INDUSTRIAL
and ENGINEERING
CHEMISTRY

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HARRISON E. HOWE, Editor

EDITORIALS

Chemistry in Medicine

ON October 21 and 22 laboratory directors, serologists, and others vitally interested in the program of the Surgeon General to wage a sustained and active campaign against the so-called social diseases, more particularly syphilis, will meet in Hot Springs, Ark. At long last there is frank discussion of diseases which have taken a frightful toll, largely because of prudish silence. Open attacks might well have resulted in curtailment, as in the case of other plagues.

The purpose of this assembly, over which Surgeon-General Thomas Parran will preside, is to make progress in the evaluation, improvement, and standardization of serological tests for syphilis. The principal tests now employed will be presented by their originators and thoroughly discussed. The program also includes the proper training of laboratory personnel and questions concerning approval by state boards of health or the licensing of laboratories for the performance of serodiagnostic tests for syphilis.

The American Chemical Society has a place on this program and President Whitmore will discuss the place of the chemist in the clinical laboratory. The tests themselves are chemical in nature. More particularly, they belong in the field of colloid chemistry. The tests of today are not the relatively simple and even crude ones earlier employed in clinical laboratories, to provide the facts upon which physicians could make their diagnoses. Many semiskilled laboratory workers, usually designated as "technicians," among whom are thousands of nurses and pharmacists, have been taught to perform by rote simple tests, just as laboratory assistants in some large industrial laboratories have learned to carry out many useful and even indispensable functions, but they can be relied upon only when constantly supervised by a director adequately trained in chemistry.

The tests of today are far more complex and difficult. Without suitable chemical training those who attempt to perform these tests are lost if something goes wrong, as not infrequently happens. It is then that the chemist thoroughly conversant with the principles of the reagents and the probable sources of error or variation inherent in the technic proves his indispensability.

It is by no means strange that the chemist plays so fundamental a part in all this work. That body processes are largely chemical in nature was long ago recognized. We are indebted to L. B. Hitchcock for the following quotation from a play written by Collins in 1860, since which time progress in chemistry has been astounding:

> The best years of my life have been passed in the ardent study of medical and chemical science. Chemistry, especially, has always had irresistible attractions for me, from the enormous, the illimitable power which the knowledge of it confers. Chemists, I assert it emphatically, might sway, if they pleased, the destinies of humanity. Let me explain this before I go further.
>
> Mind, they say, rules the world. But what rules the mind? The body. The body (follow me closely here) lies at the mercy of the most omnipotent of all potentates—the Chemist. Give me—Fosco—chemistry; and when Shakespeare has conceived Hamlet, and sits down to execute the conception—with a few grains of powder dropped into his daily food, I will reduce his mind, by the action of his body, till his pen pours out the most abject drivel that has ever degraded paper. Under similar circumstances, revive me the illustrious Newton. I guarantee that, when he sees the apple fall, he shall eat it, instead of discovering the principle of gravitation. Nero's dinner shall transform Nero into the mildest of men before he has done digesting it; and the morning draught of Alexander the Great shall make Alexander run for his life, at the first sight of the enemy, the same afternoon. On my sacred word of honor, it is lucky for society that modern chemists are, by incomprehensible good fortune, the most harmless of mankind.

A few weeks ago the *New York Times* discussed editorially the chemistry of insanity and after recounting some of the work done by leading specialists in mental diseases concluded: "Insanity as well as normal thinking must be interpreted chemically. The fact that drugs can accelerate or retard the action of both insulin and metrazol leads to that conclusion. There is work for the biochemists to do. They must discover what goes wrong with the brain's chemical factory and reduces a brilliant intellect to madness. That done, we shall have a new science of preventive psychiatry."

The American Chemical Society, under its federal charter, has a duty to perform in aiding that protection of the public which is the chief concern of the Surgeon General and his co-workers. Coöperation must be afforded through training the chemical personnel, developing properly qualified directors, and discouraging the creation of an artificial monopoly of supervision by any one profession.

It is the earnest desire of every reputable chemist and of the American Chemical Society that the program of the Surgeon General be permitted to deliver the maximum benefit to humanity in achieving this end. The trained chemist has much work to do and a real obligation in properly performing it.

The Encouraging Word

RECENT months are reported as having been more difficult for the chemist seeking employment than was the depression which began in 1929. We are informed that men with higher degrees have in most instances found places but it has been very difficult for those with but four years' work to find employment.

We have corresponded with some who have been seeking places and a recent letter from one of these men lists a number of employers who had taken the trouble to write him heartening, sympathetic, and understanding letters, even though they could offer no place while operating at part capacity and with a curtailed budget. Letters of this type, which were so highly prized as to lead our correspondent to make a list of men and their companies, certainly add to the sum of good will enjoyed by those who write them.

The other type of letter, the curt reply, seems unnecessarily discouraging. Surely a letter which will strengthen the morale of the applicant requires but little effort and is an example of the common decency which in such times is so valuable. Through our News Edition we offer employers facilities for finding men of the type they need. All who use the service are expected to reply to applicants. To make such replies in a kindly tone regardless of the news they bear is not specified, but may we not expect employers to give more attention to it?

Microchemical Division

THE Council at the Milwaukee meeting approved the constitution and bylaws offered by the Microchemical Section, which thereby became the Division of Microchemistry of the American Chemical Society.

There are many contrasts to be observed between old and new chemistry, but the differences between the technics, the apparatus, and equipment used in the laboratories of a generation ago and those which serve the specialist in microchemistry are among the most striking.

We recall well-developed courses in microchemistry early in the century. But that work was done under the microscope. The microchemist today employs equipment frequently so diminutive that a magnifying glass is used to make readings and the various tubes, beakers, combustion boats, and other apparatus appear like toys.

Microchemistry and microanalysis have already found a great variety of uses. A few years ago they made an appeal because they not only enabled saving time but permitted precise work to be done on samples a mere fraction of those formerly required. This is important both where the substances are of great value and where only small samples are procurable. Combined with other modern tools in analysis, it enables the investigator to carry his work into heretofore dark corners and to obtain results which have been quite out of reach for those who employ only the older methods and technics.

Notwithstanding the skill which must be acquired if the best work is to be done in microchemistry, it has been observed that even the student immediately handles such tiny equipment with greater care and hence does better work. As A. H. Corwin has said: "Microchemistry has ceased to be the tool belonging only to the highly trained specialist. It is now available even to freshmen in the green cap stage."

The Microchemical Section made a good record. As a division, this group of earnest workers will go on to still greater achievements in a field that is new, fascinating, and highly useful.

Three C's

HUMANITY has frequently been classified, the category depending upon the point of view of the individual observer. A particularly interesting observation has been made by W. J. Cameron, whose writings have become so well known, thanks to broadcasting. He says that people seem to gravitate into one of three classifications: creative, contributive, and covetous.

This is an interesting thought and as we look about us we can think of many men and women who have demonstrated creative ability in different fields. A considerable proportion of the chemical profession is so placed. These people create with the knowledge that everyone will have the opportunity to benefit from whatever contributions to truth they are able to make.

Then, as Mr. Cameron points out, there are many people who render important and necessary service by developing the results obtained by the creative group. Once shown, they can see clearly what must be done and frequently independent of the creative group carry their work further, overcome inherent difficulties in equipment and process, and deliver a better product.

Neither group is likely to harbor the idea that if one person has less, it is because another has more nor that one man's success means another man's failure.

Unfortunately, there is a vociferous minority who drift into the third group. They are neither creative nor contributive, but covetous. They are inclined to think of possessing in terms of dispossessing, and prefer to live by the work of the other groups. Strangely enough, their status is improved as the others progress. They may ultimately learn that the success of one man most frequently makes it more difficult for others to fail.

We hope you have not put yourself under the third C. If you even tend in that direction, do something about it.

MOTOR FUEL ECONOMY OF EUROPE

GUSTAV EGLOFF
Universal Oil Products Company,
Chicago, Ill.

Self-sufficiency strikes the keynote for the desires of most European nations. The production of substitute motor fuels derived from their own resources, such as coal, wood, oil shale, and agricultural products, is one of the goals. The economics involved is not the primary factor.

Coal is converted into liquid motor fuel by carbonization, hydrogenation, and the water gas reaction. Alcohols from farm products and methanol from hydrogenation of carbon monoxide and wood distillation are also used.

Methane, ethane, propane, and butanes, or city gas, are used in compressed form in steel cylinders (3000 to 4000 pounds per square inch pressure) in gas-driven motor vehicles. These gases are derived from coal carbonization, coal hydrogenation, and from hydrogenation of carbon monoxide, and natural gas. There are about 26,000 of this type of motor vehicle in use. Other types of gas-driven vehicles manufacture their own combustible gas en route from wood and charcoal. There are about 9000 such wood-burning motor vehicles in Europe consuming about 450,000,000 pounds of wood yearly. These vehicles are heavily subsidized by governments through direct payments, elimination of taxes on the wood and vehicle, and taxes on imported gasoline.

Total consumption of power alcohol in Europe in 1937 amounted to 510,000 tons compared with 646,000 tons during 1936. The 510,000 tons of ethanol (some methanol) represented 4.3 per cent of the total 11,882,600 metric tons of motor fuel consumed during 1937 in Europe. It is estimated that the 510,000 tons of alcohol used in Europe cost the consumer and state in additional expenditures on the order of about $100,000,000 in subsidies, tax losses, and higher operating costs of vehicles.

THE increasing tendency of nations to become autonomic in both thinking and action has been strongly felt by the author during the past ten years of European visits. As part of this nationalism, substitute motor fuels play an increasingly important role.

Countries such as Germany, England, France, and Italy have no material petroleum resources and are conducting research feverishly to utilize their own potential motor fuel supplies from coal, vegetables, cereals, wood, natural gas, and oil shale. This research is not directed solely towards producing fuel for motor vehicles such as airplanes, pleasure cars, busses, trucks, and boats, but also towards the desire to become nationally self-sufficient, to keep people employed, and to utilize their own resources. The cost of producing substitute motor fuels is not specifically involved, since gasoline produced from crude oil is markedly less in cost than any of the sources enumerated comparing over-all motor vehicle performance.

A number of European nations directly and indirectly subsidize indigenous motor fuels through taxes on imported motor fuels, partial elimination of taxes on the fuels and on the vehicles using nationally produced fuels, and, in some cases, direct part payment on the vehicles using substitute fuels.

Table I gives a bird's-eye view of European crude oil production, motor fuel consumption, motor vehicles, alcohols (methanol, ethanol), coal, and forest resources, and indicates the interplay of economic forces that motivate nations in their self-sufficiency programs.

The primary source of motor fuel in the world today is crude oil. Over 2,000,000,000 barrels of petroleum were produced during 1937, from which about 775,000,000 barrels of motor fuel were derived by distillation and cracking. Substitute motor fuels consist of compressed gases, liquids, and solids from coal, alcohols (methanol and ethanol), producer gas from wood and coal generators on motors cars, compressed natural gas, and oil shale. Acetylene, cracking of ammonia, and hydrogen have been used in an experimental way.

Coal

The primary substitute motor fuel in Europe is derived from the hydrogenation of coal and carbon monoxide. The

TABLE I. CRUDE OIL, COAL AND ALCOHOL PRODUCTION, MOTOR FUEL CONSUMPTION, FOREST AREA, AND MOTOR VEHICLE USE IN EUROPE DURING 1937

Country	Motor Car Registration (*2*)	Motor Fuel Consumption (*21*)	Crude Oil Production (*21*)	Coal Production (*23*)	Alcohol Used as Motor Fuel (*10*)	Total Forest Area (*18*)
	1000 cars	*1000 bbl.*	*1000 bbl.*	*1000 metric tons*	*1000 metric tons*	*1000 sq. miles*
United Kingdom	2,411.3	44,200	0	228,990	16	4.7
France	2,200.0	25,000	532	46,146	153	34.0
Germany	1,445.7	20,000	3,077	208,045	210	54.6
Russia	514.4	24,000	199,636	81,000	..	3,014.5
Italy	429.7	5,200	150	988	37	4.7
Belgium	220.4	4,600	0	27,876	..	...
Sweden	192.7	4,000	0	424	15	100.4
Netherlands	147.8	3,500	0	12,893	..	...
Spain	125.0	2,900	0	7,320	..	...
Czechoslovakia	95.0	1,820	185	28,432	50	18.8
Norway	76.4	1,600	0	...	..	27.0
Austria	47.4	970	33(*9*)	3,141	2	?
Finland	44.4	800	0	...	..	84.2
Poland	34.3	600	3,870	29,768	8	31.0
Rumania	26.5	700	63,533	1,928	..	29.3
Hungary	21.2	590	...	7,932	10	2.1
Yugoslavia	14.6	...	0	4,476	4	47.8

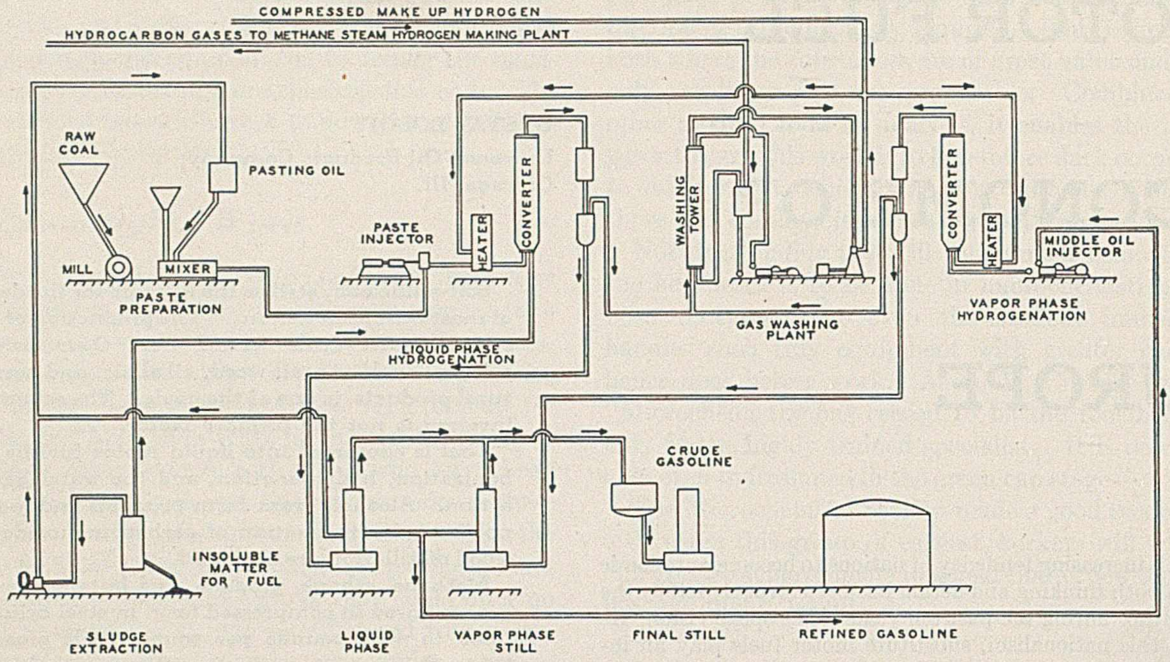


FIGURE 1. MOTOR FUEL FROM COAL HYDROGENATION

synthetic liquid motor fuel production in Germany will be at the rate of about 17,000,000 barrels a year from the units of the two processes now operating or under design and construction. In England the rate of direct coal hydrogenation to gasoline is about 1,300,000 barrels a year. France is operating a 110,000-barrel-a-year catalytic unit to convert water gas to motor fuel. No other European countries are using these processes at present. For European conditions the various sources indicate that the cost per U. S. gallon of motor fuel produced by either coal or carbon monoxide hydrogenation is about 18 cents.

Direct Hydrogenation of Coal

The hydrogenation of coal and carbon monoxide derived from coal are two processes developed in Germany. The hydrogenation of coal is carried out at pressures of the order of 4000 pounds and temperatures of about 850° F. in the presence of catalysts (Figure 1). The hydrogenation of carbon monoxide (Fischer-Tropsch process) is carried out at atmospheric or superatmospheric pressure in the presence of catalysts and temperatures of the order of 350° F. (Figures 2 and 3).

It is difficult to obtain precise figures on the cost of producing a gallon of motor fuel from the hydrogenation of coal or from carbon monoxide. However, from a number of European sources it has been learned that the cost of motor fuel production by the two processes ranged between 17 and 19 cents per U. S. gallon. These figures are fortified by the conclusions in important reports issued by the Committee of Imperial Defence of Great Britain and by the Labor Party of England (7). The Imperial Defence committee reports:

> The Billingham plant was originally intended to deal with coal only and to have a rated output capacity of 100,000 tons (30,000,000 Imperial gallons or 36,000,000 U. S. gallons) of motor spirit. It was subsequently decided to include provision for the treatment of coal tars to the extent of 50,000 tons of petrol per annum, thus making the capacity 150,000 tons (45,000,000 Imperial gallons or 54,000,000 U. S. gallons) of petrol per annum.
>
> The quantity of coal which was then expected would be required for the plant when in full operation is stated to be as follows:

	Tons
Coal hydrogenation:	
For processing[a]	150–200,000
For all other purposes (steam, power, hydrogen production, etc.)	300–350,000
	500,000
Tar oil hydrogenation[b] for steam, power, hydrogen production, etc.	100,000
Total	600,000

[a] The exact quantity depends, among other things, on the ash and moisture content of the coal.

[b] In addition, about 60,000 tons of tar oils are required.

> This gives for the coal hydrogenation 1 ton of petrol for each 1.5 to 2 tons processed, or for each 5 tons of total coal used.
>
> The spirit produced by the plant is of a high grade and during the last few months an octane rating of 75 has been achieved. This is a high standard for a straight or undoped petrol.
>
> If a new hydrogenation plant were to be built, it would have to be designed to use coal only, as there are not available supplies of creosote or low-temperature tar in sufficient quantities to provide for another mixed coal and tar plant. The plant would have a capacity of 150,000 tons of petrol, as Imperial Chemical Industries, Ltd., regard this size as the minimum from an economic point of view.
>
> The capital cost of such a plant (to include land, offices, site development and design charges, research charges essential for this new plant, working capital, interest during construction, and fees payable to the International Hydrogenation Patents, Ltd.) is estimated by Imperial Chemical Industries, Ltd., at 8,000,000 pounds ($40,000,000), made up approximately as follows:

	Pounds	Dollars
Capital cost (plant, materials, etc.):		
General services and workshops	1,035,000	5,175,000
Boilers and power plant	1,570,000	7,850,000
Gas-making, purification, and compression	1,762,000	8,810,000
Hydrogenation plant and refinery	2,880,000	14,400,000
	7,247,000	36,235,000
Sundry charges (research during construction, interest during construction, working capital, International Hydrogenation Patents fee)	750,000	3,750,000
Total	7,997,000	39,985,000

The estimated results of operations on a new plant thus calculated are shown below. The figures are set in two groups; the first deal with a calculation for depreciation of the plant on the basis of 20-year life (i. e., with no provision for obsolescence), and the second group is based on a charge for depreciation and obsolescence combined which is sufficient to write off the plant within 10 years.

	20-Year Life		10-Year Life	
	Pence/ Imp. gal.	*Cents/ U. S. gal.*	*Pence/ Imp. gal.*	*Cents/ U. S. gal.*
Assumed av. realization price at works (assuming existing rate of preference of 8d. (16 cents) per gal.)	12.00	20	12.00	20
Deduct:				
Works costs (including works overhead)	7.20	12	7.20	12
Works profit before providing for depreciation and obsolescence	4.8	8	4.8	8
Provision for depreciation at 5%	2.13	3.63	...	...
Provision for depreciation and obsolescence at 10%	...	...	4.27	7.1
Profit after charging depreciation	2.67	4.45	...	...
Profit after charging depreciation and obsolescence	...	...	0.53	0.967

On the basis of a new plant to hydrogenate coal costing $40,000,000 for the production of 150,000 tons a year of motor fuel, the production cost per U. S. gallon would be about 15.6 cents on the basis of plant life of 20 years (no obsolescence charges included). On the basis of writing off the plant in 10 years, including depreciation and obsolescence, the cost per gallon of motor fuel would be 19 cents.

