary layer are shown schematically in Fig. 1.

If a lead electrode in a solution of sodium chromate with an excess of sodium chlorate is kept at a potential at which all chromate ions approaching the electrode react with lead but practically no Pb^{++} ions leave the electrode, the thickness of the boundary layer and the value of the limiting current density may be calculated from equations derived in a previous paper (7). The concentration of chromate ions, c_1, as a function of the distance from the electrode, y, from the electrode may be approximated by the relation

$$c_1 = c_{1(0)}[1 - (1 - y/\delta)^2] \tag{I}$$

where $c_{1(0)}$ is the concentration of chromate ions in the bulk solution and δ is a parameter of the dimension of length as a measure of the thickness of the boundary layer. Since the mobilities of the other ions, Na^+ and ClO_3^-, do not differ considerably from the mobility of the chromate ions, the parameter δ may be used for the representation of the concentration distribution of all ions and likewise for the velocity profile. Then δ (cm) is found to be

$$\delta = \left[\frac{120 D_1 \nu x}{g c_{1(0)} \left(\dfrac{\partial \ln \rho}{\partial c_{\mathrm{Na_2CrO_4}}} - \dfrac{\partial \ln \rho}{\partial c_{\mathrm{NaClO_3}}}\right)}\right]^{\frac{1}{4}} \tag{II}$$

where D_1 (cm^2/sec) is the diffusion coefficient of chromate ions, ν (cm^2/sec) is the kinematic viscosity of the solution, x (cm) is the distance from the lower edge of the electrode, g = 981 cm/sec^2 is the gravitational acceleration, ρ (g/cm^3) is the density of the solution, and the concentrations in mole/cm^3 are designated by c with the respective subscripts.

The average current density $(I/A)_H$ for an electrode of height H is obtained as

$$\left(\frac{I}{A}\right)_{\mathrm{H}} = \frac{16 \mathrm{F} D_1 c_{1(0)}}{3} \cdot \left[\frac{g c_{1(0)}}{120 D_1 \nu H}\left(\frac{\partial \ln \rho}{\partial c_{\mathrm{Na_2CrO_4}}} - \frac{\partial \ln \rho}{\partial c_{\mathrm{NaClO_3}}}\right)\right]^{\frac{1}{4}} \tag{III}$$

At 25°C the following numerical values hold: $D_1 = 1.1 \cdot 10^{-5}$ cm^2/sec corresponding to a mobility of chromate ions of $0.88 \cdot 10^{-3}$ (cm/sec)/(volt/cm); $\nu = 0.90 \cdot 10^{-2}$ cm^2/sec; $\partial \ln\rho/\partial c_{\mathrm{Na_2CrO_4}} = 140$ (mole/cm^3)$^{-1}$; $\partial \ln\rho/\partial c_{\mathrm{NaClO_3}} = 70$ (mole/cm^3)$^{-1}$ (10); F = 96,500 coulomb/equivalent. Le Blanc and Bindschedler (2) investigated a solution containing 12 grams $NaClO_3$/liter and 3.0 grams Na_2CrO_4/liter corresponding to $c_{1(0)} = 1.9 \times 10^{-5}$ mole Na_2CrO_4/cm^3. For this solution equation (II) gives a value of $\delta = 0.1$ cm at a distance of x = 10 cm from the upper edge of the electrode, and equation (III) gives an average current density of 1.15×10^{-3} amp/cm^2 for an electrode of 10 cm height.

STRUCTURE OF THE BOUNDARY LAYER WHEN LEAD CHROMATE IS FORMED WITHIN THE BOUNDARY LAYER

The current density of 0.006 amp/cm^2 applied in most runs reported by Le Blanc and Bindschedler (2) exceeds the limiting current density for formation of $PbCrO_4$ at the surface of the anode. At higher current densities and under steady-state conditions, lead ions enter the solution near the anode and migrate across the boundary layer up to a certain distance δ_p where they encounter chromate ions and form a precipitate of $PbCrO_4$ as is shown schematically in Fig. 2. Since the solution near the anode is rich in lead chlorate, its density is higher than that of the bulk solution. The solution near the surface of the anode will, therefore, flow downward. The

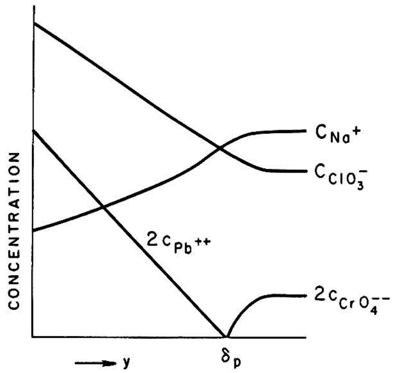

FIG. 2. Concentration distribution in the boundary layer when lead chromate is formed within the boundary layer.

thickness and the average flow velocity of the boundary layer increase with increasing distance from the upper edge of the anode. Accordingly, bulk solution flows into the boundary layer. Thereby chromate ions are transported toward the anode at a rate beyond that accounted for by electrolytic migration and diffusion. The amount of chromate ions entering the boundary layer, however, cannot be equivalent to the amount of lead ions formed at the anode, for the mechanism suggested in this paper presupposes a definite thickness and a definite flow velocity of the boundary layer involving excess lead ions at the lower edge of the anode. Consequently, lead chromate is formed not only at some distance δ_p in front of the anode, but also in a mixing zone of lead-rich boundary layer and bulk solution below the lower edge of the anode. In this respect, the present analysis differs from that given by Le Blanc and Bindschedler (2).

EXPERIMENTAL

A lead foil coated with lacquer on one side was tilted by 15° vs. the vertical direction, the free surface facing downward. The electrolyte contained 12 grams $NaClO_3$ and 3 grams Na_2CrO_4 per liter. In accordance with Le Blanc and Bindschedler (2), a current density of 0.006 amp/sec was applied. The precipitate of $PbCrO_4$ formed within the boundary layer settled downward, and separated from the tilted electrode. In addition, fringes of precipitated lead chromate were observed at the lower edge of the electrode. This confirms the conclusion that a sizable amount of lead chromate is formed at the lower edge of the electrode by virtue of mixing of the lead-rich boundary layer with bulk solution.

CONCLUDING REMARKS

Approximate calculations indicate that the amount of lead chromate formed in the mixing zone at the lower edge of the anode is a substantial fraction of the total amount of lead chromate. Calculations are omitted in this paper since the effect of $PbCrO_4$ moving downward has been disregarded and an estimate of this neglect is not possible. For this reason, only a qualitative discussion of the interplay between diffusion and convection is given.

A somewhat different situation is encountered when the electrolyte is stirred, and thereby the effective thickness of the diffusion boundary layer is determined. This case has been considered by Aten (11) with special reference to the anodic formation of silver halide at a silver electrode for the electroanalytic determination of halogen. In this case, silver halide has to be formed virtually only at the surface of the anode. Thus, the current density must not exceed the limiting value for exclusive formation of silver halide at the anode. The limiting current density is proportional to the concentration of halide in the bulk solution and, therefore, tends to zero when the electrodeposition of halogen is close to completion. An appropriate value of the current density at any time may be obtained by confining the electrode potential to such a value that the concentrations of both silver and halide ions at the anode are sufficiently low and accordingly the migration of silver ions into the boundary layer is negligible.

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

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Extractive Metallurgy of Zirconium by the Electrolysis of Fused Salts

II. Process Development of the Electrolytic Production of Zirconium from K_2ZrF_6[1]

M. A. STEINBERG, M. E. SIBERT, AND E. WAINER

Horizons Incorporated, Cleveland, Ohio

ABSTRACT

An intensive investigation of the electrolysis of K_2ZrF_6 in an electrolyte of NaCl has been carried out to determine the optimum conditions for the production of zirconium metal by fused salt electrolysis.

Cell designs and conditions of operation evolved are described, yielding a high purity zirconium powder which is ductile on consolidation. This metal can be fabricated with ease, and is comparable to Kroll zirconium sponge. Because of the stability of the raw materials, their ease in preparation and in electrolysis, coupled with lower cost equipment, it is felt that this process will yield a much lower cost zirconium metal.

INTRODUCTION

The historical and theoretical aspects of the double fluoride process for production of zirconium metal have been discussed in previous papers (1, 2). The basic concept of the process entails the electrolysis of a fused alkali halide-potassium zirconium fluoride mixture under a purified argon atmosphere. In this paper, a detailed operational procedure is given for the electrowinning of zirconium metal, including treatment of the raw materials, construction and operation of the electrolytic cell under an inert atmosphere, electrolytic procedures and conditions of current and voltage, and recovery of the metal from the deposits obtained.

A complete description of the effects produced by variations in the operating variables is given. Temperature, current density, voltage, and cell atmosphere are all significant variables in this operation. Purity of raw materials and concentration effects are of equal or greater importance.

Metal produced by this process has been thoroughly evaluated by chemical analysis and physical metallurgical techniques. A summation of this data and methods employed are included in this discussion.

EQUIPMENT AND CELL DESIGN

All electrolytic work done toward development of the fluoride process was done in cells of the type shown in Fig. 1, as compared to the work done in the small cells previously used. The design illustrated takes a charge of 5 lb. Two modifications of the cell are used, but these differ only in details, and not in capacity or operation.

The process has been successfully adapted to cells of 30- and 250-lb capacity. A subsequent paper will deal with larger scale operation in detail.

The cell design is essentially a steel shell with all-graphite interior parts. Heating is accomplished by an a-c heated carbon resistance element. This element is supported by its leads inside of a graphite shell separated from the steel casing by lampblack insulation. Silica and firebrick have been alternatively employed as insulation. The crucible is seated on a graphite pedestal inside the heating element. An inner graphite liner separating the crucible from the element and serving as a safety measure in case of crucible leakage has previously been used with this cell, but is not shown in this design.

Water-cooled copper-to-graphite element leads are used. The crucible serves as the cell anode and the positive d-c connection is made directly to the cell casing.

The head is basically a graphite dish packed with insulation and fitted with a water-cooled steel top. The cathode and thermocouple are inserted through this head. A steel bumped head with a gasketed flange is also provided to cover the whole upper assembly for evacuation of the cell.

Cells of this type are operated almost indefinitely with no corrosion of inner graphite parts if the cell interior is kept dry and free of atmospheric contamination. Crucibles are replaced after four to six runs due to salt leakage problems with commercial CS graphite.

Also, this cell can be utilized with a water-cooled

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[1] Manuscript received June 15, 1953. This paper is based on a portion of the work carried out by Horizons Incorporated for the New York Operations Office of the Atomic Energy Commission under Contract No. AT(30-1)-1144.

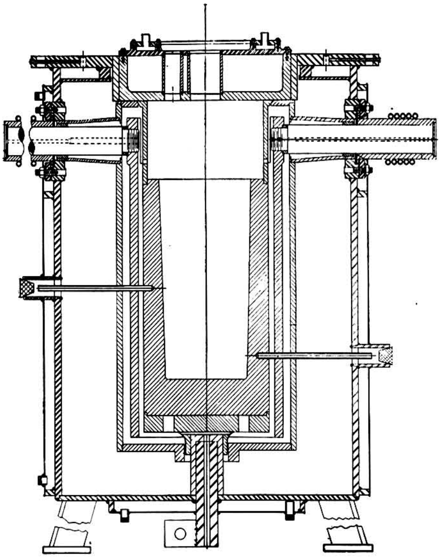

FIG. 1. Assembly drawing of inert-atmosphere zirconium electrolytic cell.

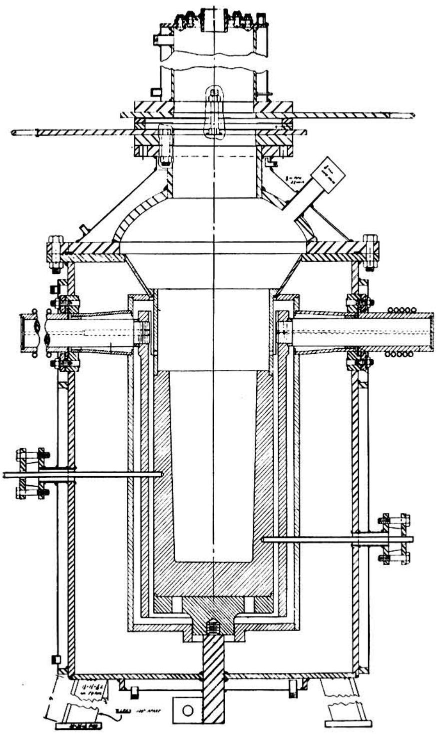

FIG. 2. Assembly drawing of modified electrolytic cell with bumped head, gate valves, and cathode removal chamber in place.

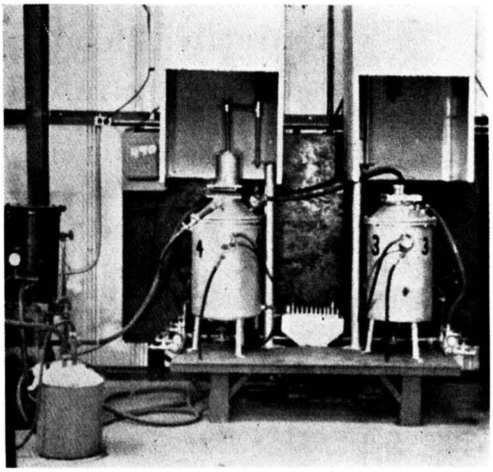

FIG. 3. External view of cells showing hood system and vacuum pump, cell 3 with vacuum head in place, and cell 4 with cathode removal chamber, cathode holder, and cathode in place.

cathode-removal chamber which fits onto the bumped head in place of the vacuum flange (Fig. 2). A photograph of two cells, one being evacuated (cell 3) and one with the bumped-head, cathode removal chamber and cathode in place is shown in Fig. 3. The two sliding gate valves shown in Fig. 2 close off both the cell and the cathode chamber so that the cathode chamber with the cathode and deposited metal can be removed from the cell proper and cooled under argon while the electrolyte and cell are sealed off under argon also. A second cathode removal chamber is placed on the cell and both gates are open, enabling a second electrolytic run to be made. A central panel board with a-c and d-c controls, temperature indicator, and argon flow-meters and valves for the operation of these cells, is shown in Fig. 4.

The argon is admitted through one of the element leads traveling down to the cell bottom, up around the crucible, and out through the head.

An a-c welding transformer has been used as a heating power source. A variety of d-c sources have been used with equal success. The most versatile is a motor generator set. A Hobart 400 amp a-c welder has been satisfactory as an a-c source. A Columbia 2000-amp motor generator has proved to be an extremely versatile and reliable d-c unit.

Linde Argon, 99.98 ± 0.02% in purity, is used as an inert atmosphere during operation. For further purification, the gas is passed through a column of phosphorus pentoxide to remove any residual moisture and then through a titanium sponge column

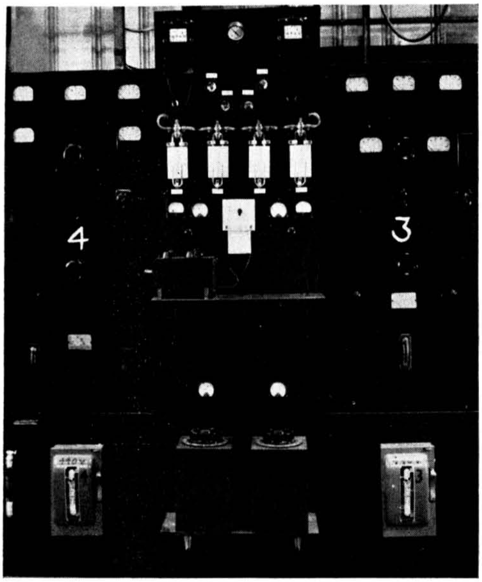

Fig. 4. Front over-all view of panel board showing a-c and d-c controls and meters, temperature indicating equipment and argon pressure controls, and manometers for the two cells and the cathode removal chambers.

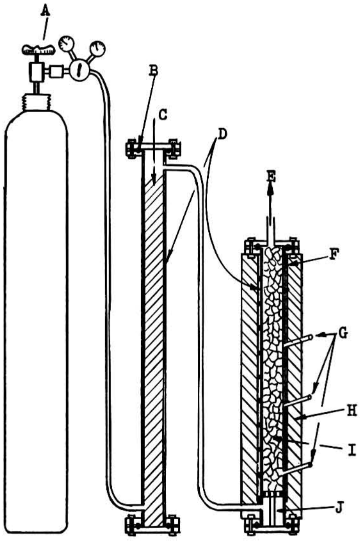

Fig. 5. Sectional drawing of argon purification train used with zirconium electrolytic cells. A—argon tank; B—copper O-rings; C—P_2O_5 packing; D—3-in. O.D. stainless steel tubes with steel flanges; E—to electrolytic cells; F—chromel "A" wire (14GA) embedded in refractory alundum cement; G—thermocouple wells; H—Kaylo pipe insulation; I—titanium sponge; and J—pedestal support.

at 700°C to remove O_2 and N_2. A sketch of this drying train is shown in Fig. 5 and is illustrated in Fig. 6.

Operational Procedures

Preparation of Cell and Materials

As will be later explained, it is essential that the cell and materials used be in an anhydrous condition; therefore, certain purification and cleaning steps must be taken. These include a hot evacuation of the cell and the vacuum drying of salts used in the electrolyte.

A new cell or one which has not been used for some time must be evacuated to remove moisture, hygroscopic salts, and certain organic materials. In the case of a new cell, insulating materials, particularly lampblack, and graphite parts contain large quantities of moisture and organic materials. The cell is first evacuated down to 100 μ or less at room temperature and then heated up to 100°–200°C above the normal operating temperature and pumped until the original pressure is again attained.

Raw materials must be pure and anhydrous. The sodium chloride used has been of reagent grade requiring, at most, an oven drying for 10–12 hr at 110°–120°C to remove surface occluded moisture. The K_2ZrF_6 is somewhat hygroscopic and is vacuum dried in a vacuum oven for 4–6 hr at 80°C at approximately 50 μ. The K_2ZrF_6 used has been of three

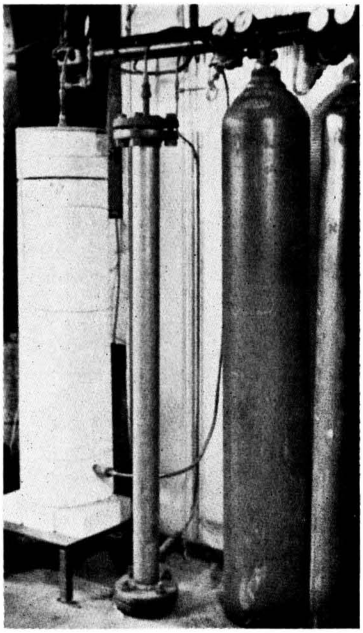

Fig. 6. Argon purification train with heaters, insulation, valves, etc., Ti column and P_2O_5 column.

types: (*a*) a C.P. grade, 99 + %, as supplied by the Kawecki Chemical Company, (*b*) a recrystallized 99.9% grade (Kawecki Chemical Company), and (*c*) a recrystallized 99.9% material produced in this laboratory.

Charging of Cell

The cell is initially heated to 850°–900°C under an argon atmosphere with the crucible in place. The dry salts are then charged and melted as rapidly as possible under a heavy argon flow.

When a fluid bath is obtained, the temperature is set at about 850°C using a chromel-alumel thermocouple embedded in the crucible wall. If purification of the bath is needed, a graphite cathode is inserted into the bath and d.c. applied to the circuit. Voltage is set at 1.5–2.0 volts. When moisture has been eliminated, a rise of 0.5–0.8 volt will be noted with a simultaneous current drop. Other more easily electrolyzable impurities are also broken down in this pre-electrolytic step. The bath is then ready for electrolysis.

Electrolysis

The cell temperature is dropped to 800°–850°C and a steel cathode with a nickel lead shaft inserted into the bath under low voltage (1–2 volts). This cathode shaft is protected by a graphite sleeve. Nickel is used as a lead because of its greater resistance to dry chlorine attack. A cylindrical cathode is used to conform to the crucible configuration. A variety of cathode designs, including cones, disks, and strips, have been tried, but these produce no outstanding changes in results. When the cathode has reached bath temperature, the current is increased to a point where the initial current density is 250–400 amp/dm². At these temperatures this yields an actual bath voltage of 3.5–4.0 volts and an indicated voltage of 4–6 volts, including the voltage drop through the cell. All reported voltages are meter readings and not actual electrode voltages. Electrolysis is carried out for a calculated number of ampere-hours based on a deposition rate of 0.5 gram/amp-hr. This is equivalent to about 60% current efficiency which is normally encountered. When the bath is near exhaustion of the available zirconium, sodium is produced and will be observed burning at the sight hole of the cell. There is little visible action during the runs aside from the evolution of copious amounts of chlorine.

When the run is over, the cathode is raised from the bath with a small voltage still across the cell. It is clamped into position just above the bath or in a sealed cooling chamber above the cell and allowed to cool to room temperature in an argon atmosphere.

A typical cathode and deposit as cooled and removed from the cell is shown in Fig. 7. An operating data synopsis for three typical runs is given in Table I, along with a summary of characteristics of the deposited metal.

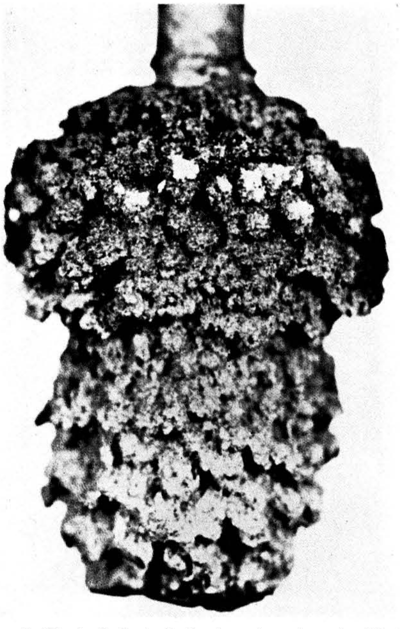

FIG. 7. Typical electrolytic zirconium deposit. (Reduced one-third in reproduction.)

Metal Recovery

The deposit as recovered from the cell or cooling chamber is a gray to black rough surfaced metal-salt agglomerate. It is roughly one-third metal and two-thirds salts. These salts are principally NaCl, NaF, KCl, and KF, with small amounts of K_2ZrF_6, and possibly other lower zirconium chlorides or fluorides.

The deposit is broken off the cathode and jaw-crushed to coarse lumps. These are allowed to soak in water for a short time until soft. They are then wet mortared to break up salt agglomerates, washed in buffered hot water solutions, and kept just slightly acidic to prevent excessive precipitation of any hydrous oxides of zirconium. A series of washings and decantations are made until there is no evidence of residual salts and no test for halide ions in the wash water. The powder is then filtered and acetone dried.

Metal Consolidation

The metal as recovered from the washing step is a coarsely crystalline powder, brilliantly metallic. Typical granules and powder particles of as-recovered metal are shown in Fig. 8. This powder may either be sintered under argon or high vacuum, arc

TABLE I. *Electrolysis of* K_2ZrF_6-NaCl-*Salt Bath*

Run No.	K_2ZrF_6 %	Electrolysis			Amp hr	Yield %	C.E. %	Remarks
		T °C	E Volts	C.D. Amp/dm²				
68-47	38	800	5.8	340	560	84	64	Commercial recrystallized K_2ZrF_6
68-61	38	800	4.9	270	600	87	62	Commercial recrystallized K_2ZrF_6
68-51	41	800	4.8	270	500	86	63	Horizons recrystallized K_2ZrF_6

Screen analysis (% retained on screen)

Run No.	+35 %	+100 %	+150 %	+200 %	+325 %	−325 %
68-47	2.9	30.0	21.0	14.8	17.0	14.3
68-61	1.4	30.1	18.4	12.7	19.8	17.6
68-51	13.7	50.2	14.9	7.6	8.4	5.2

Analysis for carbon, oxygen, and nitrogen

Run No.	Zr %	C %	N %	O %	Hardness Rockwell B
68-47	99.9	0.047	0.011	0.038	82
68-61	99.8	0.030	0.0017	0.074	85
68-51	99.8	0.029	0.002	0.049	84

Amp hr = ampere hours of electrolysis.
Yield % is based on total available Zr in electrolyte.
C.E. = Current efficiency based on number of ampere hours of electrolysis and theoretical yield of 0.85 gram/amp hr.

FIG. 8. As-recovered zirconium granules, water washed prior to compaction for arc melting. 15X

melted, or sheath rolled. The usual procedure carried out at Horizons Incorporated for evaluation purposes has been arc melting.

A small laboratory arc-melting furnace has been used, employing a water-cooled copper hearth and a tungsten tipped electrode. The unit operates under a quarter atmosphere of argon. Arc-melted, cast ingots up to 50 grams in weight are melted from each electrolytic run for evaluation. These ingots are melted from the powder, cold-pressed into compacts at 10 tsi.

EVALUATION OF THE PROCESS

Mechanism of the Reaction

The mechanism of the reaction has not been conclusively established, but certain definitive facts are known which suggest a number of possibilities all leading to the same end result.

The fused salt mixture has been essentially standardized as one of NaCl and K_2ZrF_6. All the observed by-products and end products may be accounted for by consideration of the various chemical and electrochemical reaction possibilities through the purification and deposition cycles.

Considering only the double fluoride in a bath with some moisture present, the following chemical reactions might occur.

$$K_2ZrF_6 + (\chi + 2)\, H_2O \rightleftarrows ZrO_2\cdot \chi H_2O + 2KF + \overline{4HF} \quad (I)$$

$$ZrO_2\cdot\chi H_2O \overset{\Delta}{\rightleftarrows} ZrO_2 + \overline{\chi H_2O}\ (550°C) \quad (II)$$

$$K_2ZrF_6 \rightarrow 2KF + \overline{ZrF_4} \xrightarrow{\Delta} ZrF_3 + \overline{1/2F_2} \quad (III)$$

Reactions (I) and (II) probably occur to some extent during charging and melting of the salts. It is doubtful that reaction (III) occurs at all. Fluorine is apparently replaced by chlorine, and a similar decomposition does occur to some extent as the chloride when NaCl is melted with K_2ZrF_6.

Ionization may take place in the following manner:

$$K_2ZrF_6 \rightleftarrows 2K^+ + ZrF_6^{2-} \qquad \text{(IV)}$$

$$K_2ZrF_6 \rightleftarrows K_2ZrF_5^+ + F^- \qquad \text{(V)}$$

During the dehydration or purification step, a low voltage pre-electrolysis with a graphite anode can produce the following reactions,

$$H_2O \rightleftarrows 2H^+ + O^{2-} \qquad \text{(VI)}$$

$$2H^+ + 2e \rightarrow \overline{H_2} \text{ (cathode)} \qquad \text{(VII)}$$

$$\left.\begin{array}{l} O^{2-} + C \rightarrow CO + 2e \text{ or} \\ 2\ O^{2-} + C \rightarrow \overline{CO_2} + 4e \text{ (anode)} \end{array}\right. \qquad \text{(VIII)}$$

These latter three reactions all occur as evidenced by gases evolved from the cell.

When NaCl is considered as part of the system, the chlorine replacement then can occur. Since no fluorine is evolved, this replacement is definitely known to take place, possibly according to one of the following reactions.

$$K_2ZrF_6 + 4NaCl \rightarrow 2KF \cdot ZrCl_4 + 4NaF \text{ or} \qquad \text{(IX)}$$

$$K_2ZrF_6 + 6NaCl \rightarrow 2NaCl \cdot ZrCl_4 + 4NaF + 2KF \qquad \text{(X)}$$

KCl is also found in the bath, so there is some replacement of fluorine in this instance.

$$KF + NaCl \rightleftarrows NaF + KCl \qquad \text{(XI)}$$

All ionic salts are of course present to a great extent as ions in a fluid melt.

On electrolysis the following anode reactions are possible, assuming elimination of moisture.

$$2Cl^- \rightarrow Cl_2 + 2e \qquad \text{(XII)}$$

$$ZrCl_6^{2-} \rightarrow ZrCl_4 + Cl_2 + 2e \qquad \text{(XIII)}$$

$$ZrCl_6^{2-} \rightarrow ZrCl_3^+ + 3/2\ Cl_2 + e \qquad \text{(XIV)}$$

Reaction (XII) occurs throughout the process when the voltage is greater than 2.5 volts. There is no definite proof that (XIII) and (XIV) occur, but if reaction (IV) takes place, then reactions of this type could logically follow.

The exact mechanism of the reduction from 4+ Zr(IV) to Zr° is in doubt. There is definite reason to believe it evolves through breakdown of a chloride, and some reason to think the reduction is stepwise going from 4+ Zr(IV) through 3+ Zr(III) to Zr°. The following cathode reaction types can be postulated.

$$Na^+ + e \rightarrow Na \qquad \text{(XV)}$$

$$K^+ + e \rightarrow K \qquad \text{(XVI)}$$

$$Zr^{4+} + 4e \rightarrow Zr \qquad \text{(XVII)}$$

$$Zr^{3+} + 3e \rightarrow Zr \qquad \text{(XVIII)}$$

$$\left.\begin{array}{l} Na^+ + ZrCl_4 + e \rightarrow NaCl + ZrCl_3 \text{ and} \\ 3Na^+ + ZrCl_3 + 3e \rightarrow 3NaCl + Zr \end{array}\right. \qquad \text{(XIX)}$$

$$3Na^+ + ZrCl_3^+ + 4e \rightarrow 3NaCl + Zr \qquad \text{(XX)}$$

$$3Na^+ + ZrCl_3^+ \rightarrow 3NaCl + Zr^{4+} \qquad \text{(XXI)}$$

Reactions (XV) and (XVI) are relatively unimportant, occurring only when the zirconium concentration in the electrolyte is near exhaustion. It is doubtful whether (XVII) or (XVIII) occur, as there is no concrete evidence that the simple Zr ions exist. Reactions (XIX) through (XXI) are means by which Zr could be liberated. Any such mechanism could derive Zr(IV) or Zr(III) from the anode or from the bath and produce Zr at the cathode.

The over-all cell reaction is as follows:

$$4NaCl + K_2ZrF_6 \rightarrow Zr + 4NaF + 2KF + \overline{2Cl_2} \qquad \text{(XXII)}$$

Certain side reactions enter under specific conditions. If significant oxygen remains in the bath and ZrO_2 is produced, then high oxygen deposits are produced.

$$2ZrO_2 \rightarrow 2ZrO^{2+} + 2\ O^{2-}$$

$$2ZrO^{2+} + 4e \rightarrow 2ZrO \rightarrow ZrO_2 + Zr \qquad \text{(XXIII)}$$

This reaction also occurs during the purification cycle.

If the temperature is extremely high, chlorination can occur at the cathode, the chlorine being derived from the anode.

$$2Zr + 3Cl_2 \rightarrow 2ZrCl_3 \xrightarrow{Cl_2} 2ZrCl_4 \qquad \text{(XXIV)}$$

Disproportions are also possible at higher temperatures and extreme voltages as:

$$Zr + 3ZrCl_4 \rightarrow 4ZrCl_3 \qquad \text{(XXV)}$$

$$Zr + 2ZrCl_3 \rightarrow 3ZrCl_2 \qquad \text{(XXVI)}$$

Finally, the process is definitely an electrolytic one and not a sodium reduction by secondary reaction at the cathode. There is no apparent reaction on melting of the two salts. Furthermore, metal may be produced below the decomposition potential of sodium chloride. The cathode deposit is a compact adherent one unlike a thermal reduction product. There is no evidence of sodium metal production during the reaction until the available zirconium is near depletion, or at extremely high voltages when some sodium may be codeposited.