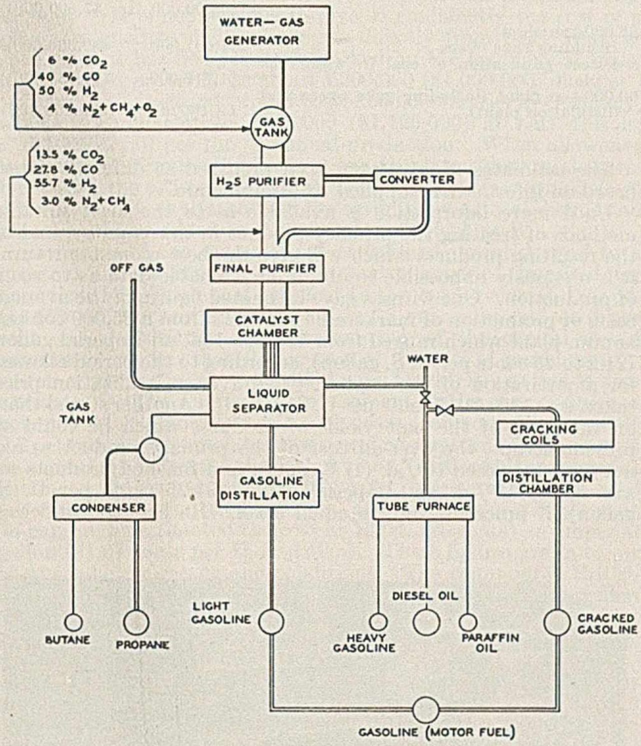


Figure 2. Motor Fuel from Water-Gas Reaction, Fischer-Tropsch Process

The British Labor Party, working independently of the Imperial Defence committee, came to the conclusion that gasoline from hydrogenation of coal "at the present time" costs about 11 pence (22 cents) per Imperial gallon or 18 cents per U. S. gallon. The following is taken from the British Labor Party's report:

> On the basis of their experimental work, I. C. I. (Imperial Chemical Industries, Ltd.) were led to believe that petrol could be produced by hydrogenation at a cost of 7 to 9d. (14 to 18 cents an Imperial gallon, or 11.67 to 15 cents per U. S. gallon), of which about 2d. (4 cents) would be due to the cost of coal. The figure realized in practice has not been disclosed, but there is some reason to think that with a reasonable allowance for interest on capital and amortization the price stands in the region of 11d. (22 cents) an Imperial gallon. The I. G. Farbenindustrie has been similarly reticent, but it is learned from an authoritative source that their cost of producing petrol (from brown coal) has been 25 pfennigs a kilogram which is about 11d. (22 cents) an Imperial gallon (18.3 cents per U. S. gallon) at par.
>
> The chairman of I. C. I., Lord McGowan, has twice referred recently to the high cost of producing petrol at Billingham. In his speech at the company's annual meeting on April 29, 1937, he said:
>
> "For general commercial reasons it is not the practice of the company to disclose the financial results of any particular activity. All that I can say, therefore, in regard to the hydrogenation plant is that up to date it has not shown results which would justify its description as a good commercial proposition, even with the advantages of the existing customs duty, and without that protection, of course, the enterprise would be uneconomic."
>
> In the House of Lords on July 14, 1937, Lord McGowan said: "Although the process is today in successful operation it does not, even with the protection afforded by the British Hydrocarbon Oils Production Act, present a favorable opportunity for the investment of large sums of private capital . . . Success from a commercial point of view in the synthetic production of petrol depends largely, as far as the future is concerned, upon the policy of the government of the day."
>
> Although the company has not disclosed its accounts, it is not difficult to form a rough idea of the principal items in the running costs of a hydrogenation plant similar to that at Billingham. The men employed on the plant are largely skilled workers, and their wages will average about £3, 15s. ($19) a week. On this basis the wages bill for 2000 men will be £390,000 ($1,950,000) a year; spread over an annual production of 45,000,000 Imperial gallons (54,000,000 U. S. gallons) of motor spirit, this is equivalent to 2.1d. (4.2 cents) an Imperial gallon (3.5 cents per U. S. gallon). The cost of the raw materials—600,000 tons of coal, 50,000 tons of creosote, and 12,000 tons of low-temperature tar—can hardly be put, at current market values, at less than £500,000 ($2,500,000), equivalent to 2.7d. (5.4 cents) an Imperial gallon (4.5 cents per U. S. gallon).
>
> Imperial Chemical Industries provided the Billingham plant out of reserves, but in a calculation of the running costs of the hydrogenation process it is necessary to allow interest on the capital expenditure. With a rate of 3.5 per cent, at which the

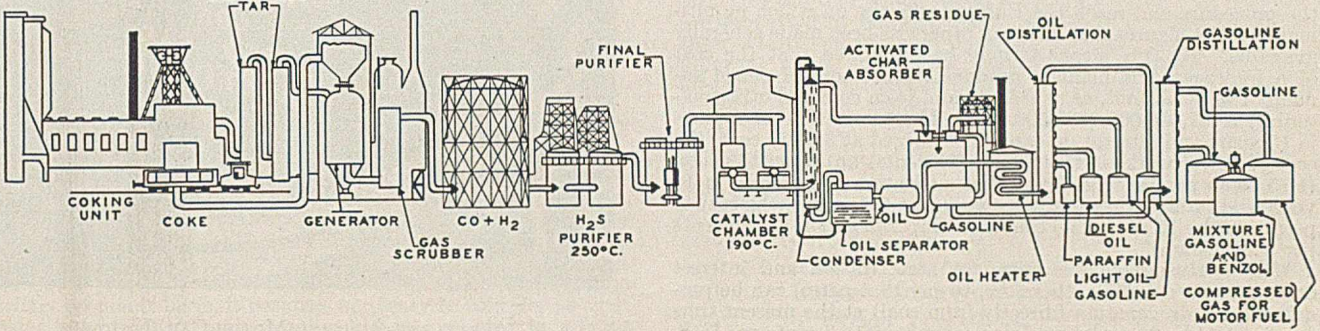
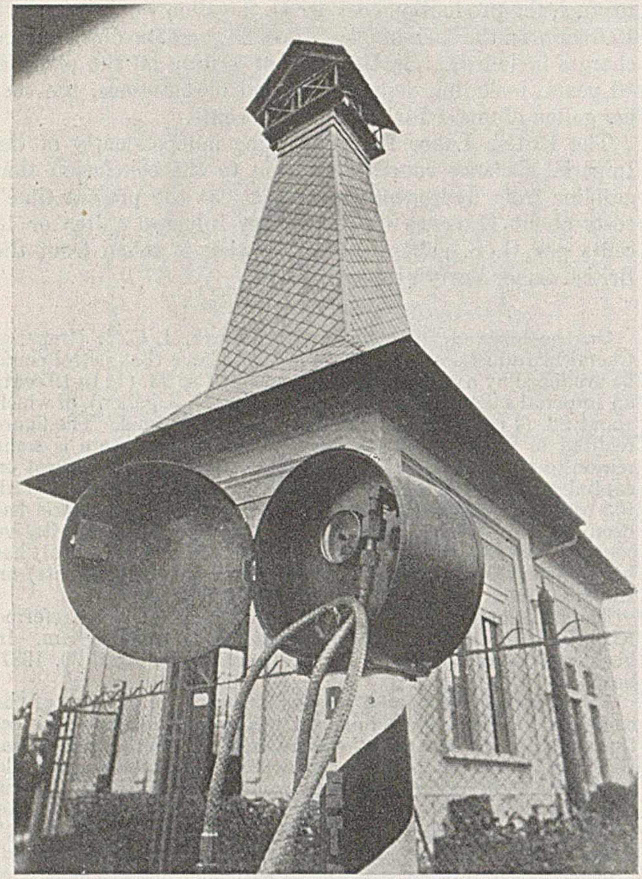


Figure 3. Motor Fuel from Coal Carbonization and Catalytic Water-Gas Reaction



COMPRESSED METHANE GAS FILLING STATION, ITALY
4500 pounds per square inch

money could be raised with a governmental guarantee, the interest on £5,500,000 ($27,500,000) would amount to £192,500 ($962,500) a year or 1.0d. (2 cents) an Imperial gallon (1.67 cents per U. S. gallon).

It is difficult to know at what figure amortization of the plant should be reckoned. Imperial Chemical Industries suggest amortization in 10 years, with compound interest at $2^{1}/_{2}$ per cent on the reserves provided. German authorities take the view that 10 years is an unnecessarily short period, and amortization in 15 years, with compound interest at $2^{1}/_{3}$ per cent on reserves, seems reasonable; on a capital of £5,500,000 ($27,500,000) this would absorb about £300,000 ($1,500,000) a year or 1.6d. (3.2 cents) an Imperial gallon (2.67 cents per U. S. gallon).

The total of these costs—wages, raw materials, interest on capital, and amortization—is £1,382,500 ($6,912,500) a year or 7.4d. (14.8 cents) an Imperial gallon (12.3 cents per U. S. gallon).

These estimates may be checked by the reports made by Sir David Rivett personally, and by a committee of which he was chairman, to the Australian Government. Sir David Rivett's estimates are based on figures supplied to him by Imperial Chemical Industries and by German firms. His final calculations are made in terms of Australian currency, costs, and wages, but by using his own multipliers as dividers it is possible to reverse the procedure and reach the European figures on which he ultimately relies, figures that have not otherwise been made generally available. By this means it may be calculated that the cost of a hydrogenation plant to produce 150,000 tons of petrol annually from coal (not, as at Billingham, from coal and other materials) is £7,500,000 ($37,500,000). If amortization takes place in 15 years and interest on capital is charged at 3.5 per cent, the cost of petrol works out at 10.5d. (21 cents) an Imperial gallon (17.5 cents per U. S. gallon); if amortization takes place in 10 years and interest on capital is charged at 6 per cent, the cost of petrol will be 12.75d. (25.5 cents) an Imperial gallon (21.25 cents per U. S. gallon).

With a reasonable allowance for amortization and interest on capital it seems fair, therefore, to say that petrol can be produced by hydrogenation (directly from coal) at the present time for about 11d. (22 cents) an Imperial gallon (18.3 cents per U. S. gallon).

Hydrogenation of Carbon Monoxide from Coal

The Fischer-Tropsch process of producing motor fuel from the hydrogenation of coal was developed in Germany. Motor fuel, kerosene, Diesel oil, and paraffin wax are produced; the mixture is called "Kogasin oil." The motor fuel production from this process in Germany will be at the rate of 530,000 tons yearly when the units now operating and those under design and construction are functioning. There is one unit in operation in France producing motor fuel at the rate of 13,000 tons a year.

The Imperial Defence committee studied the Fischer-Tropsch hydrogenation of carbon monoxide process and reported:

> Statements were furnished to the committee setting out particulars relating to the recommended size of plant, estimates of the capital and operating costs, the type and yield of products it is claimed can be produced, and estimated realization value of the products, etc. . . The following are examples of the sizes of plants and estimates of capital cost submitted to the committee:

KOGASIN OIL YEARLY PLANT CAPACITY COSTS

20,000-ton plant (including coke ovens)	£1,000,000 to £1,500,000	($5,000,000 to $7,500,000)
35,000-ton plant:		
Including coke ovens	£1,901,000	($9,505,000)
Direct gasification of coal in water gas plant	£1,717,000	($8,585,000)
60,000-ton plant (including coke ovens and distillation plant)	£3,100,000	($15,500,000)

> The estimates of cost have been prepared at different dates, based on information supplied by Ruhrchemie.
>
> Until more information is available as to the most suitable methods of treating the primary product in this country, and of the resulting products which will give the best economic return, it is obviously impossible to obtain any reliable data as to costs of production. One witness gave estimated figures of the average costs of production of marketable products from a 35,000 ton per annum plant which ranged from $12^{3}/_{4}$ to 15d. an Imperial gallon (21.2 to 25 cents per U. S. gallon), according to the period allowed for amortization of the capital. The average realization price taken was 13d. (21.7 cents per U. S. gallon). Another stated that, on the basis of the best yields of products which he could at present accept, the over-all cost of the primary product would not have to exceed $10^{1}/_{2}$d. (17.5 cents), and finished products an average of $12^{3}/_{4}$d. per Imperial gallon (21.25 cents per U. S. gallon), if proceeds were to equal costs. He had not sufficient

ACETYLENE-BURNING MOTOR CAR, ITALY
C_2H_2 from calcium carbide and water

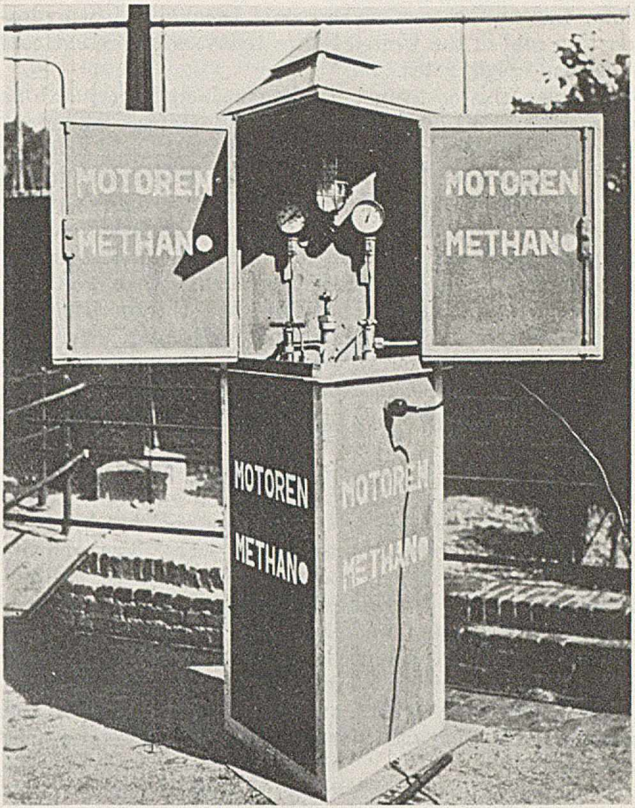
data to say whether such results were practicable. Generally the evidence appears to indicate that the costs of production in the case of this process are not likely to be less than those of the hydrogenation process.

The following is reported from the British Labor Party's report (7):

> The synthetic process (i. e., catalytic water gas reaction), unlike hydrogenation, can be worked in relatively small units. The economic unit is said to be a plant producing about 35,000 tons of primary products annually, or, if it includes its own catalyst plant, about 60,000 tons of primary products annually.
>
> The committee were given estimates for synthetic plants of two types: Plant A is a self-contained plant, with its own coke ovens, designed to produce annually 35,000 tons (11,077,500 gallons) of primary products from bituminous coal. If the "Diesel" oil fraction were "cracked," it would yield 28,350 tons of motor spirit annually, apart from subsidiary products. Plant B is a plant without coke ovens, designed to work in conjunction with a coal distillation unit and to produce from the low-temperature coke 10,000 tons of synthetic products annually.
>
> It is difficult to assess the cost of a British plant from German experience, especially in view of recent wide fluctuations in the price of steel, and all estimates must be accepted with caution.
>
> Plant A, it is stated, would cost about £1,900,000 ($9,500,000) to build, which spread over the 35,000 tons of synthetic products made annually, works out at £54 ($270) per ton of annual production. [It is not possible to give so confidently the cost of a plant designed to make water gas directly from black coal, as such a plant has not yet been worked on the commercial scale, but it would probably be about £200,000 ($1,000,000) cheaper.]
>
> Plant B, it is stated, would cost 4,500,000 marks in Germany, which is equivalent to £225,000 ($1,125,000) at par—this is, £22.5 ($122.50) per ton of annual production. When allowance is made for the omission of coke ovens, this is in substantial agreement with the estimate for plant A. To make a fair comparison, a portion of the capital costs of the accompanying coal-distillation plant should be added to the capital costs of plant B.
>
> Estimates of the over-all cost of finished petrol depend to a great extent on interest charges and the period required for amortization. With coal supplied to the coke ovens at 18s. 6d. ($4.62) per ton and amortization in 15 years, interest at 3 per cent and depreciation on three-quarters of the capital would amount to not less than 21 per cent of the cost of production.
>
> For a plant similar to plant A, Sir David Rivett made two estimates for the Australian Government of the cost of finished petrol. With amortization in 10 years, compound interest at 2.5 per cent on accumulated reserves, and a return of 3.5 per cent on capital, he estimated the cost at 15.8d. (31.6 cents) an Imperial gallon; with amortization in 15 years, compound interest at 3 per cent on accumulated reserves, and a return of 3.5 per cent on capital, he estimated the cost at 13.0d. (26 cents) an Imperial gallon (21.67 cents per U. S. gallon). These figures are in terms of Australian currency and conditions. The comparable British figures would be about 12.1d. (24.2 cents) an Imperial gallon (20.17 cents per U. S. gallon) and 10.0d. (20 cents) an Imperial gallon (16.7 cents per U. S. gallon). These are of the same order as the estimated costs of hydrogenation.
>
> For plant B, the over-all cost of the finished motor spirit is given as 20.21 pfennigs a kg., which works out at about 8d. (16 cents) an Imperial gallon (13.3 cents per U. S. gallon) at par. The lower estimate for plant B compared with plant A results from the lower capital cost, which in turn is due to the absence of coke ovens, and for this, as already explained, some allowance should be made. When allowance is made, the estimates are in substantial agreement.
>
> With reasonable provision for amortization and interest on capital, the cost of synthetic petrol at the present time may therefore be taken at 10.5d. (21 cents) an Imperial gallon.

The Falmouth committee offers the following conclusion:

> The limitations which have been referred to in the cases already dealt with do not arise with these processes (hydrogenation of carbon monoxide); for the main product is oil, and there is no residual solid fuel to be disposed of in competition with coal. The successful operation on a large scale of these processes would, therefore, produce an entirely new demand for coal, and offer greater opportunities for the creation of employment in the mining industry, as well as directly at the plants. Since, however, the development of these processes cannot be achieved on a strictly economic basis, it becomes necessary to consider at what cost the additional employment could be provided in present circumstances.



METHANE GAS FILLING STATION, GERMANY

Up to 5000 pounds pressure

> The information supplied to the committee indicates that for this hydrogenation process a plant with a production capacity of 150,000 tons per annum of motor spirit would afford direct employment to some 2000 persons in the plant, and a further 4000 in the mining and secondary industries, giving a total employment figure of 6000. Unfortunately the cost of erecting such a plant is very great, amounting, on the basis of the present cost of wages and materials, to about £8,000,000 ($40,000,000). This would work out at a capital cost of £1333 ($6665) per man employed. In addition, on the basis of the present preference of 8d. (16 cents) per Imperial gallon (13.3 cents per U. S. gallon), there would be a loss of revenue to the Exchequer which would represent at least £250 ($1250) per annum per run. The cost of providing work by this means would therefore be very high. It would represent from the revenue point of view alone a continuing assistance amounting to about £5 ($25.00) per week per person employed.
>
> Though reliable figures are not available for these processes (hydrogenation of carbon monoxide), the information furnished to the committee indicates that they are not likely to be very different from those given for the hydrogenation process.
>
> The committee, therefore, find themselves driven to the conclusion that, viewed solely from the point of view of providing a large measure of employment, the hydrogenation and synthetic processes do not at present offer a very hopeful prospect, in relation to the cost which would be involved. In this view they are supported by one important witness, who, while advocating the development of these processes for other reasons, used the following words as regards their effect on employment: "Any idea that oil from coal can provide sudden salvation for the coal industry is clearly foolish."

The foregoing cost figures and related data are interesting and instructive from the standpoint of present-day conditions in Europe. Secured from a number of wholly independent sources abroad, they conform surprisingly with figures from foreign coal hydrogenation operations translated to United States conditions of today by authorities close in touch with foreign operations. These latter data from American sources indicate 14 to 16 cents per U. S. gallon of motor fuel as the cost which would be obtained in hydrogenating coal in the United States today, with present coal prices and freight rates.

However, this cost must not be considered conclusive as regards future conditions in the United States. Abundant oil supplies make prospects rather remote that coal or other substitute motor fuels will be utilized for many years in the United States. When that distant time arrives, lower hydrogenation costs for America can well be anticipated. Since European plants were the first constructed, they have doubtless suffered from much higher capital costs than would be expected for new installations. Further, the thorough application of American engineering technic, particularly petroleum refining technology, would reduce capital and operating costs of gasoline from the hydrogenation of coal in the United States to a price materially below 16 cents a gallon.

Benzene Motor Fuel

The high-temperature carbonization of coal has been the primary source of benzene motor fuel for years. The products of high-temperature treatment of coal are gas, coal tar, and metallurgical coke. The gas is scrubbed with oil or activated carbon and the coal tar is distilled to recover the benzene motor fuel content. Benzene is produced in the gasification of coal with a maximum yield of 3 gallons per ton of coal gasified. This type of motor fuel has an octane rating of over 90 and is used as a blending agent for lower grade fuels to raise their antiknock value.

Benzene and toluene, which are present in benzene motor fuel, are diverted in wartime largely toward explosive use. The Mining and Power Commission of the French Chamber of Deputies recently reported (*11*): "Benzene would also have to be reserved in time of war for the manufacture of explosives. Its production, moreover, is limited by the activity of coke ovens and gasworks and is therefore capable only of slight expansion. The domestic output of benzene last year at 75,144 tons (64,794 tons from coke ovens and 10,350 tons from gasworks) showed only a small advance over 1936, and was well below the 1929 peak of 79,200 tons."

The production of benzene motor fuel in the different countries of Europe is as follows (*13*) in metric tons:

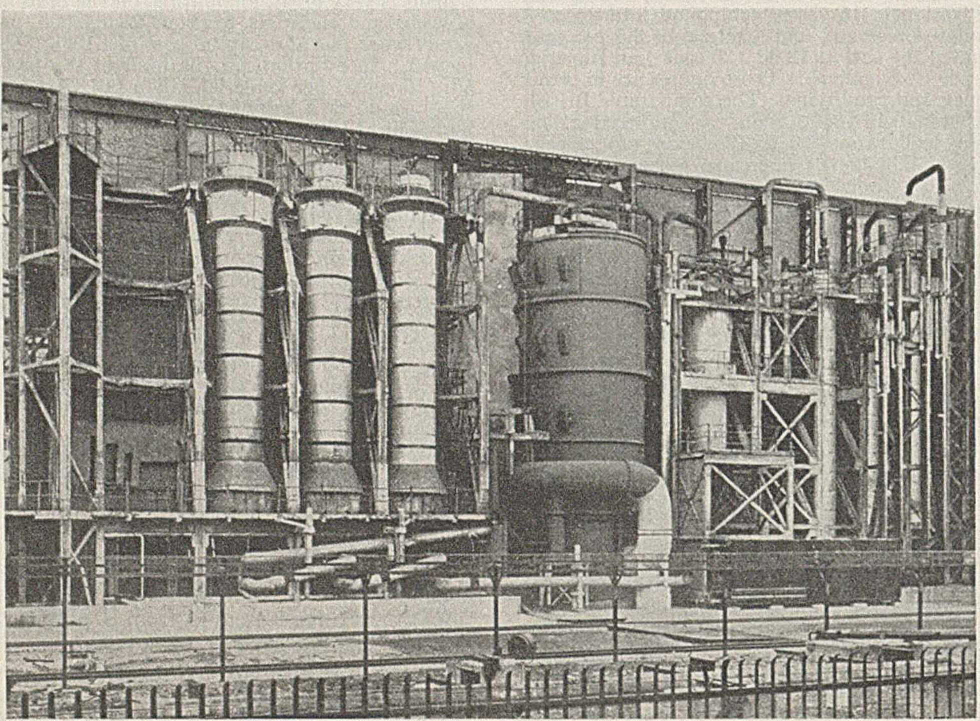
Germany	430,000	Austria	8,200
Czechoslovakia	12,000	Sweden	500
Hungary	3,100	Holland	10,800
Poland	10,000	Finland	200
Belgium	36,700	Switzerland	3,000
France	80,000		
United Kingdom	230,000	Total	824,500

The cost to consumers of Europe was $49,463,000 more for benzene motor fuel than it would have been for gasoline, as a result of loss of taxes, governmental subsidies, and benzene production costs. Expressed another way, it was 20 cents more for each gallon of benzene fuel consumed.

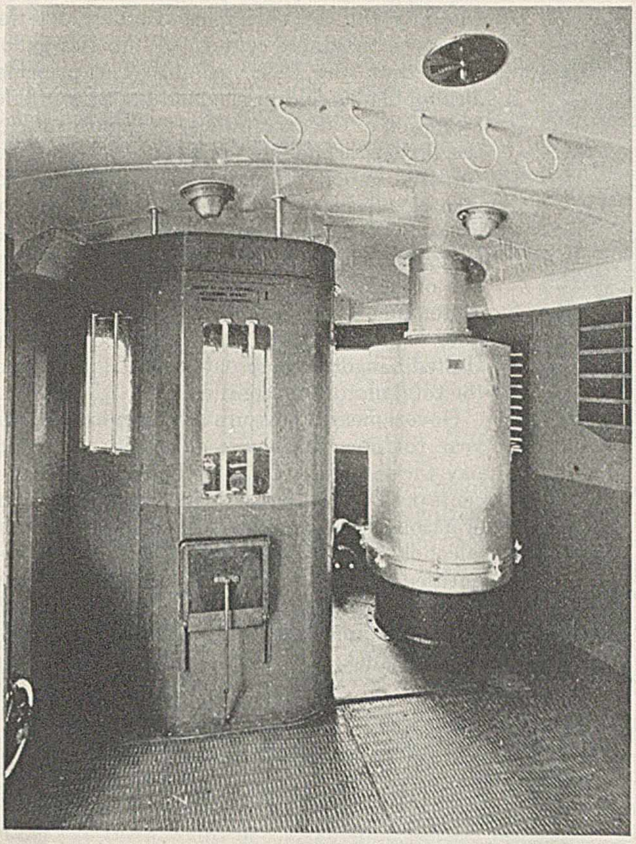
Compressed Gas

The sources of substitute motor fuels in Europe which are increasing are combustible gases from coal carbonization, coal hydrogenation, Fischer-Tropsch hydrogenation of carbon monoxide to hydrocarbons, natural gas, and the cracking process. Although during the World War England used balloons filled with city gas as motor fuel because of an "impending shortage of gasoline," its use did not increase materially. The development in Germany turned toward the light-weight alloy cylinders attached to the motor vehicle to store the combustible gas under pressure. The gases used for motor fuel are coal gas, methane, ethane, propane, and butane; they are compressed, depending on the type, up to 4000 pounds per square inch.

Motor vehicles are converted into the compressed gas type at a cost of $150 to about $300, depending on the size (*3*, *16*). The primary changes are as follows: (*a*) racks are installed to hold the steel cylinders. (Each weighs about 115 pounds empty; when filled with propane-butanes at a pressure of 150 pounds per square inch, one weighs 215 pounds or a net of 100 pounds of compressed gas (*3*), equivalent to 18 gallons



Coal Hydrogenation Unit at Billingham, England



Passenger Bus. Motorman's Place and Wood-Burning Stove, France

of gasoline.) Some of the larger trucks carry eight cylinders and some passenger busses use trailers to carry the cylinder. When methane at 3000 pounds per square inch is used, the cylinder weighs 155 pounds; it holds 28 pounds of methane, equivalent to 4.6 gallons of gasoline (*3*). When compressed city gas is used, the cylinder content in terms of gasoline equivalency is about 1.8 gallons (*5*). (*b*) The heart of the operation is the control of the pressure reduction by means of a regulating valve, so that a steady flow of gas passes to the motor. (*c*) A special gas-air mixer is used instead of the gasoline carburetor.

The greatest development in the use of compressed gas has been in Germany where, it is estimated, over 150,000 tons (*16, 17*) of gasoline during 1938 will be replaced by compressed gas, which is available at many stations (*19*) similar to gasoline filling stations.

Filling stations (*6*) dot Germany in a network which supply city gas, methane, or propane-butanes direct by filling the cylinders on the motor vehicle or replacing the empty ones. Depending upon the type of compressed gas (city, methane, or propane-butane), the distances traveled by a given vehicle when using two cylinder storage tanks are about 25, 85, and 225 miles, respectively, before they have to be refilled (*3*). It is estimated (*17*) that over 25,000 German motor vehicles are using about 250,000 cylinders as storage tanks for the compressed gas.

Italy has developed a natural gas field near Milan made up largely of methane. This gas is compressed at 3000 pounds per square inch into steel cylinders and is distributed at eight filling stations which supply about five hundred busses and trucks in the Milan and Florence areas (*3*). At present (July 1, 1938) in Italy, natural gas is replacing petroleum gasoline as a motor fuel at the rate of about 40,000 tons a year. It is expected that within two years the use of methane from natural gas and coal carbonization will be fourfold greater than it is now.

The use of motor vehicles burning compressed gases is subsidized by governments of Germany and Italy by reduction of taxes (*4, 15*). The tax on a U. S. gallon of gasoline shipped into Italy is 51 cents; Germany charges 36 cents. On the basis of 59.6 cents a gallon for motor fuel in Germany, of which 36 cents is a tax on imported gasoline (it lands in Hamburg at 11 cents an Imperial gallon or 9 cents per U. S. gallon from the United States), the cost of city gas, motor methane, and propane-butanes in Germany compared on a gallon of gasoline basis is 43, 41, and 61 cents (*4*).

It is estimated that in all Europe compressed gas will replace about 250,000 tons of gasoline during 1938.

Alcohol Motor Fuels

The increased use of power alcohol was demanded in Central Europe from 1930 to 1937 through enactment of laws. Power alcohol is supported by heavy governmental subsidies. Alcohol replaces imported motor fuel and is fostered by the national self-sufficiency programs. Power alcohol consumption increased in Europe during 1930 to 1936 from 59,000 to 648,000 tons. However, a sharp decline took place in 1937 with the use of only 510,000 tons, a drop of 25 per cent. A more drastic drop is indicated for 1938. Alcohol may be eliminated as a source of power as a result of the staggering economic losses involved, its diversion to other uses, and its encroachment upon food supplies.

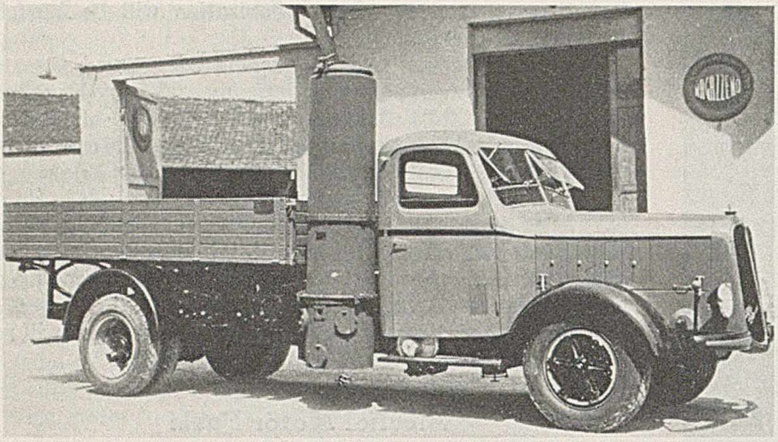
The economic strain upon the governments of Europe due to power alcohol use has been heavy. A loss of income of about $105,000,000 (*12*) was incurred during 1937 alone, based upon subsidizing the producers, tax losses, and higher fuel costs. These losses resulted from the marketing of 510,300 tons of alcohol out of a total 11,882,600 tons or 4.3 per cent of the motor fuel used in Europe.

Germany and France (*21*) have been the heaviest consumers of power alcohol in Europe, and their supply was derived primarily from sugar beets and potatoes. Germany required a 10 per cent blend of alcohol with gasoline but, four years after the legal requirement, it was found that there was insufficient alcohol produced in the country to fulfill the law. In order to meet government specifications, it was necessary to import alcohol to cover the deficiency. During 1937 synthetic methanol was used in Germany to the extent of 70,000 tons to make up the 10 per cent alcohol quota, but it was not sufficient to stop the drain on basic foodstuffs entailed by so drastic a requirement in motor fuel. The percentage of alcohol required in motor fuel was reduced from 10 to 8.5 per cent in October, 1937, and to 6.9 per cent in April, 1938.

In France the sugar beet is grown primarily for the purpose of furnishing power alcohol, so that there is no excessive drain on foodstuffs to furnish motor fuel. The laws requiring from 10 to 35 per cent alcohol in motor fuels were for the purpose of absorbing the products of the vineyards and beet farms; but as a result of drought neither group was able to produce the legal amount of alcohol required for blending.

The German subsidy to the potato alcohol producers is about $130 per ton of power alcohol or about 39 cents per gallon. In order to increase alcohol production 100,000 tons a year from farm products, France legislated in June, 1938, to the effect of paying $12,500,000 for this amount of alcohol which figures about 36 cents a gallon subsidy.

Power alcohol consumption reached a peak of 321,300 tons in France, in 1935, dropping to 153,400 during 1937, a shrinkage of over 52 per cent. During 1935 France used over 55 per cent of the total power alcohol of Europe and about 33 per cent during 1937; an estimate is given for 1938 of less than 25 per cent of the total. The power alcohol goal set



Wood-Burning Stove on Truck, Italy

by law has not been reached (the percentage alcohol blend during 1937 was 5.4 per cent) as a result of natural causes and to diversion of alcohol to other uses such as munitions manufacture.

In Germany the use of alcohol from agricultural products has fallen off sharply—i. e., 20,000 tons during 1937 compared to 1936. Of the 210,000 tons of alcohol used during 1937, methanol represented 70,000 tons, leaving 140,000 tons of ethanol derived from potatoes, etc. This alcohol tonnage of 140,000 is about the same quantity as was used in Germany five years ago.

Power alcohol consumption for Germany and France has been as follows:

Year	Germany	France	European Total
	Metric tons		
1930	?	28,000	59,000
1931	50,000	52,100	121,000
1932	95,000	69,100	182,000
1933	135,000	180,000	362,000
1934	170,000	203,000	445,000
1935	170,000	321,300	576,000
1936	207,000[a]	303,900	646,000
1937	210,000[a]	153,400	510,000

[a] Includes methanol: 47,000 tons in 1936, 70,000 tons in 1937

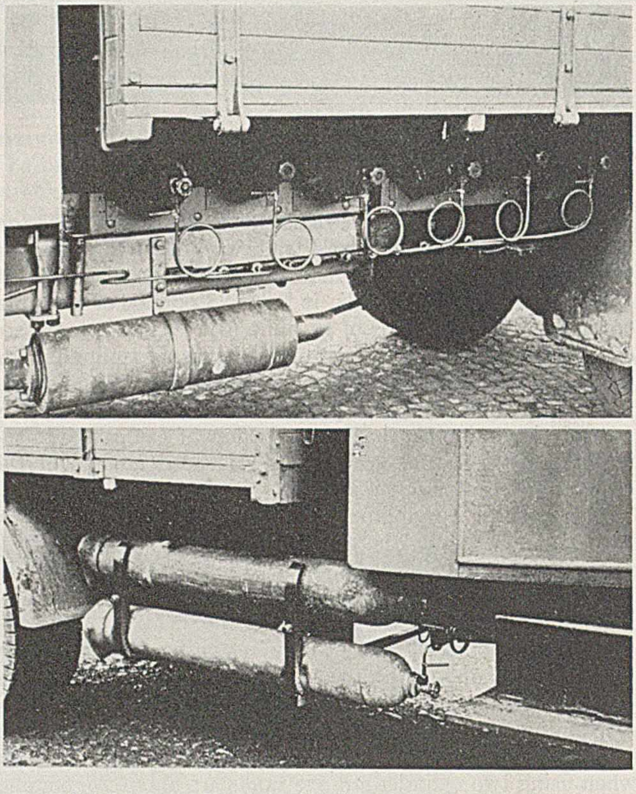
The data showing the power alcohol consumption and percentages of the total motor fuel consumed during 1937 in European countries are as follows; the alcohol used in motor fuel ranged from 0.3 per cent for the United Kingdom to 23.0 for Czechoslovakia:

Country	Power Alcohol Consumption	Total Light Motor Fuel Consumption	Alcohol
	Metric tons		%
Germany	210,000	2,640,000	8.0
France	153,400	2,827,000	5.4
Czechoslovakia	50,600	220,000	23.0
Italy	37,000	483,500	7.6
United Kingdom	16,000	4,840,000	0.3
Sweden	15,200	503,200	3.0
Hungary	10,500	69,100	15.2
Poland	8,000	98,200	8.1
Yugoslavia	3,800	30,200	12.6
Austria	2,300	146,300	1.6
Latvia	2,200	19,400	11.1
Lithuania	1,300	5,700	22.7
Total	510,300	11,882,600	4.3

Great Britain has never compelled the use of power alcohol for blending purposes in order to subsidize the agricultural industries. This is probably due largely to the fact that the raw material, molasses, must be imported.

The British Government further encourages alcohol motor fuel blends by exempting both their alcohol and benzene content from the import duty on motor fuel, which for years was 8d. per Imperial gallon (about 16 cents per U. S. gallon). Recently the tax on imported motor fuel was increased to 9d. (18 cents) per Imperial gallon or 15 cents per U. S. gallon. The principal alcohol blends sold in England have been able, by reason of tax exemptions, to compensate for the higher alcohol cost of about 7.6 cents per Imperial gallon of blend due to the governmental subsidy granted alcohol itself to the limit of 17.5 cents per Imperial gallon (14.6 cents per U. S. gallon). Alcohol blends have not occupied a significant position in British motor fuel markets in competition with gasoline, as shown by the fact that alcohol in the United Kingdom represents only 0.3 per cent of the total motor fuel consumed.

Governmental pressure has been exerted this year to force the power alcohol producers to pay the tax of 18 cents per Imperial gallon (15 cents per U. S. gallon) as do importers of gasoline or gasoline produced from imported oil, on the basis that the alcohol is derived from imported molasses and hence is not entitled to preferential treatment. However, loss of the 18 cent per gallon tax advantage for alcohol still leaves a preferential of approximately 5 cents per gallon in favor of alcohol motor fuel.



Upper. Header Connection of Steel Cylinders on Truck to Deliver Compressed Gas to Motor, Germany
Lower. Compressed Gas Cylinders on Truck and Trailer, Germany

During 1937 a changed attitude regarding the use of power alcohol was noted in various European countries. In Germany the use of foodstuffs for alcohol production was out of favor, and in Italy and Latvia the legal regulations regarding alcohol blends have been suspended for the time being because of a shortage of crops and the increased fear of war, which has diverted motor fuel alcohol to munitions manufacture.

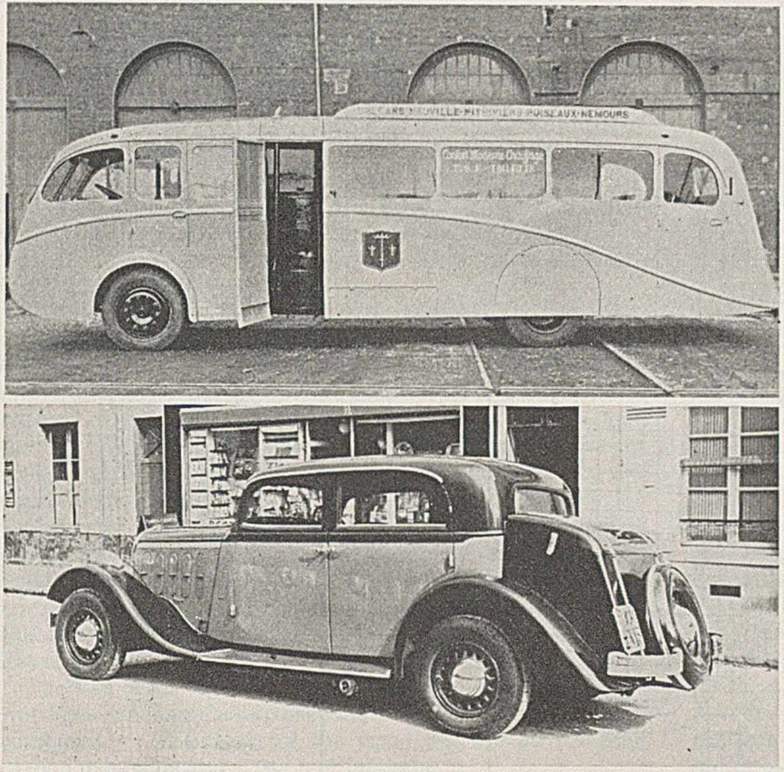
Increased gasoline taxes have formed only a part of the encouragement given to power alcohol. In most European countries alcohol is heavily subsidized—i. e., Germany 39 cents per gallon and France 36 cents per gallon; the government monopolies pay higher prices to distilleries than to distributing companies. The monetary losses entailed due to power alcohol use in the countries of Europe during 1937 was $104,060,500.

The following table (*13*) shows alcohol tax losses, subsidies, and extra cost to consumer above tax-paid gasoline:

Germany	$53,738,000	Sweden	$849,000
France	36,634,000	Poland	584,000
United Kingdom	1,538,000	Latvia	367,000
Italy	4,145,500	Austria	383,500
Czechoslovakia	3,032,500	Lithuania	181,500
Hungary	1,677,500		
Yugoslavia	930,000	Total	$104,060,500

Europe's power alcohol policies have made difficulties for motorists which have been little recognized in the United States. The instability of alcohol supplies has caused repeated changes in the octane ratings of fuel sold the public. No sooner do car operators and automobile manufacturers adjust engines to run on fuels of a given antiknock value than an increase or decrease in the supply of power alcohol results in the raising or lowering of the antiknock value of fuels and in making readjustments necessary.