The process is not operable when exposed to the air. Deposits made in air are mixtures of oxide and

TABLE II. *Effect of* K_2ZrF_6 *concentration on the electrolytic production of zirconium*

Run No.	Concentration K_2ZrF_6 %	Yield %	Current efficiency	% >100 mesh	% C	% N	% O	Hardness Rockwell B
61-147	20	82.5	57.5	ND	ND	0.012	0.061	ND
61-164	20	80.5	61	ND	0.042	0.002	0.042	79
61-171	24	81	51.3	ND	0.034	0.0013	0.055	90
75-175	26.5	94	54	ND	0.034	0.0032	ND	ND
74-4	27	93	46	25.8	0.058	0.007	ND	ND
74-6	27	90	44	36.3	0.074	0.0139	ND	ND
68-35	33	86	50	27.6	ND	ND	ND	83
68-57	38	80	69	59.9	0.023	0.0002	0.060	87
68-51	41	66	63	63.9	0.029	0.002	0.049	84

E (volts) = 5-6 volts.
Current density = 300-500 amp/dm².
Temperature = 830°-860°C.
ND = not determined.

metal, very finely divided, and analyze at best around 85% Zr.

Effect of Concentration of K_2ZrF_6

This process is operable using K_2ZrF_6 concentrations up to 50%, but considerable difference is observed in operational characteristics. A high concentration is desirable from two standpoints, lower operating temperatures and longer runs without recharging.

Maximum yields of metal have been encountered using 25-30% by weight K_2ZrF_6 concentrations. Maximum current efficiencies are obtained using the 35-40% range. Thus a 30-35% concentration has been considered the optimum concentration range.

Pertinent data for runs of various concentrations are shown in Table II and illustrated in Fig. 9. Some tendency has also been noted toward an increase in particle size with increasing concentration, but the observation is not conclusive at this time. Zirconium metal of comparable purity has been produced throughout the range of concentrations investigated.

Temperature Effect

Bath temperatures from 790° to 1000°C have been investigated. The melting point of the usual 30-35% K_2ZrF_6-NaCl bath is just under 790°C and, at this minimum temperature, the bath is quite viscous giving poor deposition characteristics and low efficiencies. At 800°C, however, the efficiency climbs to a maximum. Beyond 870°C, it falls off to a point where it is only 40% at 1000°C. With other variables affecting the process considered, the optimum operating temperature appears to be about 850°C.

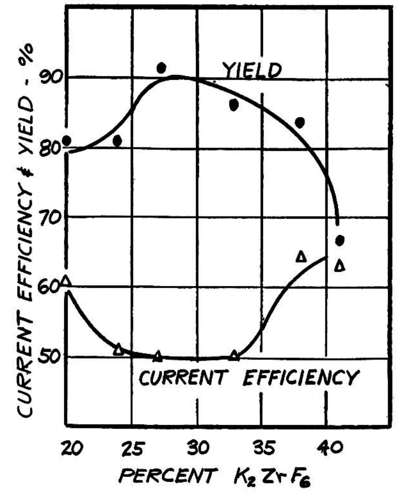

FIG. 9. Effect of initial K_2ZrF_6 concentration in the electrolyte on the metal yield and current efficiency.

TABLE III. *Effect of temperature on the efficiency of zirconium metal production by fused salt electrolysis of* K_2ZrF_6

Run No.	Temp, °C	Yield %	Current efficiency %	% C	% N	% O	Hardness Rockwell B
61-142	790	71.5	43.5	ND	0.007	0.128	—
68-33	800	76	63	ND	ND	ND	86
61-164	860	80.5	61	0.042	0.002	0.042	79
61-191	920	70	43	ND	0.0015	0.033	ND
61-44	1000	90	40	ND	ND	ND	ND

E (volts) = 5-6 volts.
Current density = 300-500 amp/dm².
Concentration of 20% by weight of K_2ZrF_6 in NaCl.

At higher temperatures, the deposits are richer in salts and the crystals of zirconium are of a dendritic type. There is also a greater tendency for pickup of impurities, and over-all metal quality is diminished.

Pertinent data for runs showing effect of temperature and efficiency are given in Table III and illustrated in Fig. 10.

Effect of Cell Feed Purity

Probably no other single factor is of greater importance in the fluoride process than is the purity of the salt bath. The most deleterious contaminants are water, oxides, and iron. Such impurities must either be absent or removed through pre-electrolysis and vacuum drying of salts. Otherwise the presence of these impurities is directly reflected in efficiency of the process and quality of the deposit.

In all experimental runs reported here, C.P. or

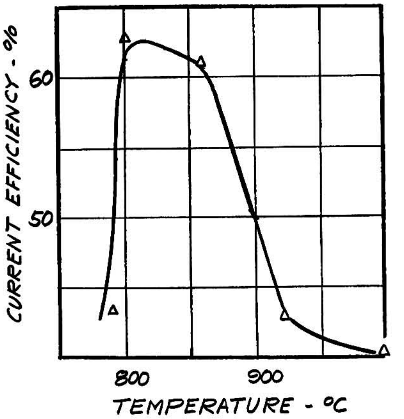

FIG. 10. Effect of temperature on the current efficiency in the electrolytic production of zirconium from K_2ZrF_6.

TABLE IV. *Spectrographic analysis of typical* K_2ZrF_6 (K_2ZrF_6 ignited to oxide for analysis)

Element	Per cent	Element	Per cent
ZrO_2	Major	MoO_3	—
SiO_2	0.05	NiO	0.002*
Fe_2O_3	0.005	Cr_2O_3	0.005
Al_2O_3	0.08	SnO_2	—
HfO_2	0.50	Ag_2O	—
CuO	0.0005*	CoO	—
TiO_2	0.001	Ta_2O_3	—
CaO	0.30	Cb_2O_5	—
MnO	0.001*	B_2O_3	0.0005*
MgO	0.001	V_2O_5	0.003
WO_3	—	Na_2O	—
PbO	0.01	K_2O	Major

* Less than.

Elements not detected: P, Bi, Ga, Cd, Y, Yb, In, Ge, Li, Ir, As, Os, Lu.

Analytical Grade NaCl has been utilized. K_2ZrF_6 obtained from several sources and also prepared at Horizons Incorporated has been investigated. However, a major portion of the work reported has been accomplished with K_2ZrF_6 with a purity as given in Table IV.

Water in the NaCl may be removed by high temperature air drying to a tolerable limit. That in the K_2ZrF_6 can be removed by a vacuum drying step. The cell of course must also be dry.

Iron in the salts can be removed by a low voltage pre-electrolysis. Since the crucible is anodic, any iron present is also removed in such a step if the amount is not excessive. No iron can be exposed in the cell or chlorination will result, and an $FeCl_3$ atmosphere will prevail in the cell. Iron serves to reduce the process efficiency and also cut down the particle size in addition to contaminating the deposit.

The presence of oxides or water in the bath is reflected in the oxygen analysis of the metal produced. This produces an extremely hard zirconium possessing little or no ductility.

Data illustrating effects of these various impurities are shown in Table V. The first six of these runs employed either a low grade zirconium source material or had a foreign substance added to the bath. Four satisfactory runs are appended for comparison.

Continuous Operation of the Process

Considerable work has been done toward extending the process beyond a single run batch-type procedure. Indications are that the process is adaptable to a semicontinuous operation. This has been done through reuse of a given bath and employment of a cathode cooling chamber. The design of such a cell was noted in Fig. 2 and 3. This cooling chamber is nothing more than a water-cooled gas tight container which can be removed from the cell with the cathode, allowing the insertion of a second cathode.

Theoretically a bath should be useful for a minimum of six runs. A bath is limited only by the buildup of NaF and KF which lowers the electrical conductivity and makes it more susceptible to polarization effects. Up to three runs have been made on a given bath with no noticeable effect on metal pro-

TABLE V. *Effect of cell feed purity*

Run No.	Type Zr source	Zr concentration %	Yield %	Current efficiency %	% >100 mesh	C %	N %	O %	Hardness Rockwell B
68-39	Recrystallized commercial, Fe in cell	11	61	58	ND	ND	ND	ND	ND
92-27	Recrystallized commercial, +1% ZrO_2	12	61	52	32.4	ND	ND	ND	Rc 34
92-29	Recrystallized commercial, +1% ZrO_2	12	51	46	28.9	0.011	0.000+	1.23	97
75-5	K_2ZrF_5, crude (contains ZrO_2)	7.2	82	56	44.3	0.049	0.033	0.255	ND
75-23	Low Hf, crude	6.4	92	34	46.1	0.070	0.007	0.207	ND
75-26	Horizons, crude	3.9	86	24	32.4	0.261	0.057	0.457	ND
68-47	Vac. dried, recrystallized, no pre-electrolysis	12	87	62	32.9	0.047	0.011	ND	82
75-175	Vac. dried, recrystallized, no pre-electrolysis	8.5	94	54	ND	0.034	0.0032	ND	ND
61-164	Vac. dried, recrystallized, pre-electrolysis	6.4	80.5	61	ND	0.002	0.042	0.042	79
74-6	Commercial, as received, no pre-electrolysis	9	90	44	55.8	0.074	0.013	ND	ND

ND = not determined.

TABLE VI. *Semicontinuous operation for electrolytic zirconium production*

Run No.	K_2ZrF_6 conc. %	Temp, °C	I Amp	E Volts	Yield %	Current efficiency %	% >100 mesh	C %	N %	O %	Hardness Rockwell B
68-31	25	850	150-200	4.5-4.2	86	43	23.9	0.027	ND	0.006	95
-33	25	800	200-60	5.3-4.1	76	63	ND	ND	ND	ND	ND
74-4	27	840	150	5.8	93	47	26.0	0.058	0.007	ND	ND
-6	27	860	120-95	7.8-5.3	90	44	36.3	0.013	0.013	ND	ND
-7	27	860	125	6.2	ND	60	ND	ND	ND	ND	ND
68-57	38	820	200	5	80	69	59.9	0.023	0.0002	0.060	87
-59	38	800	200-100	5.6-4.5	54	35	19.4	0.030	0.0017	0.112	85

ND = not determined.

duced. Certain adjustments are necessary however in temperature and operating current. Typical data for semicontinuous operation are shown in Table VI.

Effect of Other Variables

Other variables have only minor effects on the process in general. An argon atmosphere is of course important, but a highly purified argon is not necessary.

Current density has little effect within fairly large limits. The lower limit is fixed only by voltage, and a minimum of 2.0–2.5 volts must be maintained across the cell for a satisfactory deposit. The upper limit of current density is about 500 amp/dm². Beyond this point metal is produced, but particle size diminishes and the metal is more difficult to recover from the deposit.

Electrode distance and cathode design have had little effect to this point. Investigation along these lines has of course been confined to the 5-lb cells with fixed dimensions.

EVALUATION OF METAL PRODUCED

Chemical Evaluation

Zirconium produced by the fluoride process has been evaluated by means of chemical analysis, screen analysis, and spectrographic analysis. The following analytical methods have been employed:

Total Zr: Pyrophosphate gravimetric method; HF or aqua regia solution of sample; precipitation with $(NH_4)_2HPO_4$ followed by ignition to ZrO_2.

Carbon: Combustion method and KOH absorption of CO_2. Standard Leco Semi-Automatic Determinator used.

Nitrogen: Kjeldahl Method using Micro Kjeldahl apparatus (Scientific-Glass Apparatus Co.—M-3074). HF solution of sample. Titration with 0.01*N* HCl.

Oxygen: Chlorination method; ignition in purified chlorine at 400°C, followed by ignition of residue and weighing as ZrO_2. Adapted from HCl volatilization method developed at Massachusetts Institute of Technology AEC Laboratory (3, 4). Average values obtained:

Zr and Hf — 99.6–99.9% N — 0.002–0.004%
C — 0.04–0.06% O — 0.04–0.08%

Samples have periodically been sent out for spectrographic analysis. Samples of such analyses are reported in Table VII.

Particle size analyses have been done using a Ro-Tap vibrator with a standard set of Tyler screens, 35, 80, 100, 150, 200, and 325 mesh.

Typical analyses are given in Fig. 11 for two samples in the form of distribution curves. Other analyses for representative runs are reported in Table VIII. It is not unusual to have >50% of +100 mesh.

TABLE VII. *Typical spectrographic analysis of electrolytic zirconium*

(Reported in parts per million)

	Sample				
Element	6144-46 Powder	61-90 Powder	61-90 After double drip melting	Composite 1	Composite 2
Al	60	725	700	80	100
Ca	—	7	25	<50	<50
Cr	10	30	25	50	30
Cu	20	65	65	<5	<5
Fe	800	850	300	200	100
Hf	9400	—	—	15,000	15,000
Mg	<5	3	12	<10	<10
Mn	10	40	7	<10	<10
Mo	20	<10	<10	<10	<10
Ni	30	20	20	50	40
Pb	30	40	<5	<10	<10
Si	40	100	105	200	30
Sn	40	9	50	<10	<10
Ti	270	1015	690	500	500
V	—	<100	<100	ND	ND
W	100	ND	ND	ND	ND

ND = not determined.

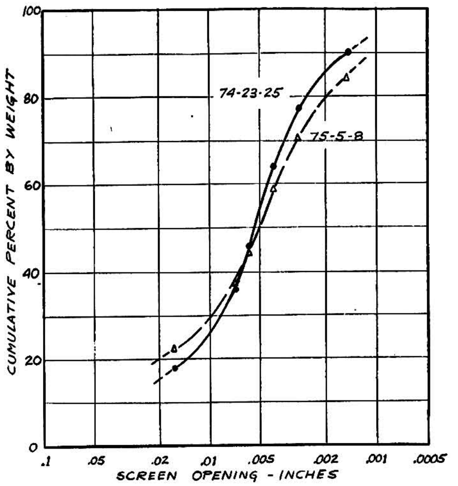

FIG. 11. Particle size and size distribution plot of two typical electrolytically produced zirconium metal powder products.

TABLE VIII. *Particle size analysis*

Run No.	+35 %	+100 %	+150 %	+200 %	+325 %	−325 %	Remarks
68-57	11.7	48.2	15.5	8.4	10.0	6.2	
68-61	1.4	30.1	18.4	12.7	19.8	17.6	
92-27	1.7	30.7	23.1	14.1	23.3	7.1	
92-31A	5.4	49.6	21.8	8.7	10.6	3.9	
68-49	5.8	37.7	21.3	12.6	14.9	7.7	High K_2ZrF_6 conc.
92-39B	6.4	43.4	17.9	10.1	15.0	7.2	

Metallurgical Evaluation

In almost all of the electrolytic runs in which sizable amounts of zirconium powder were recovered, samples were taken for arc melting to produce small ingots on which hardness and workability data were obtained.

Cold rolling, in most cases, was carried out on the as-cast ingots without prior annealing, as this is the most drastic type of treatment for the determination of ductility in forming that can be carried out. Hot working, to strip of about ⅛-in. thickness followed by cold reduction, both with and without intermediate anneals, was also carried out. Sheath rolling of both melted ingots and cold-pressed powder was conducted using mild steel as the canning material. Wire-rolling to 0.030-in. diameter was conducted on selected ingots to determine the ease of fabrication of the electrolytically produced zirconium by this method.

In general, the zirconium powder was compacted in a 1-in. diameter die, by cold pressing at 10 tsi. Compacts of 20–50 grams in weight were prepared. These were melted in a small laboratory arc-melting furnace under an atmosphere of argon of approximately 20 cm pressure. A water-cooled tungsten electrode and water-cooled copper hearth were used, each ingot being turned over and remelted to insure complete fusion and homogeneity of the cast metal.

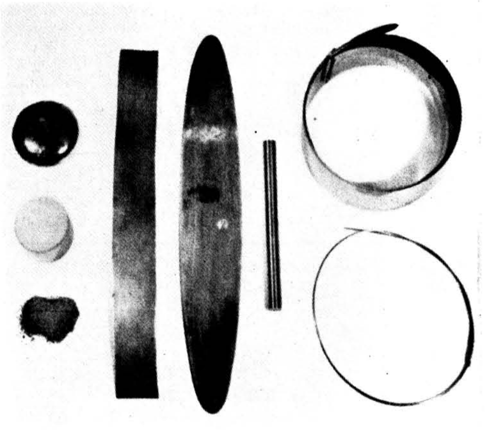

FIG. 12. Zr powder, Zr cold press compact, melted ingot, cold-rolled sheet, hot-rolled strip, machined Zr bar, coiled cold-rolled Zr foil 0.008 in. thick, and rolled Zr wire 0.03 in. diameter. (Reduced to slightly less than one-half size.)

Rockwell A and B hardnesses were taken on both sides of the ingot after first grinding parallel flat surfaces on the faces. In the case of thin sheet, Vickers hardness readings using a 5 kg load were obtained.

Fig. 12 is a photograph showing the various stages of processing of the electrolytically produced zirconium. The powder pressed to a compact of about 70% density is arc-melted and a cast ingot is obtained, as shown. Cold-rolled strip, hot-rolled plate, and a cold-rolled and machined rod are also shown. A coil of cold-rolled sheet and wire, rolled to 0.030 in., are included.

Some of this zirconium powder was melted by an arc method, using a consumable electrode. The powder was extruded and sintered and the resulting rod melted to obtain the two-pound ingot shown in Fig. 13. This ingot had an average hardness value of Rockwell B-85.

HARDNESS OF AS-CAST ZIRCONIUM INGOTS

In measuring the hardness of the cast ingots of zirconium an attempt has been made to correlate the hardness values to the oxygen contents determined on each batch of powder produced.

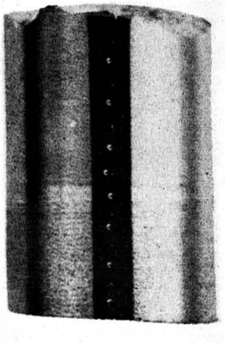

FIG. 13. Small zirconium ingot, 2 lb., melted by consumable electrode method from the sintered powder. (Reduced to ⅘ size.)

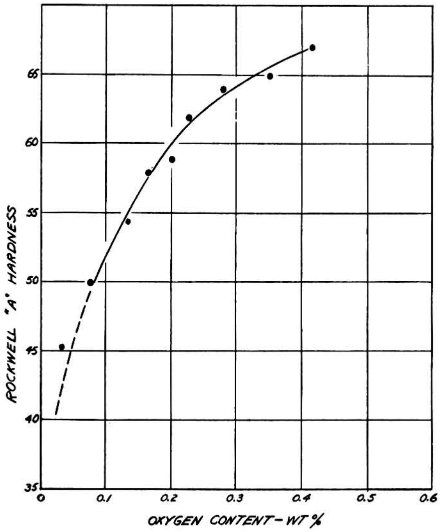

FIG. 14. Hardness as a function of oxygen content for as-cast electrolytically produced zirconium; C ≅ 0.05%; N_2 ≅ 0.003%.

Only those runs with nitrogen contents between 0.002 and 0.005 weight per cent (0.003% average) and carbon contents between 0.02 and 0.07 weight per cent (0.05% average) were chosen. With this as a basis, the oxygen contents were plotted against the hardness values obtained and this variation is shown in Fig. 14.

DUCTILITY OF ELECTROLYTICALLY PRODUCED ZIRCONIUM

The workability of the as-cast zirconium ingots was determined by rolling to sheet and determining the hardness at certain stages in the reduction. Attempts were not successful, in general, to reduce the arc-melted ingots over 50% by cold-rolling if the as-cast hardness exceeded Rockwell A 54–55. However, if the hardness of the ingot was lower than this, it was possible to cold roll strip directly from the ingot stage without intermediate anneals, provided care was taken to grind out any incipient edge-cracking that may occur. Cold reductions of up to 98% have been experienced on certain batches produced. However, almost all of the zirconium produced could be hot rolled at 700°–800°C to plate (0.125 in.) and cold rolled to sheet (as thin as 0.006 in.) with no difficulty. Typical cold reduction vs. hardness data are given in Fig. 15. This material has working characteristics that compare favorably with sponge zirconium.

Sheath rolling has been attempted both with the cold-pressed powder and with cast ingots using a mild steel sheath. Hot rolling to a reduction of about 60%, followed by an additional cold reduction of

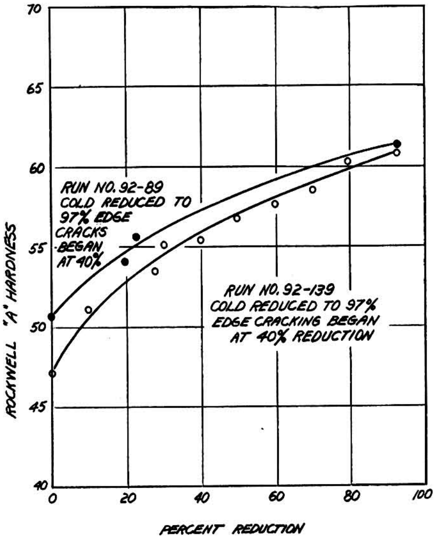

FIG. 15. Hardness vs. reduction in rolling for electrolytically produced zirconium.

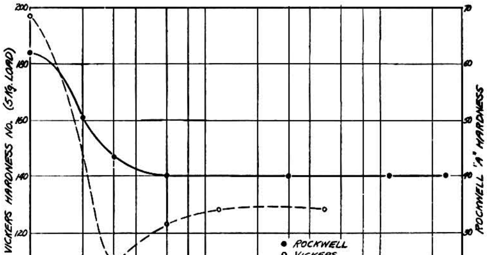

FIG. 16. Hardness as a function of annealing time for 97% cold-rolled zirconium.

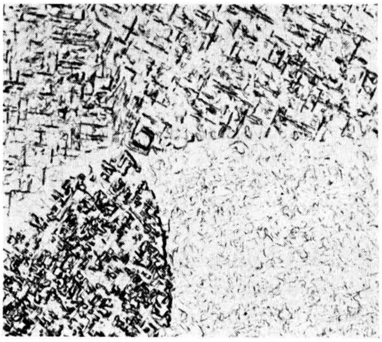

FIG. 17. As-cast zirconium ingot showing typical Widmanstatten structure of cast zirconium electrolytically polished and etched. Bright-field illumination. 100×

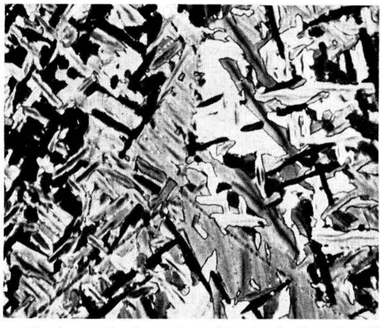

FIG. 18. As-cast zirconium ingot similar to Fig. 17, showing details of Widmanstatten structure electrolytically polished and etched. Polarized light. 250×

about 30%, was obtained. The zirconium is then removed from the steel sheath and further reduced cold to strip of the order of 0.006–0.010 in. in thickness.

The hardness variations as a function of annealing time for two different runs of zirconium, cold rolled approximately 97%, are given in Fig. 16.

MICROSTRUCTURES OF ZIRCONIUM, ELECTROLYTICALLY PRODUCED

Typical microstructures of the as-cast, cold-worked, and annealed zirconium are shown in Fig. 17 through 25.

The well identified as-cast structure of zirconium showing the Widmanstatten pattern is shown in Fig. 17 and 18, under bright light and polarized light illumination.

Specimens, cold pressed to a 17% reduction in thickness and annealed at 800°C, are shown in Fig. 19 and 20. In an annealing time of 5 min, only partial recrystallization has occurred, while 15 min at 800°C has resulted in complete recrystallization.

The structure of an as-cast ingot, cold-rolled 98% without intermediate anneal, is shown in Fig. 21.

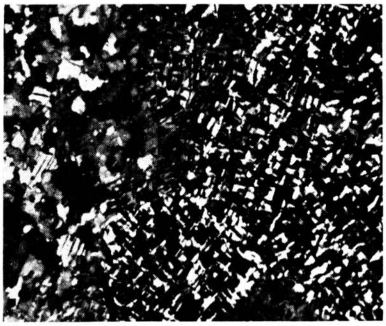

FIG. 19. Zirconium (cold reduced 17%) annealed 5 min at 800°C, showing partial recrystallization. Polarized light. 100×

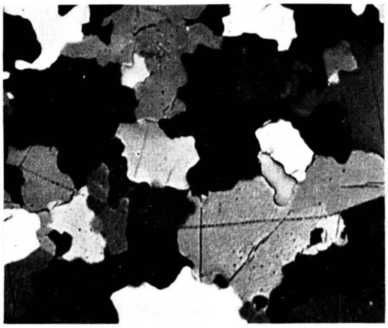

FIG. 20. Zirconium, vacuum annealed 15 min at 800°C after 17% cold reduction. Polarized light. 250×

FIG. 21. Zirconium ingot, cold rolled 98% without intermediate anneal. Polarized light. 250×

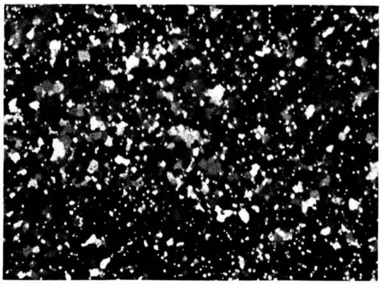

FIG. 22. Same as Fig. 21 but vacuum annealed 15 min at 800°C. Complete recrystallization has taken place. Polarized light. 100×

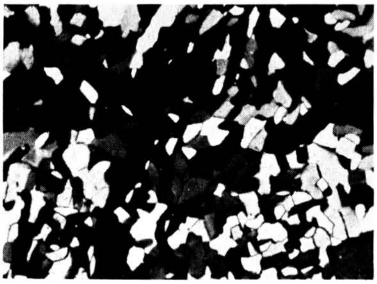

FIG. 23. Same specimen as Fig. 22 but vacuum annealed 4 hr at 800°C. Complete recrystallization and grain growth have taken place. Polarized light. 100×

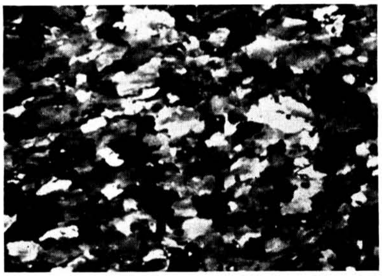

FIG. 24. Electrolytic zirconium metal, arc-melted and hot-rolled 80% from 0.375–0.07 in., at 700°C followed by 40% cold reduction from 0.070–0.030 in. Polarized light. 250×

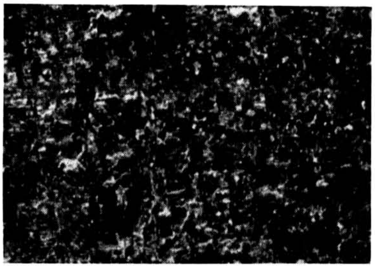

FIG. 25. Electrolytic zirconium metal, arc-melted and sheath-rolled at 900°C to 60% reduction; sheath-rolled, cold to an additional 30%, removed from sheath and cold-reduced to 0.008 in. sheet to a total of 98% reduction. Electrolytically polished. Polarized light. 250×

Annealing this specimen at 800°C for 15 min has resulted in complete recrystallization, while recrystallization and considerable grain growth has occurred in this specimen annealed at the same temperature for 4 hr.

The microstructure of a typical hot-rolled ingot, followed by a lesser amount of cold reduction is shown in Fig. 24. Fig. 25 shows the severely deformed structure of a sheath rolled zirconium specimen in which a substantial amount of cold reduction has taken place.

DETERMINATION OF PREFERRED ORIENTATION IN ROLLED SHEET AND WIRE

Cold-Rolled Sheet Texture

Pole figures were determined for cold-reduced zirconium sheet rolled from electrolytically produced metal, consolidated by both sheath rolling and by cold rolling. Samples of zirconium sheet, cold rolled to over 95%, were utilized for these determinations.

An abbreviated x-ray method was used for the determination of the pole figures. Although this method does not lend itself to high accuracy, it is wholly adequate for the purpose at hand, to determine the degree of preferred orientation obtained with electrolytically produced zirconium, cold-rolled 95% or better.

The sheet of zirconium is placed parallel to the x-ray beam, between the target and film, and bent slightly so that the x-ray beam strikes the surface at a low glancing angle and is diffracted onto the film. Only two glancing angle shots were made for each specimen, one being perpendicular to the rolling direction and the thickness direction of the sheet, and the other, perpendicular to the transverse and the normal direction of the sheet. Although it was not possible to estimate many degrees of intensity for the two poles plotted, (0002) and (10Ī0), the data were sufficient to give good approximations of the rolling textures. The average orientation is best described by representing the basal planes (0001) parallel to the rolling direction but inclined

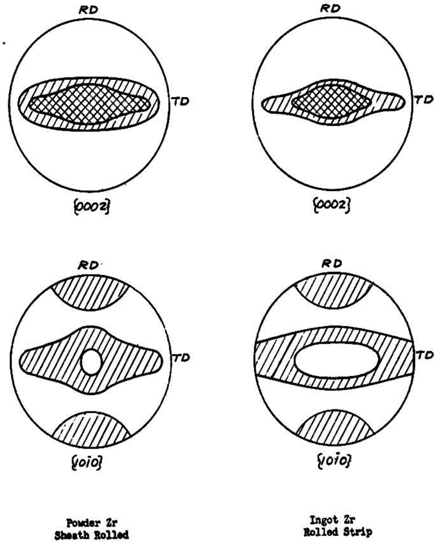

FIG. 26. Pole figures for {0002} and {10Ī0} planes of electrolytic zirconium sheet produced by indicated methods.

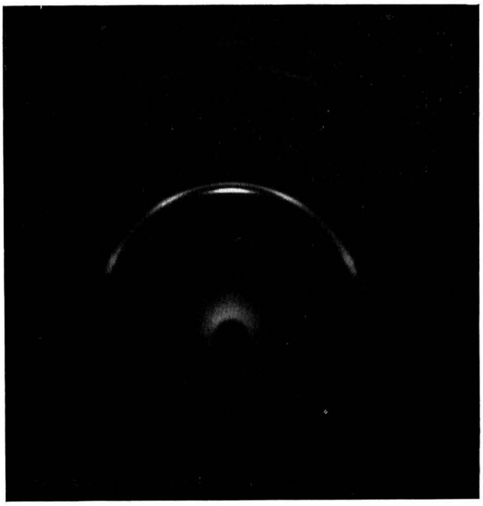

FIG. 27. X-ray photogram of rolled zirconium wire produced from electrolytic powder—MoK α radiation.

from the rolling plane by about 30° in the transverse direction and with a ⟨10$\bar{1}$0⟩ in the rolling direction. Fig. 26 shows these pole figures for the sheath-rolled and the cold-rolled zirconium specimens.

Cold-Rolled Wire Texture

The texture of cold-rolled electrolytic zirconium wire was determined from the x-ray photogram in Fig. 27. It was found that the ⟨10$\bar{1}$0⟩ direction was parallel to the wire axis. This is in agreement with the result of other investigators (5).

The results of these brief studies of preferred orientation in cold-worked zirconium metal produced by the electrolytic method show that the metal behaves in the same manner as iodide and sponge zirconium (6).

PRESENCE OF "SECOND PHASE" IN ELECTROLYTICALLY PRODUCED ZIRCONIUM

A second phase has previously been reported in both iodide and sponge zirconium of high purity. This phase, present in the annealed structure of the equiaxed alpha grains of zirconium, is acicular in nature when the zirconium is in the annealed state and suggests a preferential precipitation out of solution from the HCP lattice of the alpha zirconium.

This second phase has been present in varying amounts in almost all samples of electrolytic zirconium produced. From recent work done on titanium, reported in the literature, there is good evidence that this second phase in zirconium is a hydride (7). Thus, some simple experiments were conducted to determine if the hydride phase was present in the zirconium metal produced by this process. Determinations of hydrogen content on representative samples of zirconium from time to time have yielded values of 0.01 to 0.025 weight per cent hydrogen present in the electrolytic zirconium.

FIG. 28. Zirconium, vacuum annealed 2 hr at 800°C, furnace cooled, revealing hydride precipitation phase. Polarized light. 150×

These experiments consisted of first annealing small arc-melted zirconium ingots and slow cooling them, and then reheating to 310° to 410°C, followed by water quenching. The annealing was done at 800°C for 2 hr in a sealed-evacuated quartz tube. Fig. 28 is a photomicrograph of the structure resulting, revealing the acicular needles of the second phase in the alpha grains.