On June 17, 1938, the French Government was confronted with a surplus of wheat and imposed an additional tax of 20 centimes per liter (2.1 cents per U. S. gallon) on gasoline to subsidize the manufacture of power alcohol primarily from wheat to the amount of 1,250,000 hectoliters (32,875,000 U. S. gallons) annually, with the result that alcohol again must be blended in *essence tourisme* and a further change in octane rating is made necessary.



Upper. Wood-Burning Stove in Doorway to Passenger Bus, France
Lower. Wood-Burning Pleasure Car with Cooling Pipes Shown Underneath, Paris, France

Armaments on Alcohol Policies

Recent events have confirmed previous analyses showing that the primary reason for compulsory use of alcohol in motor fuel in Europe is the desire of the countries to develop and maintain their alcohol industries for the purpose of national defense; this is done not merely as a protection against failure of petroleum supplies in wartime due to blockades but particularly to assure adequate capacity in wartime for manufacture of a prime raw material in making munitions—namely, alcohol (*1*). Significantly, the war scare which gripped all Europe during 1937 was accompanied by a sharp decline of alcohol used in motor fuel. This decrease was far too great to be explainable solely by crop shortages in sugar beets, the main source of alcohol in France and Italy, and must be attributed to the large quantities of alcohol consumed for armament purposes. Classified as confidential military information, diversion of alcohol from motor fuel channels to use in making munitions has seldom been publicly mentioned. In at least one instance, however, it has been reported as a cause for the decline in France of alcohol for motor fuel purposes during 1937 (*10*). Numerous informed sources abroad privately acknowledge that similar diversion of alcohol is also an important factor for the decline of alcohol for use in motor fuel in Italy and probably in Germany.

Because of the natural inclination of foreign nations to avoid this sensitive topic, it is likely that the desire to maintain a vital wartime industry in a continuous condition which permits operations at peak capacity has been greatly understressed as a cause of Europe's compulsory use of alcohol in motor fuel. A realistic appraisal of the situation compels the conclusion that this consideration has been a basic incentive for Europe's power alcohol policies, possibly outweighing even the desire to overcome vulnerability to wartime failure of petroleum supplies due to blockade. At times incapable of meeting all peacetime requirements as in 1937, most European nations clearly do not have alcohol industries of sufficient capacities to meet motor fuel needs and wartime scale of munitions manufacture simultaneously. Indications are that at least one major European nation does not contemplate the use of any alcohol in motor fuel in the event of war. Reports are that it has rejected pleas of automobile manufacturers and others to advance the octane ratings of various fuels on the grounds that in wartime no alcohol would be available for that purpose, that the country's limited supply of tetraethyllead would be used up in military fuels, and that commercial vehicles consequently should not be adapted to fuels of high antiknock value in face of the probability they would have to run on straight gasoline of relatively low antiknock value in time of war.

The Mining and Power Commission of the French Chamber of Deputies recently reported (*11*): "So far as alcohol is concerned, wartime requirements for the explosives industry, for solvents, and for medicinal purposes would be so great that they would far exceed domestic production. This is borne out by the experience of the Great War, when French consumption amounted to between 5 and 6 million hectoliters, of which domestic output was able to supply 1 million hectoliters only. In time of national emergency alcohol would be far too valuable to be used as a motor fuel."

Producer Gas from Wood

Wood and coal as gas producers are not primary sources of motor fuel even in those countries urging their wider adoption. Despite drastic laws and government subsidies, the number of wood-burning motor vehicles is relatively small. The total number in Europe is estimated to be about 9000. These motor cars are made up of specifically designed wood-burning (producer gas) stoves and motors, or gasoline engines converted to wood-burning motors. Passenger busses, trucks (up to 20 tons), pleasure cars, and two taxicabs in Paris are using wood as the motor fuel source.

France has about 4500 wood-burning vehicles, Germany 2200, and Italy about 2200. Many wood filling stations dot France, Germany, and Italy where the wood is sold in packages varying from about 30 to 60 pounds. In Germany there are over 1000 wood filling stations at distances between 20 to 25 miles apart.

At Holten, Germany (May, 1938), the cost of dried wood (at a filling station) was at the rate of 51 cents for a sack of 82 pounds. In order to start the motor readily, charcoal costing 70 cents for 33 pounds is used at the beginning of producer gas production. It has been estimated that 25 pounds of wood, costing 16 cents, will give the same distance performance as 1 gallon of gasoline. This comparison gives the effect of a cheap fuel source when compared to Berlin prices of motor fuel of 59 cents per gallon (filling station price, June, 1938). However, this gives but part of the picture; we must take into consideration the high gasoline tax (36 cents per gallon), absence of taxes on wood, one-half tax rate on wood-burning vehicles, governmental subsidy in converting the vehicle from a gasoline burner to wood burner, and the greater labor, repair, and depreciation costs involved in using wood-burning vehicles compared to gasoline.

Wood as a power substitute for motor transport is a factor in those countries where the natural resources encourage it. The use of wood is desired primarily in France, Germany, and Italy to replace imported petroleum. It is estimated that 450,000,000 pounds of wood were substituted for the equivalent of 18,000,000 gallons or 53,000 tons of gasoline.

A number of motor vehicle manufacturers fabricate equipment directly for the purpose of using producer gas from wood. The vehicles are more expensive in initial cost compared to gasoline type. Many of the wood burners have been converted from gasoline types at costs ranging from $300 to over $500, depending upon the size and work required. The additional parts of wood-burning vehicles over those using gasoline are: stove to burn the wood; cooling pipes to reduce the producer gas temperature; tank to collect condensed water, tar, and acids; filtering agent to extract solid particle from the producer gas; blower in some units to draw the producer gas from the source and then inject it into the motor.

The flow diagram of a gas producer, called in Europe "Gasogene," is illustrated in Figure 4. It consists of a light steel cylinder 2 feet in diameter and 8 feet high, and may or may not be lined with a ceramic material for insulation. It has openings at top and bottom, through which wood, wood charcoal, coal, briquets, or mixtures of them may be charged into the gas generator. Air flows into the solid fuel bed to ignite the producer-gas-forming material. A torch dipped in oil may be used to start the fire (actually observed by the

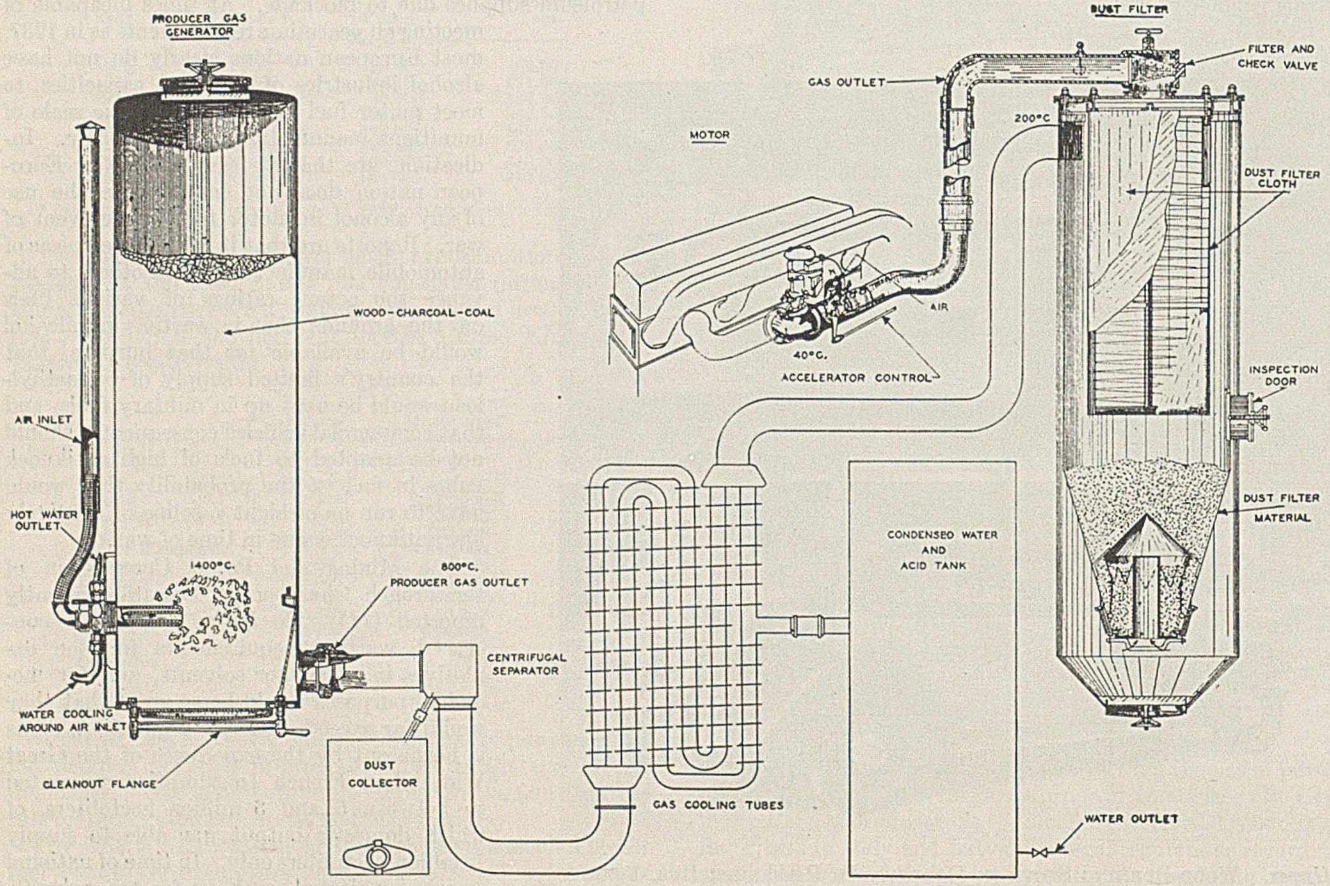


FIGURE 4. PRODUCER GAS MOTOR FUEL SYSTEM

author). Air is admitted into the bottom of the generator, and combustion takes place at about 1400° C.; the producer gas leaves the bottom of the generator at about 800° C. as the gas passes through a series of air-cooling pipes connected to a knockout cylinder to collect water, tar, acids, and a solid-particle catcher, then into a filtering chamber to take out the colloidal particles of dust in the gas stream as it passes through a solid filtering material such as activated char and filtering cloth. The purified producer gas mixed with air is then discharged by means of a blower into the motor.

Wood-Burning Taxicab, Paris

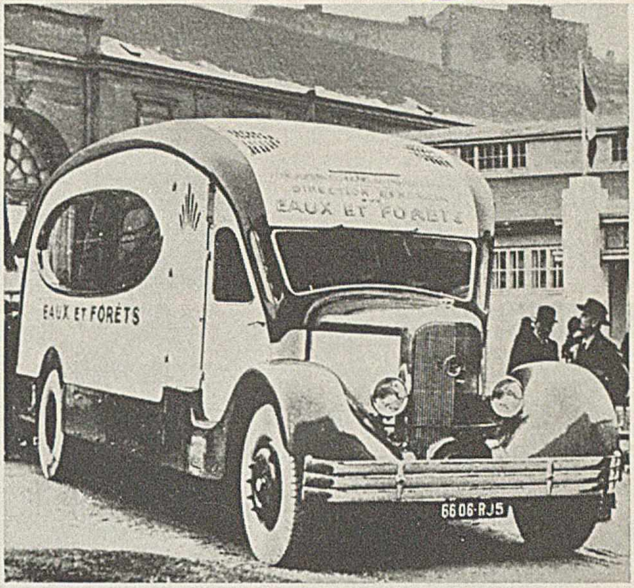
Charcoal–anthracite coal mixture

Green wood is not as suitable for producer gas production as wood which has been air-dried in order to remove excess moisture. The drying period may take from 7 to 18 months. Beech, oak, and birch with a moisture content of 20 per cent are used. Part of the wood is converted into charcoal for "quick" starting of the motor on a cold morning. From 10 to 20 minutes may be required, and in some cases gasoline is used first to warm the motor. Depending upon the duty that the motor vehicle has to perform, the wood is cut into sizes of 0.5 × 0.5 × 0.5 inch to about 2 × 2 × 3.5 inches. Some waste (sawdust) is briquetted with wood tar or coal tar and pitches.

In addition to the fact that the initial cost of the Gasogene vehicles is higher than that of gasoline vehicles, other economic factors have to be considered. One lies in the bulk and weight of the generator equipment. The transporting capacity is reduced about 20 per cent in comparison with gasoline motors on trucks. A wood gas generator capable of operating a 90-horsepower 5-ton truck weighs 1850 pounds. When a charcoal gas generator is used, the weight is 1575 pounds but the price of charcoal is about $2.18 higher per 100 miles of operation than wood which nullifies the excess loading possible in that type of truck. The general over-all performance of the engine using charcoal is considerably better than that using wood because fewer cleanings are necessary and less water is produced.

The loss of power output based upon the heat content of wood gas in comparison to gasoline is about 30 per cent. The combustible constituents of the wood gas are 30 per cent carbon monoxide and 1 per cent methane.

The inconvenience and delay in starting are other objections; when combined with the delays necessitated by cleaning and reduced efficiency, the over-all picture of wood as a motor fuel compared to gasoline does not appear favorable except as necessity demands its use.



Wood-Burning French Government Motor Bus

To interest people in this kind of vehicle shown in Vienna Fair at French concession

If all the wood produced in France yearly were used as a motor fuel, it would displace about 500,000 tons of oil or 10 per cent of the nation's requirement. Should this ever go into effect, there would be no wood left over for other purposes. This conclusion holds in general for other European countries as well.

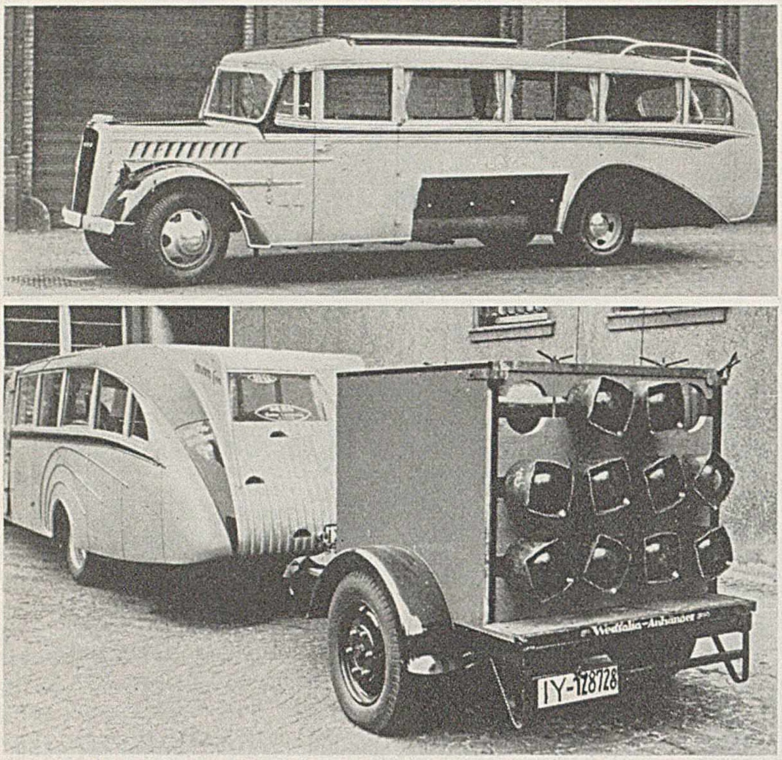
Producer Gas from Charcoal and Anthracite

The gas producer motor vehicle may operate on brown coal, lignite, anthracite coal, and peat coke alone or mixed with wood or wood charcoal. One taxicab in Paris operates on producer gas from a mixture of 20 per cent charcoal and 80 per cent anthracite coal. Gasoline was used to warm the motor, and the charcoal-anthracite mixture was ignited from a torch dipped in oil. It actually took about 5 minutes before the taxi was in smooth running order. In general, it has been found that the use of coal gives somewhat more difficulty in operation than dried wood or wood char.

Producer Gas from Brown Coal, Lignite, and Lignite Briquets

On account of the high water content of brown coal and lignite fuels, they should be converted to coke. The resultant cokes are similar to wood charcoal in activity but have considerable ash which gives rise to clinkers. In forming brown coal briquets, tar decomposition is accomplished by precarbonization in order to remove volatile matter.

Coal in general has not met with favor as a producer gas fuel because of its high gasification temperature. Nevertheless, Belgium favors an 80 to 20 mixture of anthracite and charcoal; a lower fuel expense is claimed than when city gas is used. The disadvantages which have halted the use of coal are slag formation, leading to sintering of the ceramic lining of the generators, and discharge of high percentages of sulfur dioxide in the exhaust gases. It was impossible to obtain information as to the number of coal-burning vehicles in Europe.



Upper. Passenger Bus with Cylinders of Compressed Gas, Germany
Lower. Bus and Compressed Gas Trailer, Germany

Oil Shale Motor Fuels

Oil shale in Europe is found in the following countries: Great Britain, Estonia, Finland, France, Latvia, Sweden, Spain, and Czechoslovakia. The latter countries have little or no commercial production at present. Since these countries have practically no crude oil, the exploitation of the shale deposits has become increasingly important from the economic standpoint. The following table shows the metric tons of shale motor fuel produced in Europe during 1937:

United Kingdom	26,000
Estonia	7,300
Finland	2,700
France	1,500
Latvia	1,300
Total	38,800

The Scottish oil industry started about 90 years ago to yield products such as motor fuel, kerosene, Diesel oil, wax, and ammonium sulfate. The reserves are estimated at 280,000,000 tons or a potential 6,160,000,000 gallons of oil, assuming 22 gallons of oil per ton of shale. The shale oil industry antedates the petroleum, and many of the processes developed in this industry were subsequently applied to crude oil. The output of oil shale annually (1937) is approximately 1,400,000 tons from which 100,000 tons of marketable products were obtained. The shale motor fuel industry is protected by an 18 cent tax per Imperial gallon (15 cents per U. S. gallon) against imported gasoline, but even this protection has not served to stabilize the industry.

Because of the more efficient motors of today, the fuel produced from shale oil has required increased blending with higher octane fuels or cracking to raise the octane rating which in turn increases the cost of production. The motor fuel yield is at the rate of about 26,000 tons a year. It is estimated that the cost of producing motor fuel from oil shale is about 15 cents per U. S. gallon.

The Estonian oil shale deposits have been exploited commercially since about 1922 when a fuel shortage made extensive developments desirable. The deposit has a total average thickness of 10 feet and an area of about 965 square miles. The oil shale reserve is estimated at 3,500,000,000 tons with a potential oil production of about 675,000,000 tons. During 1937 about 112,000 tons of shale oil (*8*) were produced from which 14,000 tons of motor fuel were derived. It is estimated that 18,000 tons of motor fuel will be produced during 1938 from 150,000 tons of shale oil.

The oil shale deposits of France are estimated at 21,000,000 tons of workable shale in the Autun region. The shale mined per year is about 120,000 tons with a yield of about 9000 tons of oil a year. The motor fuel production during 1937 was about 1500 tons.

Semiscale tests have been carried out in Italy on the shale oil production from the deposits in Ragusa, Frosinone, and Abruzzi. The 1,800,000 estimated tons of shale of this area would probably produce over 100,000 tons of motor fuel; however, to date there has been no commercial production of shale motor fuel.

Sweden has oil shale deposits to the extent of about 5,000,000,000 tons. It is estimated that of this quantity 630,000,000 tons can be mined cheaply in open cuts and converted into 32,000,000 tons of oil. A retorting unit is in operation which processes 75 tons of oil shale a day, producing 3 tons of oil.

At present, competition with petroleum products has made oil shale motor fuels a nationalistic problem.

The following table shows the extra costs of shale gasoline above imported gasoline, in losses in taxes, government subsidies, and production costs for the countries where it was marketed during 1937.

Country	Cost above Imported Gasoline	Extra Cost per Metric Ton of Motor Fuel
United Kingdom	$1,309,000	$50.00
Estonia	282,500	37.00
Finland	98,000	36.30
France	105,500	70.00
Latvia	53,500	41.00
Total	$1,848,500	

The production and use of shale motor fuel have cost the consumer and governments about 15 cents per U. S. gallon above that of imported gasoline, owing to losses in taxes.

Ammonia, Hydrogen, and Acetylene as Motor Fuels

The desperate desire of nations to make themselves self-sufficient in substitute motor fuels is reflected in the experimental work going on with such substances as ammonia, hydrogen, and acetylene.

Synthetic ammonia has been used in Italy as a motor fuel substitute. The ammonia is cracked into hydrogen and nitrogen by means of a so-called disintegrator (probably catalytic). Vaporization of the liquefied ammonia is accomplished by releasing the pressure in the storage tank and counteracting the refrigerating effect thus encountered, by means of a disintegrator which utilizes the heat from the motor exhaust. In Cherso, Italy, a test using a Fiat passenger car developed

TABLE II. EUROPEAN PROPORTIONS OF SUBSTITUTE FUELS IN 1937[a]

Country	Alcohol	Benzene	Oil from Coal and Synthetic Gasoline	L. T. C.[c] Gasoline	Shale Spirit	Total Substitutes	Total Light Motor Fuel Consumption	Per Cent Substitutes
				Metric tons				
Germany	210,000	430,000	800,000	[b]	..	1,440,000	2,640,000	54.5
Estonia	...	...	...	...	7,300	7,300	14,300	51.9
Czechoslovakia	50,600	12,000	...	...	...	62,600	220,000	28.5
Lithuania	1,294	...	...	...	...	1,294	5,700	22.7
Hungary	10,516	3,100	...	...	...	13,616	69,100	19.7
Poland	7,955	10,000	...	...	...	17,955	98,200	18.3
Latvia	2,154	...	...	...	1,300	3,454	19,400	17.8
Yugoslavia	3,806	...	...	...	...	3,806	30,200	12.6
Belgium	...	36,700	...	...	...	36,700	408,800	9.0
France	153,400	80,000	13,000	...	1,500	247,900	2,827,000	8.8
United Kingdom	16,000	230,000	116,000	4,000	26,000	392,000	4,840,000	8.1
Italy	37,000	...	...	...	...	37,000	483,500	7.7
Austria	2,300	8,200	...	...	...	10,500	146,300	7.2
Sweden	15,247	500	...	...	...	15,747	503,200	3.1
Holland	...	10,800	...	...	...	10,800	392 600	2.8
Finland	...	200	...	...	2,700	2,900	112,500	2.6
Switzerland	50	3,000	...	...	...	3,050	203,900	1.5
Total	510,322	824,500	929,000	4,000	38,800	2,306,622	13,014,700	17.7

[a] Total European light motor fuel consumption, including countries not enumerated, 14,344,000 metric tons.
[b] Included under synthetic gasoline. [c] Low-temperature carbonization.

TABLE III. RETAIL PRICES, IMPORT DUTY, AND TAXES ON MOTOR FUEL (*22*)

Country	City	Gasoline Price	Import Duty	Import Duty and Tax
		Cents per U. S. gal.		
Italy	Rome	73	49	51
Germany	Berlin	59.6	31	36
Lithuania	Kaunas	63.1	23.2	23.2
Bulgaria	Sofia	50	28	39
Czechoslovakia	Prague	42.4	5	16.1
Palestine	Jerusalem	41.4	20.7	20.7
Yugoslavia	Belgrade	40.9	6.7	23.5
Switzerland	Zurich	38.2	19.2	19.2
Hungary	Budapest	38	8	26
Estonia	Tallinn	38	8.1	21.1
Latvia	Riga	37.8	14.4	21.6
Greece	Athens	37.5	19.9	21.2
United Kingdom	London	36.2	15	15
Belgium	Antwerp	36	20	20+ 9% ad valorem
France	Paris	31.8	18.5	19.5
Norway	Oslo	27.5	None	9.5
Denmark	Copenhagen	26.4	None	11

31 miles per hour in a road test. As a motor fuel the low heating value of ammonia (4.450 kcal. per kg.) does not lend itself to wide use. The high cost involved in the use of ammonia is another factor retarding its use.

Experiments on acetylene as a fuel indicated that acetylene cannot do the full work of a gasoline engine and that thermal efficiency is highest with dilute air-gas mixtures.

Hydrogen as motor fuel in the form of compressed gas has also been tried. The results so far do not look very promising.

100-Octane Fuels

There are no units operating in Europe at present on substitute fuels to produce 100-octane motor fuel. While there is one plant producing such fuel and several others are under way, the source material is petroleum. However, 100-octane fuel can be produced from Europe's substitutes, providing some of the catalytic processes developed and introduced in the United States are employed. This may be done in one of the following ways:

1. Isomerize the normal butane which they produce from hydrogenation of coal and the water gas reaction, dehydrogenate and polymerize to isoöctenes and hydrogenate to isoöctanes.
2. Isomerize their normal pentane to isopentane which has an octane rating of 90, whereas the normal has 64. The isopentane, because of its boiling point, will be blended with the isoöctanes and then leaded to 100 octane.
3. Alkylation of normal or isobutylene with isobutane or isopentane.
4. Catalytic cracking process, which is highly selective in the production of high octane gasoline.
5. Catalytic isomerization and cyclization of gasoline made by Fischer-Tropsch water-gas reaction and hydrogenation of coal.

There is nothing at present to indicate that 100-octane fuel, which has become practically necessary in the operation of military air craft, can be made from these *Ersatz* materials by any other methods.

Summary of Substitute Motor Fuels (*13*)

The substitutes for petroleum gasoline in Europe in 1937 composed of synthetic gasoline and benzene from coal, alcohol, and oil shale amounted to 203,306,622 tons or 15,250,000 barrels, or about 18 per cent of the total gasoline consumption. The tonnage of substitute fuels for each country is shown in Table II.

In addition to the liquid substitutes given, two other types are produced from the gases of coal and wood. It is estimated for 1938 that compressed and producer gas from coal and wood will substitute for 243,000 tons of petroleum gasoline or 1,823,000 barrels.

For the year 1938 about 25 per cent of the total European requirements for motor fuel will come from substitutes.

Import Duty, Taxes, and Prices

The highest gasoline prices in Europe are in Italy, Germany, and Lithuania and are 76, 63, and 59.6 cents per U. S. gallon, respectively. The import duty and tax per gallon of gasoline in Italy is 51 cents and for Germany 36 cents. Detailed data are shown in Table III.

As a matter of contrast, the average retail price for regular grade gasoline in the United States was 19.5 cents a gallon, of which 5 cents was tax (June, 1938).

TABLE IV. COST OF EUROPEAN SUBSTITUTE FUELS AT AVERAGE RATES OF EXCHANGE DURING 1937 (*14*)

Country	Alcohol Tax, Losses, Subsidies, and Extra Cost to Consumer above Tax-Paid Gasoline	Benzene	Synthetic and L.T.C. Gasoline	Shale Spirit	Total
Germany	$ 53,738,000	$33,238,500	$70,952,000	.....	$157,928,500
France	36,634,000	6,564,500	2,523,500	$105,500	45,827,500
United Kingdom	1,538,000	9,660,000	6,039,000	1,309,000	18,546,000
Italy	4,145,500	......	......	.....	4,145,500
Czechoslovakia	3,032,500	Not calcd.	......	.....	3,032,500
Hungary	1,677,500	Not calcd.	......	.....	1,677,500
Yugoslavia	930,000	......	......	.....	930,000
Sweden	829,000	Not calcd.	......	.....	829,000
Poland	584,000	Not calcd.	......	.....	584,000
Latvia	367,000	......	......	53,500	420,500
Austria	383,500	Not calcd.	......	.....	383,500
Estonia	....	......	......	282,500	282,500
Lithuania	181,500	......	......	.....	181,500
Finland	....	Not calcd.	......	98,000	98,000
Total	$104,040,500	$49,463,000	$79,514,500	$1,848,500	$234,866,500

Excess Costs of Substitute Fuels over Gasoline

For 1937 the extra cost to the consumer and state above the cost of imported gasoline (*24*) and losses in taxes amounted to about $235,000,000, or 32 cents for every gallon of substitute fuel consumed. The monetary losses involved in European countries are given in Table IV.

There will be an estimated loss of $300,000,000 due to the use of substitute fuels over petroleum gasoline costs (during 1938) to the consumers and governments of Europe.

Acknowledgment

The photographs of compressed gas used as motor fuel were furnished through the courtesy of Benzol-Verband G. m. b. H., Bochum, Germany, and C. Padovani, Instituto di Chimica Industriale, Milan, Italy. Appreciation is also expressed to Prudence M. Van Arsdell of Universal Oil Products Company for assistance.

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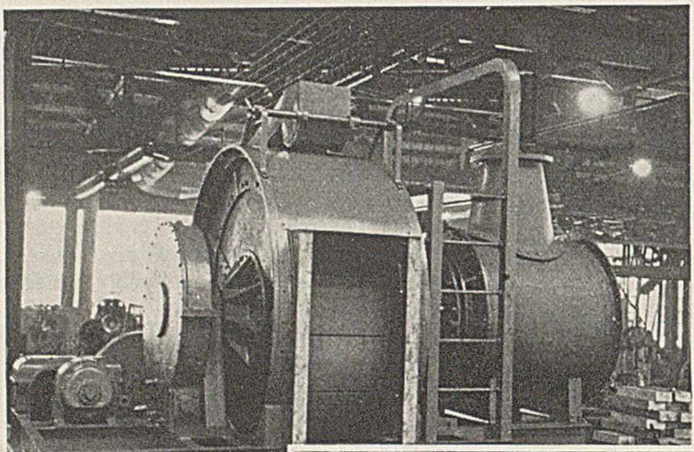
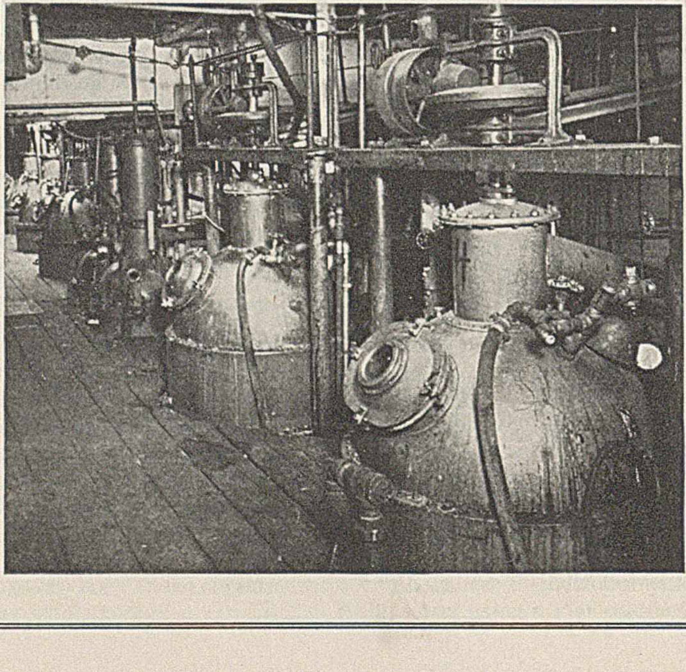


A SHOP CONSTRUCTION VIEW SHOWING OLIVER-ROBISON FILTER DRYER WITH MONEL HOUSING AND ACCESSORIES, AND FILTER CLOTH SCREENS

This unit has a drum 6 feet in diameter by 2 feet wide and a daily capacity of 200 tons of dry salt. Designed by Clinton S. Robison and Associates and built by Dominion Engr. Co., Ltd., Montreal, Canada

Courtesy, International Nickel Company, Inc.



BATTERY OF JACKETED NICKEL PROCESSING KETTLES AT THE PLANT OF THE MARBLETTE CORP., LONG ISLAND CITY, N. Y.

Built by Sholes Inc., Orange, N. J., and by George Keller (Copper Works), Brooklyn, N. Y.

Courtesy, International Nickel Company, Inc

Centrifugal Pumps for the PROCESS INDUSTRIES

H. E. LaBOUR
The LaBour Company, Inc., Elkhart, Ind.

THE centrifugal type of pump is the unit most commonly used in the process industries, but the characteristics of this pump, as well as its advantages, are best explained by comparison with other available types of pumping equipment. The term "pumping equipment" as here used refers only to apparatus for moving liquid by mechanical action and does not refer to devices utilizing the displacement action of compressed air.

The pumps under discussion may be placed in two general classifications: (1) positive displacement pumps as represented by the reciprocating or piston pump and by the rotary pump; (2) the centrifugal type of pump.

Although they differ widely as to mechanical construction, the two varieties of displacement pumps employ the same principles of operation and have the same fundamental operating characteristics. In all cases the liquid flows or is drawn into the pump and then in a relatively quiescent condition is moved through the pump and expelled by the mechanical displacement action of a part of the pump. The mechanical motion may be of a reciprocating nature, such as a moving piston, or it may be in the form of revolving vanes which displace and push the liquid at moderate velocity.

Positive Displacement Pumps

Because of their slow speed positive displacement pumps are vitally dependent upon close clearances between the moving and stationary parts, and this makes them unfit to handle corrosive or highly abrasive liquids. They will produce a positive suction and will lift liquids from a lower level. They will develop high pressure, and the discharge pressure is not determined by the speed of operation or the specific gravity of the liquid but is limited fundamentally only by the limits of the mechanical construction of the pump and the power available for operation. Since this pump operates by mechanical displacement, its capacity is directly affected by the speed of operation.

In all displacement pumps, if the speed remains constant the capacity also remains relatively constant, and the power input increases as the head, against which the pump must deliver this constant capacity, increases. Inversely the power decreases with reduction in head but the capacity remains nearly constant. This characteristic is just the reverse of that displayed by the true centrifugal type of pump (Figure 1).

Centrifugal Pumps

The centrifugal type of pump operates at a relatively high speed, and the energy from the driving unit is imparted to an impeller revolving within a body of liquid. This impeller imparts energy and motion to the liquid. The kinetic energy thus imparted to the liquid is converted to pressure within the pump, and the liquid is discharged purely because of difference in pressure, not because of displacement, as in the positive displacement pump.

The ordinary centrifugal pump must be filled with liquid or primed before it can develop pressure. It can lift liquid from a lower level on the suction side if the suction line is at all times kept filled with liquid. However, if air is admitted to the pump suction, the pump drops its pressure and ceases to function.

Special types of centrifugal pumps, designated as self-priming centrifugal pumps, have the ability to handle air. These will be discussed in more detail, but their general pressure and capacity characteristics are the same as those of other centrifugal pumps.

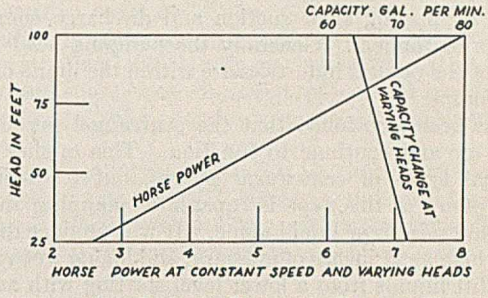


FIGURE 1. TYPICAL CURVE OF ROTARY POSITIVE DISPLACEMENT PUMP

Since the centrifugal pump develops its discharge pressure through the medium of motion, the factors of speed and the weight or specific gravity of the liquid are of prime importance. Disregarding such accompanying factors as viscosity, slip, etc., the pressure which a centrifugal pump will develop varies directly with any change in the specific gravity of the liquid being handled and varies approximately as the square of any change in the peripheral speed of the impeller.

If a centrifugal pump operates against a given static head and the specific gravity of the liquid is increased, the pump at its discharge will show an increased pressure, but this will be offset completely by the increased pressure at the base of the column of liquid in the discharge line, due to the increase in the specific gravity of the liquid being handled. The change in the specific gravity will have no effect on the quantity discharged. The power input, however, will increase as the specific gravity increases.

Unlike the positive displacement pump, the centrifugal type of pump tends to increase its capacity and to increase its power input as the head is decreased. Also, inversely, the power input and capacity decrease as the head is increased until that head or pressure is reached which is the maximum the pump will develop. Here the power input is a minimum. This characteristic permits the operation of centrifugal pumps with varying capacities from a maximum down to nothing without the use of unloading devices and without danger to the pump. A positive displacement pump requires the use of a by-pass or unloading valve to limit the pressure or damage to the equipment will result (Figure 2).

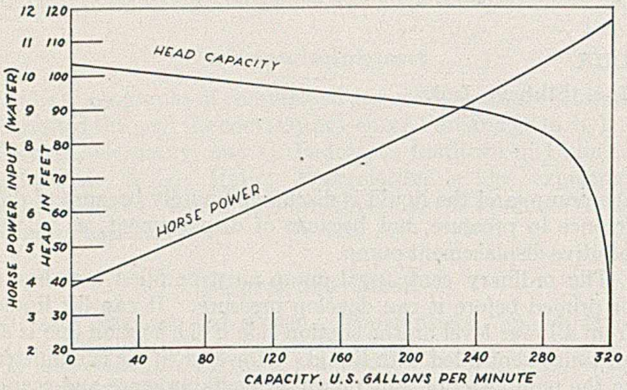


FIGURE 2. TYPICAL CURVE OF CENTRIFUGAL PUMP, CHEMICAL TYPE

Since the pressure which a single-impeller pump of given design and size will develop is limited by its speed of operation, if pressures are required beyond the practical limits of this impeller, it is necessary to stage two or more individual pumps by placing their suction and discharge connections in series or tandem. Generally the pumping head requirements of the process industries are within the limits of single-stage pumps.

It has been mentioned that the centrifugal pump cannot handle air and continue to function. This applies to conventional types of centrifugal pumps, but a specially designed pump of this type is capable of pumping air, or air and liquid mixed, or liquid alone. It will produce dry vacuums as high as 27 inches of mercury, and higher wet vacuums. It will lift liquids from a lower level starting with an empty suction line and will successfully handle, intermittently, liquid and gas. This pump is known as a self-priming centrifugal pump.

The self-priming centrifugal pump has the same pumping characteristics as the simple standard centrifugal pump, but in the more commonly used design it obtains its self-priming action by a special type of impeller and casing which permits the recirculation of a part of the liquid only when priming is being accomplished. This recirculated liquid mixes with gas from the pump suction, and the mixture is discharged into a separator where the gas is removed before the recirculated liquid returns to the pump for more gas. In the best design the recirculation of liquid is automatically stopped by hydraulic balance after priming is completed.

This self-priming type of pump combines the advantages of the centrifugal pump with the suction ability of the positive displacement pump and can be made so simple in construction as to permit its general use in the process industries.

There is one more variation of the centrifugal type of pump which must be considered—the turbine pump. It is a centrifugal pump in so far as its pressure is affected by its rotative speed, and it is operated at centrifugal pump speeds.

The pressure capacity characteristics of the turbine pump are more those of the direct-acting or the positive displacement pump than of the centrifugal pump, since the load on the driving unit increases with increased pressure (Figure 3).

Roughly, this pump may be pictured as a single-impeller pumping unit having a multiplicity of small vanes on or near the periphery of the impeller and so arranged as regards the casing design that discharge and reëntry occur in sequence a number of times before final discharge. This has an effect similar to multistaging a standard centrifugal pump in so far as the building up of pressure is concerned. However, this pump has some characteristics peculiar to itself.

The turbine pump is quite dependent upon close clearances and is primarily of value in the smaller sizes where high heads and small capacities are desired and where the close clearances may be maintained. It is available in the self-priming type.

History

The real development of centrifugal pumps for handling corrosive liquids has taken place within the last twenty years. Prior to this, various types of pumping equipment were used, running the whole gamut from conventionally designed centrifugal pumps made of lead, down to piston pumps of lead, bronze, or other materials, with rubber ball valves. Mechanical pumping equipment, however, had at that time only a small part in the handling of corrosive liquids, as by far the most commonly used transferring device for liquids was some form of the "blow case" using compressed air as a displacing medium.

Just prior to the World War, interest in corrosion-resistant materials was stimulated by the introduction from Germany of alloys of the chromium-nickel type, and about this time a demand also developed for more flexible and safe methods of conveying corrosive liquids. Toward the close of the World War some centrifugal pumps of special design appeared on the market but still their use was limited in scope by the absence of adequate materials of construction. The available materials were confined almost entirely to lead and one or two high-priced chromium-nickel alloys.