The photomicrograph of the specimen, heated to 310°C for 4 hr and water quenched, shows a decreased amount of this second phase (Fig. 29), while the one heated to 410°C for 1 hr and water quenched shows the complete absence of the phase. Only equiaxed alpha grains are present with a few mechanical twins resulting from polishing (Fig. 30).

To further substantiate this second phase, a second sample was annealed at 850°C for 5 hr in a sealed off-evacuated quartz tube, and furnace cooled. The acicular second phase is again present (Fig. 31). However, when this specimen is heated to

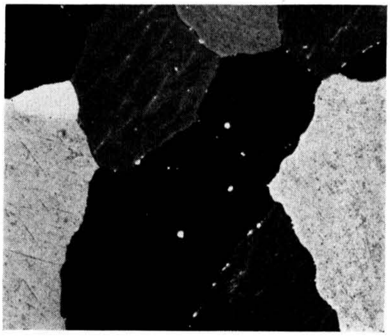

FIG. 29. Zirconium, same as Fig. 28 but 4 hr at 600°F and water quenched. Note decreased amount of hydride phase. Polarized light. 150×

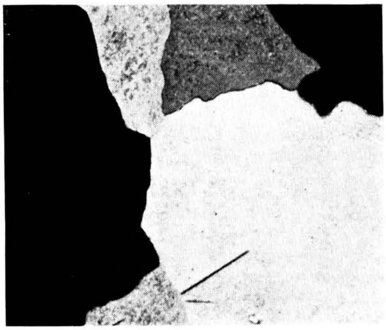

FIG. 30. Zirconium, same as Fig. 28 but 1 hr at 800°F and water quenched. Note hydride phase completely dissolved and only one phase, α zirconium is evident. Polarized light. 150×

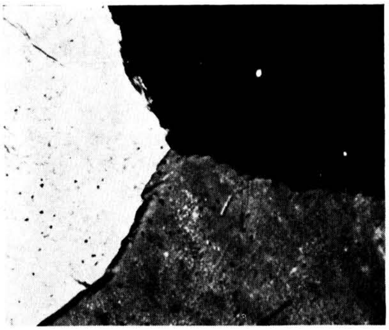

FIG. 31. Electrolytically produced zirconium metal, vacuum annealed 850°C for 5 hr, and furnace cooled. Hydride phase is still evident. 150×

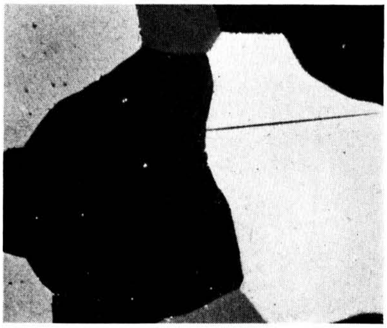

FIG. 32. Same as Fig. 31. Heated in a vacuum at 850°C for 5 hr but degassed in an actively pumping system at 0.02 μ pressure for 5 hr. Hydride phase has disappeared. Polarized light. 250×

850°C in a vacuum system which is being actively pumped, and a pressure of less than 0.02 μ is obtained, and this specimen is then furnace cooled, this second phase has disappeared, as is shown in the photomicrograph of Fig. 32. The fact that the acicular phase, present in the annealed specimen, disappears on heating to a relatively low temperature followed by quenching and by degassing at a higher temperature in a vacuum, establishes this phase as a hydride. Neither the oxide, carbide, or nitride becomes soluble at these low-solution treatment temperatures, nor can zirconium be degassed of them by an 850°C vacuum treatment.

CONCLUSIONS

A practical electrolytic process has been evolved for the production of pure zirconium metal. The method entails the electrolysis of K_2ZrF_6 in molten NaCl under a protective argon atmosphere.

Metal so produced is in the form of coarse crystalline dendrites which may be consolidated by standard arc melting or powder metallurgical techniques. The resultant product is satisfactory from a purity, hardness, and ductility standpoint, and is comparable to sponge produced by magnesium reduction of the chloride. Improvements in purity of the starting material and refinements in the recovery procedure have made this possible.

The fluoride process utilizes readily available materials. The double fluoride itself is easily prepared from the oxide, silicate, or zirconate by normal chemical procedures.

Standard electrolytic equipment with some modification could be employed for commercial operation. Provision must be made for a protective atmosphere and elimination of chlorine corrosion.

The process may be run on a semicontinuous basis, a number of runs being made on the same salt bath simply by charging fresh K_2ZrF_6 to the electrolyte. The bath life is limited only by the buildup of NaF and KF in the salt system, making it more refractory and less conductive. A high fluoride bath is also more susceptible to polarization.

The process is operable within broad limits with respect to temperature, voltage, current, and zirconium concentration. The bath may be run from 790°–1000°C, but maximum efficiency is obtained from 800°–850°C. Voltages over 2.0–2.5 volts must be used to obtain a satisfactory deposit. An upper current density limit of about 500 amp/dm^2 is necessary to avoid a very fine particle size deposit. An optimum initial K_2ZrF_6 concentration lies in the range of 30–35 weight percent, although the process functions with less efficiency using baths of 1–40% K_2ZrF_6.

Zirconium produced by the fluoride process is of 99.8–99.9% in purity with average values of about 0.05% carbon, 0.05% oxygen, and 0.003% nitrogen being obtained. It has a hardness of Rockwell B 80–85. Aside from titanium and hafnium, metallic impurities are very low.

The process, as developed to this point, gives a product satisfactory for most applications. The prime factors contributing to this development are use of pure materials, a protective atmosphere, and a careful recovery procedure.

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

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Corrosion Inhibition in Acid Solution[1]

CECIL V. KING AND EDWARD HILLNER

Department of Chemistry, New York University, New York, New York

ABSTRACT

Cylinders of iron, zinc, and cadmium were rotated in a highly corrosive solution of acid containing nitrate ion as a depolarizer, as described previously. Three kinds of inhibitors were added to the solution: (*a*) dichromate ion plus complexing or chelating agents for metal ions; (*b*) a wetting or emulsifying agent which is strongly adsorbed; and (*c*) a reagent which forms a very insoluble precipitate with ferrous and ferric ions. Measurements of the effectiveness of these inhibitors are given.

INTRODUCTION

As shown previously (1), iron, zinc, and cadmium dissolve at approximately the same diffusion or transport-controlled rate, in dilute hydrochloric acid with excess of a suitable depolarizer present. Low concentrations of dichromate ion reduce the dissolution rate considerably. Fluoride ion improves the inhibiting effect of the dichromate; presumably, it converts ferric and chromic ions formed to soluble complexes, and prevents precipitation of nonadherent or porous hydroxides.

One objective of the present work was to find if complexing or chelating agents for ferrous, ferric, and chromic ions would be generally effective as inhibition "promoters" with dichromate, and if any would be superior to fluoride ion in this respect.

A second objective was to investigate the effect of emulsifying certain water-insoluble chelating agents, and other insoluble compounds which have been reported to confer low reactivity to solid surfaces by strong adsorption. The emulsifying agents were found to be just as effective when used alone, and experiments with one of them are reported below.

As a third objective of this exploratory work, a search was made for a reagent which would form a very insoluble, adherent precipitate with the first metal ions dissolved, since this should be an effective method of inhibition. With iron, cupferron was found to be a good inhibitor of this type; unfortunately, the compound is not very stable in acid solutions.

EXPERIMENTAL

The pure metals used were described previously (1). The cylinders varied from 1.75 to 2.0 cm in diameter, and were always rotated at 15000 ± 200 cm/min peripheral speed. Cylinder lengths were: iron 3.2 cm, zinc 2.5 cm, cadmium 2.6 cm.

The metals were abraded with No. 600 silicon carbide paper and weighed before each run; afterward, they were wiped with filter paper wet with water or alcohol, rinsed with alcohol, dried, and reweighed. Only total weight losses for the time specified are given. Most of the experiments were carried out at room temperature, as given in the tables.

For a reference corroding solution, a mixture containing $0.02M$ HCl, $0.06M$ KNO_3 was used. In each experiment with this and other mixtures, the solution volume was 250 ml. Since some of the reagents change the *p*H, measurements were made with a Beckman meter. All solutions were exposed to the air.

Many of the experiments were repeated once or more, and the reproducibility was, in general, no worse than ±0.2 mg. When longer runs were made, or when the cylinders were reimmersed in the same or a fresh solution after weighing but without repolishing, the corrosion rate usually increased with time. This was especially true of iron, where pitting was quite evident, as noted below.

Dichromate of course cannot be used with reagents which reduce it. No such reduction was noticed except with cupferron, and dichromate was not needed in experiments with this compound.

Chemicals used were of the best commercial grades. Cupferron (the ammonium salt of *N*-nitrosophenylhydroxylamine) is commonly available for analytical purposes. Sodium gluconate and glucono-δ-lactone were supplied by Charles Pfizer and Company, Brooklyn, N. Y. Ethylene diaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) were supplied by Alrose Chemical Company, Providence, R. I. Thenoyltrifluoroacetone (TTA) was from the Dow Chemical Company, Pittsburg, Calif.

RESULTS

Table I shows the weight loss of the cylinders in the $0.02M$ HCl, $0.06M$ KNO_3 solution alone and

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TABLE I. *Weight loss, mg in 5 min, in 250 ml 0.02M* HCl, *0.06M* KNO_3, *30 ± 1°C, 15,000 cm/min peripheral speed*

$K_2Cr_2O_7$	Fe	Zn	Cd
—	76	78	148
0.01*M*	5.7	4.8	6.7

TABLE II. *Weight loss in mg, in* HCl, *0.06M* KNO_3, *sodium gluconate, 28-30°C, 15,000 cm/min*

	HCl *M*	Gluconate *M*	$K_2Cr_2O_7$ *M*	Time	Wt loss	*p*H
Iron	0.02	0.01	—	5 min	2.3	2.1
	0.02	0.01	0.01	5	1.4	2.1
	0.02	0.04	0.01	5	1.4	3.5
Zinc	0.02	0.01	—	5	44	2.1
	0.02	0.01	0.01	15	2.3	2.1
	0.02	0.04	0.01	15	−0.3	3.5
	0.03	0.04	0.01	2 hr	−0.2	3.4
	0.04	0.04	0.01	3 hr	−0.2	2.6

with added $K_2Cr_2O_7$ under the conditions of these experiments. Without dichromate, about 50% of the acid is used up in five minutes, and if the initial concentration were maintained, the weight loss would be about 30% greater.

Sodium gluconate is widely used as a complexing agent for iron and other metal ions. The salt increases the *p*H of the acid solution, and in some experiments additional HCl partly compensated for this. Results of experiments with gluconate are given in Table II.

The dissolution rate of iron is decreased by the gluconate alone, even more when dichromate is present. In the latter solutions, the cylinder became coated with a light orange film, which wiped off easily with alcohol. On longer runs the dissolution rate became higher and the iron cylinder started to form pits.

The gluconate-dichromate mixture was more effective with zinc than with iron, being fully protective for 3 hr at a *p*H of 2.6. The weight increases shown in Table II are probably due to an oxide film, although this was invisible and the metal surface remained bright. In the runs in which weight was lost the zinc acquired a very light yellow film.

In similar solutions containing dichromate and gluconate, a cadmium cylinder lost a few mg in 5 min.

Gluconic acid is easily formed by hydrolysis of glucono-δ-lactone. To obtain solutions containing gluconic acid with a *p*H of 1.8, the lactone was added to the 0.02*M* HCl, 0.06*M* KNO_3 mixture and the solution allowed to stand for about 2 hours. The corrosion rates with both iron and zinc were larger than those given in Table II at *p*H = 2.1.

TABLE III. *Weight loss in mg, in* HCl, *0.06M* KNO_3, *in solutions saturated with EDTA, 25°-28°C, 15,000 cm/min*

	HCl *M*	$K_2Cr_2O_7$ *M*	Time	Wt loss	*p*H
Iron	0.02	—	5 min	7.0	1.7
	0.02	0.01	5	2.8	1.7
	0.01	0.01	5	0	2.0
	0.01	0.01	15	0.7	2.0
	0.01	0.01	2 hr	5.5	2.0
Zinc	0.02	—	5 min	96	1.7
	0.02	0.01	5	10	1.7
	0.01	0.01	2 hr	0	2.0
	0.01	0.01	20 hr	0	2.0
Cadmium	0.01	0.01	5 min	3.1	2.0

EDTA is not very soluble in water (about 0.005*M*) and is commonly used in the form of the more soluble salts, as a sequestering or chelating agent in neutral or basic solutions. In the present experiments, the solutions were saturated with the acid form of the compound, and in some cases the hydrochloric acid was reduced to 0.01*M* to keep the *p*H near 2.0. Dissolution experiments with EDTA are summarized in Table III. With dichromate present the iron acquired a light yellow film, the cadmium a light brown film; both rubbed off easily with alcohol. The zinc remained bright when no weight was lost.

DTPA has been reported to be a more effective chelant for some metal ions in acid solutions than EDTA. Solutions to which it was added, with a *p*H of 1.9, proved to be somewhat more corrosive than those described in Table III.

Citric acid forms chelates with both bi- and trivalent metal ions (2, 3). Experiments were run with citric acid in the corroding solution as shown in Table IV.

A number of substances, added to a hydrochloric

TABLE IV. *Weight loss in mg in solutions containing citric acid, 0.06M* KNO_3, *21°-25°C, 15,000 cm/min*

	HCl *M*	$K_2Cr_2O_7$ *M*	Citric acid *M*	Time	Wt loss	*p*H
Iron	—	—	0.2	5 min	2.4	1.85
	—	0.01	0.2	5	9.0	1.85
	0.01	—	0.01	5	4.4	2.1
	0.01	0.01	0.01	5	1.2	2.1
Zinc	0.01	—	0.01	5	74	2.1
	0.01	0.01	0.01	5	0	2.1
	0.01	0.01	0.01	1 hr	0.9	2.1
	0.01	0.01	0.01	3 hr	6.4	2.1
	0.01	0.01	0.01	23 hr	21	2.1
Cadmium	0.01	—	0.01	5 min	85	2.1
	0.01	0.01	0.01	5	31	2.1

TABLE V. *Weight loss in mg, in 0.5M acetic acid, 0.06M* KNO$_3$, *p*H = *2.5, 27°–29°C, 15,000 cm/min*

	K$_2$Cr$_2$O$_7$ *M*	Time	Wt loss
Iron	—	5 min	5.5
	0.01	5	0
	0.01	3 hr	75
Zinc	—	15 min	986
	0.01	15	−0.1
	0.01	48 hr	+0.1

acid-nitrate mixture or to nitric acid alone, decrease the dissolution rate of iron (4). Nitrate does not act well as a depolarizer with citric acid alone; the acid probably enhances protection by an air-formed oxide film. The same is true of sodium gluconate (Table II).

Citric acid has no such protective effect with zinc unless dichromate is present also.[2] The experiments with zinc in Table IV were repeated several times with different cylinders of both SP and reagent grade zinc, in runs of several hours duration. The weight loss averaged about 1 mg/hr, but it should be noted that an appreciable fraction of the acid is neutralized in 23 hr. The metal remained bright and shiny, but in every case two or three comparatively deep pits appeared near the lower end of the rotating cylinder. At first it was thought that there were flaws in the metal but in the repeated experiments this proved not to be the case.

Acetic acid.—It was shown by Abramson and King (4) that iron dissolves in acetic acid-potassium nitrate solutions about one-tenth as fast as in strong acids, indicating that the rate is not diffusion-transport controlled. It has also been shown by Hackerman and Hurd (5) that dichromate reduces the corrosion of iron in air-free acetic acid solutions of *p*H near 3. The experiments of Table V were run to test the effect of dichromate in more concentrated acetic acid with air and nitrate ion present, with both iron and zinc.

Dichromate protects iron temporarily in this solution, but the effect breaks down and pits appear on the surface. When the iron was removed and repolished after a 1 or 2 hr run, it was again completely protected for 5 or 10 min in the same solution. The zinc cylinder was left in the solution without dichromate for 15 minutes inadvertently. The protective effect of dichromate is remarkable; cadmium was not similarly protected.

Other complexing agents.—Many reagents form complexes or chelates with the metal ions concerned here, and some which looked more promising as inhibition "promoters" with dichromate were tried as mentioned below.

Sulfosalicylic acid forms soluble complexes with ferrous and zinc ions (2), with ferric ion (3), and a rather unstable complex with chromic ion (6). When added to the dichromate-containing corroding solution making the *p*H = 1.7, it increased the dissolution rate of all three metals.

Acetylacetone chelates with bi- and trivalent metal ions (3). When added in concentrations of 0.05 and 0.1*M* to the dichromate-containing corroding solution, it reduced the dissolution to about 2 mg in 5 min in all three cases. Visible films were formed; the chelates are apparently not very soluble.

TTA was originally made to assist in extracting metal salts into nonaqueous solvents (7). It is slightly soluble in water, and with a trace of ferric ion added to the saturated solution, a pink coloration and eventually a precipitate appear. When the HCl-KNO$_3$-K$_2$Cr$_2$O$_7$ solution was saturated with TTA, no effect was found on dissolution rates, however.

Emulsions of TTA were no more effective than the emulsifying agent alone. The same was true of emulsions of reagents which are reported to be strongly adsorbed and to deactivate the surface of metals. Two such reagents tried were perfluorodecanoic acid (8) and tricresylphosphate.

Aerosol OT (dioctyl ester of sodium sulfosuccinate) was one of the emulsifying agents used. When it alone was added to the HCl-KNO$_3$ solutions, the results shown in Table VI were obtained. Dichromate did not increase the inhibition. The results indicate that Aerosol is strongly adsorbed and that the metal surface becomes approximately saturated at a low concentration. However, the adsorbed film is not completely protective.

Cupferron.—This compound has long been used to precipitate ferric iron quantitatively (9). The

TABLE VI. *Weight loss, mg in 5 min, in 0.02M* HCl, *0.06M* KNO$_3$, *with Aerosol OT; 25° ± 1°C, 15,000 cm/min*

Aerosol wt %	Wt loss		
	Fe	Zn	Cd
0.001	67	60	126
0.005	2.5	11	4.8
0.01	2.9	1.7	0.9
0.05	2.9	1.6	1.5
0.10	2.5	1.5	2.5
0.20	2.7	1.5	5.7

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[2] Loss of dichromate is never important in the experiments. The concentration used, 0.01*M*, is twice the amount which gives maximum inhibition when used alone (1). While 15 meqs of dichromate was present in the solutions, 21 mg of zinc (Table IV) corresponds to only 0.64 meq, assuming that only dichromate was reduced. Nitrate may have been reduced as well, but there was no way of testing this.

TABLE VII. *Weight loss of iron cylinder, mg in 5 min, in 0.02M* HCl, *0.06M* KNO_3, *with cupferron; 30°–33°C, 15,000 cm/min*

Cupferron M	Wt loss	Cupferron M	Wt loss
0.001	69	0.0034	−0.1
0.0025	62	0.0038	−0.1
0.003	1.3	0.005	−0.1
0.0032	0.2	0.01	−0.2

TABLE VIII. *Weight loss of iron cylinder in mg, in cupferron solutions with 0.06M* KNO_3, *0.5 gram acetphenatidin/liter, 15,000 cm/min*

Cupferron M	HCl M	Time hr	Wt loss	Temp, °C	pH
0.01	0.02	3	0.9	15–17	2.5
0.10	0.02	19	0	14–20	5.2
0.05	0.04	19	0.8	28–30	3.5
0.05	0.06	19	5.3	28–30	2.0

ferrous salt is similarly insoluble; both are no doubt chelates. Cupferron was found very effective in protecting iron in 5-min runs, as shown in Table VII. After each run the iron was covered with a golden brown film, most of which came off with alcohol, leaving a very shiny surface. The small weight gain at concentrations above 0.0032*M* must have been due to precipitate which was not removed.

The protective effect broke down in longer runs, apparently due to decomposition of the cupferron. The compound is more stable at lower temperatures, and is possibly stabilized by the addition of small amounts of acetphenatidin (acetophenetidine) to the solution, as suggested by F. G. Germuth. Some experiments with various concentrations of cupferron and HCl are given in Table VIII.

Cupferron does not act as an inhibitor with zinc or cadmium, since no insoluble compounds are formed.

Potentials of the corroding metals.—The potentials of the rotating cylinders were measured against a saturated calomel half-cell. In 0.02*M* HCl, 0.06*M* KNO_3 the values were as follows: iron, −0.48 volt; zinc, −0.98 volt; cadmium, −0.71 volt. On addition of 0.01*M* dichromate the potentials were decreased numerically (became less anodic) by 0.15 to 0.20 volt. The solutions which gave best inhibition showed no greater, and generally a smaller effect. The potentials were followed for 5 min only, since there was no evidence of a rapid drift. The behavior is quite different from that of iron in neutral or slightly alkaline, aerated solutions of oxidizing or nonoxidizing inhibitors (10).

DISCUSSION

Previously the authors (1) followed the view of Mayne and Pryor (12) that chromate acts as an inhibitor by direct oxidation of iron to the oxide, probably after first being adsorbed on the metal surface. In the acid solutions employed here this would apply to the dichromate ion, and to zinc and cadmium as well as iron. To be protective, the oxide films would have to be of the anhydrous, crystalline types which are not easily dissolved by acids.

The ordinary dissolution of these metals has to be accompanied by a rise in *p*H at the surface; when nitrate is present, ammonium ion and other reduction products are formed (11):

$$\left.\begin{array}{l} 4Fe + NO_3^- + 10H^+ \\ \qquad \rightarrow 4Fe^{++} + NH_4^+ + 3H_2O \\ 4Zn + NO_3^- + 10H^+ \\ \qquad \rightarrow 4Zn^{++} + NH_4^+ + 3H_2O \end{array}\right\} \qquad (I)$$

It is quite possible that ferrous and zinc hydroxides precipitate and are later redissolved. In fact, it is almost certain that the surface of iron is never quite clean in such solutions, at least in the presence of air.

Direct oxidation of the metal by dichromate also increases the *p*H at the surface. Since Cr_2O_3 or $Cr(OH)_3$ is formed in only small amounts along with Fe_2O_3, even in chromate inhibition in neutral solutions (12), Cr^{+++} is written in the following equations:

$$\left.\begin{array}{l} 2Fe + Cr_2O_7^= + 8H^+ \\ \qquad \rightarrow Fe_2O_3 + 2Cr^{+++} + 4H_2O \\ 3Zn + Cr_2O_7^= + 8H^+ \\ \qquad \rightarrow 3ZnO + 2Cr^{+++} + 4H_2O \end{array}\right\} \qquad (II)$$

If any ferrous ion is formed by reaction (I) it would also be oxidized rapidly by dichromate, using up hydrogen ions.

The function of complexing or chelating agents is, then, to prevent precipitation of oxides or hydroxides by forming soluble complexes with ions not involved in forming the tightly adherent film of impervious oxide. An alternative view is that these reagents act to clean the surface of air-formed, less protective films, thus allowing free access of dichromate ion to be adsorbed. Since fluoride ion is an effective promoter with dichromate ion on zinc, its main action would appear to be to keep chromic ion in solution rather than to clean the surface. However, it has been reported that chromic and fluoride ions form a stable complex only very slowly (13). Gluconic acid and EDTA are rather nonselective; it would be useful to have rapid, specific chelants for each of the ions involved.

Chelants which form very stable complexes will probably prove to be the best promoters with dichromate. The chelates, however, must be soluble; acetylacetone forms moderately stable complexes, but is not very protective because a porous, adsorptive film is formed. Citric and sulfosalicylic acids form the least stable complexes of the reagents used. TTA is too insoluble in water, and chelates are formed too slowly in the very dilute solution. EDTA forms very stable compounds with ferrous and ferric ions. Not many stability constants with chromic ion are known.

It is possible that extremely stable chelates will prove undesirable in inhibition, since they may cause, rather than hinder, dissolution. It has been reported that inactive metals such as copper can dissolve, with evolution of hydrogen, in solutions of strong chelants for their ions [(3) p. 57].

The data show that protection is obtained more easily when the *p*H is above 2 than when it is lower. Gluconic acid, DTPA, and sulfosalicylic acid may have seemed more favorable at a somewhat higher *p*H. The effect of *p*H is evident with EDTA in Table III. At least two factors are involved: some chelants form weak acids, or chelate with hydrogen ion; and strongly acid solutions dissolve oxide films, or attack flaws in them, more rapidly.

Cadmium is less easily protected than iron and zinc in these acid solutions. This no doubt indicates that the oxide formed is more rapidly soluble in acids, or does not have a suitable crystalline form to be adherent and protective. The effect of a simple adsorption inhibitor (Aerosol) is at least as great as on zinc and iron (Table VI).

Iron is more difficult to protect than zinc, and preliminary study shows that the reason lies in the nature of the iron surface as prepared for the experiments. The breakdown of protection in the best solutions (Table III) is accompanied by pitting, which is visible under a microscope at an early stage and in some cases definitely takes place along abrasion marks left in polishing. Finer polishing, or a short chemical etch, results in longer protection before pits become visible. This aspect of protection is under further study.

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

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Microstructure and the Corrodibility of Steel in Inhibited Hydrochloric Acid Solutions[1]

P. H. Cardwell

Dowell Incorporated, Tulsa, Oklahoma

ABSTRACT

In a study of the corrodibility of steels it was found that the degree of annealing as measured by the resolution of the pearlite, the grain size, and the presence of the Widmanstatten structure has considerable influence on the corrosion rate of the steels. Two acid inhibitors were examined in order to investigate materials which could be used satisfactorily to protect different grain structure steels during industrial applications of inhibited hydrochloric acid solutions.

Introduction

Heat treating a steel changes its resistance to corrosion by certain media (1). Under specific corrosive conditions a martensite steel may have a different corrodibility than other structures such as ferrite with lamellar pearlite or spheroidite, and tempered martensite. Since the corrosion of a metal takes place upon its surface, which is composed of crystal faces, edges, corners, boundaries, and disturbed crystal layers (2), and since the surface property of a metal is a composite of all the properties of these many types of exposed surfaces, it is understandable that the corrodibility is related to the surface property of the metal. Thus, it is not too surprising that a major change in the grain structure of steel, as from martensite to pearlite and ferrite, has an influence on the corrodibility of the steel; however, there seems to be very little information available as to the influence of only slight changes in the grain structure on the corrodibility of specific types of steel such as pearlite.

The studies reported in this investigation of microstructure and corrodibility were made on samples of steels which are in commercial use. In the examination of the steels the following items were studied: importance of the degree of annealing of steels, the influence of grain size, the effect of Widmanstatten and spheroidite structures, the significance of cold-worked metal, and the value of two different types of acid inhibitors to protect metals of various microstructures. It is realized that the preferred method of study is to vary only one variable, e.g., grain size, maintaining all others constant; however, the object of this investigation was somewhat different in that it was desired to know the effect of these various items in relationship to the other items upon the steels in actual commercial use. It should be realized that, due to the nature of this investigation, definite conclusions as to the effect of any one variable could not be measured. However, certain indications can be pointed out when specific combinations of these items are present. Such information is of commercial importance.

Degree of Annealing

Recently, it was reported (3) that the corrodibility of 16 different steels in 10% inhibited hydrochloric acid increased slightly with increase in carbon content. Many of the steels did not show this relationship as well as others, and, for this reason, the present study was made of microstructures to determine its influence on the relationship of the corrodibility to carbon content.

Experimental results.—The various steels investigated and their corrodibility in 10% inhibited hydrochloric acid are given in Table I. The steels were in the form of tubing, with the exception of the SA-70, SA-212A, and SA-105I which were plate stock, and SA-7 and SAE-1035 which were forged boiler handhole plates. This table regroups data previously reported (3).

The metals were then annealed and the corrosion rates redetermined. With the majority of the metals there was no change, but with two of the SA-83A samples, one of SA-192, one of SA-210, and with SA-53, SA-7, and SAE-1035, the annealed specimens gave lower corrosions rates. These last two steels might have been expected to give lower corrosion rates after annealing because of the change from a cold-worked structure produced from machining. The annealing was accomplished by heating the metal specimens for an hour at a temperature of 857°C in a neutral salt bath, followed by slow cooling to atmospheric temperature.

The inhibitor used in concentration of 0.4% in the hydrochloric acid solution was an aromatic nitrogen-

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TABLE I. *Corrosion rates, grain size, and magnification required to resolve pearlite of various steels*

Metal	Corrosion rate 10% inhibited HCl, mdd	Percentage carbon	Grain size	Resolution of pearlite
SA-7	7320	0.21	Medium-fine ASTM No. 5-6	Partially 500×
SA-7 annealed	1950	0.21	Fine ASTM No. 6-7	Almost completely 500×
SA-53 annealed	2540	0.28	Fine ASTM No. 7	Almost completely 500×
SA-70	1710	0.16	Medium ASTM No. 5	Partially 500×
SA-83A S.1	2780	0.17	Very fine ASTM No. 8	Partially 1000×
SA-83A S.2	4300	0.16	Fine ASTM No. 6-7	Not resolved 1000×
SA-83A S.2 annealed	2200	0.16	Fine ASTM No. 7	Almost completely 500×
SA-83A S.3	7420	0.16	Very fine ASTM No. 8	Not resolved 1000×
SA-83A S.3 annealed	3030	0.16	Medium ASTM No. 5	Partially 1000×
SA-105I	2340	0.17	Fine ASTM No. 7	Almost completely 1000×
SA-106A	2680	0.23	Fine ASTM No. 7-8	Partially 1000×
SA-192 S.1	1810	0.16	Fine ASTM No. 7-8	Partially 500×
SA-192 S.2	3180	0.17	Fine ASTM No. 6-7	Not resolved 1000×
SA-192 S.2 annealed	2640	0.17	Fine ASTM No. 6-7	Partially 1000×
SA-210 S.1	4740	0.32	Very fine ASTM No. 8	Partially 1000×
SA-210 S.2	2780	0.29	Medium-coarse ASTM No. 3-4	Almost completely 500×
SA-210 S.2 annealed	2240	0.29	Very fine ASTM No. 8	Almost completely 500×
SA-210 S.3	5270	0.35	Fine ASTM No. 6-7	Partially 1000×
SA-210 S.4	2680	0.24	Medium-fine ASTM No. 5-6	Partially 750×
SA-212A	2440	0.28	Medium-fine ASTM No. 6	Partially 500×
SAE-1035	7360	0.23	Fine ASTM No. 6-7	Almost completely 500×
SAE-1035 annealed	2680	0.23	Medium-fine ASTM No. 5-6	Almost completely 500×
Boiler tube inner surface	31,100	0.15	Medium-fine ASTM No. 5-6	Spheroidized
Boiler tube outer surface	2000	0.15	Medium-fine ASTM No. 5-6	Spheroidized
Boiler tube outer surface annealed	1860	0.15	Medium-fine ASTM No. 5-6	Almost completely 100×

sulfur coal tar material.[2] The inhibitor contained a saturated straight chain (average 10 carbon) hydrocarbon sodium sulfonate wetting agent to increase its efficiency (4).

In the investigation of the microstructure by means of metallographic examination, the steel specimens were mounted, polished, and etched with 5% nital. The specimens were examined under the microscope at various magnifications in order to resolve the pearlite. The results of this investigation are summarized in Table I.

Discussion.—In the metallographic study of the various boiler metals, it was found that of steels which were examined, all were pearlitic except the SA-53 which had a Widmanstatten structure. This is the structure obtained by heating to a relatively high temperature and then cooling rapidly. It is of interest to note that the Widmanstatten structure was changed to pearlite upon annealing, and this was accompanied by a decrease in corrosion rate.

In this study, the degree of annealing was determined by means of the magnification necessary to resolve the pearlite. The lower the magnification necessary to resolve the pearlite, the more complete is the annealing. It was found that the degree of annealing varied considerably from steel to steel. In some of the steels, the pearlite was almost completely

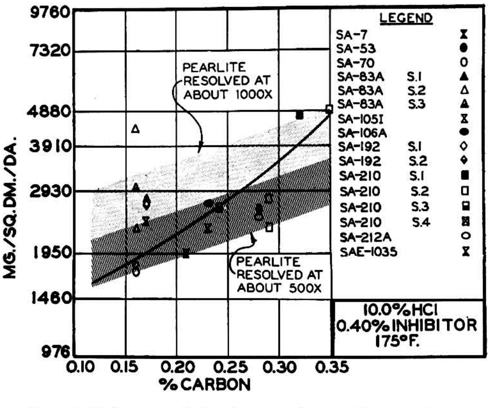

FIG. 1. Influence of the degree of annealing on the corrodibility.

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[2] Dowell Incorporated A25.

resolved at 500 diameters while in others the pearlite was not resolved at 1000 diameters.

The influence of the degree of annealing on the corrodibility of the steels is given in Fig. 1, a previously published curve (3) to which have been added shaded areas of corresponding degrees of annealing. It shows that degree of annealing has considerable influence on the corrodibility of steels in inhibited hydrochloric acid solutions. The more complete the annealing, the lower is the corrosion rate of the metal in the acid. This graph indicates that the variation of these data from the mean curve when corrosion rates are plotted against carbon content is partly due to the difference in the degree of the annealing of the steel.

INFLUENCE OF GRAIN SIZE

There has been considerable work (1, 5) reported as to the influence of grain size on corrodibility. At first glance, the work seems confusing, but, undoubtedly when the complete system of metal, microstructure, and corrosive media are taken into consideration, the results are not contradictory. While it would be expected that the large crystals would be more stable than the small ones, there are other factors which must be considered, such as presence and location of the cementite. In addition to this, consideration has to be given as to which is the most susceptible to attack by the corrosive media, the grain boundaries or the grain itself. It would be expected that with inhibited hydrochloric acid solutions the crystals would be more susceptible to attack than the cementite grain boundaries. If this is the case, then the large grains will be attacked in preference to the fine grains.

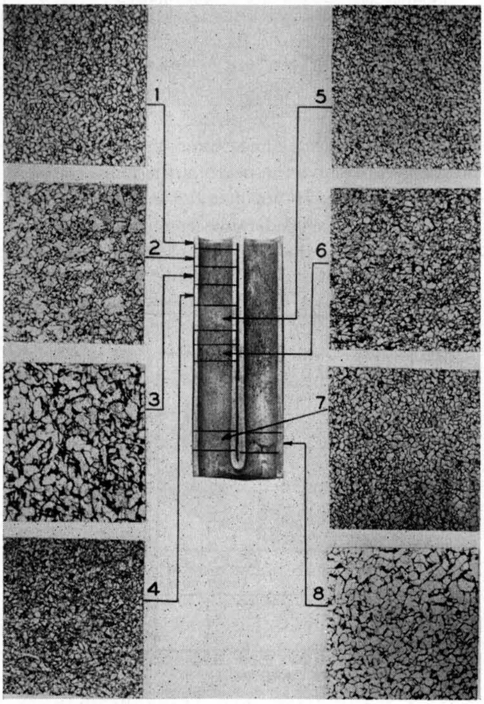

FIG. 2. Microstructure of section of bifurcate tube

In the study of the resolution of the pearlite of the boiler steels, the grain size was determined. The grain size of the majority of these steels varied from medium fine to fine (ASTM No. 5–8); the only exception was one of the SA-210 samples which had a medium-coarse (ASTM No. 3–4) grain. Upon annealing, this SA-210 sample had a very fine (ASTM No. 8) grain size and the corrosion rate was lowered slightly, from 2780 to 2240 mdd.

A considerable amount of information as to the effect of grain size has been obtained from a study of microstructure and corrodibility of bifurcate tubes. The metallographic examination of the metal showed that the structure beyond the weld-heat affected zone, that is, the normal nonaffected metal, was of a smaller grain size than were the grains in the heat affected zone. When such tubes were exposed to the nitrogen-sulfur coal tar inhibited hydrochloric acid solutions, pitting occurred in the areas of large grains. The microstructures of a tube are shown in Fig. 2 and 3.

The upper part of the double tube end ([1], Fig. 2)

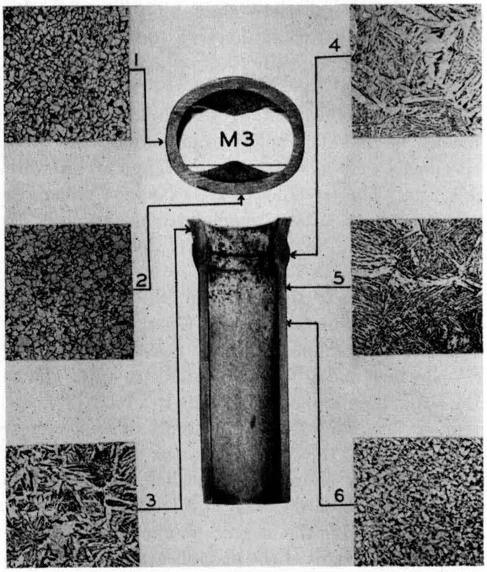

FIG. 3. Microstructure of section of bifurcate tube

showed only a small amount of pitting and had a fine grain structure ASTM No. 8. The metal farther down the tube toward the juncture between the double and the single tube showed considerable pitting in the area of larger grain structure ASTM No. 6–7 ([2], Fig. 2) and ASTM No. 5–6 ([3], Fig. 2). Below the ptted area closer to the juncture was a section of the double tube which had a very fine grain structure, ASTM No. 8 ([4] and [5], Fig. 2). The fine grains of this area merged into an area of slightly larger grains, ASTM No. 7, ([6], Fig. 2) which were pitted. A large pit was noted in one of the tubes which was found to be in an area of medium-fine grain structure, ASTM No. 6, ([8], Fig. 2).

The section of the tube between the double and single tube was pitted and showed a fine grain structure, ASTM No. 7, ([1] and [2], Fig. 3). The single end of the bifurcate showed pitting at and around the welded area. The crystal structure of the weld metal is shown by [4], Fig. 3 and of the heat affected zone by [3] and [5], Fig. 3. Below this area was a very fine grain, ASTM No. 8, which was not pitted.

Whenever metal is welded together, there always seems to be a change in crystal structure (6) from that of the metal before welding, usually fairly fine grains going to a larger grain structure. The net result of the welding is to bring about an area of larger grain structure which merges on both sides into finer grain structures. The size, location, and amount of larger grain depends upon the temperature gradient brought about within the metal by the welding process (7).

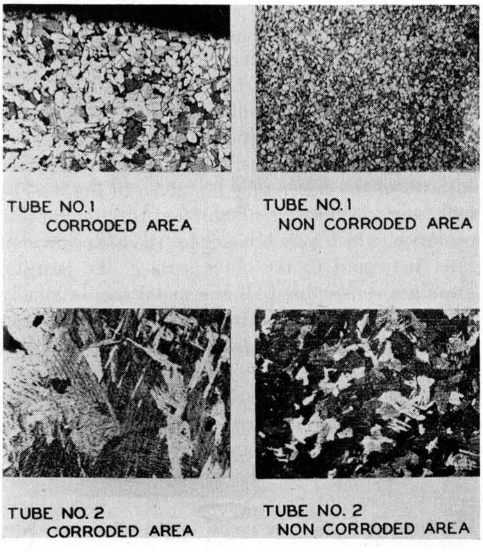

FIG. 4. Corrosion adjacent to welds. Magnification, approx. 75×.

This change in crystal structure has been found also in boiler tubes which have been welded. In such tubes, a pitting type of corrosion has been found. The corrosion in these cases was discovered adjacent to the welds as shown in Fig. 4. The corrosion took place in the areas of large crystals and, in addition, in tube No. 2, the Widmanstatten structure was also found in the corroded area.

Other investigations (8) have shown that in metals in which there is a variation of crystal sizes, the attack is in the areas of large grains. The steel tubing used in gas distillate wells is usually upset on the ends in order to reinforce the strength at the threaded areas. The process of upsetting changes the crystal structure, and, if the tube is not heat treated sufficiently, there are areas of coarse grain structure adjacent to fine grains. With the upset tubing, the corrosion has been found in the areas of coarse grain structure which are always adjacent to the fine grain zones.

The reason for the pitting in the areas of large crystals seems to be due either to the large grains being more susceptible to attack, or to a galvanic effect of dissimilar metal structures in contact with each other. In studies of corrodibility in inhibited hydrochloric acid solution of metals possessing uniform but different grain structure, only slight variations in corrosion rates are found. This is shown in Table II. These data were obtained at 74°C using SAE 1020 steel in nitrogen-sulfur coal tar inhibited 10% hydrochloric acid solution. Thus, it is believed that the corrosion is caused in the main by the presence of dissimilar metal structures and, secondarily, by larger grains.

EFFECT OF WIDMANSTATTEN STRUCTURE

The presence of Widmanstatten structure is fairly common in boiler steels. Such structures are usually found in tubes which have been welded and in forged handhole caps, as well as manhole plates. The presence of the Widmanstatten structure and its influence on corrodibility has already been mentioned in the SA-53 steel of Table I and the boiler tube of Fig. 4. Additional information on Widmanstatten structure is given in Fig. 5 which shows the photomicrographs of boiler handhole caps. The first

TABLE II. *Grain size and corrodibility*

Crystal structure	Corrosion rate, mdd	Magnification to resolve pearlite
Medium—ASTM No. 4 and 5	1560	500×
Fine—ASTM No. 7 to 8	1270	1000×
Very fine—ASTM No. 8	1320	Not resolved 1800×
Partially spheroidized ASTM No. 6	1220	Not resolved 1800×

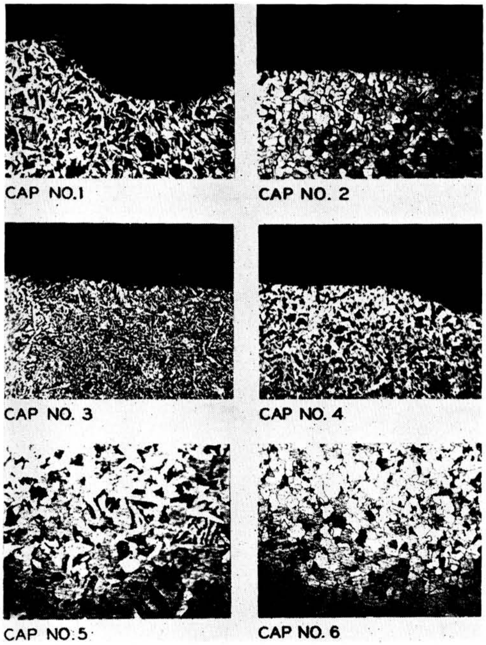

FIG. 5. Microstructure of boiler handhole caps. Magnification, approx. 75×.

TABLE III. *Boiler handhole caps*

Cap	Grain size ASTM	Corrosion rate, mdd	Magnification to resolve pearlite
1	5-6	585	Half at 1700×
2	5-6	391	Nearly all at 1700×
3	7	830	No resolution at 1700×
4	6	244	Nearly all at 400×

four caps were exposed to the nitrogen-sulfur coal tar inhibited 3.5% hydrochloric acid solutions for 6 hr at 65.5°C, and, of these, the only cap which showed any evidence of pitting was cap. No. 1. The corrosion rate, grain size, and magnification necessary to resolve the pearlite for the handhole caps are given in Table III.

The structure of the steel in cap No. 1 is chiefly pearlitic with the presence of some Widmanstatten structure. The grain size is medium fine (ASTM No. 5-6). In cap No. 2 the grain size is about the same as that of cap No. 1, whereas cap No. 4 has somewhat smaller grain size; but in both of these caps the crystals are more regular in shape and there is no Widmanstatten structure present. In the case of cap. No. 3, the grain size is fine and irregular. It appears that this cap may have been forged while fairly cool; as a result, the grains which were broken up by the forging had little or no opportunity to reform.

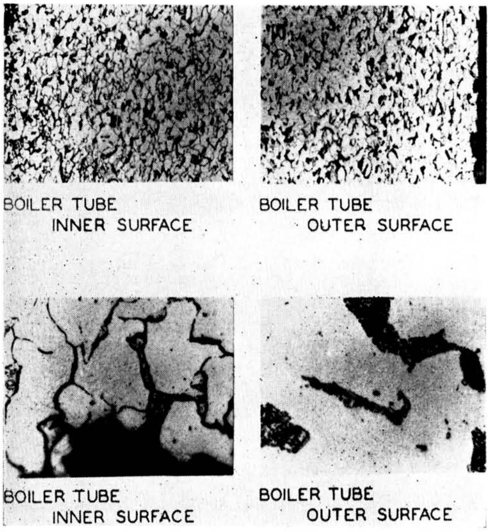

FIG. 6. Intergranular oxidation and spheroidite. Magnification, top, approx. 25×; bottom, approx. 500×.

As in the case of the boiler metals discussed earlier, the degree of annealing as measured by the resolution of the pearlite has considerable influence on the corrodibility of the handhole caps.

SPHEROIDITE

When the corrosion rate of a boiler tube taken from a superheater header of a high-pressure boiler was measured in the nitrogen-sulfur coal tar inhibited 10% hydrochloric acid solution at 74°C, it was found that the inner surface of the metal had a higher corrosion rate than the outer surface. The corrosion rate of the inner surface was 31,100 mdd, whereas for the outer surface the corrosion rate was 2,000 mdd, this latter result being about what would be expected for a steel containing 0.15% carbon.

The photomicrographs of the inner and outer surfaces of the boiler tube are given in Fig. 6. The inner surfaces have been subjected to intergranular oxidation, which may account for the high corrosion rate. In regard to the outer surface, the pearlitic areas are spheroidized. If the metal was originally pearlite, then this indicates that the tube has been heated for a considerable period of time at a temperature of 590° to 700°C.

The spheroidite can be changed into normal pearlite by annealing. The corrosion rate of the annealed pearlite specimen was found to be 1860 mdd. This would indicate that the spheroidization of the pearlite does not have an appreciable effect upon the corrodibility of the metal in the nitrogen-sulfur coal tar inhibited hydrochloric acid at 79°C.

This conclusion agrees with the corrodibility of laboratory-formed spheroidite as is given in Table II. In this connection, it is of interest to note that in the case of gas distillate well tubing (8, 9) the steel is more susceptible to attack when the pearlite becomes spheroidized. The reason for this was believed to be due to the corrosion protective film which, because of the crystal structure, gives better protection to pearlite than to spheroidite. It may be that the hydrochloric acid removes this protective film, resulting in spheroidite and pearlite steels having about the same corrosion rates in inhibited acid solutions.

PRESENCE OF COLD-WORKED METAL

In the construction of steel equipment, it is often necessary to use stressed metals. Boilers contain a considerable amount of cold-worked or stressed metals such as the rolled tube ends, the machined surfaces on the handhole caps, and the seats for these caps in the headers. When such metal is exposed to the usual inhibited hydrochloric acid solutions, pitting may occur in the stressed areas.

A handhole cap was subjected to 5% hydrochloric acid with the nitrogen-sulfur coal tar inhibitor for 19 periods of eight hours each at 65.5°C. It was mounted in a manner simulating boiler conditions so that acid contacted only the underside of the cap. The lip was pitted and a deep groove formed at the point of contact between the handhole cap and gasket. The crystal structure of the lip is given as cap No. 5 in Fig. 5. The grain size is rather large and angular, which indicates a stressed condition within the metal. It is possible to change the crystal structure of the handhole caps by annealing to give caps which are more resistant to corrosion.

A similar handhole cap was annealed and then subjected to the nitrogen-sulfur coal tar inhibited 5% hydrochloric acid solution. There was very little corrosion on the annealed plate. Its crystal structure is shown in Fig. 5, cap No. 6. Annealing reduced the grain size somewhat and the crystals are not angular.

EFFECT OF DIFFERENT TYPES OF INHIBITORS

Since industrial equipment is designed and built with steels containing different crystal structures which it is impossible to change once the unit is erected, it becomes necessary to select the inhibitor for the specific crystal structure conditions. In order to determine the effect of other inhibitors to prevent the pitting type of corrosion as obtained by the nitrogen-sulfur coal tar inhibited acid solutions, tests were performed using a rosin amine-ethylene oxide condensate as an inhibitor. This material polyethanol RAD-1112 (13) is surface active and functions as a combination inhibitor and wetting agent to prevent the attack of acid more effectively.

Using the polyethanol amine inhibitor in 5% hydrochloric acid solution, an unannealed handhole cap was treated. It showed slightly more attack than the annealed one above, but was much better than the unannealed one exposed to the nitrogen-sulfur coal tar inhibited hydrochloric acid solution.

Another comparison between the nitrogen-sulfur coal tar and the polyethanol amine inhibitors was made using bifurcate tubes. Two bifurcates which had identical crystal structures were subjected for 16 periods of six hr each to 7.5% hydrochloric acid solutions inhibited with these two materials.

In the case of the nitrogen-sulfur coal tar inhibitor, the acid caused pitting in the areas of the large crystals, and in these same areas Widmanstatten structure was also present. The tube subjected to the polyethanol amine inhibited acid solution did not pit even though the tube had the same crystal structure. An investigation of other bifurcate tubes containing only dissimilar metal structures, medium and fine grain, but no Widmanstatten structure, has shown that the polyethanol amine inhibited hydrochloric acid solutions do not cause pitting, whereas the nitrogen-sulfur coal tar inhibited hydrochloric acid solutions do.

The reason why the polyethanol amine is a more satisfactory inhibitor for hydrochloric acid solutions than a coal tar material, when dissimilar grain sizes and Widmanstatten structure are present, is not understood at this time. Part of the explanation may be that the polyethanol amine molecule is both a wetting agent and an inhibitor, whereas in the case of the coal tar inhibitor two different chemical molecules are used, a wetting agent and an inhibitor.

CONCLUSIONS

This investigation indicates that the crystal structure of the metal has considerable influence on its corrodibility in inhibited hydrochloric acid solutions. The more complete the annealing, as measured by the resolution of the pearlite, the lower is the corrodibility. When there is a variation in the grain size, pitting occurs in the area of larger crystals. This may be due, in part, to the larger crystals, but what seems to be more important is the presence of two dissimilar metal structures. The corrodibility is increased by the presence of Widmanstatten structure and cold-worked metal, whereas very little if any effect is obtained by spheroidizing the pearlite. The degree of influence of these various crystal structures is dependent upon the inhibitor used in the hydrochloric acid solution. The effect is much more pronounced in the case of a nitrogen-sulfur coal tar type inhibitor than with a polyethanol amine type.

ACKNOWLEDGMENTS

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

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Positive D-C Corona on Polyethylene-Insulated Wire in Air[1]

D. S. RODBELL,[2] J. B. WHITEHEAD, AND C. F. MILLER

The Johns Hopkins University, Baltimore, Maryland

ABSTRACT

An investigation of an apparent anomaly in the electric strength of air about polyethylene-insulated wires, under atmospheric conditions, when direct voltages are applied to the wire is described. Results show that the air surrounding the wire does break down when the gradient, due to the applied voltage, exceeds the accepted value for the electric strength of air, but the discharge is not maintained. An explanation of this self-quenching action is given.

INTRODUCTION

The corona discharge has been known and studied for many decades (1). The major objective of these investigations was either to establish accurate quantitative laws governing this phenomenon, or to explain the mechanisms involved in terms of fundamental processes (2–6).

From the work done to the present, it is felt that the corona discharge, in principle, is understood in terms of fundamental processes (3–5). The "Law of Corona" has been established as a valid empirical criterion for corona formation.

Some recent work at the Naval Research Laboratory (Appendix I) indicates an anomaly in the formation of positive corona on polyethylene-insulated wire in air under atmospheric conditions. It is the purpose of this paper to explain this apparent departure from a heretofore well-established law.

For the relatively simple geometry of a coaxial arrangement of a bare, round wire and a conducting outer cylinder with a potential difference between them, the gradient at the surface of the central conductor is given by

$$E_r = \frac{V}{r \ln R/r}$$

where V = the applied potential difference, r = the radius of the inner conductor, and R = the inner radius of the outer cylinder.

It is known from the Law of Corona (1, 7, 8) that the voltage gradient, at the surface of a wire of radius, r, at which the initial formation of corona occurs is given by

$$g = Am\delta + Bm\sqrt{\frac{\delta}{r}} \quad \text{max kv/cm}$$

where A and B are constants, m is an irregularity factor (= 1 for smooth uniform wires), and δ is the density factor (= 1 at STP).

So accurate is this law for predicting corona onset, that a Corona Voltmeter built upon this principle has been used as a secondary high voltage standard (9).

The theory of the positive corona discharge requires that there be one free electron in proximity to the corona-forming surface in order to initiate the avalanches (3, 4). The only requirement of the anode surface is that it establish an electric field at its surface which exceeds the dielectric strength of the air. Thus, assuming a smooth cylinder at atmospheric conditions, specification of only the radius of curvature establishes, by the Law of Corona, the critical gradient at the surface of the cylinder.

From the foregoing considerations, for a coaxial arrangement of cylinders with the outer being a conductor and the inner being at a positive potential with respect to the outer cylinder, and as long as the inner cylinder has quantitatively describable parameters, the field may be calculated, and prediction of the applied voltage that yields corona is possible. Corona onset is usually established by a visual glow, an audible hiss, or observing the abrupt increase in the average current flowing to the electrode. For polyethylene-insulated wire as the inner cylinder and positive direct voltage applied, no such indications can be observed (for alternating voltage no discrepancy is encountered). Direct voltages exceeding ten times predicted onset values fail to yield corona in this sense, and result in dielectric rupture of the polyethylene (see Appendix I).

This would indicate an anomaly in either the dielectric strength of air, or in the Law of Corona, both well-established. This paper will give experimental evidence that neither of these properties are, in reality, violated, and the explanation will be given which anticipated these results.

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[1] Manuscript received June 26, 1953. This paper was prepared for delivery before the New York Meeting, April 12 to 16, 1953.

[2] Present address: General Electric Research Laboratory, Schenectady.

DESCRIPTION OF APPARATUS

The direct voltages required for the experimental work were obtained from two power supplies, both having outputs positive with respect to ground. The first was a (0–22.5)-kv doubler rectifier; the second d-c supply was a (0–30)-kv r.f. rectified type.

The 60 cps alternating voltage employed was obtained from a G.E. testing transformer. The step-up voltage ratio of this transformer is 150:1 when connected as used.

The polyethylene wire samples were in two sizes. One was the aircraft antenna wire on which the phenomenon was first observed; the outer diameter of this wire is 0.462 cm (0.182 in.), the central conductor diameter is 0.128 cm (0.0505 in.). The other polyethylene wire was obtained from the American Phenolic Corporation, and has an outer diameter of 0.292 cm (0.115 in.), and an inner conductor diameter of 0.08 cm (0.0315 in.). A bare brass rod of 0.3175 cm (0.125 in.) diameter and a bare copper rod of 0.203 cm (0.081 in.) diameter were also employed, as described in the next section.

The two outer cylinders used had inside diameters of 2.34 cm (0.910 in.) and 1.27 cm (0.50 in.). The 2.34-cm (0.910-in.) cylinder was 20.3 cm (8 in.) long; the 1.27-cm (0.50-in.) cylinder was 30.5 cm (12 in.) long. Both of these cylinders had, attached to their ends, cylindrical wooden fillets, flaring outward, with a radius of curvature of about 2.5 cm. The inner surface of these fillets was covered with several coats of Du Pont conducting silver paint (No. 4817) which was carried into the cylinder itself far enough to insure an equipotential surface. The purpose of these fillets was to decrease uniformly the gradient on the wire as it left the cylinder. The same conducting paint was also used to make a tight-fitting outer cylinder on the 0.462-cm (0.182-in.) polyethylene wire when examination of the polyethylene alone was made.

The central wire was used in lengths of about 61 cm (24 in.). It was mounted in a tower made of wood, Bakelite, and ceramic insulation. The members of the tower were coated with Dow-Corning four-silicone compound in order to minimize surface leakage. Several small Lucite disks were made to assist the centering of the wire and cylinder. These disks had a central hole, 0.00254 cm (0.001 in.) larger than the wire diameter, and an outer diameter 0.00254 cm (0.001 in.) smaller than the cylinder with which they were to be used. When the wire was drawn tight by means of brass machine screws soldered to its ends, and the appropriate disks placed on the wire, the cylinder holder was adjusted until the Lucite disks dropped through the cylinder. The cylinder holder was then locked in place by suitably placed bolts.

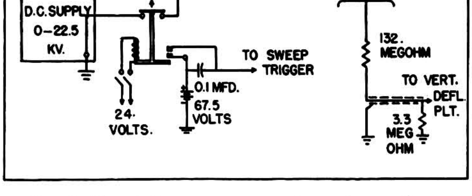


FIG. 1. Circuit for current wave shape observations

A Tektronix 511 A.D. oscilloscope was used for observing the charging current wave form. Permanent records of these wave forms were made photographically using a DuMont Type 296 oscilloscope record camera. The oscilloscope was equipped with a 5CP11A cathode ray tube to obtain an easily photographed trace. Voltage applied to the oscilloscope was obtained from a voltage divider through which the charging current passed. This divider was constructed of forty 3.3 megohm resistors in series in the upper arm; the lower section was usually one 3.3 megohm resistor, but another could be paralleled with this to change the division ratio by a factor of approximately two. A very low capacity shielded cable (7 $\mu\mu$f/ft at 1000 cps; 3-ft length) connected the upper and lower sections of the divider. The voltage divider was reasonably compensated for capacity without further adjustment, as was indicated by its attenuating a 100-kc square wave without noticeable change in wave shape. The voltages were applied directly to the vertical deflection plates of the cathode ray tube in order to avoid any distortion that might be caused by the transient response of the input amplifiers and associated circuitry.

The high voltage switching was obtained using a Western Electric Type 217-B rapid close relay. The relay was operated on 25 volts d.c. A secondary set of contracts on the relay was used to trigger the driven sweep of the oscilloscope; this allowed a time delay between the start of the sweep and the application of the high voltage to the specimen. The voltage wave obtained was a good approximation to a step function for the purposes of investigation.

Measurements of total charge were made using a ballistic galvanometer whose undamped characteristics are: sensitivity—0.002 microcoulombs/mm (on a scale 1 meter distant); C. D. R. X.—9000 ohms; period—30.5 sec; resistance—2325 ohms.

An Ayrton universal shunt with a resistance 10,000 ohms was used to obtain nearly critical damping resistance.

Also employed were a General Radio Type 716-B capacity bridge, and a General Radio beat frequency oscillator, Type 713-B.

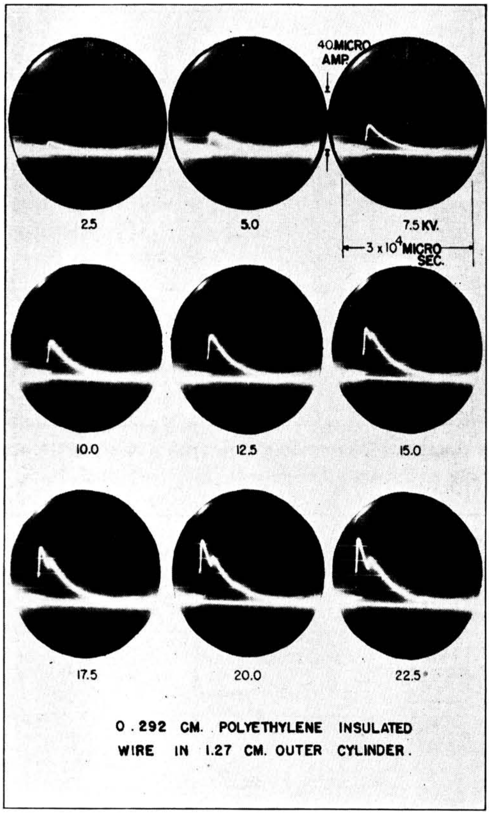


FIG. 2. Current vs. time—polyethylene-insulated wire in air; 0.292 cm polyethylene-insulated wire in 1.27 cm outer cylinder.

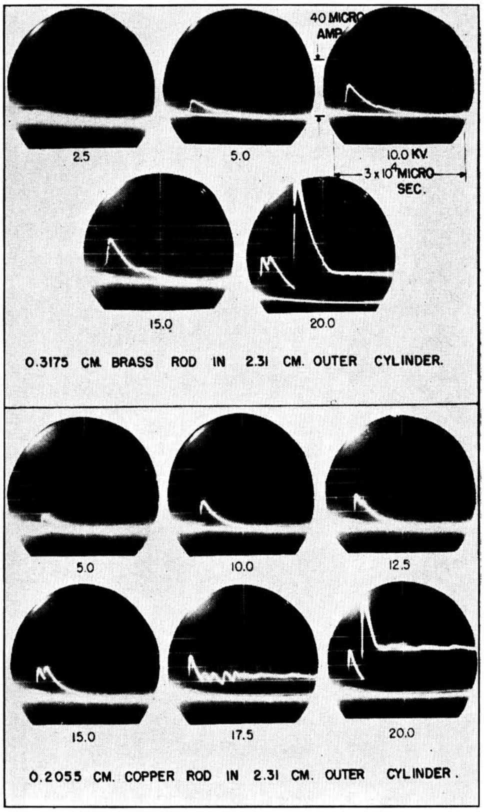


FIG. 3. Current vs. time—bare central conductors in air

MEASUREMENTS, OBSERVATIONS, AND RESULTS

Current Wave Shape

The circuit employed in observing current wave shape is shown in Fig. 1. The voltage supply available at the time these data were recorded had a maximum output of 22.5 kv. The current wave shapes shown throughout this paper have, for their axes, ordinates proportional to current, and abscissae proportional to time. The time between the left and right vertical grid lines (i.e., the 0 and 10th horizontal divisions), unless otherwise noted, is 3×10^4 microsec. The ordinate scale is of interest in relative magnitudes between wave shapes of a given set, and is the same for a given set, unless otherwise noted (its value is about 10 microamp/vertical division). These coordinate scales shall be referred to hereafter as "normal."

Fig. 2 shows a typical set of current wave shapes for polyethylene-insulated wire in a conducting outer cylinder. Fig. 3 shows current wave shapes for bare central wires.

To examine what primary contribution the polyethylene might make to the wave shapes (in the sense of interfacial polarization, etc.) when it is part of the dielectric circuit, some observations of current wave shapes for polyethylene alone were made. This was accomplished by excluding air from the concentric arrangement. The 0.462-cm (0.182-in.) wire was covered along a central section, about 30.5 cm (12 in.) in length, with several coats of conducting silver paint. When dry, this painted surface was a tightly-fitting, outer conductor. With this arrangement as the coaxial specimen, photographs of the current wave shapes were made. These are given in Fig. 4.

Measurement of Total Charge

Employing a ballistic galvanometer, measurement of the total charge flowing to the coaxial arrangements of polyethylene wires in the two outer cylinders was obtained for various voltages up to 30 kv. The Ayrton shunt was used to assure a constant value of damping, and one which was very closely the critical damping resistance for the galvanometer used. The shunt was used throughout at a multiplying power of unity. Since, for a given arrangement,

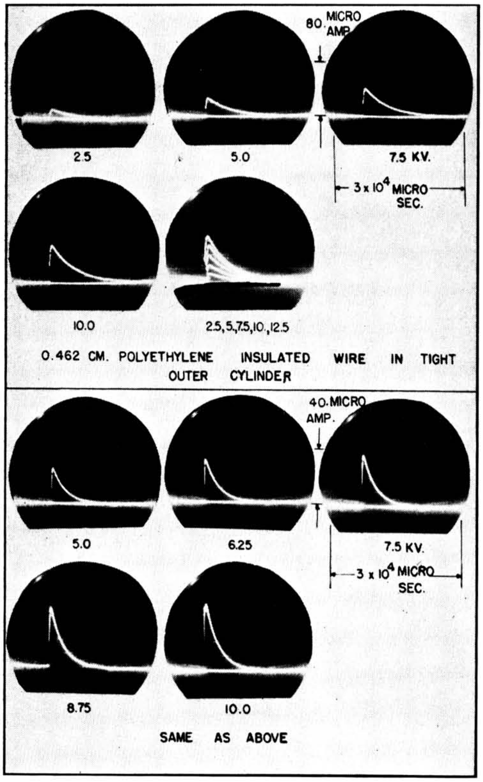


FIG. 4. Current vs. time—polyethylene-insulated wire in tight-fitting outer cylinder.