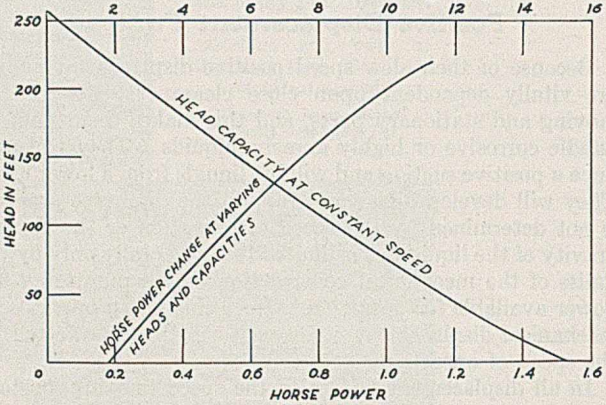


FIGURE 3. TYPICAL CURVE OF TURBINE TYPE PUMP

The really rapid growth in the use of centrifugal pumps may be traced directly to two separate developments. First was the introduction of the self-priming centrifugal pump which occurred in 1922; second was the tremendous development in the production of corrosion-resistant alloys, beginning about 1923 with the general interest in the use of high-chromium steels and the chromium-nickel alloys. Some of the latter, as represented by the "Parr" alloys, had been available for some years but were handicapped by high costs and by uncertain composition and performance.

The self-priming centrifugal pump for handling corrosive liquids inherently combined many of the performance characteristics of both the centrifugal and displacement types of pumps. This pump, for the first time, made it possible for the chemical plant operator to locate a centrifugal type of pump above the source of supply.

Materials of Construction

Except for some of the chlorine group of acids and their salts, practically every chemical commonly encountered today can be handled successfully with available materials of construction which are suitable for use in fabricating pumps. Materials, such as rubber, ceramics, and the high silicon-iron alloys, are not so classified because of structural limitations that prevent their fabrication for general use.

A high percentage of the resistant alloys available are special products of individual manufacturers. Each of these alloys has its particular advantages and its limitations.

However, these fall into a few general groups with certain group characteristics.

No particular reference need be made to the fields of application of the old and well-known metals such as lead, bronze, aluminum, and cast iron, but these will be discussed later in connection with specific pump applications.

The newer alloys which have contributed heavily to the development of pumps for the process industries consist basically of (1) iron and chromium, (2) iron, nickel, and chromium, and (3) nickel and chromium. Any discussion of characteristics of these alloys can, at best, be only general since variations in composition and even in methods of manufacture influence inherent resistivity by affecting size and type of grain structure, distribution of impurities, density of castings, or other factors.

Because of the tremendous variety of these alloys now available, the selection of materials of construction permits considerable variation. It is often much easier to point out what types of materials should be avoided than to offer definite guidance as to what to select unless the details of the specific application are known.

Experience has demonstrated that in most cases nitric acid is best handled in the chromium-iron alloys of the 18 per cent chromium and 8 per cent nickel type. These may or may not contain some molybdenum, but it is advisable to maintain at least a 200 to 1 chromium to carbon ratio.

The materials used for handling sulfuric acid will vary with the strength and temperature of the acid. Weak acid solutions at moderate temperatures may be handled in lead or in some of the chromium-nickel alloys. It may be handled also in some of the better chromium-nickel-iron alloys. Lead should not be used if erosive conditions are encountered.

The most corrosive range encountered in pumping sulfuric acid lies approximately between 40° and 55° Bé. Lead and the best of the chromium-nickel alloys are still serviceable here but the iron-base chromium alloys should not be used.

In the middle ranges of strength of sulfuric acid—say approximately from 15° to 60° Bé.—there is a great tendency for the iron-base chromium alloys to show serious intercrystalline corrosion, even when other corrosion resistance appears satisfactory. A great many lead pumps are in use for handling 60° Bé. sulfuric acid, and lead has been employed successfully up to 66° Bé.; but above 60° Bé., lead should be used only in special cases. On the other hand, cast-iron pumps are utilized to some extent with indifferent results for handling 60° Bé. acid and are commonly used for 66° Bé. acid. Either iron-base or nickel-base chromium alloys of proper composition are suitable for this range.

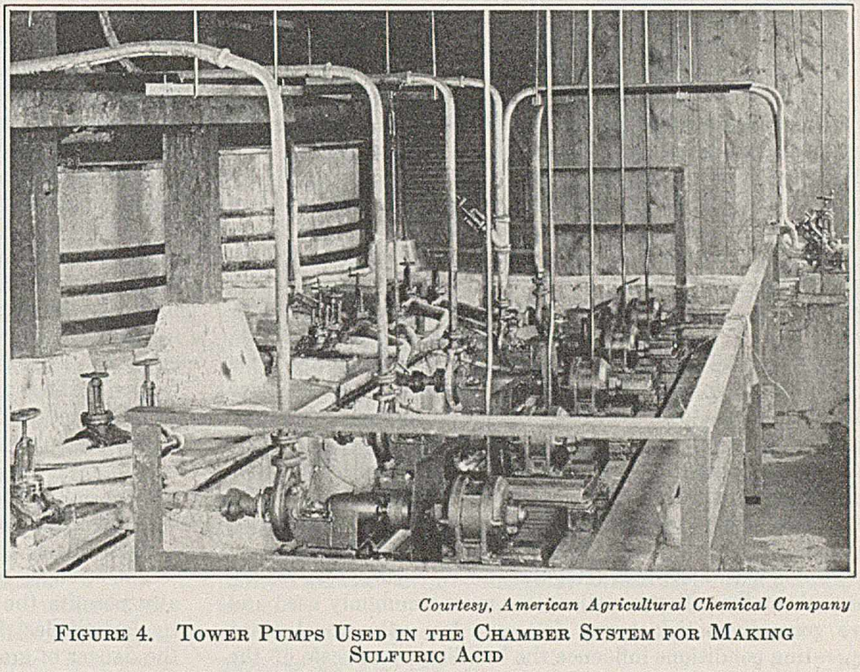
Cast iron is commonly used from the middle ranges up to 100 per cent acid and may be successfully employed for handling oleum if the iron is free from graphitic carbon segregations. Again, chromium alloys with either an iron or nickel base may be used.

No alloys have yet been found which may be regarded as generally satisfactory for handling the chlorine group of acids. Instances of successful behavior of a few alloys are numerous, but just as numerous are the records of failures. Probably local conditions and impurities in the solutions have much to do with this lack of uniformity, but in pumping hydrochloric acid one point stands out prominently—namely, that the presence of air mixed with the acid tremendously increases the rate of corrosion.

Some alloys are offered for the handling of the above-mentioned solutions in which dependence for resistance to corrosion is placed almost entirely upon the development of a protective film of an insoluble salt. Obviously, if this is removed, either as a result of abrasive materials being present with the liquid or of the washing action of the rapidly moving liquid itself, then immunity is lost.

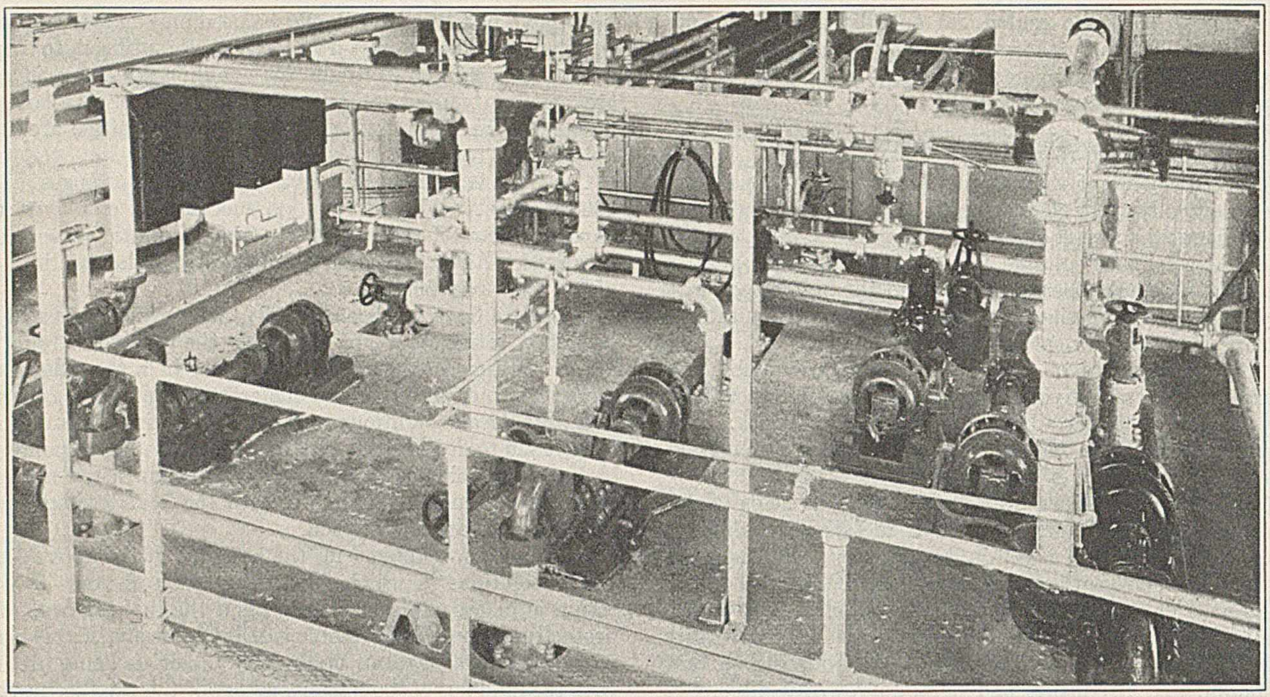
The handling of alkaline or caustic solutions presents far less of a problem than the handling of many acid solutions, since cast iron can be used in the large majority of cases. The factor of liquid contamination rather than corrosion of the materials of construction must be considered in the handling of caustics to be used in the rayon industry. Generally this industry specifies high-nickel alloys essentially low in iron and copper. Pure nickel may be employed. Most of the iron-base and nickel-base chromium alloys will handle alkaline or caustic solutions successfully in so far as corrosion is concerned.

No definite recommendation can be offered for materials used in contact with the great mass of the chemical solutions encountered. Exact composition and even impurities in these solutions may be important as far as their corrosiveness



Courtesy, American Agricultural Chemical Company

Figure 4. Tower Pumps Used in the Chamber System for Making Sulfuric Acid



Courtesy, Rumford Chemical Works and Chemical Construction Corporation

FIGURE 5. PUMPS IN A CONTACT TOWER INSTALLATION

is concerned. For instance, mixed sulfuric and nitric acids are easier to handle than either of the acids alone, but the presence of even a small quantity of hydrochloric acid with sulfuric acid enormously increases the rate of corrosion.

The variations in the composition and in the methods of manufacture of different alloys which belong in the same general classification may be sufficient to produce widely different results. This seemingly unaccountable variation is most confusing to the pump user, but as yet no practical method has been developed for predicting the behavior of any alloy under all conditions of operation. It is this uncertainty which induces the constant increase in the large number of alloys already available.

Service Applications

CIRCULATING PUMPS. The two most commonly encountered applications under this classification are both found in connection with the manufacture of sulfuric acid; yet these two applications are so vitally different that they must be considered separately.

In the manufacture of sulfuric acid by the chamber system as commonly used in the phosphate fertilizer industry (Figure 4), the method of circulating acid over the Glover and Gay-Lussac towers is almost standard. A nonpriming type of pump is used which receives its supply by gravity from low tanks, usually not more than 3 or 4 feet deep, and located below the level of the base of the tower. This system calls for the maintenance of a constant acid head or pressure at the top of the tower, and the pumping methods therefore involve delivering the acid to the tank at the head of the tower at as constant a rate as possible. Generally the rate of delivery is small (not over 20 gallons per minute), and the static head seldom exceeds about 70 feet in plants in the United States. There are a few 90-foot towers in operation.

Pumps with hard-lead (Regulus metal) casings and nickel-base chromium alloy impellers are most commonly used and are generally satisfactory. In some few cases local plant operating conditions influence the building up of scale on the inside of the pump casings, and in such applications the casing should be made of one of the resistant chromium-nickel or chromium-nickel-iron alloys. Pumps in this service will give a minimum of trouble if they are operated continuously rather than intermittently.

Pumps for service in contact systems for the manufacture of sulfuric acid encounter more severe conditions (Figure 5). The temperature of the liquid is often nearly 200° F., and the liquid may be in such condition that gas is easily liberated from it. The corrosive action on the pump packing, particularly under pressure, is so severe that gravity-fed centrifugal pumps of the conventional type are not successful.

The modern contact plant generally uses the self-priming type of centrifugal pump and locates it above the source of supply. This keeps the packing gland continuously under some vacuum, which, in combination with water cooling of the glands, the use of proper packing, and proper gland lubrication, gives very satisfactory packing life. Records of service conditions indicate that when the pumps are kept in continuous operation, it is possible in many cases to obtain several months of service before repacking is necessary.

The vertical centrifugal pump of the "boot" type is used to some extent in tower service. This pump receives its supply by gravity, as the pump casing is located at or near the bottom of the supply tank. The pump is driven through a long shaft which extends upward through an enclosed pipe or boot with the driving unit located above the maximum acid level. The packing may be entirely eliminated in some cases, or at worst it is so located as to be out of pressure contact with the acid (Figure 6).

When pumps of the self-priming type are used, consideration must be given to the fact that they are lifting the liquid from a lower level. Hence the capacity of the pump in terms of acid delivered will be affected by any gas which may be released from the acid under the vacuum equivalent to the suction lift.

The strength of acid handled in contact tower service usually permits the use of pumps with cast-iron casings, particularly if electric-furnace cast iron is used, so as to eliminate the danger of graphitic carbon segregations. In self-priming pumps the impellers are generally made of chromium-nickel iron and often it is justifiable to make the entire pump of such an alloy. The vertical type of centrifugal pump for this service is generally of such size as to permit the use of cast-iron impellers as well as cast-iron casings.

TRANSFER SERVICE. Within this classification is found the great bulk of pump applications, and so great a variety of conditions is encountered that only a limited number may be mentioned or classified.

The most simple type of installation involves the location of the pump so that liquid from the supply source flows to the pump suction by gravity. Such service can be handled successfully with a nonpriming type of centrifugal pump except in cases where air or gas is drawn into the pump regularly or along with the liquid. Under such conditions the ability of the self-priming pump to handle air will prove beneficial.

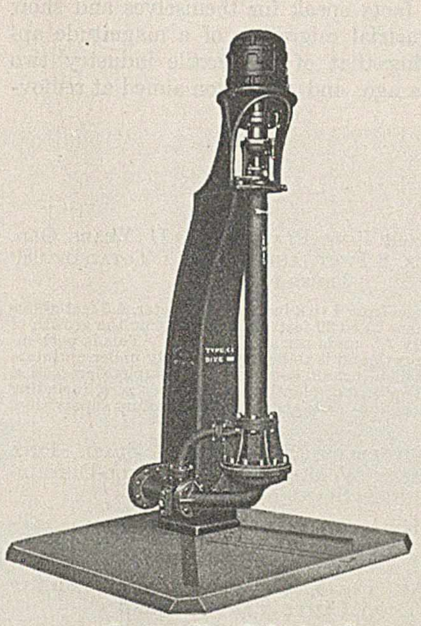
When the pump is to be located so that it must lift the liquid by suction, several factors must be considered if best operation is to be obtained.

When well made, self-priming centrifugal pumps will produce high dry vacuums, but it is well never to require a suction lift of more than 20 feet on the basis of water equivalent. The effective height of suction lift is directly affected by the specific gravity of the solution. For instance, a pump capable of lifting water 20 feet by suction could lift a liquid of 1.82 specific gravity only about 11 feet.

Because of the ability of self-priming pumps to handle considerable quantities of gas, it is quite possible that air leaks in the suction line may not be detected as such, but the reduction in capacity may be erroneously ascribed to corrosion, wear, or even misapplication.

When pumps of the positive displacement type operate under any specified condition, they actually displace a definite volume of fluid whether this be gas or liquid. On the other hand, a self-priming centrifugal pump displaces gas by mixing it with liquid, and the resultant mixture has a specific gravity lower than that of the liquid alone. Thus, reduction in liquid-handling capacity in a self-priming centrifugal pump takes place both because of the actual volume occupied by the gas being handled and because of the loss in pressure differential resulting from the lowered specific gravity of the fluid within the pump.

If volatile liquids are to be handled, the problem is further complicated by the necessity for consideration of the vapor pressure of the liquid and the fact that gas may be liberated on the suction side of the pump as a result of the lowered pressure. This gas may be reabsorbed within the pump during its transition from the low-pressure condition on the suction side of the pump to the elevated pressure on the discharge side.



Courtesy, Chas. S. Lewis & Company

FIGURE 6. VERTICAL CENTRIFUGAL ACID PUMP

Another type of installation which is a combination of the two already mentioned involves the location of the pump at a level below the maximum liquid level but with the suction line elevated before it reaches the pump. A typical installation of this kind is found in tank car unloading. Here the suction line enters the top of the car, but the pump may be at ground level. After flow has once been started, the pump is assisted by siphoning action, but a self-priming centrifugal pump should be used, since pumping is usually noncontinuous and more or less gas must be handled.

Many interesting applications which are difficult to handle in any other way are possible with self-priming centrifugal pumps. For instance, liquids can be mixed and gases can be absorbed in liquids. Decantation may be accomplished with self-priming pumps. An interesting variation of the decantation application is in constant use in the oil refining industry where self-priming pumps are utilized to skim and reclaim waste oil from the surface of water reservoirs. Portable pumps may be used for the emptying of small containers such as drums or storage-battery-forming tanks.

PUMPING FROM VACUUM. The continuous removal of liquids from vacuum apparatus, such as evaporators, condensers, and filters, employs centrifugal pumps as auxiliaries to vacuum producing pumps.

The centrifugal pump is always located below the source of supply but may have to withdraw liquids under vacuums as high as 28 inches of mercury. In this service two fundamental principles must always be kept in mind: (1) In a centrifugal pump the flow of liquid is produced by pressure difference; and (2) the ability to develop vacuum is definitely limited, regardless of speed or size of pump.

Many gravity-feed types of centrifugal pumps will operate successfully under relatively high wet vacuums. Self-priming pumps will work under as high or higher wet vacuums and will also handle gases at the same time. Every centrifugal pump, whether of the gravity-feed or of the self-priming type, must be located far enough below the vacuum apparatus so that a sufficient liquid head can be developed on the pump suction to permit the pump to produce the pressure differential necessary to discharge the requisite amount of liquid.

This suction head varies with different makes and types of pumps, but a head of at least 1.13 feet should be provided for each inch of vacuum above 20 inches of mercury.

In a few isolated applications self-priming pumps have successfully removed liquid from vacuum apparatus and at the same time produced the vacuum under which the apparatus was working. This has been done with certain types of deep-submergence rotary filters and in some types of open filter bed applications.

PRESSURE FILTER FEED. The centrifugal type of pump is ideal for this service, and the selection of gravity-feed or self-priming pumps will depend entirely upon the location of the source of supply. Usually the gravity-feed type is used. Pressure filter service calls for a maximum flow at a minimum pressure when the filter is first started. This tapers off until, at the time of finishing the cake, the maximum pressure is desired and the flow is negligible. This exactly meets the pressure characteristics of the centrifugal pump; in addition, unlike the positive pressure pump, the maximum head which the centrifugal will develop is limited and there is no danger of bursting the filter cloths as a result of excess pressure.

The building of pumps for the process industries is a highly specialized field of endeavor. For best results this requires on the part of the pump manufacturer a rather thorough understanding of the chemical problems to be met, and on the part of the user, at least a fundamental knowledge of the limitations and characteristics of available pumping equipment.

RECEIVED March 30, 1938

PAPER GOES SOUTH

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AMERICAN independence of foreign sources of pulp and paper is being found in the swiftly developing industry which utilizes fast-growing southern pines. In this development implications in other directions are of equal, if not actually greater, consequence. The rapidity of this movement of paper and pulp manufacture to the pine regions of the South Atlantic and Gulf states has been phenomenal. New mills have increased the productive capacity of this region by 150 per cent in the brief span of two years, and plans awaiting a favorable time to be put into execution call for another substantial increment in plant capacity. The significance of this southward trek of paper has been frequently clouded by misstatements, and accounts deeply tinged with wishful thinking have received wide circulation.

The facts speak for themselves and show an industrial migration of a magnitude approaching that of the textile industry two decades ago, and expansion aimed at remov-

(*Top*) SLASH PINE PLANTATION, 11 YEARS OLD, SPACED 8 × 8 FEET, AND GIVING A TOTAL OF 680 TREES PER ACRE

The trees range from 4 to 8 inches in diameter, 4.5 feet above ground, and are 25 to 30 feet tall, representing the growth of approximately 2.5 cords per acre per year. This is particularly good growth and is to be expected only under optimum conditions, which include good soil and complete protection from fire. The cost of planting is $2.50 per acre, including the cost of seedlings and labor for plant but not supervision.

(*Center*) EXCELLENT GROWTH OF SLASH PINE REPRODUCTION WORKED UNDER A WELL-DISTRIBUTED STAND OF SEED TREES

In the slash pine region beef cattle production offers an additional supplement to timber growing.