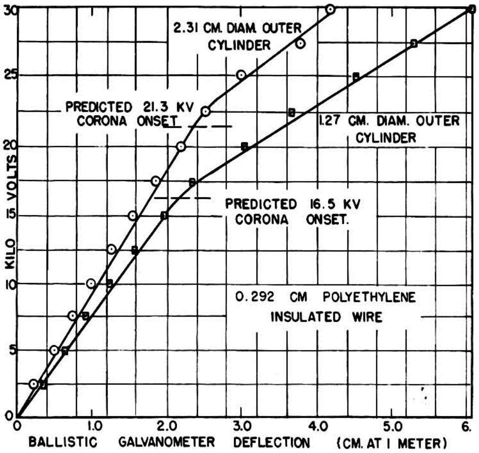


FIG. 5. Voltage vs. charge—polyethylene-insulated wire

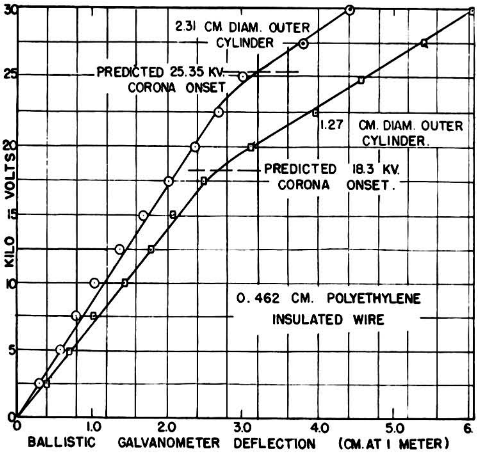


FIG. 6. Voltage vs. charge—polyethylene-insulated wire

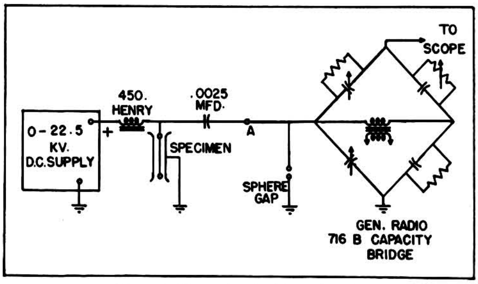


FIG. 7. Capacity bridge circuit

the external circuit parameters are not changed, the deflection of the galvanometer is directly proportional to the total charge which flows, provided only that the time of charge flow is much less than the period of the galvanometer (10). This is realized in these measurements since the time for charge flow is of the order of 0.02 sec, and the period of the galvanometer is 30.5 sec.

Fig. 5 and 6 show plots of initial deflection of the ballistic galvanometer (in centimeter on a scale 1-meter distant) as abscissa vs. applied voltage as ordinate. The abscissa is directly proportional to total charge. Each point represents the average of at least three observations. The deviation is not greater than 3%.

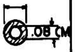
Auxiliary Observations

Using the General Radio 716-B capacity bridge, the General Radio beat frequency oscillator 713-B, and associated apparatus connected as in Fig. 7, capacity measurements were made using a substitution technique. With the circuit opened at [A], the bridge was balanced with the 0.004-μf capacitor and the 500-kilohm resistor in parallel in the unknown arm. The specimen arm was then connected, and the capacitor, C_s, was readjusted to balance the bridge. The direct voltage was then slowly raised from 0 to 22.5 kv, while watching the oscilloscope for a change in the balanced condition.

In the case of the 0.318-cm (0.125-in.) brass rod in the 1.27-cm (0.5-in.) outer cylinder, the bridge became unbalanced at a voltage very close to theoretical corona onset value; the amount of unbalance (as estimated from the amplitude of the signal on the oscilloscope) increased as the voltage was increased. When the 0.292-cm (0.115-in.) polyethylene-insulated wire replaced the brass rod and the same procedure was followed, a momentary unbalance was observed as theoretical corona onset voltage was reached, but the balanced condition was reestablished in less than 1 sec. The bridge settings remained untouched. As the direct voltage was further increased, similar unbalances were observed, but these also returned to the balanced condition in a short time (less than 1 sec) without any external changes to the apparatus. These same observations were noted for bridge frequencies from 1000–20,000 cps.

TABLE I. *Corona onset values in kv for the geometries investigated*

(A-C values are given as peak, i.e., $\sqrt{2} \times$ rms) S.I.C. for polyethylene taken as 2.35

CENTRAL CONDUCTOR OUTER CYLINDER		POLYETHYLENE INSULATED				BRASS		COPPER	
		462 CM. 		.292 CM. 		.3175 CM. 		.2055 CM. 	
	CALC.	25.35		21.3		17.3		15.0	
	MEAS.	A.C.	D.C.	A.C.	D.C.	A.C.	D.C.	A.C.	D.C.
		23.15	——	20.1	——	17.0	16.8	14.85	15.0
	CALC.	18.3		16.51		12.1		11.29	
	MEAS.	A.C.	D.C.	A.C.	D.C.	A.C.	D.C.	A.C.	D.C.
		17.81	——	15.7	——	12.01	12.0	11.65	11.1

60 CPS and D-C Corona Onset Measurements

Measurements of corona onset voltages were made for the configurations for which a normal type corona could be observed. The results are given in Table I along with the calculated values. Onset was determined by a microammeter in series with the specimen in the d-c case, and a neon bulb across part of a series resistance for the a-c case. An audible hiss accompanied the onsets observed.

DISCUSSION OF RESULTS

Examination of the charging current vs. time curves for the various configurations reveals that, for values of voltage well below calculated corona onset, the shape of the curve is the exponential form, anticipated for a capacitor in series with a resistor. In the ideal case, where there is no inductance present, the initial amplitude of such a current form is given by E/R, where E is the magnitude of the step function voltage wave, and R is the series resistance; furthermore, the rise is instantaneous and the exponential decay begins distinctly at the peak of the initial rise with no rounding of the peak. However, due to the finite inductance present in any physical network, these ideal conditions are only approximated, and there is noted the rounded peak and initial slope of the leading edge. This departure from ideal is also contributed to by the form of the step function voltage wave, itself an approximation.

As the amplitude of the applied voltage approaches the predicted onset value for the configuration (see Table I), secondary peaks are observed. These occur, in time, a few milliseconds after the initial peak. It is to be noted here that the voltage actually appearing across the coaxial cylinders is not the step function voltage wave, but something of the form of an increasing exponential whose asymptotic amplitude is equal to the amplitude of the step function voltage applied. In fact, the voltage across the cylinders vs. time would closely resemble the current wave form inverted.

These secondary peaks occur in all cases when the applied voltage amplitude is in the vicinity of calculated corona onset. In the case of the bare center conductor, however, as the voltage exceeds the corona onset value, the current stops decreasing with time and assumes a steady value whose magnitude is determined by the applied voltage and the geometry. That is, the magnitude of the steady corona current is that value for which the potential drop in the series resistance, subtracted from the applied voltage amplitude, leaves a value of voltage across the cylinders which is equal to or greater than the critical corona onset value. For the insulated wires, no such steady-state value is ever observed; regardless of the form and number of the secondary peaks, the current magnitude tends toward zero with increasing time. From the time scale on the current vs. time curves, it is seen that the current is essentially zero within 3×10^4 microsec for the insulated wires (the value being somewhat different for each configuration due to small differences in geometric capacity).

Any steady current beyond this time would be due to interfacial polarization—d-c leakage and/or volume conduction in conjunction with a corona discharge.

That polyethylene has practically no interfacial polarization could be assumed after examination of the published data of dielectric constant vs. frequency, which is essentially constant from d.c. to well beyond 100 megacycles/sec.

Interfacial polarization manifests itself as a drop in the dielectric constant accompanied by an increase in the absorption (loss) (11). This occurs within the lower frequency end of the electromagnetic spectrum for materials with high resistivities (polyethylene has a resistivity of the order of 10^{15} ohm-cm).

The results obtained show that for polyethylene alone there is no indication of appreciable steady-state current.

The maximum voltages employed on the 0.462-cm (0.182-in.) polyethylene wire alone exceed the maximum stress when this wire is employed in the normal air-surrounded configurations. Hence, any contribution to the charging current wave shape by the polyethylene, in a primary sense, would be reproduced here for the polyethylene alone. There is no indication that anything of the correct order of magnitude is present from these data.

Surface leakage current over the specimen and apparatus would be observed on these same data. Examination reveals that if any surface leakage, volume conduction, and/or interfacial polarization exist in or on the dielectric circuit studied, their magnitude combined is too small to be observed by the techniques employed here, and for the purposes of this investigation they can be considered negligible.

From the data of the polyethylene alone, it is clear that any internal discharges (due to voids, for example) would appear on the current-time trace as discontinuities in the exponential decay. Austen and Hackett (12) report these void discharges in extruded polyethylene cable, occurring at a maximum stress of 46.9 kv/cm for 50 cps. This stress corresponds to 7.8 kv applied to the 0.462-cm (0.182-in.) polyethylene wire alone; from the data no such discharges are observed for the direct voltages employed. The discharges reported by Austen and Hackett occur in the order of 10^{-7} sec, and hence if these occur in the 0.462-cm (0.182-in.) wire used here, they might not be seen due to time considerations alone. Furthermore, it is quite likely that, since the mechanisms of the a-c and d-c discharges are somewhat different, the void discharges may not occur at all in the d-c case for this value of stress.

If the secondary peaks of the current wave shapes are not due to primary contributions of the polyethylene, then they must be due to temporary breakdown of the air surrounding the inner cylinder, this breakdown becoming permanent in the case of the bare center conductors when the applied voltage exceeds the corona forming gradient. In the case of the polyethylene-insulated wire, some mechanism exists which prevents permanent breakdown of the air for applied d-c potentials exceeding the critical value. The fact that the air molecules actually are ionized when voltages exceeding the critical value are applied should lead to an increase in the total charge that would flow in the circuit if they did not ionize. This is, in fact, verified by the results of applied voltage vs. total charge (measured with a ballistic galvanometer) for the configurations employing polyethylene wire and air.

The slope of the voltage vs. total charge plots is proportional to the reciprocal of the effective capacity of the configuration during the time of charge flow. It would be expected then that the capacity would be different at voltages above critical corona value. This was observed as a transient condition in the capacity measurement using the superposition technique described. When the charge stopped flowing, the effective capacity returned to its previous value. For the bare conductor as the central member, when the direct voltage exceeded the critical corona value, there was a maintained change in capacity as long as the direct voltage was applied.

THEORY AND CONCLUSIONS

The criterion for a self-sustained corona discharge about a conductor, at a positive direct voltage, may be written [after Loeb (3)] as

$$\beta f \left(\exp \int_r^{r+a} \alpha \, dx \right) = 1$$

Where f = factor giving the number of photons produced by an electron avalanche capable of photoionizing the gas; β = the geometrical chance factor that these photons will ionize the gas molecules and build up the discharge; the expression

$$\left(\exp \int_r^{r+a} \alpha \, dx \right)$$

represents avalanche formation due to ionization by a single electron as it moves from $a + r$ in the gap to r (the surface of the corona-forming electrode); α = the first Townsend coefficient, representing the number of ionizing collisions per unit path length in the direction of the field. The position $r + a$ is the location in the gap at which the field is great enough to give α a value different from zero.

When the electron avalanche arrives at the anode, it is absorbed; in its wake it has left many excited atoms and positive ions. Production of other electrons to initiate new avalanches is due, according to the classical Townsend theory, to positive ion bombardment of the cathode. Loeb (3, 5, 13) and English (14) present evidence that this is not necessary, but that photo-ionization of the gas due to photons emitted from excited gas atoms is sufficient to produce the required electron to trigger the next avalanche. This electron must occur in the gap at a distance $r + a$, or greater, in order to satisfy the previously mentioned criterion. The only further requirement is that the applied field be maintained in the gap so that α shall not become zero.

In the preceding sequence, the surface at r was a conductor. If this conductor is now covered with a good insulator, such as polyethylene, then the electron avalanches reaching this surface cannot be absorbed, either conductively through the dielectric, or as absorbed charge in the interfacial sense. They must, therefore, reside on the surface and, as such, become a negative surface charge on the dielectric (perhaps a space charge very closely surrounding the dielectric). The field, due to this surface charge, will be superimposed on the field due to the applied system voltage. This clearly reduces the field strength in the gap. If the resultant field is still high enough to give α a value different from zero, so that another avalanche may follow, then this electron avalanche succumbs to the same fate as its predecessor, and the charge contained in it adds to the previous surface charge to further lower the electric field strength in the gap. By this process, a condition is reached where α is negligibly small, and no more avalanches are possible at the same applied voltage.

If the voltage is now increased, more negative charge builds up around the insulating surface, and equilibrium is again established in the gap. This process of increasing voltage is culminated when the dielectric strength of the insulation has been reached due to the resultant field. What is occurring in the configuration is that the electric field in the air gap is being maintained at a value just below critical (i.e., approximately 30 kv/cm) by the surface charge process, whereas the field in the dielectric is much greater than would normally exist without the surface charge. A simple calculation reveals that only 1 particle in 10^{12} need be ionized to supply sufficient charge to reduce the field strength below corona value for the configurations used here. The stress at breakdown for the N.R.L. data (Appendix I) is of the order of 3000 kv/cm in the polyethylene. Although this seems quite high, it is known that in highly uniform geometries the intrinsic dielectric strength may be approached, and this for good, solid dielectrics is in the range of 10^7 volts/cm. It is quite likely that this ratio of electric stresses of about 100:1 in the configuration is the answer to why the outer cylinder size of the N.R.L. data makes only a small difference in the rupturing value of applied direct voltage required for the concentric arrangement of polyethylene wire in air. When the dielectric breaks down, the surface charge in the vicinity of rupture is absorbed by the inner conductor, and breakdown of the total gap follows by the previously described mechanism.

The first pulse (after initial peak) observed on the current traces presented in the data corresponds, therefore, to the arrival of the voltage applied to the coaxial cylinders, to a value which allows an avalanche to occur in the gap. The secondary pips on the current traces are secondary avalanches which may occur only for higher voltages since now a surface charge exists on the polyethylene (the voltage across the cylinders is increasing approximately in an exponential fashion, as noted earlier). The field in the gap is distorted due to surface charge; these secondary avalanches, therefore, are not as sharp or well-defined as the initial one.

In the case of the 60 cps applied voltage, normal corona is observed. This is in agreement with the theory set forth here since, in the a-c case, the d-c volume conductivity of the dielectric is not important, and the necessary current is of the displacement type, not requiring transport of charges through the dielectric, but only displacement of electrons or positive ions in the dielectric itself about their equilibrium positions.

For bare wires in air, with coaxial symmetry, pulses on the current vs. time curves are also observed. These are similar to those observed for the polyethylene-insulated wire, except that when the voltage across the cylinders exceeds the value corresponding to corona formation, corona is observed in the normal sense. Brown (15) reports that when a secondary cylinder is introduced between, and insulated from, a bare wire and its outer cylinder, the direct voltage applied between the wire and outer cylinder may exceed many times the predicted corona onset value without observing corona in the normal sense. This is, in fact, due to a lowering of the gradient about the central wire caused by the initial breakdown charge residing on the intermediate cylinder (the charge on the cylinder being of the same sign as the polarity of the central wire).

The pulses observed on the current traces presented here that occur at voltage values below critical corona onset magnitudes are probably what Loeb (3, 13) terms pre-onset streamers and burst pulses, due in part to ambient ionization below avalanche-forming gradients.

CONCLUSIONS[3]

From the arguments presented in this paper, the following conclusions may be drawn:

(*A*) There exists no gross discrepancy in either the

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[3] It is to be expected that insulators other than polyethylene should behave in a similar manner under the conditions described herein, provided they possess comparably high values of volume resistivity. No observations were made for the wire negative. Since the mechanisms for positive and negative corona are considerably different, no conclusions concerning the negative case can be made here. In speculation, knowledge of the behavior of polyethylene under positive ion bombardment is required. Such information is notably lacking in the available literature.

accepted d-c dielectric strength of air, or the Law of Corona as applied here.

(*B*) The phenomena described at the outset have been explained in terms of fundamental processes.

(*C*) The data obtained are in agreement with this explanation.

ACKNOWLEDGMENT

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

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APPENDIX I

The following data[4] represent direct kilovolts, wire positive, at which rupture of the dielectric occurs. No normal corona was observed during the measurements which were performed in air under atmospheric conditions. The wire is the 0.463-cm (0.182-in.) diameter polyethylene-insulated conductor used in the experimental work described in this paper.

Large cylinder (18 in. I.D., 36 in. long).—During these tests the voltage was increased from 0 to 240 kv at the rate of 100 kv/min, held at 240 kv for 2 min (if breakdown had not yet occurred), and then increased at 100 kv/min until breakdown occurred.

Breakdown voltage for wire kv	*No. of samples*
190	1
220	1
240	3
260	1
270	1
280	1
290	3
300	1
310	1
320	1

Small cylinder (0.68 in. I.D., x 8 in. long).—Rate of rise procedure same as that given above for large cylinder.

Breakdown voltage for wire kv	*No. of samples*
170	1
200	1
220	1
240	3
275	1
310	1
320	1
330	1

Small cylinder (0.68 in. I.D. x 8 in. long).—During these tests the voltage was increased from 0 to 240 kv at rate of 50 kv/min, held at 240 kv for 2 min (if breakdown had not previously occurred), and then increased at 50 kv/min until breakdown occurred.

Breakdown voltage for wire kv	*No. of samples*
240	5
260	1
275	2
280	1
285	1

In addition to the above, a few tests were made with a small cylinder having $\frac{3}{16}$ I.D. These tests gave a voltage scatter at breakdown in the same range as given for the two cylinders above. These data seem to indicate that the size of the cylinder is not much of a factor in the breakdown voltage.

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[4] The presented data are extracted from a letter sent to Dr. C. F. Miller by Dr. J. E. Dinger of the Naval Research Laboratory, Aerology Branch, Mechanics Division, Washington, D. C.

The Preparation of Phosphor Screens for Color Television Tubes[1]

SIDNEY LEVY[2] AND ALBERT K. LEVINE[3]

Physics Laboratories, Sylvania Electric Products Inc., Bayside, New York

ABSTRACT

A method is described for producing accurately registered, fine-detail patterns of color phosphors for use in making screens for color television cathode ray tubes. The method is photographic in nature, and the desired phosphor pattern is produced by irradiating a thin film of a photosensitive resin material containing dispersed phosphor with an appropriate light pattern and developing the pattern by suitable means.

INTRODUCTION

One of the important aspects of color television research is the development of practical and economical methods for the construction of color television kinescopes for picture display. The phosphor screen in color kinescopes is much more complex than the screen in any other type of cathode ray tube. This paper describes the preparation of color television screens by a novel method using commercially available materials and relatively inexpensive equipment.

REQUIREMENTS

Phosphor screens for color television tubes consist of finely detailed discrete patterns of three different color-emitting phosphors. These patterns may be in the form of circular dots or thin lines. On a screen measuring 9 in. x 12 in., these dots would have a diameter of about 12 thousandths of an inch. Similarly, a line screen would have lines of about this thickness. The location and size of these dots or lines must be accurate within a thousandth of an inch over the entire screen area. A tube employing the shadow mask principle is shown disassembled in Fig. 1. The screen for such a tube has a mosaic pattern of dots of three different phosphors. Details of the pattern are shown in Fig. 2. A short distance from the screen, toward the gun end of the tube, there is a thin, perforated metal mask which is parallel to the screen and of nearly the same area. For each hole in the mask there is a corresponding trio of phosphor dots. Three electron guns are mounted symmetrically about the axis of the tube. The guns, mask, and dotted screen are so positioned that the electron beam from each gun, when deflected, is directed through the holes in such a way as to strike dots of one color only. Thus, by modulating the current in each beam, the relative magnitudes of the primary colors emitted by the tri-dot element can be adjusted so that the desired visual color for that element is produced by physical mixture. Satisfactory performance of the tube depends upon accurate registration of the electron guns, the perforated metal mask, and the dotted screen plate.

Several methods have been proposed for preparing such screens, e.g., settling phosphor through masks, silk-screen printing, letterpress printing, and electrostatic printing. To date, the silk-screen process is the only published method (1) which has been successfully applied to color-screen preparation. The photobinder process, which will be described in this paper, has also been used successfully to prepare screens for the shadow-mask tricolor kinescope. The method is photographic in nature, and the perforated shadow mask of the tube itself, or a photographic reproduction of the mask, is used as the master pattern.

In the photobinder process, a photosensitive resin binder is blended into a paste with one of the color-emitting phosphors. The paste is applied to the glass screen plate in a thin film by knife coating or other suitable means. Light from a suitable small-area source is allowed to pass through the openings of the master pattern in an exposure device, exposing portions of the film. The exposure device is positioned in such a way that the exposed portion of the film will constitute the desired dot pattern for the particular phosphor being used. Then the unexposed, and hence unfixed, areas are washed away by a solvent. The entire process is then repeated for each of the phosphors to be applied. When the dot patterns for all three colors have been obtained, the light-fixed photosensitive binder is removed by baking at 400°C, and a permanent silicate binder is applied by spraying.

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[1] Manuscript received July 20, 1953. This paper was prepared for delivery before the New York Meeting, April 12 to 16, 1953.

[2] Present address: American Safety Razor Company, Brooklyn, N. Y.

[3] Assistant Professor, Brooklyn College, Brooklyn, N. Y.; Consultant, Physics Laboratories, Sylvania Electric Products Inc., Bayside, N. Y.

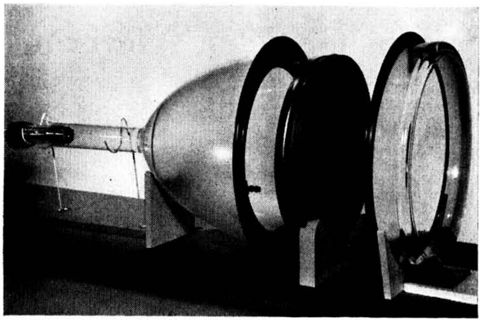

FIG. 1. Exploded view of shadow mask color kinescope

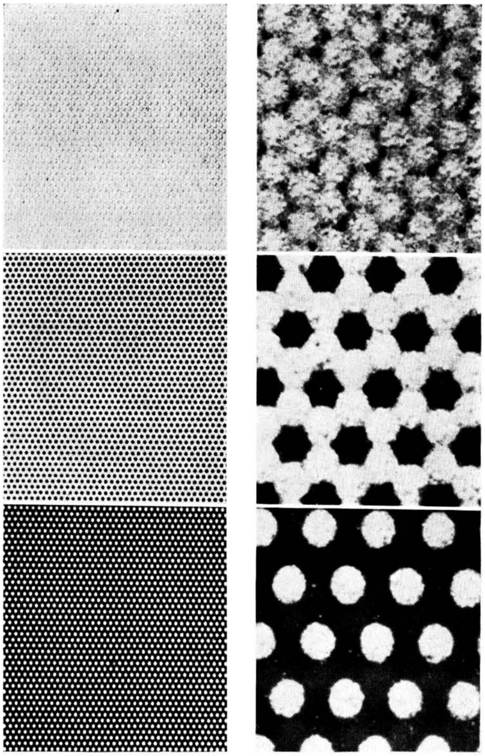

FIG. 2. Portion of tricolor phosphor screen with one-dot, two-dot, and three-dot patterns, showing successive stages of mosaic dot pattern, natural size, and enlarged.

Resist Materials

The use of photosensitive resist materials is well known, especially in the field of graphic arts. Photographically fixed gelatin-type materials are used to prepare halftone and line reproductions for press printing. Photo stencils, which are used extensively in silk-screen printing, and photo-offset printing are also based on the use of photographically set materials of various types.

It was proposed at these laboratories to use such resist materials directly on the glass screen plates either as a contact stencil or, if a suitable material could be found, as a photosensitive temporary binder for the phosphor, permitting direct photographic reproduction of the dot pattern on the glass screen plate. The method which was most promising, and which has been successfully developed, is the one using the photosensitive material as a temporary binder for the phosphor.

The criteria for a suitable photosensitive vehicle are: (*a*) adequate photosensitivity; (*b*) noninteraction with the phosphor materials; (*c*) suitable viscosity and other rheological properties to give stable dispersions of phosphor; (*d*) ease of incorporation into a practical coating system; (*e*) absence of interfering residue.

Several photosensitive materials were tested and one is being used successfully to prepare color screens. The materials tested were: (*a*) gelatin (photographic); (*b*) polyvinyl alcohol; (*c*) polyvinyl acetate; (*d*) Kodak Photosensitive Lacquer (an experimental material manufactured by Eastman Kodak and available on special order).

A number of other materials exhibit the photochemical sensitivity required, but the investigation was limited to the materials readily available. It is possible that additional research will lead to better and more effective systems. The material which was successfully used was Kodak Photosensitive Lacquer (KPL). All of the materials investigated were suitable in every respect except for the requirements that the material should leave no interfering residue and have no effect on the phosphor or tube life. However, a residue develops with all of the materials, other than KPL, since the required sensitization is effected by use of ammonium, potassium, or sodium dichromate, any one of which leaves a chromic oxide residue on ignition. In addition, these materials themselves leave a residue after firing at 400°-500°C.

Additional research is required on gelatin and the polyvinyl resins to find new sensitizers and to obtain high purity materials and thus make them useful systems. In contrast, the Kodak material has a volatile sensitizer incorporated, leaves no residue after bakeout at 400°C or lower, and has all the other required characteristics. KPL and polyvinyl acetate require an organic solvent such as trichloroethylene or a ketone for the process, whereas the others are water soluble.

A solution of KPL, which was 30 % solids by weight, was used to make up the phosphor pastes. The composition of the paste was approximately 25 % KPL (dry), 25 % phosphor, and 50 % solvent. After preliminary stirring, this mixture was blended by passing through a three-roll ink mill. The viscosity of the resulting paste ranged from 1000–5000 centipoise, depending on the particular phosphor, and the paste offered no problems in knife coating.

The phosphors employed were Sylvania #160 green (zinc orthosilicate), #150 red (zinc phosphate), and #170 blue (calcium magnesium silicate).

Coating Process

The photosensitive resist materials which were used in this investigation are relatively unaffected by ordinary room illumination. Nevertheless, to avoid complications, all steps of the procedure through the development of the exposed pattern were carried out in darkened rooms under red safelight.

In the investigation of coating problems, a thin film of the phosphor paste made from one of the various photoresists was applied to a glass plate with one of the various types of knife coaters, and the coated plate was then allowed to dry in air. A Bradley blade was employed for some of the test work. To meet the requirements of television tube face plates, a special knife-coating fixture was designed for coating flat glass panels with curved outlines. The device, which is illustrated in Fig. 3, features a sliding flat plate with a concave curved end. With the coating blade resting on this plate, the knife coater is filled with the phosphor paste. As the blade slides toward the screen plate, the concave edge of the sliding plate meets the convex edge of the screen plate and is held there while the blade continues across the screen plate. This makes it possible to do the complete coating operation with a single stroke.

The knife-coating process occasionally resulted in nonuniform coating weights over large areas. This was traced to variations in glass flatness. To overcome this, a spray coating system is now under investigation that should produce more satisfactory coatings. The spray coating method uses a traversing spray mechanism with a wide-angle spray gun and a pressurized can. As shown in Fig. 4, the fan-shaped spray is aligned across the panel, and the traverse moves the gun along at right angles to the alignment of the fan spray. By control of the can pressure and feed rate, a relatively uniform film can be attained.

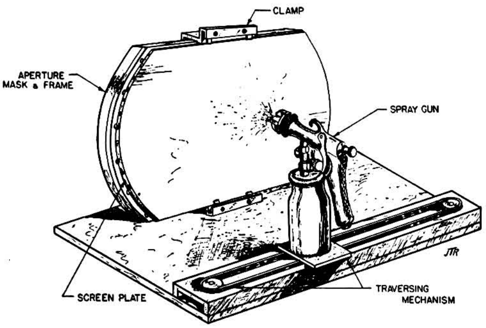

FIG. 4. Spray coating device

Exposure and Development

Several different methods of exposure were employed. In the first, the panel was exposed with the emulsion side in contact with a negative of the required pattern. In the second, the panel was exposed from the emulsion side by point-light shadow projection, an optical analogy to the situation in the shadow-mask tube. In the third, the panel was exposed from the glass side by point-light shadow projection (see Fig. 5). This method gave the best over-all results because good adherence of film to glass resulted from the exposure at the glass-emulsion interface. In addition, the dot size was photographically reproduced. This was not the case in either method of emulsion-side exposure, probably because of light scattering in the emulsion.

Exposure from the glass side introduces a slight uncorrectable displacement in the pattern produced

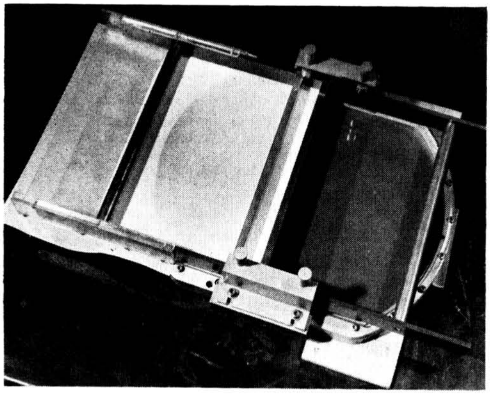

FIG. 3. Knife coater in use

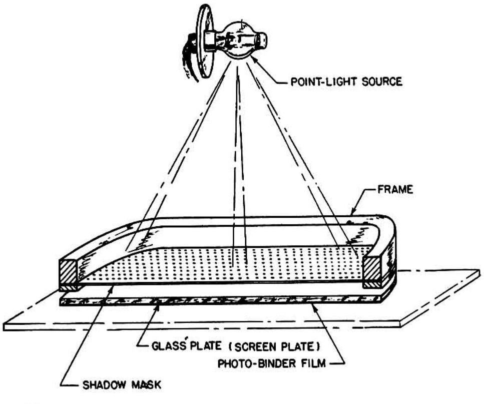

FIG. 5. Exposure arrangement in photobinder process

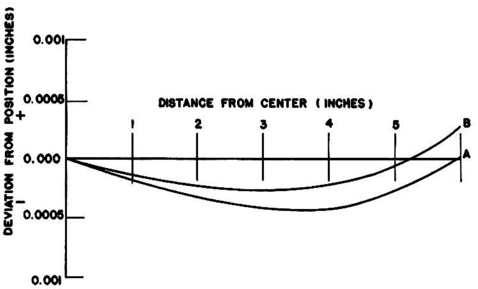

FIG. 6. Refractive error in shadow projection through glass. Curve A—compensated to zero at edge; curve B—compensated for minimum deviation.

by the refraction in the glass. The magnitude of this displacement can be calculated. Fig. 6 gives the location error vs. distance from the center of the screen for a particular setting of the exposure device. The maximum error can be reduced to a value which is negligible by suitable design of the geometry of the exposure device. In the present case, the maximum error in dot location due to refraction is less than 0.0003 in.

The apparatus actually employed is shown in Fig. 7. It consists of a vertical optical bench with a precision milling machine table attached to the base. The light source is a Sylvania 300-watt zirconium, enclosed, concentrated arc lamp. This lamp has a crater 0.116 in. in diameter. A crater of this size produces shadowed dots of adequate size to be covered by the electron beam in the tube. The master pattern can be either the aperture mask or a photographic reproduction of it. The coating, exposure, and developing are carried out with the screen panel and aperture mask clamped together in such a way that the outside of the screen plate faces the side of the aperture mask which faces the guns in the finished tube. To position the dots for the different colors, the milling table is used to move the aperture mask and screen assembly relative to the arc lamp. The distance traversed by the milling table in this operation is about 0.3 in. and is measured to the nearest thousandth.

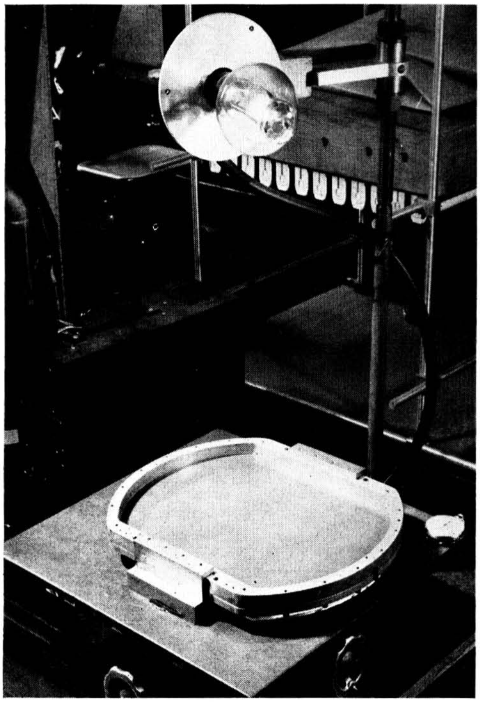

FIG. 7. Optical bench for point shadow projection

The distance from the arc lamp to the master (or aperture mask) is calculated from the desired pattern size, using the known spacing between the screen plate and the aperture mask and the thickness and refractive index of the screen panel. The refractive effects taking place at the glass-air interface enter into this calculation. When the spacings used are essentially those to be used in the color tube, the uncorrectable deviation due to refraction is less than 0.0003 in. (see Fig. 6).

The exposure time for each batch of each color phosphor is determined by a step exposure. The emulsion is exposed for the appropriate length of time and the film is developed by washing away the unexposed areas with a suitable solvent (trichloroethylene). The washing was done in several ways, including a condensing vapor type solvent wash, immersion in solvent, and a flush spray; the last was found most effective. The panel is recoated, the table is indexed to the position for the second set of dots, and the exposure is repeated for a time appropriate for the second phosphor. The procedure is repeated for the third phosphor.

After all three sets of dots have been developed, the photosensitive binder is removed by baking the plate at 400°C for several hours. The phosphor

TABLE I. *Color and brightness measurements for green phosphor No. 160 (zinc orthosilicate)*

Binder	Relative brightness, % of control	Color*	
		x	*y*
Control	100	0.260	0.715
Kodak Photosensitive Lacquer	96	0.260	0.725
Polyvinyl alcohol	39	0.262	0.720
Gelatin	9	0.185	0.540

* Chromaticity values, based upon the color measurement system of the International Commission on Illumination.

deposit is very fragile at this point and the screen is sprayed with a 14% solution of potassium silicate, using an air brush, to form a permanent binder. The subsequent operations are: (*a*) floating on a lacquer film; (*b*) aluminizing by high vacuum evaporation; (*c*) baking out lacquer film. These operations have been summarized elsewhere in the literature (2).

Luminescence of Experimental Screens

Three sets of panels were prepared with the green phosphor (zinc orthosilicate), using Kodak Photosensitive Lacquer, polyvinyl alcohol, and gelatin, respectively, as binders. The luminescent output and color of the KPL sample were not significantly different from the control, a liquid-settled panel. However, the efficiency of the polyvinyl alcohol and gelatin panels were markedly reduced, being, respectively, 39% and 9% that of the control; the color of the gelatin panel was also changed as shown by the chromaticity values. These results are summarized in Table I.

Test runs on full-size color screens showed that the KPL screens can give uniform screens with brightness comparable to screens prepared by the silk-screen method. Registration of the several sets of dots was excellent, and the reproduction of the dot size and location was photographic within measureable limits.

CONCLUSION

The photobinder technique for the preparation of mosaic phosphor patterns for color kinescopes offers considerable promise. By its nature, it is more precise than the silk-screen method, and it may be useful in overcoming the lack of interchangeability of units in the matching tube members, particularly in the case of the aperture mask of the shadow-mask tube.

The technique is applicable to the production of other mosaic surfaces in tubes, e.g., memory tubes, where precisely registered and accurately sized areas of sensitive materials are required.

ACKNOWLEDGMENT

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

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2. N. S. FREEDMAN AND K. M. MCLAUGHLIN, *Proc. I.R.E.*, **39,** 1230 (1951); D. W. EPSTEIN AND L. PENSAK, *RCA Rev.*, **7,** 5 (1946).

Electrolytic Reduction of Benzoic, Phenylacetic, and Cinnamic Acids and Esters at a Platinized-Platinum Cathode[1]

SHINICHI ONO, TADAO HAYASHI, AND JYUNICHI NAKAYA

Department of Chemistry, Naniwa University, Osaka, Japan

ABSTRACT

A study has been made of the electrolytic reduction of certain aromatic carboxylic acids and esters at a platinized-platinum cathode (Pt-pt) in alcoholic sulfuric acid solution.

It was found that the reduction at a Pt-pt cathode was quite different from that pursued at a lead or a mercury cathode. At a Pt-pt cathode, the reduction of benzoic, phenylacetic, and cinnamic acids and esters gave rise to cyclohexyl compounds. In no case was the carboxyl group reduced.

A special study of the electrolysis at a Pt-pt cathode under elevated pressure was made. The results confirm the catalytic nature of the process.

INTRODUCTION

Numerous studies have been made of electrolytic reduction of benzoic (1), phenylacetic (2), and cinnamic (3) acids, using high hydrogen overvoltage cathodes, such as Pb, Cd, Hg, and Hg-Zn cathodes, but no attempt has been made to determine the effect of platinized-platinum cathode (Pt-pt) on them, except in the case of cinnamic acid (4).

This has now been done. It has been found that the reduction of these acids at a Pt-pt cathode in alcoholic sulfuric acid solution gave rise to cyclohexyl compounds, but no alcohols. The esters also gave the corresponding cyclohexyl compounds.

Earlier work showed that the reduction of benzoic- (1) and phenylacetic- (2) acids at a Pb cathode gave benzyl- and phenylethyl-alcohols, respectively. Cinnamic acid at a Hg or a Pb cathode produced bimolecular compounds as well as phenylpropionic acid, but no phenylpropyl alcohol. With cinnamic acid it has now been found that the reduction of the double bond took place first, and then that of the benzene ring. The carbonyl groups in these compounds were quite resistant to the catalytic action of a Pt-pt cathode. It is also of interest that the interposition of a CH_2 or a CH_2CH_2 linkage between phenyl- and carboxyl- groups has no essential influence on the course of reduction.

Differences in the electrolytic reduction using Pb and Pt-pt cathode are summarized in Table I.

It is apparent that the course of the reduction at a Pt-pt cathode contrasts sharply with that pursued at a Pb or a Hg cathode. The characteristic properties of the Pt-pt cathode have been mentioned by several authors as follows.

Fichter and Stocker (5) and also Bancroft and George (6) observed the formation of cyclohexanol by the electrolytic hydrogenation of phenol using a Pt-pt cathode, and it was stated that a Pt-pt cathode had a specific effect on the hydrogenation of phenol. Sitaraman (7) found that the 3-isomeric cresols gave the corresponding methylcyclohexanols and methylcyclohexanones.

Wilson (8) suggested that there were close analogies between the prepared cathodes of Pt or Ni and catalytic hydrogenation in the reduction of sorbic acid and beta-vinylacrylic acid. Thus the reduction of sorbic acid at a Pt-pt cathode gave considerable amounts of 2-hexenoic acid and the fully saturated hexoic acid, whereas Hg or Pb cathode produced only a mixture of 3- and 4-hexenoic acid. This author pointed out that catalytic hydrogenation must proceed through electrically neutral intermediates, whereas electrolytic reduction may or may not, since it proceeds only in ionizing media. Much more important must be the condition of the hydrogen on the surface of the Pt-pt cathode.

In the present experiments, judging from the fact that (*a*) benzene rings were hydrogenated independently of the distance from the carboxyl group, and (*b*) both benzene rings in phenyl and benzyl esters were hydrogenated at the same time, it can be said that the reduction at a Pt-pt cathode takes place independently of the proton affinity of parts of the molecules. It is probable, therefore, that the reduction, under these conditions, involves the combination of an active center of the organic molecules with a chemisorbed hydrogen atom, in the manner envisaged by Horiuti (9).

Little attention has been paid in the past to the effect of external pressure on electrolytic reduction of organic compounds. Ipatiev, *et al.* (10) measured the

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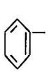
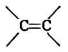
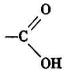
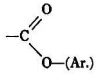
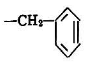
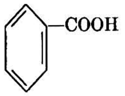
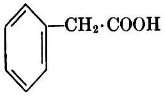
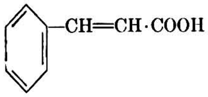
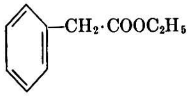
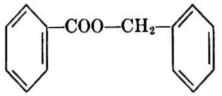
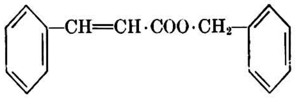
[1] Manuscript received January 7, 1952. This paper was prepared for delivery before the Detroit Meeting, October 9 to 12, 1951.

TABLE I. *Effect of cathode on reduction of various groups*

Group										
Cathode / Compound	Pb	Pt-pt	Pb	Pt-pt	Pb	Pt-pt	Pb	Pt-pt	Pb	Pt-pt
	−	+			+	−				
	−	+			+	−				
	−	$+_2$	+	$+_1$	−	−				
	−	+					−	−		
	−	$+_1$					+	−	−	$+_1$
	−	$+_2$	+	$+_1$			−	−	−	$+_2$

Note: + and − indicate reducibility and nonreducibility, respectively; $+_1$ and $+_2$ give the order in which the groups are reduced.

overvoltage on the Pt-pt in acid and alkaline solutions under pressures up to 100 atm. They observed that the potential of the cell increased with pressure.

Assuming that the reduction at a Pt-pt cathode consists mainly in a catalytic mechanism, there could be a correlation between the reduction products and the external pressure. Since no data are available, the present series of experiments was designed.

EXPERIMENTAL

Materials.—Benzoic and phenylacetic acids (C. P. products) were purified by recrystallization. Cinnamic acid and esters were prepared by standard methods. The mp or bp of samples was as follows:

	Acid	Ethyl ester	Phenyl ester	Benzyl ester
Benzoic	122	87–8/10 mm	71	145–7/5 mm
Phenylacetic	76	124–5/18 mm	42	172–4/12 mm
Cinnamic	132	144–5/16 mm	72	195–8/5 mm

Reduction technique.—The catholyte was 75, 50, 40, and 28% of sulfuric acid to which ethyl alcohol had been added. A sheet lead anode was used. The platinized-platinum cathode was prepared as follows. A platinum (100 cm^2) cylinder of gauze or sheet was platinized by electrolysis of platinic chloride solution (3 grams of platinic chloride in 100 ml of distilled water and 0.03 gram of lead acetate added).

The usual type of electrolytic cell was used. The porous cup (17 cm x 4.6 cm, Japan Chemical Ceramic Company, permeability, 3.94×10^{-4} cm/sec, porosity, 57.31) was used as a cathode compartment, and the cell was immersed in a water bath to maintain the desired temperature. The samples were dissolved in alcoholic sulfuric acid solution and placed in the cathode chamber. Sulfuric acid was used as an anolyte. Current density was varied between 0.5 and 6.5 amp/dm^2.

In the case of reduction under high pressure, the electrolytic cell was placed in an autoclave especially designed for this purpose (Fig. 1) and hydrogen was allowed to enter to a little more than the desired pressure. The valve between the tank and bomb was then closed and current was switched on.

Isolation and characterization of products.—When the reduction was completed, the catholyte was diluted with water and extracted with ether. The ether extracts were collected, washed with water, and dried over anhydrous sodium sulfate. The ether was evaporated and the residue was distilled under diminished pressure The fractions obtained were characterized and weighed. The physical properties of cyclohexyl compounds obtained are shown in Table II.

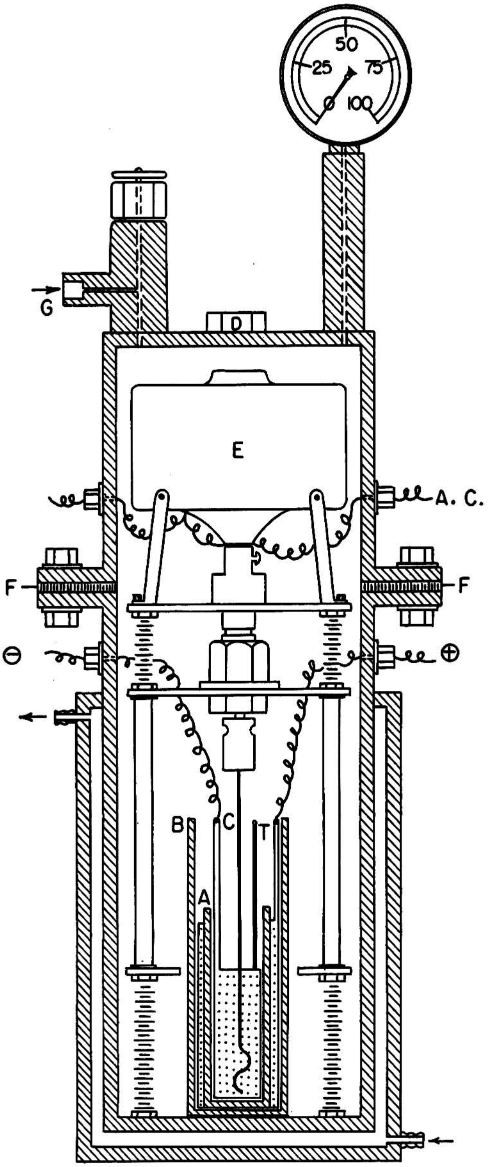


Fig. 1. Autoclave specially designed for pressure electrolysis. A—porous cup; B—electrolytic cell; C—cathode; D—safety disk; E—stirring motor; F—rubber packing; G—gas inlet; T—maximum thermometer.

Typical Experiments

(*a*) *Phenylacetic acid.*—13.5 grams (0.1 mole) of phenylacetic acid was dissolved in 40 ml of ethyl alcohol and 40 ml of sulfuric acid (50%) and placed in the cathode chamber. Sulfuric acid (30%) was used as an anolyte. A current of 2.0 amp was passed for 14 hr (theoretical for 13.6 grams phenylacetic acid, 16.1 amp hr). The temperature was kept between 25°-30°C.

When the reduction was completed, the catholyte was diluted with 50 ml of water and extracted with ether. The ether extracts were washed with water and dried over anhydrous sodium sulfate. After evaporating the ether, the residue was distilled under diminished pressure giving two fractions: (f_1) 65°-80°/6 mm Hg (10.2 grams) and (f_2) 114°-119°/6 mm Hg. Redistillation of (f_1) gave ethyl cyclohexylacetate, bp 68°-70°/6 mm Hg, $D_4^{25} = 0.9475$, $n_4^{25} = 1.4472$,

TABLE II. *Physical constants of reduction products*

Compound	M.P. (°C)	B.P. (°C/mm Hg)	D_4^{25}	n_D^{25}
$C_6H_{11}COOH$	29			
$C_6H_{11}CH_2COOH$	33			
$C_6H_{11}CH_2CH_2COOH$	16	132-3/9	0.9966	1.4658
$C_6H_{11}COOC_2H_5$		80.5-81.5/11	0.9525	1.4398
$C_6H_{11}CH_2COOC_2H_5$		68-70/6	0.9475	1.4472
$C_6H_{11}CH_2CH_2COOC_2H_5$		92-94/8	0.9674*	1.4488*
$C_6H_{11}COOC_6H_{11}$		60-62/7	0.9517	1.4395
$C_6H_{11}CH_2CH_2COOC_6H_{11}$		72-75/6	0.9741	1.4700
$C_6H_{11}CH_2COOCH_2C_6H_{11}$		70-73/8	0.9765	1.4510

* at 20°C.

TABLE III. *Effect of current density—(a) ethyl benzoate*

Catholyte: ethyl benzoate, 10 g; ethanol, 50 ml; 75% sulfuric acid 30 ml; temp: 25°-30°C; quantity of current: 16 amp hr; cathode: Pt-pt, gauze, (100 cm^2)

Run No.	Current density (amp/dm^2)	Yield† (%)	Current efficiency (%)
1	0.8	78.8	52.8
2	1.2	78.0	52.2
3	2.0	60.5	40.5
4	3.0	65.3	43.7
5*	4.0	74.0	49.5
6*	6.0	74.0	49.5

† Ethyl hexahydrobenzoate. * Temp: 35°-40°C. Yield is calculated on consumed depolarizer. Current efficiency is the percentage of current used in producing the product.

and (f_1) was distilled again under diminished pressure giving bp 117°–119°/6 mm Hg, mp 30°C, identified as cyclohexylacetic acid.

(*b*) *Ethyl benzoate* (*under pressure*).—Ten grams (0.67 mole) of ethyl benzoate was dissolved in 50 ml of ethyl alcohol and 30 ml sulfuric acid (75%) and placed in the cathode chamber. Sulfuric acid (50%) was used as an anolyte. The electrolytic cell was placed in the autoclave and hydrogen was admitted to 20 atm pressure. The reduction was carried out at a current density of 1.2 amp/cm^2 for 16 amp hr (theoretical for 10 grams ethyl benzoate, 10.7 amp hr).

TABLE IV. *Effect of current density—*(*b*) *ethyl phenylacetate*
Catholyte: ethyl phenylacetate, 10 grams; ethanol, 50 ml; 75% sulfuric acid, 30 ml; quantity of current: 16 amp hr (theory 9.8 amp hr); temp: 25°–30°C; cathode: Pt-pt, gauze (100 cm^2)

Run No.	Current density (amp/dm^2)	Yield† (%)	Current efficiency (%)
1	0.5	76.0	46.6
2	1.0	56.8	34.8
3	2.0	56.8	34.8
4	3.5	63.6	39.0
5*	5.0	63.6	39.0
6*	6.5	66.5	40.7

† Ethyl cyclohexylacetate. * Temp: 40°–45°C

TABLE V. *Effect of current density—*(*c*) *phenylacetic acid*
Catholyte: phenylacetic acid, 13.6 grams; ethanol, 40 ml; 50% sulfuric acid, 40 ml; quantity of current: 28 amp hr (theory 16.1 amp hr); temp: 30°–35°C; cathode, Pt-pt, sheet (100 cm^2)

Run No.	Current density (amp/dm^2)	Yield† (%)	Current efficiency (%)
1	1.0	76.5	44.0
2	2.0	80.2	46.1
3	3.0	74.6	42.9
4*	4.0	77.5	44.6
5*	5.0	75.5	43.4

† Cyclohexylacetic acid and its ethyl ester. * Temp: 40°–45°C.

During reduction, the temperature in the cell was uncontrolled, but a maximum thermometer inserted in the catholyte showed that this had not been higher than 25°C.

The catholyte was diluted with water, neutralized with sodium carbonate, and extracted with ether. The ether was evaporated and the residual solution was distilled under diminished pressure. The fraction bp 78°–82°/11 mm Hg was collected. Redistillation gave bp 80.5°–81.5°/11 mm Hg, $D_4^{25} = 0.9525$, $n_D^{25} = 1.4398$. Saponification with 20% alcoholic potassium hydroxide gave a hexahydrobenzoic acid, mp 28°C.

(*c*) *Cinnamic acid to hydrocinnamic acid.*—Cinnamic acid (7.5 grams) in 75% sulfuric acid and alcohol solution was electrolyzed with 6.0 amp hr of current (theoretical for 7.5 grams of cinnamic acid, 2.7 amp hr) and gave (f_1) 3.5 grams, bp 140°–54°/10 mm Hg, mp 48°C, (f_2) 1.5 grams, bp 159°–64°/10 mm Hg, mp 85°C, and (f_3) 1.3 grams, unchanged cinnamic acid. The (f_1) was recrystallized from ligroin, mp 49°C, identified as hydrocinnamic acid. It was shown that (f_2) was a mixture of hydrocinnamic and cinnamic acids.

(*d*) *Cinnamic acid to cyclohexylpropionic acid.*—

TABLE VI. *Effect of acid concentration—*(*a*) *benzoic, phenylacetic, and cinnamic acids*
Catholyte: compound, 0.1 mole; ethanol, 40 ml; sulfuric acid, 40 ml; temp: 30°–35°C; cathode: Pt-pt, sheet, (100 cm^2)

Run No.	Compound (g)	H_2SO_4 (%)	Current density (amp/dm^2)	Product*		Yield (%)	Current efficiency (%)
				f_1 (g)	f_2 (g)		
1	Benzoic (12.3)	28	1.0	5.0	4.4	66.0	53.1
2	Benzoic (12.3)	75	1.0	8.1	1.8	66.0	53.1
3	Phenylacetic (13.6)	28	2.0	6.0	6.0	77.5	44.6
4	Phenylacetic (13.6)	50	2.0	9.5	3.0	77.5	44.6
5	Phenylacetic (13.6)	75	2.0	10.5	1.5	72.5	41.7
6	Cinnamic (14.8)	28	3.0	4.0	6.0	60.0	42.8
7	Cinnamic (14.8)	40	3.0	6.8	6.0	76.0	54.2
8	Cinnamic (14.8)	75	3.0	11.4	2.2	76.5	54.6

Quantity of current: Run No. 1-2, 20 amp hr (theory 16.1 amp hr) 3-5, 28 amp hr (theory 16.1 amp hr) 6-8, 30 amp hr (theory 21.4 amp hr).

* Products: f_1, ethyl esters of cyclohexyl acids; f_2, cyclohexyl acids.

Cinnamic acid (7.5 grams) in 75% sulfuric acid and alcohol solution was reduced at 3.0 amp/dm² for 5 hr (theoretical for 7.5 grams cinnamic acid, 10.8 amp hr) and gave (*a*) bp 91°–94°/8 mm Hg, 5.7 grams, and (*b*) bp 124°–6°/8 mm Hg, 1.0 grams. The fraction (*a*), D_4^{20} = 0.9674, and n_D^{20} = 1.4488, was identified as ethyl cyclohexylpropionate.

TABLE VII. *Effect of acid concentration—(b) ethyl benzoate*

Catholyte: ethyl benzoate, 10 grams; ethanol, 50 ml; sulfuric acid, 30 ml; temp: 40°–45°C; quantity of current, 16 amp hr (theory 10.7 amp hr); cathode: Pt-pt, gauze, (100 cm²)

Run No.	H_2SO_4 (%)	Current density (amp/dm²)	Yield* (%)	Current efficiency (%)
1	40	2.0	58.7	39.3
2	75	2.0	64.5	43.1
3	80	2.0	65.4	43.7
4	96	2.0	64.5	43.1

* Ethyl hexahydrobenzoate.

TABLE VIII. *Effect of temperature—(a) ethyl benzoate*

Catholyte: ethyl benzoate, 10 grams; ethanol, 50 ml; 75% sulfuric acid, 30 ml; quantity of current: 16 amp hr (theory 10.7 amp hr); cathode: Pt-pt, gauze, (100 cm²)

Run No.	Temp (°C)	Current density (amp/dm²)	Yield* (%)	Current efficiency (%)
1	7–11	4.0	54.8	36.6
2	25–30	4.0	74.0	49.5
3	55–60	4.0	76.0	50.8
4	8–10	2.0	43.3	29.0
5	25–30	2.0	60.5	40.5

* Ethyl hexahydrobenzoate.

TABLE IX. *Effect of temperature—(b) phenyl benzoate*

Catholyte: phenyl benzoate, 10 grams; ethanol, 70 ml; 75% sulfuric acid, 30 ml; quantity of current: 20 amp hr (theory 16.2 amp hr); cathode: Pt-pt, gauze, (100 cm²)

Run No.	Temp (°C)	Current density (amp/dm²)	Yield* (%)	Current efficiency (%)
1	30–35	5.0	19.8	16.0
2	45–50	5.0	24.6	19.9
3	50–55	5.0	34.0	27.5

* Cyclohexyl hexahydrobenzoate.

TABLE X. *Effect of duration of reduction of ethyl benzoate*

Catholyte: ethyl benzoate, 10 grams; ethanol, 50 ml; 75% sulfuric acid, 30 ml; current density: 4.0 amp/dm²; temp: 30°–35°C; theoretical amount of current: 10.7 amp hr

Run No.	Duration of run		Yield* (%)	Current efficiency (%)
	(hr)	(amp hr)		
1	4.0	16.0	74.0	49.5
2	5.0	20.0	73.0	39.1
3	6.0	24.0	72.0	32.1
4	7.5	30.0	74.0	26.4

* Ethyl hexahydrobenzoate.

(*e*) *Phenyl cinnamate.*—Phenyl cinnamate (11.2 grams) in 75% sulfuric acid (30 ml) and alcohol (50 ml) was electrolyzed at a current density of 1.0 amp/dm² for 20 hr (theoretical for 11.2 grams of phenyl cinnamate, 16 amp hr) at 25°–30°C. The

TABLE XI. *Effect of pressure—(a) ethyl benzoate*

Catholyte: ethyl benzoate, 10 grams; ethanol, 50 ml; 75% sulfuric acid, 30 ml; quantity of current: 16 amp hr (theory, 10.7 amp hr); cathode: Pt-pt, gauze, (100 cm²)

Run No.	Pressure (atm)	Current density (amp/dm²)	Temp (°C)	Yield* (%)	Current efficiency (%)
1	1 (H_2)	4.0	30–35	74.0	49.5
2	10 (H_2)	1.2	20–25	84.5	56.5
3	20 (H_2)	1.2	20–25	85.5	57.2
4	10 (H_2)	4.0	30–35	75.0	50.2
5	20 (H_2)	4.0	30–35	75.0	50.2
6	30 (H_2)	4.0	30–35	77.0	51.3
7	40 (H_2)	4.0	30–35	73.1	49.0
8	20 (CO_2)	2.0	25–30	64.5	43.2
9	40 (CO_2)	2.0	25–30	58.6	39.2

* Ethyl hexahydrobenzoate.

TABLE XII. *Effect of pressure—(b) phenylacetic acid*

Catholyte: phenylacetic acid, 13.6 grams; ethanol, 40 ml; 50% sulfuric acid, 40 ml; quantity of current: 28 amp hr (theory 16.1 amp hr); temp: 40°–45°C; cathode: Pt-pt, sheet, (100 cm²)

Run No.	Pressure of hydrogen (atm)	Current density (amp/dm²)	Yield* (%)	Current efficiency (%)
1	1	5.0	75.5	43.4
2	15	2.0	75.5	43.4
3	25	4.0	77.0	44.3
4	35	4.0	75.5	43.4
5	25	5.0	78.2	45.0
6	40	5.0	77.0	44.3

* Cyclohexylacetic acid.

TABLE XIII. *Effect of pressure—(c) cinnamic acid*

Catholyte: cinnamic acid, 7.5 grams; ethanol, 60 ml; sulfuric acid, 20 ml; temp: 25°–35°C; quantity of current: 15 amp hr (theory 10.8 amp hr); cathode: Pt-pt, sheet, (100 cm²)

Run No.	Pressure of hydrogen (atm)	Current density (amp/dm²)	Yield* (%)	Current efficiency (%)
1	1	3.0	60.3	43.4
2	15	3.0	62.8	45.2
3	30	3.0	69.3	49.9
4	1	5.0	74.5	53.6
5	35	5.0	74.5	53.6
6	45	5.0	70.5	50.8

Note: Concentration of sulfuric acid: Run No. 1–3 28%; Run No. 4–6, 40%.

* Cyclohexylpropionic acid.

reduction gave cyclohexyl cyclohexylpropionate, bp 72°-75°/6 mm Hg, $D_4^{25} = 0.9741$, $n_D^{25} = 1.4700$. Saponification with 20% alcoholic potassium hydroxide solution gave cyclohexylpropionic acid, mp 16°C, and cyclohexanol.

RESULTS AND DISCUSSION

Effect of current density.—It was found that better yields could be obtained at lower current densities. This is shown in Tables III, IV, and V.

Effect of acid concentration.—It may be seen from the data in Tables VI and VII that stronger acid solution caused the formation of esters; otherwise acid concentration had no noticeable influence on the reduction.

Effect of temperature.—It is seen in Tables VIII and IX that the reduction was favored by high temperatures.

Effect of duration.—Table X shows that yield of product was almost independent of duration of the run. Current efficiency fell, of course, as the run was prolonged beyond the theoretical time.

Effect of pressure.—A special study was undertaken of the effect of high pressure in the course of the reduction. It is seen in Tables XI to XIII that the reduction was favored at high hydrogen pressure, although the effect was not great. Assuming that the reduction at a Pt-pt cathode proceeds by a catalytic mechanism, it would be expected that pressure would increase the rate of reduction of organic compounds. The results obtained, however, are irregular. More detailed conclusion must await further results.

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

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Flexible Leads for Low-Frequency Electric Furnaces[1]

M. EATON

Shawinigan Chemicals Limited, Shawinigan Falls, Quebec

AND

S. B. THOMAS

Northern Electric Company Limited, Montreal, Quebec

ABSTRACT

Special problems are encountered in designing cables to transfer power from the bus system to the electrodes of arc furnaces. The requirements for cable are outlined and a brief study made of the various types used. The development of water-cooled cables is traced, and data are given on construction, current ratings, life expectancy, and other characteristics. The conclusion is that this type of cable is a practical solution of the problems encountered.

INTRODUCTION

Water-cooled flexible leads, consisting essentially of a flexible conductor inside a flexible metal tube with suitable terminals and water passage, have been in use for many years. One of their most important applications pertains to calcium carbide furnaces.

The electrical resistance of a calcium carbide furnace is low (usually between 1200 and 2500 microhms, depending on the power taken and the nature of the charge). In order to obtain a satisfactory power factor, it is therefore necessary to limit the reactance to a corresponding value. Since reactance is directly proportional to frequency, it presents a greater problem in the design of 60-cycle furnaces than it does for furnaces with power supplied at lower frequencies. The reactance, X, equals $2 \pi fL$ ohms. The inductance, L, depends mainly on the size, shape, length, and arrangement of current-carrying parts.

Fig. 1 and 2, showing schematically the arrangement of low-voltage connections to the electrodes of a carbide furnace designed for low reactance, serve to show the advantage gained by the use of water-cooled flexible leads. Current supplied by transformer [2] is carried to the contact shoes, [10], on the electrodes, [11], [12], and [13], by interlaced bus bars, [3], and uninterlaced connections, [7], [8], and [9], including water-cooled flexible leads, [16]. Single circuits are indicated, whereas in practice multiple circuits, with a corresponding number of electrode contact shoes, are used. Minimum reactance is obtained mainly by (*a*) making all parts of the circuit as short as practicable, (*b*) the use of multiple circuits, (*c*) carrying the interlaced (alternatively plus-minus) bus bars from the transformer to points as near the electrodes as practicable, and (*d*) by completing the delta connections at the electrodes. In this arrangement of current-carrying parts, the flexible leads are exposed to the radiant heat of the furnace and, therefore, they must be water-cooled. If, alternatively, flexible leads made with multiple thin copper strips or bare stranded conductors are located outside the furnace, the length of the uninterlaced connections is increased with a corresponding increase in reactance.

Further advantages are gained in the use of water-cooled flexible leads if they can be mounted in the form of an upright arch, as indicated in Fig. 2. The height of the horizontal connections between the interlaced bus bars, [3], and the electrode, [13], is determined by the amount of clearance under them that is required for furnace operation. Since flexible lead [16] is self-supported, when its terminal connections are arranged to hold it in an arched position it may be installed as indicated. In order to obtain the same clearance with a suspended flexible lead, it would be necessary to raise the interlaced bus bars, [3], together with the horizontal tube, [9], and to increase the length of tube [19]. The self-supported flexible lead of this design therefore provides means for reducing the length and, consequently, the reactance of the electric circuit. Another advantage of the arched position is that the flexible lead has a minimum exposure to the radiant heat of the furnace and to damage by tools used in the operation of the furnace.

The development of a self-supported water-cooled flexible lead suitable for low-frequency electric furnaces is the main subject of this discussion.