(*Below*) AN EXCELLENT STAND OF LONGLEAF AFTER CUTTING AND PENNING

A cut of 7.4 cords per acre was made, leaving a residual of 4.7 cords for future harvest. This conservative cutting ensures the landowner, as well as the pulp mill, a permanent supply of timber in the future.

ing pulp and paper from a leading position among imports to one of far less prominence among the "also rans."

Involved in the situation is no new technology. In part a migration and in part a development, the building of this new section of the paper industry is based primarily on increasing demand for its product and on lower production costs in the South.

As an important present phase of the development, imports of pulp are being replaced by less significant imports of salt cake, raw material of the kraft process. Presumably, this phase will pass as realignment in the chemical industry meets the rising need for this raw material. Meanwhile, salt cake is used by Germany to pay for German imports of American goods.

Despite emphasis on the success of the sulfite process for treating southern pine, the new industry is utilizing the kraft, or sulfate, pulping process. This consists of an alkaline digestion, as distinct from the acid treatment in the sulfite process, of wood chips with a solution of a mixture of sodium hydroxide and sulfide. It is characterized by the strength of the pulp made by it and by the fact that losses of sodium in the process are made up by the addition of cheap sodium sulfate, salt cake. Its principal advantages are cheapness, recovery of most of the active constituents of the digester liquor for re-use, and the ease with which it can be applied to pine wood. Most kraft pulp is used for purposes in which color is of minor consequence. Lately modifications of the digestion process and improved methods of bleaching by steps have enabled kraft mills to make pulps equaling the sulfite product in whiteness. Although bleaching costs are high, the low original cost of the pulp itself allows bleached sulfate to compete in the market.

Kraft pulp has been made from southern pine since 1911, when two mills, one at Orange, Texas, and the other at Roanoke Rapids, N. C., were put into production. During the twenty years following, eleven other mills were added to make a total of thirteen kraft mills from Virginia to Texas. By 1931 the total output of these mills was approximately 2500 tons of pulp per day in the form of wrapping paper and liner board for corrugated box manufacture. Thus at the end of what may be called the "predepression era" a substantial pulp industry was already at work in the South.

Herty's Work

At about this point, work was undertaken by the late Charles H. Herty to show that sulfite pulp and groundwood, required for newsprint paper, can be successfully made from pine wood. Test runs completely proved this point and showed that young pines require at most only trifling modifications of the standard processes to yield newsprint of a quality equal to that imported or made from other woods.

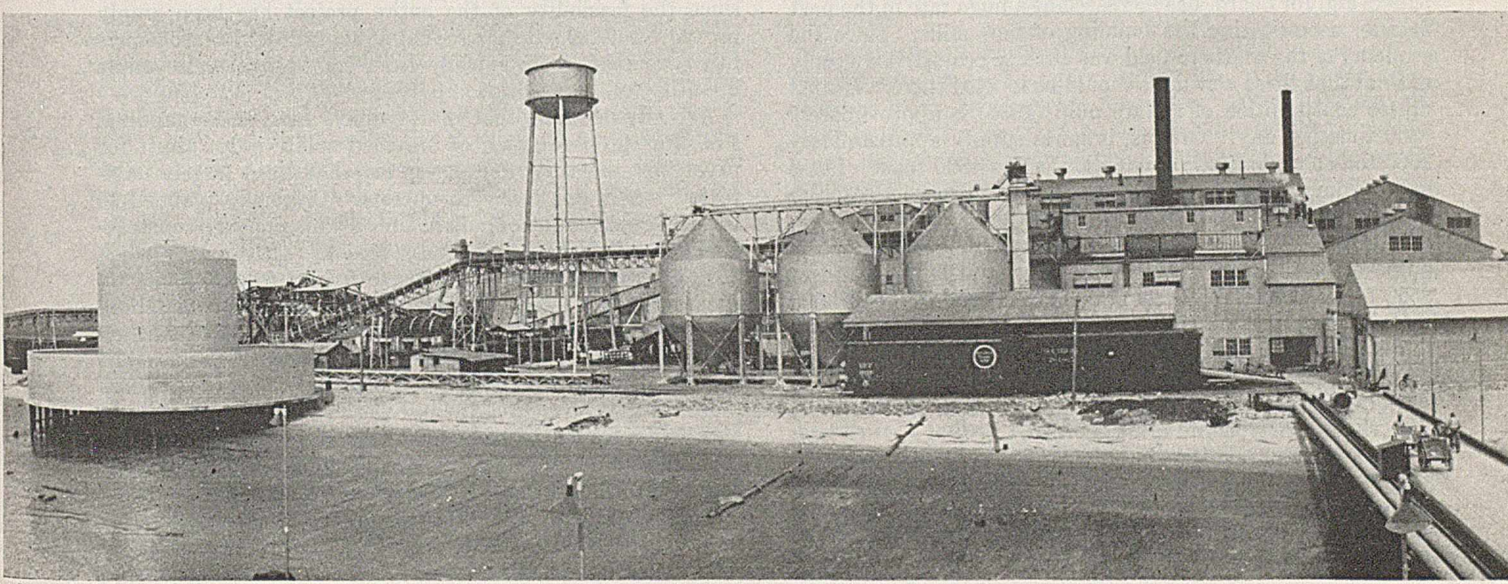
The significance of these findings lies in our relatively large imports of sulfite pulp. The fundamental fact on which they are based is that the sapwood of pine is but little more resinous than spruce, contrary to generally accepted belief. Commercial oleoresin (gum turpentine) is formed in pine as a result of wounding the tree. In older trees heartwood builds up a resin content. The former is a pathological process, the latter a physiological one.

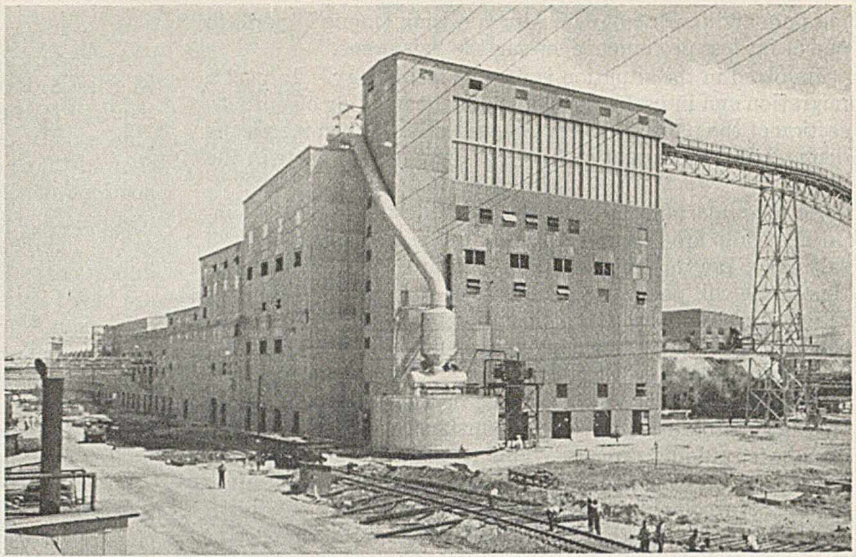
These findings have received wide publicity and as a result a misconception of what is commonly known as the Herty process has gained wide currency. Actually there is no Herty process (nor did Herty claim any). Rather there is a Herty idea that southern pine is a useful pulpwood which can produce pulp and purified cellulose of a quality and at a price attractive to papermakers and to the rayon industry. The process used and its products are familiar to the pulp industry. Only the raw material is different.

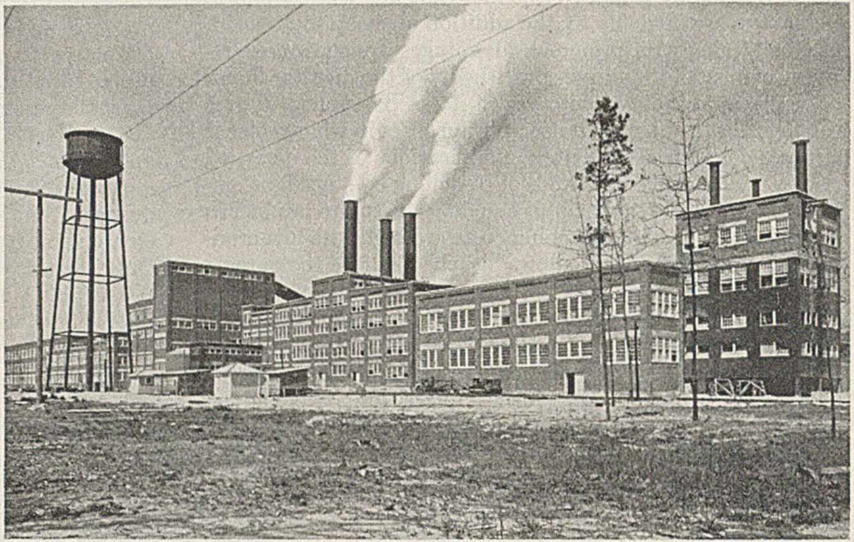
The Herty idea as set forth above is incomplete. Primarily it is based on three important concepts: America must be made independent of imports; the South needs industries; and pine is a crop growing under practically ideal circumstances for the economical production of cellulose. Only the third of these points needs special comment here.

The pine lands along our southeastern seaboards have relatively little value for other crops, yet on them pine grows luxuriantly. Several species attain full growth from seed in twenty years or less. Natural reseeding generously provides for reforestation if only two or three adult trees are left to the acre. As many as forty thousand seedlings may spring up on each acre of cut-over land. Such a number cannot grow to maturity, and hence during the first few years the new forest must be thinned to about four hundred trees per acre to provide a satisfactory stand for turpentining and lumbering. A large proportion of these thinnings can be

THE BRUNSWICK PULP AND PAPER COMPANY MAKES BLEACHED SULFATE PULP FROM PINE AT BRUNSWICK, GA.







(*Above*) Kraft Paper Mill of the West Virginia Pulp and Paper Company, Charlestown, S. C.

(*Below*) Kraft Mill of the Crossett Paper Mills, Crossett, Ark.

taken off when they have attained a size usable as pulpwood. Under favorable conditions of planting, seedlings may in ten years grow large enough to be profitably worked for turpentine, an operation that can be continued for eight to ten years. Subsequently, the trees can be cut as timber. Thus, by combining papermaking with present utilization of pine forests for timber and naval stores, a virtual third crop could be harvested during the growing cycle of the pine.

Such a forest utilization plan is difficult to put into effect, and pulpmakers prefer to use all the forest as they go rather than to complicate their operations by timing them with others. Rather, they prefer to harvest a single pulpwood crop on a cycle established to give a maximum yield of their raw material from the land.

This desire to use all the yield of the forests for a single purpose is in part responsible for preference for the kraft process. No selection of logs is necessary unless bleached pulp is to be produced. For bleaching, logs which have turpentine blazes or are otherwise injured, and are hence highly resinous, are discarded. The sulfite process, on the other hand, requires careful sorting to ensure that only logs of young trees free from injury are used.

Economic considerations, too, have fostered the growth of kraft production. Demand for kraft, both for wrapping papers and for board, has increased at a huge rate in the past decade, necessitating the building of new mills. Since the economy of the southern field was already proved, it was only natural that these new mills should be located there. United States consumption of sulfate pulp (1936) is approximately 6800 tons per day. Of this, imports supply approximately 2000 tons and domestic production, some 4800 tons. These figures compare with a total of less than 3000 tons per day consumed in 1927.

The rise of demand for bleached and unbleached sulfite pulp has been somewhat slower. Consumption in 1936 was 8500 tons per day, made up of 5000 tons produced and 3500 tons imported. These figures compare with 7200 tons per day consumed in 1927, of which 4400 tons were produced and 2800 tons imported. This more gradual increase in sulfite consumption has not stimulated the building of new mills with the urgency behind kraft demand.

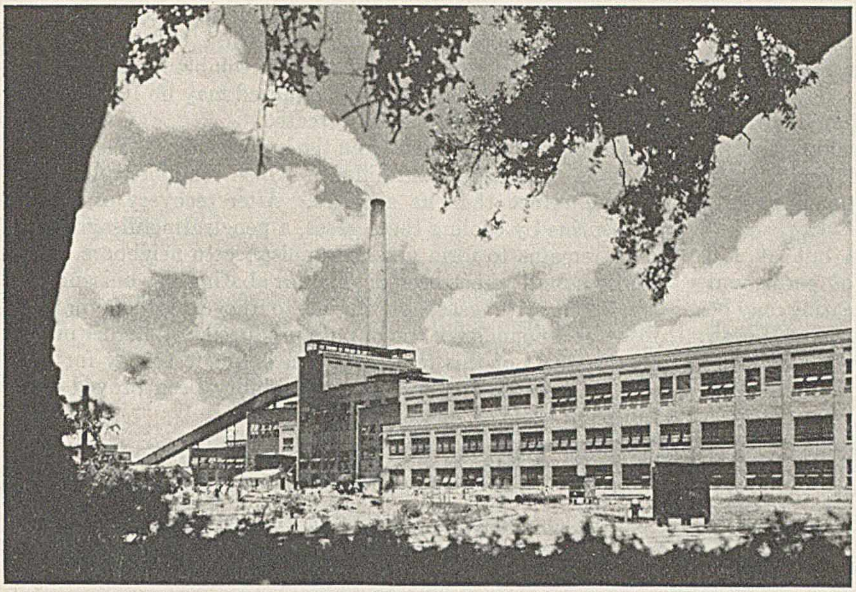
The answer of investors in pulp production to this situation is obvious. A market which more than doubles in a decade and which shows evidence of continuing expansion is more attractive than one whose demand increased by one-sixth during the same period.

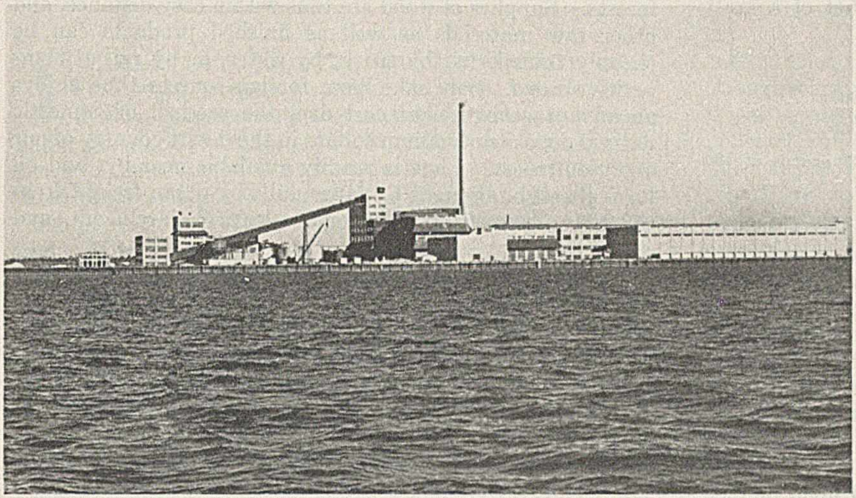
On the other hand, imports of 3500 tons per day offer a field for exploitation by many mills producing sulfite pulp at low cost. Obviously there is an opportunity here, especially since the feasibility of the entire project has been amply proved. Sulfite pulp for rayon, newsprint, and book papers has been made economically from southern pine in ample quantity for demonstration purposes.

Actually one mill, that of Rayonier, Inc., at Fernandina, Fla., for the production of bleached sulfite pulp (albeit for rayon manufacture, not newsprint) has been largely completed but is not ready to operate. Originally planned to begin the production of pulp in June of this year, the construction of this mill was well advanced by early spring when falling demand caused by reduced exports to Japan and by the nationwide slump in business postponed its completion, presumably until fall. This sulfite mill is based in part on the Herty researches, confirmed and expanded by the mill's owners, who are experienced pulpmakers.

A mill to make newsprint in East Texas has been planned and was expected to be under construction late in 1937 or early in 1938. Difficulties in financing have faced this project and at this writing it is held up on that account.

This in broad outline was the situation of the southern paper industry in the spring of 1938. To understand why these developments have been made and to learn something of what





(*Above*) THE UNION BAG & PAPER COMPANY, SAVANNAH, GA., WAS THE FIRST OF THE NEWER MILLS TO CONVERT PINE INTO KRAFT PAPER BAGS

(*Below*) KRAFT MILL OF THE ST. JOE PAPER COMPANY, PORT ST. JOE, FLA.

●

may be expected in the future, it is necessary to consider the fundamental factors in greater detail.

Factors in Future Development

First in importance is the supply of wood available and its essential qualities. Careful estimates place the area of forest extending from Virginia down the Atlantic and across the Gulf Coast into East Texas between 125 and 150 million acres. On approximately three-fourths of this land pine grows at a rate between 0.33 and 1.0 cord per acre per year. The average is conservatively half a cord per acre per year. Forest control can easily double this. Fires, sometimes set to improve grazing for cattle, now destroy large sections of forest, particularly seedlings, and efficient patrol of woodland together with fencing can minimize this huge loss. The remainder of this forest area grows gum and other woods, most of which are available for pulp making but some of which are more valuable as lumber.

Aside from the 700 or so million cords of standing timber on this land, the replacement growth will continuously yield more than 20 million cords of lumber per year and 40 million cords for pulp making. This amount of pulpwood will yield approximately 25 million tons of pulp annually, or more than treble the 1936 United States consumption of all types of pulp. If as much as half of the standing timber is used as pulpwood, it would make available some 200 million additional tons of pulp, an amount apparently ample to make up any deficiency during the initial period of expansion of the industry until such a time as reforestation programs can be put into effect throughout the area.

The character of the wood of the slash, loblolly, and longleaf pines, the predominant fast-growing species, has been widely misunderstood. Actually the principal constituents of the sapwood of these species, in addition to cellulose and lignin, are free fatty acids, glycerides of fatty acids, and unsaponifiable matter consisting of waxes and sterols. The resin acid content of sapwood is negligible. In contrast, resin acids and turpentine form in the hard heartwood cores of older trees. The principal difference from a pulping standpoint between the fast-growing southern pines and spruce is in the sharper contrast between the thin-walled cells of the springwood and the thick-walled cells of the summerwood; the latter are produced in larger proportion in the mild southern climate. This fact requires a somewhat different cooking in the sulfite digesters, but no difficulty is encountered in making the necessary adjustments. Where the kraft process is practiced, only minor differences in treatment are required.

Kraft Process

The kraft process, in contrast to the sulfite process, yields the digesting liquor in a form which can, and for reasons of economy must, be recovered for re-use. After digestion, the alkaline black liquor contains the lignins and other noncellulose constituents of the wood in a form which can be burned after suitable concentration. The organic matter in the black liquor amounts to approximately half of the original dry weight of the wood treated. After concentration in multiple-effect evaporators to about 56 per cent total solids, it is burned under boilers for the dual purpose of supplying steam and recovering the sodium compounds required in the cooking of subsequent batches. The burning of this concentrated black liquor produces from 8000 to 10,000 pounds of steam per ton of pulp and at the same time yields its sodium compounds in a molten stream for re-solution and re-use in the process. Losses are made up by the addition of salt cake to the black liquor before it is burned so that the added sodium sulfate appears in the smelt as sodium sulfide.

The smelt from the recovery furnace is dissolved in water (forming "green liquor"), clarified by sedimentation, and causticized in a continuous causticizer with lime. This yields "white liquor" which is returned to the digesters. The calcium carbonate from the causticizers is reburned to quicklime for re-use.

The white liquor, containing a mixture of sodium hydroxide and sulfide, is run into the digesters with fresh chips, and an amount of untreated "black liquor" from a previous cook is added to bring the whole to the desired proportion of caustic to wood.

Ordinarily the digesting process is carried out at 110 pounds gage pressure with frequent release of permanent gases during the heating period. The time of heating may be half an hour, and the cook may be held at temperature for an hour or longer, depending on the results desired. Pulp for subsequent bleaching is cooked longer than that intended for direct use.

From the digester, the cook is blown by its own pressure to diffusers, large tanks with internal screen bottoms, from which the black liquor, containing about 19 per cent total solids, is drawn off and the pulp given a preliminary wash. Subsequently the pulp is screened and refined, size is added, and it is sheeted on the Fourdrinier machine.

Approximate requirements per ton of product of a kraft mill using southern pine are:

Wood, cords	1.66
Salt cake, pounds	300
Process steam,[a] pounds	16,000
Power, kw-hr.	1,000

[a] Process steam requirements are approximately 3000 pounds at 130 pounds gage and 13,000 pounds at 40 pounds gage.