Consideration of means for making the flexible leads self-supported when mounted in an arched

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position led to the choice of a design in which this characteristic is obtained by the use of one or more flat strips of resilient metal which make the leads flexible in a longitudinal plane at right angles to the flat surfaces of the spring strips and comparatively rigid in a transverse direction.

Four arrangements of the spring strips, comprising successive steps in the development, are illustrated by Fig. 3 to 6. The results of accelerated aging tests are tabulated in Table I.

Fig. 3 and 4 serve to illustrate the arrangement of the component parts of both flexible leads I and II, Table I. As indicated in Fig. 3, a conventional water-cooled flexible lead, consisting of flexible conductor [10] soldered in receptacle [9] of terminal [5], having water passages [6]-[7]-[8]-[15] and outer flexible metal tube [30], is provided with spring strips (phosphor-bronze), [20] and [25], firmly fixed to the terminals, [5], by means of silver solder. Fig. 4 is a sectional view of this arrangement. The spring strips make the flexible lead self-supported when its terminal connections are made to hold one end in the position indicated by Fig. 3, and the cable is looped around laterally to a similar parallel terminal in suitable spaced relation. Since in a bend of this shape one spring strip is longer than the other, a flexible lead of this design must be fabricated and maintained with a predetermined shape of bend, i.e., with suitably spaced terminals either parallel or inclined toward one another at a predetermined angle.

Flexible Lead I

The first flexible lead of this design was made with only one spring strip located on the under side of the flexible conductor and having its ends brazed to the conductor strands at the terminals. An accelerated aging test was made on a test lead of this design with results as shown in Table I. The testing apparatus was made to hold the terminals vertical and parallel and with a suitable bending diameter. With one terminal fixed, the other terminal was moved up and down a distance of 3 ft until failure occurred, water pressure being maintained throughout the test. The tabulated results show the number of cycles and the distance traveled by the moving terminal before leakage of the cooling water occurred.

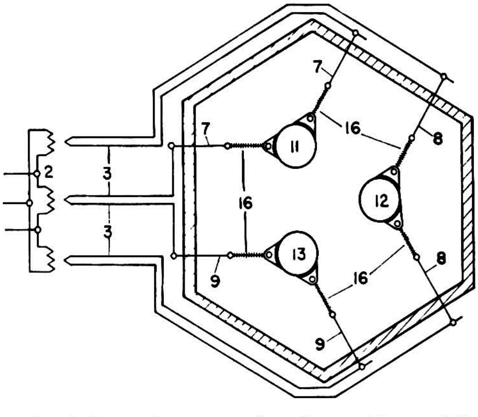


Fig. 1. Low voltage connections for a calcium carbide furnace.

Although measurement of the movement of carbide furnace electrodes indicated that flexible leads with a test performance equal to that of flexible lead I might remain in service two or three years without trouble, in practice it was found that leakage occurred after only about six months of operation. Through breakage of the conductor strands to which the spring strips were brazed and by other causes the spring strips became displaced, thus failing to support the flexible leads in a uniform arch and causing wear on the outer flexible tubes with final leakage.

The discrepancy between the actual life and the life expectancy based on test results is accounted for by the difference between furnace operating conditions and test conditions. The flexible lead on test

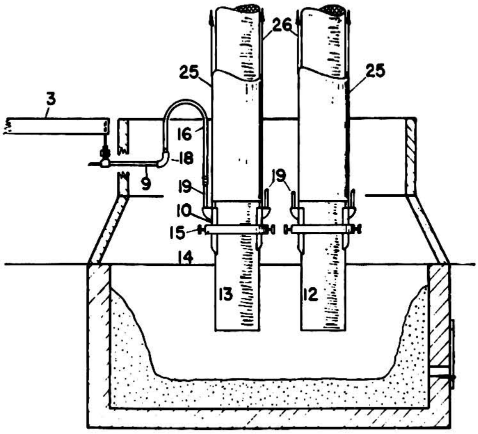


Fig. 2. Low voltage connections for a calcium carbide furnace.

TABLE I. *Results of accelerated aging tests on self-supported flexible leads*

Ref. No.	Description	Cycles traveled free end	Traveled distance ft
I	1 spring strip in water passage	3,770	22,620
II	2 spring strips in water passage	12,616	75,696
III	Spring at center of 4-segment conductor	11,120	66,720
IV	Spring at center concentric design	31,594	189,564

was constantly held at the bending diameter for which it was made and with the spring strip flexing only in a vertical plane passing longitudinally through its center, whereas, because of limited horizontal movement of the electrodes at the elevation of the contact shoes, flexible leads in service were subjected to stresses resulting from changes in bending diameter and alignment.

FLEXIBLE LEAD II

The design of the flexible leads was then changed to that shown in Fig. 3 and 4. The use of two spring strips, firmly fixed to the terminals, served to give the flexible leads more adequate support and, at the same time, the additional spring strip reduced wear on the outer flexible tube caused by relative motion between the flexible conductor and the flexible tube.

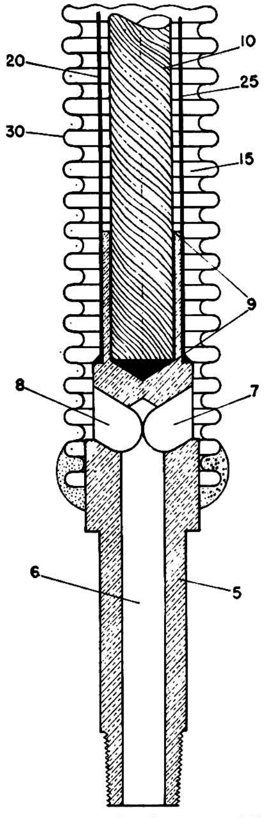


FIG. 3. Sectional views of self-supported flexible leads

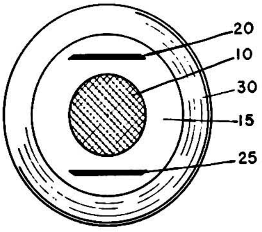


FIG. 4. Sectional views of self-supported flexible leads

The accelerated aging test indicated considerable improvement as compared with flexible lead I. It has been found that the life of the lead in service was approximately doubled by the changes in its construction. However, the spring strips still tended to become displaced with results as described above. Improvement was only in the length of service obtained before leakage occurred.

FLEXIBLE LEAD III

A further development of the flexible lead was made by securing a single spring strip, [20], at the center of a flexible conductor, [10], made in four segments as shown in Fig. 5. The assembly was held together with a neoprene-insulated binding wire, [35], which was also designed to prevent frictional wear on the inner surfaces of the flexible tubing.

The accelerated aging test (see Table I) indicated that a flexible lead of this construction was not improved with respect to life expectancy. The test life was limited because of irregular bending of the outer flexible tube. The flexible tubing tended to bend sharply at two or three points, with final failure caused by leakage at one of them. It was later found that the irregularity of the flexing was caused by displacement of the binding wire, [35], Fig. 5. A wire braid is now used to hold the segments in place.

FLEXIBLE LEAD IV

Flexible lead IV (Fig. 6) includes a flexible conductor with a core of unusual construction. A strip of resilient metal, [20], is embedded at the center of

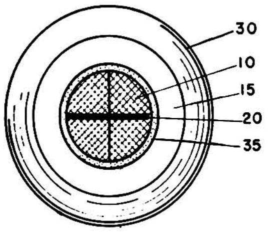


FIG. 5. Sectional views of self-supported flexible leads

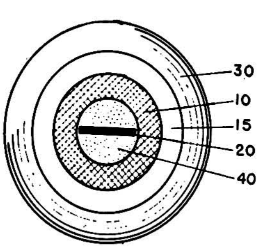


FIG. 6. Sectional views of self-supported flexible leads

an elongated core, [40], of circular cross section and made of elastic material such as neoprene. The flexible conductor, [10], is stranded around the core. The cored conductor is then soldered into the terminals and the outer flexible tubing is applied as indicated in Fig. 3. The results of the accelerated aging test are shown in Table I.

A number of advantages are derived from the concentric construction of this flexible lead, its essential characteristic being that the length of any element, except elastic parts, remains unchanged no matter how the flexible lead is bent in a longitudinal plane at right angles to the flat surfaces of the spring strip. (*A*) The flexible lead may be fabricated in straight lengths and supported in the form of an upright arch with its terminals either vertical or inclined toward one another at any desired angle, whereas a flexible lead having nonelastic elements of different bending radii must be fabricated and maintained with a predetermined shape of bend, i.e., with its terminals suitably spaced and parallel or inclined toward one another at a given angle. (*B*) The flexible lead is adapted to accommodate changes in the shape of bends and alignment such as occur in service. Lack of this property in other flexible leads referred to above introduced internal stresses which greatly reduced their useful life. (*C*) The construction of the flexible lead is such that none of its elements can become displaced. Deficiency in this respect has been a source of trouble with other water-cooled flexible leads as already related. (*D*) The electrical characteristics of the flexible conductor are improved as a result of its cored construction. This feature is of particular importance because of the magnitude of the currents carried (5–8 amp/1000 cir mils).

Flexible leads of the concentric design have been in service for several months. Their length of life in service is not yet known, but the results of the accelerated aging test indicate that they should operate two to three years without trouble. Failure on test resulted from fatiguing of the metal in the outer flexible tube with final cracking and leakage of the cooling water.

It seems that any further improvement in the life of these flexible leads will depend on improving the resistance to metal fatigue in the outer flexible tubing. Flexibility is obtained by means of annular or helical corrugations and by the use of metal having suitable thickness and resilience.

It is suggested that the resistance to fatigue of the metal used in the construction of flexible tubing of this type might be improved by the use of metal having two or more laminations separated from one another by a film or films of a suitable lubricant. An inner lamination of thinner metal would provide greater flexibility without loss of mechanical strength. The object is to obtain a tire-and-tube effect which will make the tubing still serviceable after cracks form in the outer lamination and until the equivalent of a "blow-out" occurs.

Flexible leads of the class referred to will operate without trouble for much longer periods if made with nonmetallic outer flexible tubing. Water-cooled flexible leads with neoprene outer tubes are being used. Unfortunately, nonmetallic tubes cannot continuously withstand the heat of flames or the radiant heat from furnace charges even when protected with asbestos fabric, as has been proven by trial.

It is found that if water-cooled flexible leads, with outer flexible tubing made of metal, are mounted in such a way that they may touch one another or other objects at a different electrical potential, they must be protected with insulation, such as that provided by asbestos sleeving, in order to prevent damage from arcing contacts.

The main sources of trouble with a self-supported flexible lead of the type described have been eliminated. A long-felt need for a water-cooled flexible lead suitable for low-frequency electric furnaces is therefore realized.

The previous portion of this paper dealt with the development, usage, characteristics, and advantages of self-supported, water-cooled furnace cables. The other aspects of these cables which are pertinent to this discussion are those of design and manufacture.

DESIGN

It has been found that the requirements vary to such an extent that a new design must usually be prepared for each application. However, while the designs are all basically similar, there may be considerable difference in details.

The designer must know, or must determine from the operating engineers, certain limiting conditions under which the cables are to function. These include the electrode current, the vertical travel required, the spacing between the bus bar and the electrode terminals, and any details regarding clearance, etc., which may be applicable.

Usually, more than one cable per electrode is required to carry the current. A 3-phase 20,000 kva furnace may draw as much as 75,000 amp/electrode, and a multiple cable system is obviously required. The number of cables is often limited by certain features of furnace design. If so, a preliminary choice of conductor size is made, using current densities of from 5–8 amp/1000 circular mils of copper area. These correspond approximately to current densities of from 6000 to 10,000 amp/in.^{2} which are considerably higher than the average density of 1000 amp/in.^{2} often used in bus bar design. However, these current densities, or even higher ones, are satisfactory as long as there is sufficient cooling water available to carry away the heat resulting from conductor losses, and as long as the cost of this heat loss can be tolerated. Based on these values of current density, the closest standard conductor size to that required is calculated.

The method of designing the conductor is not of particular interest here except to provide good flexibility. This can be achieved by using a large number of wires of annealed copper stranded together in the conventional manner to form a flexible conductor.

If the furnace is totally enclosed and near-normal ambient temperature conditions prevail, it is advantageous to use a reinforced neoprene hose which has almost unlimited ability to withstand flexing. Tests similar to those previously described were carried out on a cable having a hose of this type, and were concluded after 100,000 cycles of flexing without the cable having failed. The reinforcing is necessary to operate the hose under water pressure and must be nonmetallic to prevent the flow of induced currents which would overheat the reinforcing material and damage the hose.

If the cable is to be subjected to excessive heat or if there is danger of "blow-outs" of molten material from the furnace, a metallic hose is used. The type which has proved most successful is a seamless, flexible phosphor bronze hose. No wire braid reinforcement is necessary on this hose because the ends are restrained against longitudinal expansion and because the pressures used are such that the hose itself has ample strength against radial stresses.

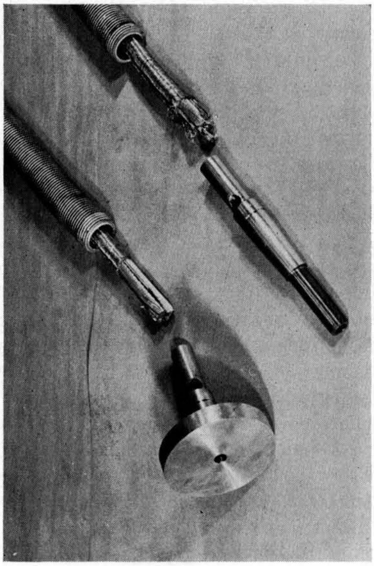


FIG. 7. Component parts of a self-supported, water-cooled cable with segmental conductor.

Knowing the conductor size, the designer can now calculate the approximate diameter of the terminals and decide on a size for the hose. This must be such that the hose can safely withstand continued flexing at the bending diameter corresponding to the required distance between the bus system and the electrode shoe. If this condition is not satisfied, the conductor size, and hence the number of cables required, must be revised.

The terminals are usually machined from copper rod and in general conform to the style shown in Fig. 3, although they may be modified somewhat to provide for different methods of making electrical and mechanical connections to the furnace. Clamps, tapered fittings, and solidly brazed connections are suitable connecting media. The cross-sectional area of the water passages, [6], [7], and [8], is made approximately equal to the area of the annular space, [15], between the conductor and hose. Only a moderate flow of water is required under a pressure of 30–60 psi. With current densities of the order previously mentioned, a water temperature rise of approximately 20° F above intake temperature is to be expected over the length of one cable.

The only main point left to consider is the length of the cable. This is dependent upon the vertical travel required. A simple arithmetical calculation involving the travel and mean bending diameter gives a minimum length for the hose. To this must be added a certain amount to insure that the hose is not subjected to bending at the point of connection to the terminals under extreme positions of travel. In practice, the length of a cable in its arched position is surprisingly short. The one with reinforced neoprene hose is 4 ft 9 in. in height. It has a 1,500,000 CM conductor, a $2\frac{3}{8}$ in. ID hose, and is capable of a maximum safe travel of 4 ft 9 in.

MANUFACTURE

It is evident from the preceding discussion that there are considerable differences in the various cables and, since relatively small numbers of these cables are made, mass production or assembly line procedures are not usually possible. Therefore, it is necessary to design tools, jigs, and methods of assembly.

Fig. 7 depicts the component parts of a cable. The larger terminal is intended for bolting to the electrode shoe, and the smaller one is intended to be fastened into a tapered fitting on the bus bar system. The conductor in this case is of segmental construction, two flexible segments being laid on either side of the supporting strip of spring phosphor bronze and held in position by a bronze wire braid. One end of this conductor is shown cut and prepared for insertion in the terminal. The conductor is soldered into the terminals while fixed in a jig of the correct

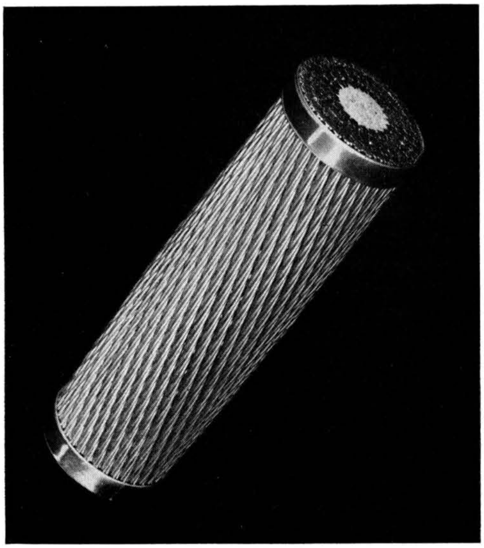


FIG. 8. 2,000,000 CM asbestos-cored cable

dimensions. For shipping, a clamp is fastened across the ends of the cable, between the two terminals, to maintain it at the proper bending diameter until installation is complete.

OTHER TYPES OF CABLES

Other types in use may be classified as: (*A*) water-cooled cables (*a*) supported by external means, and (*b*) unsupported; (*B*) bare cables (*a*) standard concentric stranded, and (*b*) special types, i.e., asbestos or spring cored.

A cable is said to be self-supporting if it can be installed in the form of an upright arch without external means of support. This is the type of cable which has already been described. When external support is required, it usually takes the form of a system of pulleys and counterweights. Some cables are not supported and hang in a loop between the bus bar and electrode. In general, water-cooled cables of these types are subject to much the same limitations regarding current carrying capacity length and bending diameters as are self-supported cables.

Bare flexible leads are commonly used for electric furnaces. Obviously, a proportionately greater cross-sectional area of copper is required than for water-cooled cables. Sufficient copper area must be provided to maintain a heat balance such that the cable is not damaged by excessive temperature rise. The cable is heated by resistance losses and by radiant heat from the furnace, and this heat must be dissipated into the air. Damage of the copper conductor from oxidation will result if its temperature exceeds 350°–400° F. There is thus a definite limit to the current which may be carried by a given cable under known conditions.

These cables may be of the usual concentric design, or they may be annular. The latter construction decreases alternating current losses and increases the surface area so that, for equivalent copper area, it has advantages over the standard concentric design. The annular construction is derived by stranding wires concentrically around a core of asbestos, a spiral spring, or similar material. Fig. 8 is a view of an asbestos-cored cable of 2,000,000 CM. It consists of 756 wires of #16 B&S annealed copper stranded around a ¾-in. asbestos rope. There is little advantage to be gained from using this construction in sizes less than 2,000,000 CM. Both standard concentric stranded and annular cables must be fitted into suitable terminals for attachment to the furnace.

CONCLUSION

In this paper the writers have attempted to present certain data which have been accumulated over the past 15 years in designing, manufacturing, and operating self-supported, water-cooled furnace cables. Several patents have been granted as a result of this work. The authors do not contend, nor has experience shown, that this type of cable is to be preferred above all others for every installation. However, it is suggested that under certain conditions self-supported, water-cooled cables can be used to advantage.

The following characteristics have been mentioned:

1. The power factor of the furnace can be improved by the use of short, interlaced multiple bus circuits combined with short flexible connections between the bus system and the electrodes. High effective electrode travel and low electrical reactance can be achieved by the use of arched cables.
2. Further reductions in reactance can be achieved by maintaining these flexible cables in an upright arch so that the length of all associated connections can be reduced to a minimum.
3. Advantages are derived from supporting the cables in this manner because the cable is farther away from the heat of the furnace.
4. The need for any auxiliary supporting apparatus is eliminated by the use of self-supporting cables.
5. More space is available for furnace operations because fewer cables are required and because more space is available directly over the "melt."

These advantages can only be fully realized when the cables can be operated with a reasonable freedom from maintenance and when the operating life is at least comparable to that of bare flexible leads.

Development has now progressed to such an extent that the authors believe these conditions can be fulfilled. Several such installations are in use in Canada and others are contemplated in the future in Canada, the United States, and Europe.

ACKNOWLEDGMENTS

Credit is due to W. R. Tims, power cable design engineer of the Northern Electric Company, for originating the idea of placing the spring strip at the center of the flexible lead as shown in the 4-segment-conductor design, Figure 5. The authors also wish to acknowledge the cooperation of other associates in the development of flexible leads suitable for electric furnaces.

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

Society Spring Meeting in Chicago in May

Chicago's Michigan Avenue skyline

The Spring Meeting of the Society will be held May 2 to 6, 1954, at the LaSalle Hotel, Chicago. The 105th General Meeting will feature sessions of the Electric Insulation, Electronics, Industrial Electrolytic, and Theoretical Electrochemistry Divisions.

Reservations

The LaSalle Hotel is reserving a large block of rooms for Society members. If you plan to attend the meeting, you are urged to request accommodations directly from the hotel. Address: Room Reservations, LaSalle Hotel, Chicago 2, Illinois. It will be extremely helpful both to the hotel and to the local committee if you will specify that your reservation is for The Electrochemical Society meeting. As always, the earliest possible reservations are desired. Of course, reservation cards will be included when the Program Booklet is distributed, but advance reservations are strongly recommended.

Technical Meetings

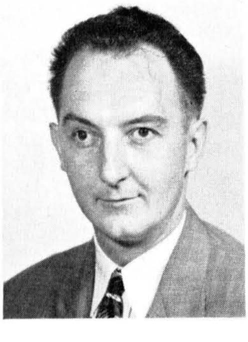
In addition to the General Sessions of the four Divisions, special symposia and round tables will be held on Rare Metals, Molten Bath Electrolysis, Electric Insulation, Compression of Halogens, Luminescence, Instrumental Measurements, Screen Applications, and Semiconductors. Although plans are not yet complete, an exceedingly full technical program is anticipated, comprising about 20 half-day sessions.

Other Functions

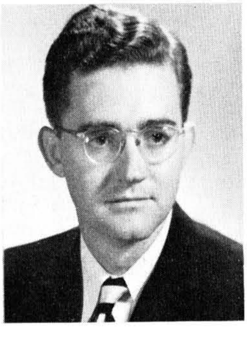
In addition to the usual meetings of the Ways and Means Committee and the Board of Directors on Sunday, May 2, there will be a general Society luncheon and business meeting on Tuesday, and a meeting of the Local Section Advisory Committee. The Division Luncheons which are planned at present include Electric Insulation, Electronics, and Industrial Electrolytic.

An informal dinner and entertainment is planned for Monday evening,

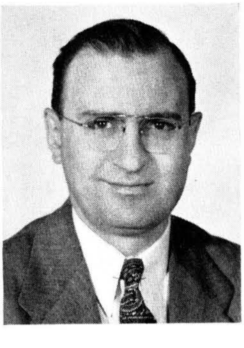
O. W. Storey
Honorary Chairman



H. T. Francis
General Chairman



A. H. Roebuck
Registration



Clifford Hampel
Entertainment

and the President's Reception and Banquet for Tuesday evening. A Section Q session is scheduled for Wednesday.

A series of very interesting plant trips to some of Chicago's diverse industries is being scheduled, as well as varied activities for the ladies.

Members of the Chicago Section who are planning the Spring Meeting include Oliver W. Storey, Honorary Chairman; H. T. Francis, General Chairman; A. H. Roebuck, Registration; C. A. Hampel, Entertainment; Simon Gary, Finance; D. V. Louzos, Plant Trips; Ben Freeberg, Arrangements. Miss Marguerite Wall of Armour Research Foundation is in charge of the Ladies' Program. Acting as advisors are R. S. Modjeska and E. L. Koehler.

Notice to Members

Members of the Society *who are residents of New York City*, when ordering "Modern Electroplating," must make their checks payable to John Wiley & Sons, Inc., *for the sum* of $5.84 to cover the New York City sales tax. Orders for the volume, including the check, should be sent to Society Headquarters, 216 West 102nd St., New York 25, N. Y.

Members *outside of New York City* must make their checks payable to John Wiley & Sons, Inc., *for the sum of* $5.67. Send order for volume and check to Society Headquarters.

Dr. Prasad Visits Niagara Falls

The Niagara Falls Section was host to a distinguished visitor, Dr. B. K. R. Prasad of the Bombay Government, during his four-day visit to Niagara Falls. As the first Chairman of the India Section of The Electrochemical Society, Dr. Prasad was instrumental in the founding of that Section and has been an outstanding leader in India's electrical and electrochemical industry.

A series of tours to local industries and a dinner at the Red Coach Inn in Niagara Falls were arranged to enable Dr. Prasad to meet a number of the outstanding personalities in the electrochemical-metallurgical field in the Niagara area. The members of The Electrochemical Society present at the dinner were fortunate in hearing a first-hand account given by Dr. Prasad on the achievements, aims, and problems of India's industry.

C. E. E. R. I. in India

The Prime Minister of India laid the foundation stone of the Central Electronics Engineering Research Institute at Pilani, Rajasthan State, in September 1953. This will be the fourteenth institute in the chain of national laboratories set up by the Council of Scientific and Industrial Research all over India. Mr. G. D. Birla, the well-known Indian industrialist, has donated Rs.21 lakhs on behalf of the Birla Education Trust for its establishment. The Government of India has recognized the national importance of the proposed institute and made a provision of Rs.29 lakhs for it in the first five-year plan.

The object of the institute will be to undertake research and development on all aspects of electronics engineering. Special attention will be devoted to the utilization of indigenous raw materials in the manufacture of components, development and use of electronic circuits for industry, building of standard electronic instruments for test purposes, investigations on radar and other types of equipment, and applications of electronics in metallurgy. The institute will undertake projects sponsored by industry and close liaison will be maintained between the institute and industry.

The institute will consist of the following divisions: (*a*) electronic circuits, (*b*) electronic components, (*c*) electronic instruments, (*d*) acoustics-audio equipment, (*e*) ultra-high frequency and very-high frequency, (*f*) library and information, and (*g*) workshop.

T. L. Rama Char,
Regional Editor, India

Polyethylene Unit Being Built by Monsanto

Construction is now under way for the first polyethylene production plant of the Monsanto Chemical Company at Texas City, Texas. Located adjacent to Monsanto's existing Texas City plant, the new polyethylene unit, operated by the Plastics Division, is expected to produce commercial quantities of polyethylene starting the fourth quarter of 1954. Plans announced last March set initial annual capacity at about 66 million pounds, with a 50% increased capacity scheduled for 1957.

Burgess Chemical Changes Name to Cary Chemicals

Directors of the Burgess Chemical Company have announced a change in corporate name to Cary Chemicals, Inc., following a directors' meeting at which Kenneth B. Cary was elected president and George F. Blasius was made executive vice-president and general manager.

The laboratory and plant of Cary Chemicals, Inc., are located in Milltown, N. J., and the executive sales offices are in Paterson, N. J. Cary Chemicals, Inc., manufactures its own line of products, including vinyl compounds, reclaiming oils, pitch compounds, tall oil esters, stearine pitches, and other related materials, and also markets, as sales agents, other essential compounding ingredients for the rubber and plastics industries.

Zirconium Company Formed

Formation of the Zirconium Corporation of America has been announced by its president George R. Sylvester. The new company plans to manufacture various zirconium compounds, but will concentrate on production of zirconium oxide. The new, patented process to be used by the corporation was developed by Sylvester & Company of Cleveland under the direction of R. A. Schoenlaub. A pilot plant was run successfully for over a year, producing stabilized zirconium oxide. Present plans call for full-scale production at the new Solon, Ohio, plant in January.

Foxboro Establishes New Branch in Amarillo

The opening of a branch office in Amarillo, Texas, is announced by The Foxboro Company, of Foxboro, Mass., manufacturer of industrial instruments for the measurement and control of process variables. Located at 1117 La Paloma Street, the new branch was made necessary by expanded industrial activity in the region, particularly in the oil and gas, chemical and petrochemical industries.

MEETINGS OF OTHER ORGANIZATIONS

Chemical Institute of Canada, 6th Divisional Conference, Analytical Chemistry Division, Royal Hotel, Guelph, Ontario, February 18–19, 1954; 8th Divisional Conference, Protective Coatings Division, Montreal, February 25, 1954; 8th Divisional Conference, Protective Coatings Division, Toronto, February 26, 1954; 3rd Divisional Conference, Chemical Engineering Division, Montreal, March 1–2, 1954.

NATIONAL ASSOCIATION OF CORROSION ENGINEERS, Tenth Annual Conference and Exhibition, Kansas City, March 15–19, 1954.

FOURTH INTERNATIONAL CONFERENCE ON ELECTRODEPOSITION AND METAL FINISHING, sponsored by The International Council for Electrodeposition, Hotel Russell, London, April 21–24, 1954. Hothersall Memorial Lecture to Institute of Metal Finishing on Tuesday, April 20, by Dr. William Blum.

TENTH INTERNATIONAL PRINTING, MACHINERY AND ALLIED TRADES' EXHIBITION, The Grand and National Halls, Olympia, London, July 5–16, 1955.

Change of Address

The Columbia-Southern Chemical Corporation, subsidiary of Pittsburgh Plate Glass Company, has moved its General Offices from Fifth Avenue at Bellefield, Pittsburgh, to One Gateway Center, 420 Fort Duquesne Boulevard, Pittsburgh 22, Pa.

SECTION NEWS

Cleveland Section

The 182nd meeting of the Cleveland Section was held on Tuesday, December 8, 1953, at the Cleveland Engineering Society. Mr. Robert J. McKay, Society President, was speaker of the evening.

Prior to the meeting, dinner was served, after which Mr. McKay held an informal discussion on "Representation of Local Sections in the National Society."

As his lecture topic, Mr. McKay spoke on "Metal Ion and Oxygen Concentration Cells in Corrosion." He stressed the need for fundamental corrosion data in the electroplating field. He has had extensive experience in this field; he described some of his work including equipment, reactions involved, and conflicting theories on corrosive actions.

MERLE E. SIBERT, *Secretary*

Midland Section

Robert J. McKay, President of The Electrochemical Society and a Vice-President of the International Nickel Company, was the guest of honor at a dinner given by the local section on December 10 at the Midland Country Club.

Later he spoke on the subject of oxygen and metal ion corrosion before a joint meeting of the Midland Section of the Society and the Midland Section of the American Chemical Society. Mr. McKay gave a brief history of the theory of corrosion, and the problems involved in testing a satisfactory plate. He explained how corrosion may be measured by means of voltage and minute currents, and described the fundamental corrosion cell. He concluded that oxygen concentration is one of the biggest factors in metal corrosion.

M. P. NEIPERT, *Secretary-Treasurer*

Philadelphia Section

On Wednesday, December 16, 1953, the Executive Committee of the Philadelphia Section met at the Engineers' Club. After discussing current Section business, Dr. Eckfeldt read the following tribute to Dr. Lukens.

"Science is built in no small measure on the good faith, good will, and cooperation of the persons comprising the scientific community. Thus it is proper from time to time for the members of a scientific society to turn from scientific matters and give thought to their fellow members. The Electrochemical Society at large and our Philadelphia Section in particular have endeavored with success to foster a spirit of fellowship. To this end, the Executive Committee of the Philadelphia Section of The Electrochemical Society has traditionally held a meeting each year in the month of December, preceding the holiday season. This Christmas meeting always has a special significance to those persons in attendance who take this opportunity to express personally to each other their warmest and heartfelt wishes for a Merry Christmas and a Happy New Year.

"We of the Philadelphia Section have been fortunate in having members who, through their interest in the welfare and objectives of The Electrochemical Society, have unselfishly given their time and talents on behalf of this organization. It is fitting that an expression of appreciation should be given to such a person. Therefore, the members of the Executive Committee of the Philadelphia Section have designated that their meeting held on Wednesday the sixteenth day of December 1953 be set apart to honor and thank one of their beloved fellow members. Through his loyal and unceasing efforts for many years, Hiram Stanhope Lukens has given our Society and Section invaluable guidance, encouragement, and cooperation.

"Dr. Lukens has faithfully served our Section, as Secretary in 1930–31, as Chairman in 1931–32, and from 1931 down to the present time as an active member of the Philadelphia Executive Committee, throughout this whole period contributing his vital share in effective leadership and responsibility. All who enjoyed the national meetings of our Society sponsored by the Philadelphia Section, at Wernersville in 1940 and the meetings in Philadelphia in 1937, 1949, and 1952, are indebted in no small measure to the part played by Dr. Lukens in making these meetings successful.

"Dr. Lukens has rendered outstanding service to our Society at large. In 1934–35 he was President of our Society. He has served on various national committees including the Board of Directors and has carried the responsibility of chairmanship of several of these.

"Dr. Lukens has our sincere appreciation. We look forward to many more years of rewarding association with him in our activities. To him and his family at this Christmas season go our best wishes."

GEORGE W. BODAMER, *Secretary*

Washington-Baltimore Section

At the meeting of the Washington-Baltimore Section of The Electrochemical Society on November 19, 1953, Dr. C. G. Abbot of the Smithsonian Institution spoke on the subject, "Utilizing Solar Energy." Dr. Abbot reviewed the early work of the Smithsonian Institution in establishing stations in various locations throughout the world for daily measurements of solar radiation in order to determine the solar radiation constant which led to his interest in this field.

Dr. Abbot reviewed the early unsuccessful attempts to use lenses to power solar engines and subsequent attempts to use mirrors. Recently developed techniques in the preparation of mirror surfaces offer promise of more efficient machines. Dr. Abbot described an engine he has designed which can develop 2 hp using a spherical mirror ten feet in diameter. This mirror is approximately 25% efficient in the conversion of solar energy. However, spherical mirrors are difficult to fabricate and are expensive, so that the first practical engine probably will use a rectangular mirror which is less efficient and much cheaper. Dr. Abbot expressed the opinion that, as our fuel supplies decrease in availability and increase in cost, solar engines will find increasing use in areas that experience sunny days most of the year.

Dr. William Blum, consultant and former Chief of the Electrodeposition Section, National Bureau of Standards, was the guest speaker at the December 17 meeting of the Washington-Baltimore Section.

Dr. Blum has recently returned from Australia where he spent several months as a guest of the three Australian Branches of the American Electroplaters' Society. During his trip, he visited a number of research laboratories and industrial concerns employing electrochemical processes. Dr. Blum's account of his experiences, which was accompanied by numerous slides, was extremely interesting.

FIELDING OGBURN, *Secretary*

NEW MEMBERS

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

Active Members

SIDNEY M. BLITZER, Ethyl Corporation, mailing add: 2826 Terrace Avenue, Baton Rouge, La. (Industrial Electrolytic and Theoretical Electrochemistry)

WAYNE M. GAUNTT, Reynolds Metal Co., 2000 S. Ninth St., Louisville, Ky. (Corrosion, Electrodeposition, Electronics, Electro-organic, and Theoretical Electrochemistry.)

ROBERT A. GILBERT, Battelle Memorial Institute, mailing add: 921 Oxley Rd., Columbus 12, Ohio (Electrothermic)

ALBERT E. HENDRICKSON, Sylvania Electric Products Inc., mailing add: 75-14 Vleigh Pl., Flushing, N. Y. (Electronics)

NORBERT IBL, Swiss Federal Institute of Technology, mailing add: Steinwiesstr. 52, Zurich 32, Switzerland (Theoretical Electrochemistry)

JEROME KRUGER, Naval Research Laboratory, mailing add: 8101 14th Avenue, Hyattsville, Md. (Corrosion)

MANLEY W. MALLETT, Battelle Memorial Institute, mailing add: 1285 Arlington Ave., Columbus, Ohio (Corrosion and Electrothermic)

RICHARD W. MOONEY, Sylvania Electric Products Inc., 60 Boston St., Salem, Mass. (Electronics)

MARGIE M. NICHOLSON, Humble Oil and Refining Co., mailing add: 120 Marion Ave., Baytown, Texas (Theoretical Electrochemistry)

FRANK P. SCHIRO, Signal Corps, Ft. Monmouth, mailing add: 14 Queens Dr., Little Silver, N. J. (Battery)

DONALD M. SOWARDS, University of Texas, mailing add: 2917 West Ave., Austin, Texas (Theoretical Electrochemistry)

PERSONALS

WILLIAM N. DUNLAP has accepted the position as assistant project engineer with the Friez Instrument Division, Bendix Aviation Corporation, Baltimore, Md. He was formerly supervisor of Plating Laboratory, Chrysler Corporation, New Orleans, La.

W. L. HADEN, JR., research chemist, Attapulgus Minerals and Chemicals Corporation, Camden, N. J., has been promoted to research supervisor of the company.

TADAYUKI NAKAYAMA, previously with the Scientific Research Institute, Tokyo, Japan, is now associated with Castings Research Laboratory in Tokyo.

FERNAND PORTAIL, Compagnie Industrielle des Piles Electriques, France, has been awarded the Gaston Plante Medal from the Société des Electriciens.

HOWARD A. ACHESON was recently re-elected president and chairman of the board of Acheson Industries, Inc.

BOOK REVIEWS

ION EXCHANGERS IN ANALYTICAL CHEMISTRY by Olof Samuelson. Published by John Wiley & Sons, Inc., New York, 1953. XVIII plus 291 pages, $6.50.

"Ion Exchangers in Analytical Chemistry" represents the first successful effort by any author to provide the analytical chemist with a practical working introduction to the field of ion exchange. The book is not intended as a comprehensive source of references but rather as an indication of the possibilities of ion exchange methods as analytical tools.

The first part of the book consists of an explanation of ion exchange phenomena. Theoretical discussion is kept to a minimum with the emphasis being placed on properties of ion exchangers, experimentally determined principles of ion exchange, and empirical equations governing equilibria and kinetics. Operating techniques of ion exchange procedures are discussed from a practical standpoint in the second section. The final (and major) portion of the book illustrates the applications of these techniques in inorganic, organic, and biochemical analysis. The many detailed procedures given in this section should be of help to the analytical chemist who desires to apply ion exchange methods to his own particular problems.

Because of the wide range of subject matter covered, this work will be of general interest to analytical chemists in all fields. The book is very readable and, coming as it does from one of the recognized experts in this new field, should be authoritative.

THOMAS C. LOOMIS

INTRODUCTION TO SOLID STATE PHYSICS by Charles Kittel. Published by John Wiley & Sons, Inc., New York, 1953. 396 pages, $7.00.

In the last decade the number of physicists working in the field of solid state has expanded greatly. To a large extent this increase has come about because of the growth of industrial laboratories. There has been no corresponding expansion of university instruction in the physics of solids. One of the reasons for this state of affairs may very well be the difficulty of organizing our information in a form suitable for classroom instruction. The "Introduction to Solid State Physics" by Charles Kittel recognizes this difficulty and sets out to overcome it. In accordance with this purpose, it contains neither a logical buildup of the theory of solids from first principles, nor a comprehensive review of all the accumulated information. Instead, it treats certain limited topics which have been handled successfully by experimental methods and for which the results can be understood through simple (although not always rigorous) reasoning. Since it has proved almost impossible to design a course around the two other viewpoints above, this new departure is to be commended.

The book starts out with the topics of ionic crystals and lattice vibrations which are of outstanding importance because of their historical impact upon physics as a whole. The central part deals with dielectric and magnetic phenomena. The book then passes to the theory of free electrons, band theory of metals and semiconductors, and finally to theories of crystal imperfections. In most of these sections the aim of developing a simple exposition suitable for classroom use is brilliantly realized, so much so that a word of caution may be in order here and there about the rigor and completeness of the reasoning presented. One such case is, for instance, the theory of order-disorder transformations which is given, justifiably, a very simple form; however, even the references which are supposed to review the field and present "a careful discussion" of slurred-over points share this simplicity so that the reader does not even get an inkling of the intensive thinking which has been going on in this field. Another case in point arises in the theory of lattice vibrations which Van Hove has advanced beyond the position indicated either by the book itself or the references quoted. The opposite type of difficulty, namely that of a reasoning too obscure for classroom exposition arises seldom; one such case is, perhaps, the theory of metallic conduction, which is a notoriously recalcitrant field from the expository viewpoint.

In conclusion, it may be said that Professor Kittel has created an excellent introductory textbook in a field where this type of exposition was never tried before. It is to be hoped that the student for whom it is designed will like it, and get from it a sympathetic viewpoint toward physical reasoning in the study of solids.

G. H. Wannier

Chemical Constitution by J. A. A. Ketelaar; translated by L. C. Jackson. Elsevier Publishing Company, Houston, Texas, 1953. VIII + 398 pages, $6.50.

"Chemical Constitution" subtitled "An Introduction to the Theory of the Chemical Bond" is intended by its author, Dr. J. A. A. Ketelaar, to serve as " . . . a complement to the usual textbooks of inorganic and organic chemistry which will enable [the chemist] to build up the great mass of data into a coherent body." This first English edition is a translation from the Dutch by Dr. L. C. Jackson.

The book is divided into four major parts concerned with the ionic bond, the atomic (covalent) bond, the metallic bond, and van der Waals bonding, in that order, and, although each bond type is considered separately, the essential similarities are stressed. The author strives to relate physical and chemical properties to molecular structure and is notably successful in this endeavor. The presentation is systematic and, where possible, general principles or rules are stated and illustrated by numerous examples. Recent experimental data are included in many sections of the text.

After a short introduction, in which the periodic table and the wave properties of electrons are discussed, the ionic bond is considered in detail. Crystal structure, ionic radii, and lattice energies are taken up generally, and the conclusions derived are applied to specific systems. In addition to simple ionic compounds, complex systems are treated at some length. The sections on polynuclear complexes and glasses contain good descriptive material but would be more readily comprehended if more structure diagrams were included. Properties such as electrolytic dissociation, acid-base strength, volatility, hardness, and solubility are discussed in relation to the ionic bond.

Discussion of the atomic bond is prefaced by a brief review of quantum mechanical principles with the hydrogen atom, the hydrogen molecule ion, and the hydrogen molecule receiving most emphasis. The resonance concept is given a lucid treatment. Hybridization is presented qualitatively and a large number of examples are given with reference to directional characteristics and the magnetic criterion of bond type. Double and triple bonds, the concept of pi-electrons, and conjugation are introduced qualitatively. A section is included on the theory of color, followed by a review of approximate methods of calculation used in quantum theoretical chemistry.

The metallic bond receives brief treatment from the point of view of quantum mechanics and the band model. Semiconductors and alloys are discussed as is Pauling's theory of metals. An interesting section on the factors responsible for mechanical properties of metals is included.

The final chapter is an excellent treatment of van der Waals forces and their influence on physical and chemical properties. Use of van der Waals equation of state in theoretical considerations regarding boiling points and solubilities is given in considerable detail. The final section is a good summary on hydrogen bonds.

The attention of the author to the dependence of physical and chemical properties on molecular structure is outstanding and makes this text a worth-while contribution. It is felt, however, that the mathematical parts of the quantum mechanical sections will not be readily comprehended by persons not previously trained in quantum theory.

The text is relatively free of typographical errors and the translation is adequate. Insufficient references limit the utility of the book for reference purposes.

David W. McCall

RECENT PATENTS

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

November 3, 1953

Faust, C. L., and Hespenheide, W. G., 2,658,032, Electrodeposition of Bright Copper-Tin Alloy
Ferris, D. E., 2,658,033, Electrolytic Method and Apparatus for Sterilizing Water
La Burthe, P. H., 2,658,093, Manufacture of Glass
Nonken, G. C., 2,658,094, Combined Electrode and Skimmer for Electric Glass Melting Furnaces
Arbeit, P., Dubois, R., and Lambert, R. E., 2,658,095, Process and Apparatus for Making Glass
Peyches, I., 2,658,096, Apparatus for the Manufacture of Multicellular Glass
√Orsino, J. A., 2,658,097, Manufacture of Positive Plates for Lead Storage Batteries
√Coleman, J. J., and Kurlandsky, S., 2,658,098, Dry Battery with Conductive Tape Intercell Connections
√Basset, L. P., 2,658,099, Microporous Carbon and Graphite Articles, Including Impregnated Battery Electrodes and Methods of Making the Same
√Kendall, T. L., 2,658,100, Vent Cap

November 10, 1953

Du Rose, A. H., and Little, J. D., 2,658,266, Laminated Coating
Talmey, P., and Crehan, W. J., 2,658,839, Process of Chemical Nickel Plating
Gutzeit, G., and Krieg, A., 2,658,841, Process of Chemical Nickel Plating and Bath Therefor
Gutzeit, G., and Ramirez, E. J., 2,658,842, Process of Chemical Nickel Plating and Bath Therefor

Society Prizes and Awards

The Edward Goodrich Acheson Medal and Prize

The Edward Goodrich Acheson Gold Medal and $1,000 Prize were founded by Dr. Acheson in August 1928.

The award is made once every two years (first award at the Fall Meeting, 1929) to the person who shall have made a distinguished "contribution to the advancement of any of the objects, purposes, or activities . . . of the Society. Such contribution may consist of but shall not be limited to (*a*) a discovery pertaining to electrochemistry, electrometallurgy, or electrothermics, (*b*) an invention of a plan, process or device, or research evidence by a paper embodying information, useful, valuable, or significant in the theory or practice of electrochemistry, electrometallurgy, or electrothermics, and/or (*c*) distinguished services rendered to the Society or its successor."

The award is made without distinction on account of sex, citizenship, race, or residence. See *Trans. Electrochem. Soc.*, **54**, 6 (1928).

The Palladium Medal

The Palladium Medal of The Electrochemical Society was founded in 1950. The source of funds for the establishment of the medal is the royalties derived from sales of the *Corrosion Handbook* which was sponsored and largely written by members active in the Corrosion Division of the Society. Dr. H. H. Uhlig served as Editor-in-Chief.

The award of the medal is to be made every two years to a scientist, in recognition of original and outstanding contributions to the knowledge of corrosion in one or more of the following fields: the theory of corrosion or corrosion control, electrode potentials, properties of electrolytes, electrode reactions, and the surface properties of metals. The jury for the selection of the medalist is appointed by the Board of Directors of the Society and consists of three members, including one member from the Corrosion Division and one from the Theoretical Division, both of whom are active in their respective fields. See *J. Electrochem. Soc.*, **98**, 95C (1951).

The Joseph W. Richards Memorial Lectureship

Dr. Joseph William Richards was one of the founders of The Electrochemical Society, and its first President. He was Secretary and Editor of the Society's TRANSACTIONS from 1904 to 1921. His very active and untiring interest in the Society and in the science and art of electrochemistry reflected itself in the rapid growth of the Society and of the electrochemical industry throughout the world. From the very start, Dr. Richards fostered the international spirit.

The Joseph W. Richards Memorial Lectureship was established in 1929 by a group of friends and admirers of Dr. Richards. The interest of the fund is used to meet the expenses incurred by inviting and entertaining distinguished scientists. See *Trans. Electrochem. Soc.*, **57**, 30 (1930).

The Electrochemical Society Prize to Young Authors

An annual prize of one hundred dollars was established by the Board of Directors in July 1928. The prize is awarded to the author of the best paper printed in the yearly volume of the JOURNAL of the Society. The judges to pass upon the merits of the paper are the Chairman of the Publication Committee, the Secretary of the Society, and three members of the Society, and two alternates, selected by the Chairman of the Publication Committee, the Committee being at liberty to invite the opinion of members not on the Committee.

The prize is open to students and graduates, under thirty-one years of age, of any technical school, college, or university, no matter where located. See *Trans. Electrochem. Soc.*, **55**, 22 (1929); **92**, viii (1947).

Francis Mills Turner Award, Sponsored by the Reinhold Publishing Corporation

For several years, Francis Mills Turner personally offered an annual prize consisting of $50.00 worth of scientific and technical books published by the Reinhold Publishing Corpora-

Honorary Members of the Society

Charles F. Chandler,* New York, N. Y.	Volume 35 (1919)
Edgar F. Smith,* Philadelphia, Pa.	Volume 35 (1919)
Carl Hering,* Philadelphia, Pa.	Volume 41 (1922)
Edward G. Acheson,* Niagara Falls, N. Y.	Volume 43 (1923)
Wilder D. Bancroft,* Ithaca, N. Y.	Volume 47 (1925)
Edward Weston,* Montclair, N. J.	Volume 50 (1926)
Thomas A. Edison,* Orange, N. J.	Volume 54 (1928)
W. Lash Miller,* Toronto, Canada	Volume 55 (1929)
Edward Dean Adams,* New York, N. Y.	Volume 57 (1930)
Charles F. Burgess,* Chicago, Ill.	Volume 62 (1932)
Frederick Mark Becket,* New York, N. Y.	Volume 66 (1934)
L. H. Baekeland,* New York, N. Y.	Volume 69 (1936)
Robert A. Witherspoon, Montreal, Canada	Volume 78 (1940)
Archer E. Wheeler, New York, N. Y.	Volume 80 (1941)
W. R. Whitney, Schenectady, N. Y.	Volume 85 (1944)
Paul J. Kruesi, Chattanooga, Tenn.	Volume 85 (1944)
Colin G. Fink,* New York, N. Y.	Volume 89 (1946)
John W. Marden, Bloomfield, N. J.	Volume 91 (1947)
William Blum, Washington, D. C.	Volume 100 (1953)

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* Deceased

tion. At the time of his demise, the Reinhold Publishing Corporation established the "Francis Mills Turner Memorial Award, Sponsored by the Reinhold Publishing Corporation," consisting of $100.00 worth of scientific and technical books to be given each year to an author under 31 years of age. This revision was gratefully accepted by the Board of Directors at the Society convention held in Philadelphia, May 4 to 8, 1952. See *J. Electrochem. Soc.*, **99,** 162*C* (1952).

Consolidated Fellowship Fund

Due to the deterioration of the Weston Fellowship funds, the Board of Directors on October 26, 1952 established a Consolidated Fellowship Fund from the accumulated earnings of the Weston Fellowship Fund, the entire Roeber Research Fund, the excess earnings of the Acheson Fund, and the $1000 returned by John W. Marden (Acheson Award) at the Montreal Meeting. This fund will be accumulated until such time as the Society has available sufficient yearly income from this source to justify offering a fellowship, at which time the Society again will be in a position to sponsor graduate studies in electrochemistry.

Former recipients of the Acheson Medal and Weston Fellowship are listed below.

Prize Essay Contest

The Electrochemical Society sponsors an essay contest, which is open to undergraduate and graduate students, on a selected subject. Two prizes are awarded for the two best essays submitted: first prize is $100, plus a one-year subscription to the JOURNAL; second prize is $50, plus a one-year subscription to the JOURNAL.

Prizes for the contest are financed by royalties from the sale of the "Corrosion Handbook," a widely used technical publication sponsored by the Corrosion Division and published by John Wiley & Sons, Inc., in 1948. See *J. Electrochem. Soc.*, **100,** 68*C*, 282*C* (1953).

Winners of Society Prizes and Awards

Acheson Medalists

EDWARD G. ACHESON*—Artificial Graphite and Carborundum—**56,** 7 (1929).

EDWIN F. NORTHRUP*—Induction Furnaces—**60,** 8 (1931).

COLIN G. FINK*—Electrochemistry—**64,** 2 (1933).

FRANK J. TONE*—Electrothermics—**68,** 2, 8 (1935).

FREDERICK M. BECKET*—Electrothermics—**72,** 3 (1937).

FRANCIS C. FRARY—Electrometallurgy—**76,** 4 (1939).

CHARLES F. BURGESS*—Electrochemistry—**82,** 3 (1942).

WILLIAM BLUM—Electrodeposition—**86,** 4 (1944).

H. JERMAIN CREIGHTON—Electro-Organic Chemistry—**90,** 5 (1946).

DUNCAN A. MACINNES—Electrochemistry—**94,** 4*P* (1948).

GEORGE W. VINAL—Batteries—**97,** 231*C* (1950); **98,** 11*C* (1951).

JOHN W. MARDEN—Electronics—**100,** 37*C* (1953).

Weston Fellowship Holders

EDWARD B. SANIGAR—"The Titration of Potassium Cyanide and of Free Cyanide in Silver-Plating Solutions by Means of Silver Nitrate"—**58,** 435 (1930); "Electrodeposition of Silver from Sulfate, Nitrate, Fluoborate and Fluoride Solutions"—**59,** 307 (1931).

KARL SOLLNER—"An Experimental Study of Negative Osmosis. Part I"; "Experimental Verification of a New Theory Concerning the Mechanism of Anomalous Osmosis. Part II"—**61,** 477, 487 (1932).

MARLIN E. FOGLE—"A Study of Cuprous Oxide Solid Photoelectric Cells"—**66,** 271 (1934).

ROBERT D. BLUE—"Electrodeposition of Aluminum from Non-Aqueous Solutions"—**65,** 339 (1934).

PIERRE A. JACQUET—"Effect of Colloids on Electrodeposition"—**65,** 21 (1934).

MYRON A. COLER—"Electrolytic Processes in the Magnetic Field"—**72,** 247 (1937).

HENRY B. LINFORD—"The Effect of the Speed of Rotation on the Electrode Potentials of Copper and Zinc"—**72,** 461 (1937).

GARTH L. PUTNAM—**71,** 26 (1937).

VITTORIO DE NORA—**73,** 39 (1938).

WALDEMAR P. RUEMMLER—**75,** 52 (1939); **77,** 50 (1940).

RODNEY E. BLACK—**79,** 44 (1941).

WILLIAM E. ROAKE—**81,** 46 (1942).

ROBERT D. MISCH—**93,** 14*P* (1948).

MASSOUD T. SIMNAD—**94,** 3*N* (1948)†; **97,** 161*C* (1950).

Joseph W. Richards Memorial Lecturers

JOHN A. MATHEWS,* Vice-President and Director of Research, Crucible Steel Company, New York, N. Y. "The Electric Furnace and the Alloy Age," **61,** 143 (1932).

R. S. HUTTON, Goldsmiths' Professor of Metallurgy, University of Cambridge, England. "Faraday and His Electrochemical Researches," **64,** 13 (1933).

W. S. LANDIS,* Vice-President and Director, American Cyanamid Company, New York, N. Y. "Joseph W. Richards, The Teacher—The Industry," **66,** 6 (1934).

KARL K. DARROW, Physicist, Bell Telephone Laboratories, New York, N. Y. "Electricity in Gases," **69,** 67 (1936).

CHARLES H. HERTY,* Director, Herty Foundation Laboratory, Savannah, Ga. "The Utilization of Southern Pine," **73,** 50 (1938).

BRADLEY STOUGHTON, Dean of Engineering, Lehigh University, Bethlehem, Pa. "Modern Marvels of Electrometallurgy," **76,** 29 (1939).

VLADIMIR K. ZWORYKIN, Associate Director of RCA Research Laboratories, Camden, N. J. "The Electron Microscope," **80,** 14 (1941).

B. D. SAKLATWALLA,* Metallurgical Consultant, Pittsburgh, Pa. "Thermal Reactions in Ferro-Alloy Metallurgy, the Basis of Alloy Steel Development," **84,** 13 (1943).

STEWART J. LLOYD, Professor of Chemical Engineering, University of Alabama, University, Ala. "Freedom in Science," **89,** 9 (1946).

OLIVER W. STOREY, Consultant, Burgess Battery Company, Chicago, Ill. "Research in Industry—Is Government Antagonistic to It?" **96,** 3*P* (1949); **97,** 9*C* (1950).

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* Deceased.

† *J. Electrochem. Soc.*

* Deceased.

J. O'M. Bockris, Lecturer, Department of Inorganic and Physical Chemistry, Imperial College of Science and Technology, London University, London, England. "Overpotential," **98,** 153*C* (1951).

Palladium Medalists

Carl Wagner, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass. "The Electrochemistry of Ionic Crystals," **99,** 346*C* (1952).

Nathaniel Howell Furman, Chairman, Department of Chemistry, Princeton University, Princeton, N. J. "Coulometry—Related Phenomena of Electrolysis and Current-Sweep Polarography," **101,** 19*C* (1954).

Winners of Young Authors' Prize

William C. Gardiner—"Hydrolysis of Mercurous Sulfate by Cadmium Sulfate Solution in the Weston Normal Cell"; "Oxidation of the Depolarizer in Preparing Standard Cells"; "Crystalline Mercurous Sulfate and the Weston Normal Cell"—**56,** 111, (1929).

Dwight K. Alpern—"Engineering Development of Photovoltaic Cells"—**58,** 275 (1930).

Frank L. Jones—"Electrodeposition of Tungsten from Aqueous Solutions"—**59,** 461 (1931).

F. W. Godsey, Jr.—"Alternating Current Capacities of Electrolytic Condensers"; and "Potential Gradients in Anodic Films"—**61,** 515, 549 (1932).

B. L. Bailey—"Hardness Values for Electrochemical Products"—**63,** 369 (1933).

Joseph R. Heard, Jr.—"Electro-Organic Oxidations in Concentrated Aqueous Organic Salt Solutions"—**65,** 301 (1934).

Upton B. Thomas, Jr.—"Electrochemical Behavior of Lead, Lead-Antimony and Lead-Calcium Alloys in Storage Cells"—**68,** 293 (1935).

W. A. Johnson—"Studies of Overvoltage: Effect of Fusion of the Cathode and Effect of Temperature on Gas Polarization"—**70,** 259 (1936).

R. Spencer Soanes—"Potential Distribution in High Current Carbon Arcs in Air"—**72,** 281 (1937).

N. B. Nichols—"The Cathode Ray Oscillograph Applied to the Dropping Mercury Electrode"—**73,** 193 (1938).

G. A. Moore—"Comportment of Palladium-Hydrogen System toward Alternating Electric Current"—**75,** 237 (1939).

J. S. Mackay—"Photoelectric Cells Sensitive to Long Wave Length Radiation: The Bismuth Sulfide Cell"—**77,** 299 (1940).

Edward Adler—"Photovoltaic Effect"; "Semi-Conductor Photocells and Rectifiers"—**79,** 367, 377 (1941).

Sidney Speil—"Electrophoretic Dewatering of Clay"—**81,** 119 (1942).

Walter G. Berl—"A Reversible Oxygen Electrode"—**83,** 253 (1943).

John P. Coyle—"The Extraction of Indium from Complex Lead-Tin Alloys"—**85,** 223 (1944).

Austin E. Hardy—"The Photoconductivity of Zinc-Cadmium Sulfide as Measured with the Cathode-Ray Oscillograph"—**87,** 355 (1945).

Norman A. Nielsen—"Passivation of Stainless Steels"—**89,** 167 (1946).

Henry Leidheiser, Jr.—"The Influence of Crystal Face on the Electrochemical Properties of a Single Crystal of Copper"—**91,** 95 (1947).

Michael A. Streicher—"The Dissolution of Aluminum in Sodium Hydroxide Solutions"—**93,** 285 (1948).

J. C. Griess, Jr.—"The Electrodeposition Behavior of Traces of Silver"—**95,** 33 (1949).

George W. Murphy—"The Separation of Simple Electrolytes in Solution by an Electro-Gravitational Method"—**97,** 405 (1950).

John T. Byrne—"Critical Interpretation of Electrodeposition Studies Involving Traces of Elements"—**98,** 457 (1951).

W. E. Kuhn—"Production of Titanium Ingots by Melting Sponge Metal in Small Inert-Atmosphere Arc Furnaces"; "Development of Graphite Electrodes and Study of Heat Losses with Different Electrodes in the Single Electrode Inert-Atmosphere Arc Furnace"—**99,** 89, 97 (1952).

Winners of Turner Book Prize

Sidney Speil—"Electrophoretic Dewatering of Clay"—**81,** 119 (1942).

Walter G. Berl—"A Reversible Oxygen Electrode"—**83,** 253 (1943).

John P. Coyle—"The Extraction of Indium from Complex Lead-Tin Alloys"—**85,** 223 (1944).

James T. Waber—"Stress Corrosion

(*Continued on page 60C*)

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(*continued from page 58c*)

Cracking of Mild Steel"—**87,** 209 (1945).

Burke Cartwright—"Electrolysis of Manganese into a Metal Cathode from Suspensions of Manganese Oxide and Carbon in Molten Manganous Chloride"—**89,** 373 (1946).

Austin E. Hardy—"A Combination Phosphorometer and Spectroradiometer for Luminescent Materials"—**91,** 221 (1947).

Michael A. Streicher—"The Dissolution of Aluminum in Sodium Hydroxide Solutions"—**93,** 285 (1948).

Ralph F. Hoeckelman—"Salt-Bath Chromizing"—**96,** 262 (1949).

Paul Delahay—Parts I and II of the paper "A Polarographic Method for the Indirect Determination of Polarization Curves for Oxygen Reduction on Various Metals"—**97,** 198, 205 (1950).

Kurt H. Stern and Charles C. Templeton—"The Electrical Conductance of Solutions of Cobalt (II) Nitrate Hexahydrate in Acetophenone at 25°C"—**97,** 443 (1951).

P. T. Gilbert—"The Nature of Zinc Corrosion Products"—**99,** 16 (1952).

Correction

Through error, the incorrect price for "Modern Electroplating" was given in the John Wiley and Sons, Inc. ad which appeared in the January 1954 Journal. The correct price of "Modern Electroplating" is $8.50.

NEW PRODUCTS

Electronics Equipment. A 16-page summary of equipment available for use in the electronics industry can now be obtained. This booklet gives descriptions, applications, and operating ranges for such equipment as surge comparison testers, portable balancers and vibrographs, magnetic amplifiers, transistors, capacitors, relays, and many others. Also gives information on such semifinished material as transformer cores and magnetic materials and alloys. Westinghouse Electric Corp. P-184

Glass Pipe and Fittings. New revised catalogue entitled "Pyrex brand 'Double-Tough' Glass Pipe and Fittings" introduces a new line of sink traps and some new fittings, and lists the standard items of stock lengths that are available. The physical properties of glass pipe that make it an ideal material for the processing industries are discussed, as well as ease of cleaning and installation, and economy of operation and maintenance. Corning Glass Works. P-185

Cold Galvanizing Process. Pamphlet announces an entirely new method of cold galvanizing for surface protection of steel and iron. The new process is not a paint but actually a cold galvanizing compound called "Galvicon." It equals and in many cases outperforms other surface protection techniques, including electroplating, hotdipping, cementation, spraying, and painting. Galvicon Corp. P-186

Electron Microscope. A new 4-page folder entitled "Some Reasons Why The World's Most Powerful Electron Microscope Deserves Your Consideration" is available. Forty-four typical applications are listed, together with design and operating information concerning the viewing screen, accelerating potential, magnification, electron diffraction, focus determination and control, image stability, resolution, and other features. North American Philips Co., Inc. P-187

LITERATURE FROM INDUSTRY

Laboratory Stirrer. The Flexa-Mix, a new magnetic stirrer, answers the space problem found in many laboratory bench assemblies. Magnetic lines of force eliminate the contaminant-collecting shaft and impellers of mechanical stirrers and permit full access to the top of the sample container. Includes a stirring motor in a functional aluminum housing; a cast-iron support plate with integral clamp; two Alnico stirring bars, one sealed in glass, one sealed in polyethylene. Fisher Scientific Co. N-46

Photo-Responsive Relays and Meters. A line of industrial photo-relays and photometers suited to a wide variety of laboratory research and industrial control duties has been developed. The photometers are available in models specifically adapted to: measurement of solution concentration by the monochromatic light method; film densitometry testing; ultraviolet radiation intensity measurements; gas analysis and gas detection by the ultraviolet absorption method, etc. The photo-relays are available in models designed for: timing control; response to specific machine speeds; turbidity control and alarm work; safety alarm in danger areas; temperature control, etc. Techniflex Corp. N-47

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Regulated Tubeless D-C Supply. A new tubeless, regulated d-c supply, using magnetic amplifier principles, is now available. The unit (Nobatron Model MA2850) delivers 50 amp at 28 volts (adjustable between 23 and 32 volts). Regulation accuracy is ±1% against line and load combined. Designed for testing aircraft heaters, pitch changers, inverters, radar installations, and fire control systems. Sorensen & Co., Inc. N-48

Potassium Silicate. A new potassium silicate—Kasil #22—has been designed to meet the demands for rapid settling of cathode ray screens. Spectrographic analyses indicate a high degree of purity by the absence of copper, nickel, and other contaminating materials. Can be used over a wide range of conditions and permits increased dry strength of screen without the sacrifice of wet strength. Philadelphia Quartz Co. N-49

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