Power is ordinarily furnished by generating superheated steam at high pressure in boilers burning oil or coal and waste wood and bark, and passing this through bleeder turbines from which process steam is drawn at appropriate pressures. This power is supplemented by either purchased or separately generated power to fulfill the requirements. Approximately 3000 pounds of steam per ton of pulp is generated by burning bark and waste wood. Another 9000 pounds per ton of pulp come from the black liquor recovery furnaces. This leaves 4000 pounds per ton of pulp to be generated by purchased fuel for process purposes and an additional 4000 pounds needed for power generation.

On the whole, the operation is planned for maximum economy and is as nearly as may be self-sustained. Salt cake, lime, wood, and a minimum amount of fuel are purchased, the first two only to make up process losses. Reductions in the salt cake requirement of as much as two-thirds are already anticipated through the application of more efficient recovery of alkali from the flue gases of the black liquor recovery furnaces. Chemical by-products recovered from the operation will affect only its fuel requirement and this probably only to a negligible extent.

Both pine and spruce yield by-products from the cooking operation of some value. These consist of a low-grade turpentine, fatty oils, and soaps. Just how important they may become in the economics of the industry is not yet clear, since few southern mills now recover by-products, but the expectation is that they may add as much as two or three dollars per ton of kraft pulp to the income of the producers.

If bleached pulp is to be made, and this can have the whiteness of the sulfite pulp if desired, the cook is prolonged by as much as several hours to complete the solution of lignins, and the pulp is subjected to bleaching by stages. First, the washed pulp is treated with a relatively heavy dosage (4 per cent) of chlorine whose primary purpose is to make residual lignin soluble. This step is followed by a thorough washing and several subsequent treatments with smaller dosages (2 per cent) of chlorine as bleaching powder with washing between. As many as five such successive treatments with washing between may be given, depending upon the whiteness desired in the finished pulp. Chlorine is used first to convert noncellulose constituents of the pulp into soluble form and later as a true bleach. The amount required may be 10 to 12 per cent of the weight of the pulp treated.

The only present waste from the kraft process is the blowoff gases from digesters and diffusers which are more important as a nuisance than as a waste. After recovery of sulfate turpentine by cooling these gases, a penetrating disagreeable odor remains to form a serious nuisance to neighbors. Recently a method has been devised for abating this nuisance by treatment with gaseous chlorine to the extent of approximately 25 pounds per ton of pulp produced. Whether or not the products of this treatment can be made to pay for it is not yet known, nor has its practicability been proved on a full-plant scale.

Economics

From an economic standpoint, the southeastern pine belt offers many real advantages to the pulp and paper industries. Mills can be conveniently located on tidewater close to pine forests. Supplies of wood are thus within easy distance, and other raw materials as well as finished products can be cheaply transported by truck, by water, or by rail at competitive rates. Salt cake from foreign sources thus enjoys an advantage in freight cost over the product of domestic natural deposits of sodium sulfate in the desert country of our own Southwest. Lime is readily available near by, and oil for fuel can be brought to paper mills by ocean freight from the East Texas fields. Labor is plentiful, intelligent, and cheap.

The question of domestic salt cake is one on which considerable thought is being spent. With present American demands for hydrochloric acid amply met by processes which yield no salt cake by-product, other possibilities are being explored. Freight costs are too high to permit natural sodium sulfate to compete seriously with the imported by-product at present. There is little hope, for the same reason, of increasing production of domestic by-product salt cake at plants remote from paper mills. Even if the western natural mineral or a domestic by-product should be able to compete at present prices, it is probable that the delivered price of the imported product might be adjusted to meet the change, in part at least.

Recent attention has been directed toward the possibility of producing salt cake as a by-product of acidulating phosphate rock. This proposal is based on the treatment of salt with sulfuric acid and the use of the hydrochloric acid produced to convert phosphate rock to a calcium hydrogen chlorophosphate. Chlorophosphate thus made contains a higher percentage of available P_2O_5 than acid phosphate made by the direct treatment of rock with sulfuric acid, and the salt cake by-product is readily marketable to the kraft mills. Although this possibility is still in the early experimental stages, it seems admirably adapted to the conditions found in the Florida phosphate areas to which salt from Louisiana and sulfur from Texas can be brought cheaply by water.

The probable expansion of demand for chlorine for bleaching as salt cake requirements grow suggests the treatment of salt with sulfuric acid to yield hydrochloric acid and oxidizing this to yield the needed chlorine. This method, since it produces two necessary raw materials for the paper industry, also merits consideration.

Forecasts of future expansion of pulp and paper manufacture in this territory have been justifiably optimistic. One of these, made by D. G. Moon on the basis of a careful analysis, will suffice to round out this picture. From a consideration of all the factors involved, he reaches the conclusion that southern production will quadruple within a decade:

	Present (1938) Southern Capacity	Expected Additional Southern Capacity
	Tons/day	*Tons/day*
Writing and book papers	450	3,550
Wrapping papers	2,000	2,500
Newsprint	...	2,000
Board	3,000	3,500
Tissue	50	700
Miscellaneous	250	2,000
	5,750	14,250

Moon further forecasts that the production of this additional 14,250 tons per day will require the investment of approximately 500 million dollars of capital—60 per cent in new mills, 16 per cent in forests, 8 per cent in converting plants, and 16 per cent in housing for employees. The entire southern branch of the industry thus forecast will consume annually an estimated total of 800 thousand tons of salt cake, 300 thousand tons of chlorine, and fuel equivalent to 3 million tons of coal.

Obviously the realization of any substantial part of this expectation will result in an important industry.

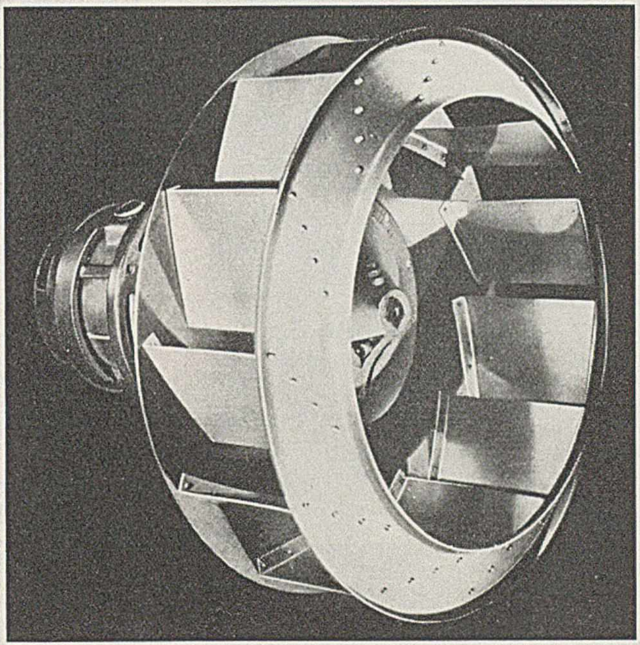
RECEIVED August 8, 1938.

DRYING MACHINERY

FRED KERSHAW

Proctor & Schwartz, Inc., Philadelphia, Pa.

THE need for good drying equipment today is great. Chemicals, ceramics, casein, tobacco, textiles, soap, leather, pharmaceuticals, plastics, rayon, gun powder, and a multitude of similar products must be dried one or more times in the course of their manufacture; and they must be dried properly and economically. The drying operation for these products is a more vital operation today than ever before. With the extended use of brand-name products, standards of quality in all these industries have been raised to a point which makes it imperative that the drying system be intelligently and scientifically engineered; otherwise the quality of the product may easily be brought below that of its competitors, with a resulting loss of sales. Cigarets, for instance, are vastly better today than those made 15 or 20 years ago, and consequently they have a wider consumer acceptance. Modern drying systems, scientifically engineered, have played an important part in this improvement, keeping step with the exacting requirements of the cigaret manufacturers in their constant drive for better quality and economy. When tobacco is being dried, a gum or sap comes to the surface of the leaf under the action of the heat. If this gum condenses on the leaf and is not completely evaporated, the tobacco will have a bitter and unpleasant taste. Modern drying machines are now designed to aerate and separate the leaves so completely while they are being dried that none of this bitter sap remains to spoil the flavor.



ONE TYPE OF FAN WHICH IS USED IN MANY DRYERS IS MOUNTED DIRECTLY ON THE MOTOR SHAFT

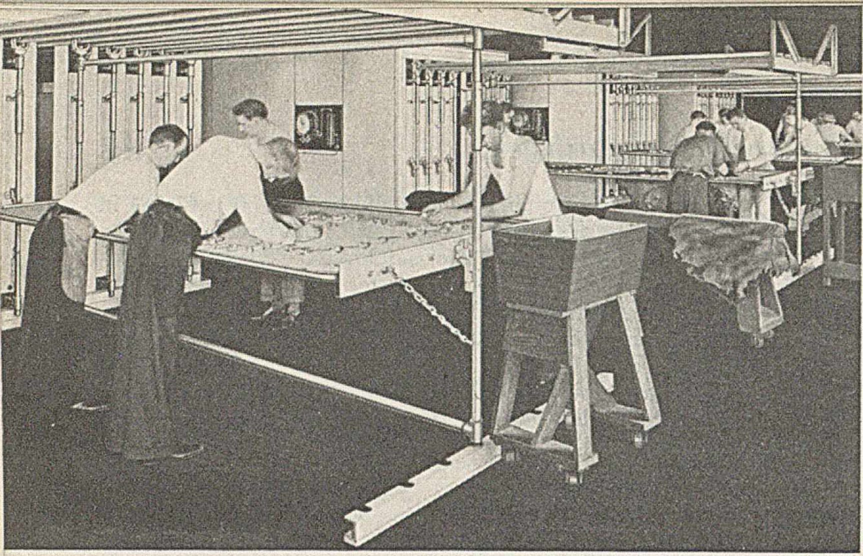
In the past 15 years the world production of rayon has increased 1500 per cent. This would not have been possible if the manufacturers of rayon had not done such a splendid job of improving their product. The wet strength of rayon, for instance, is 80 per cent greater today than it was 15 years ago. Its elasticity, dye absorption, uniformity of denier, and other qualities necessary for its manufacture into finished products have likewise been greatly improved. The refinement of the drying operation has played an important part in this improvement of quality. Rayon dryers today are scientifically designed for the particular plant in which they are to operate. The velocity, direction, and distribution of air flow necessary to give the best results have been scientifically determined for each type of rayon. Complete, accurately controlled air-conditioning equipment is made an integral part of the dryer. The rayon in its travel through the dryer passes through various zones; each zone is of a predetermined length, and in each of them definite dry- and wet-bulb temperatures and air flow are maintained. All of these factors in drying rayon have a decided effect on its shrinkage, strength, elasticity, uniformity of denier, dye absorption, and other qualities.

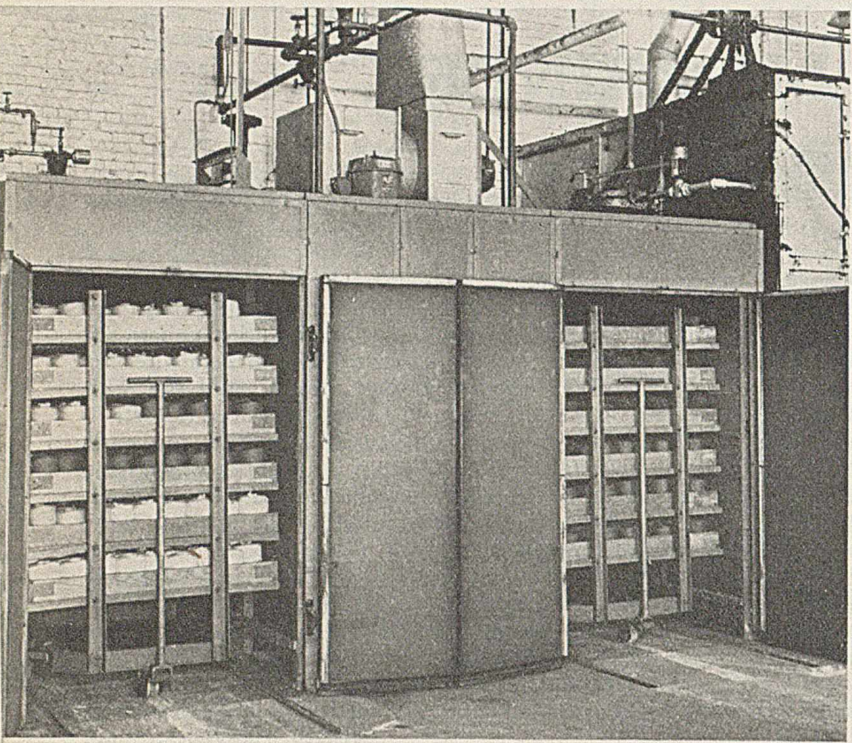
Twenty-five years ago, when competition was not so keen as it is today, when the standards of quality of commercial articles were not so rigid or so high as at present, when products were much simpler in their construction and make-up, and when labor costs were not such vital factors, the drying operation was much simpler and was not considered of sufficient importance to warrant the extensive scientific study that is given to these problems today by the leading designers and builders of drying machinery. Consequently, many companies at that time either used homemade dryers or bought standardized ready-made dryers, and obtained results that today would be ruinous in the face of existing standards of quality and costs.

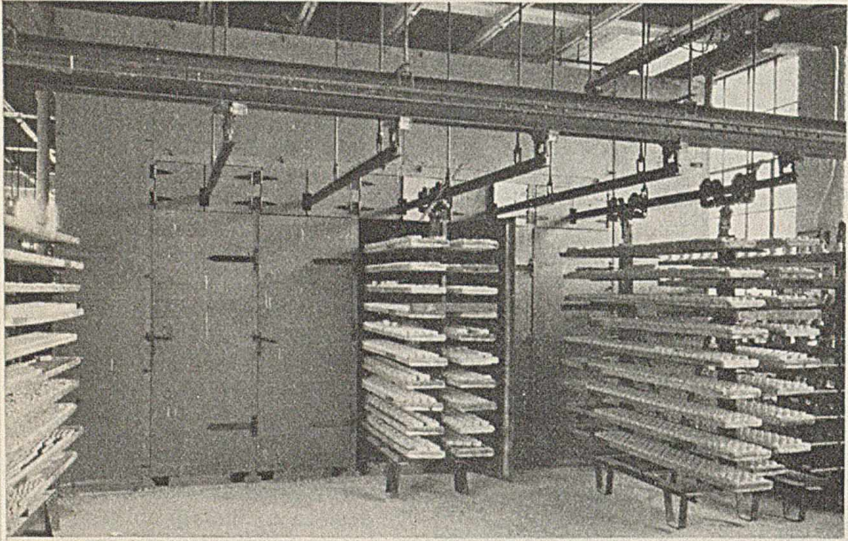
For years a well-known company which manufactures white lead used a homemade rack dryer on which they dried their product in pans. It took them 7 days to dry it. Because of this long drying time there was considerable discoloration from one cause or another. To keep in step with their competition, they wanted to improve their product. They recently called in a well-known organization of drying experts and put the problem up to them. As a result they are now producing a much whiter and cleaner product, they dry their lead in an hour and a half instead of 7 days, they are saving 60 per cent of the floor space formerly occupied by their homemade dryer, and the handling of their product is completely automatic from storage tank to finished-product storage bin. Their dust problem has also been greatly minimized.

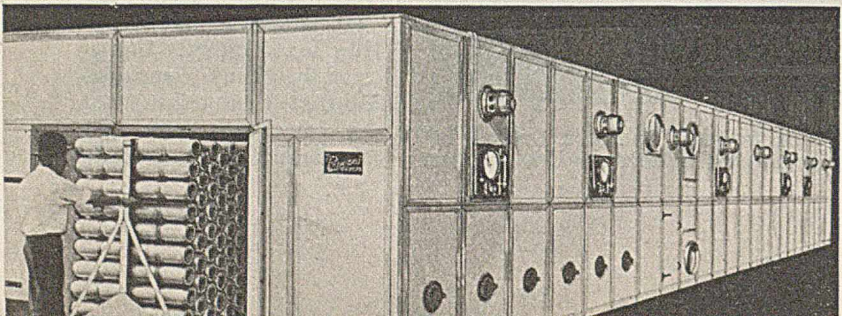
Diversity of Drying Problems

Seldom are any two drying problems exactly alike. A slight difference in processing a material will sometimes make it either harder or easier to dry. Ordinary dyed rayon skeins without any oil treatment will dry in about 1 hour, whereas dyed rayon skeins that have been processed with oils, waxes, or gums will take from 2 to 4 hours to dry, depending on the kind and amount of oil used. A tallow-base toilet soap dries much faster and easier than an olive oil soap. It takes twice as long to dry Paris green in one plant as in another because of a slight difference in the method of processing, although the drying systems are exactly alike. Veneer from a gum tree grown in the lowlands of Mississippi takes 50 per cent longer to dry than veneer from the same kind of a gum tree grown on land farther north. The textile fibers and fabrics dyed with dark colors take longer to dry than those dyed with lighter shades. Many bitter disappointments and failures have been recorded when someone without sufficient experience and knowledge of drying has assumed that, because a material in one plant could be dried in a certain time,









(*Reading from top to bottom*)

BATCH-TYPE DRYER FOR DRYING AND STRETCHING SKINS

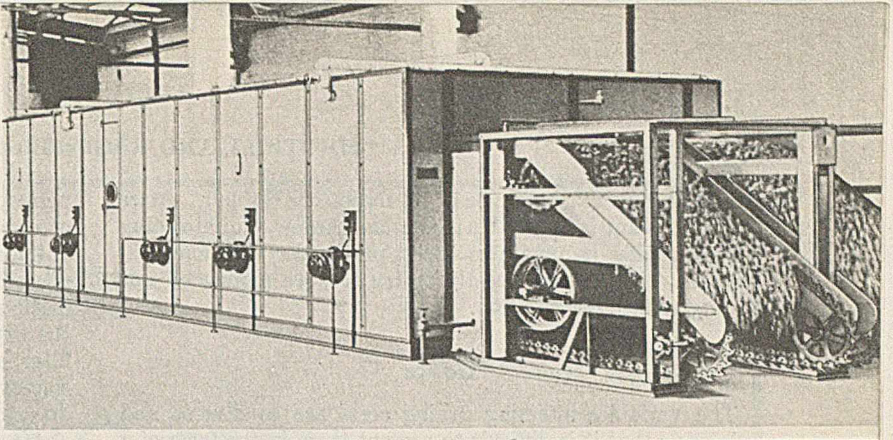
BATCH-TYPE DRYER FOR DRYING PACKAGES OF CLOSELY WOUND COTTON AFTER DYEING

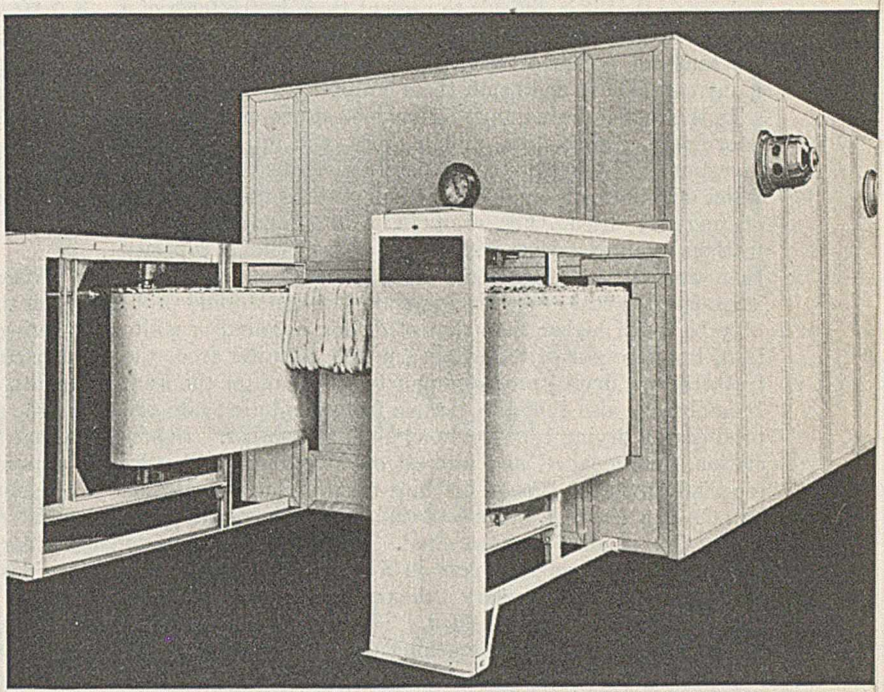
SEMIAUTOMATIC DRYER FOR DRYING SMALL PORCELAIN OBJECTS PRIOR TO FIRING

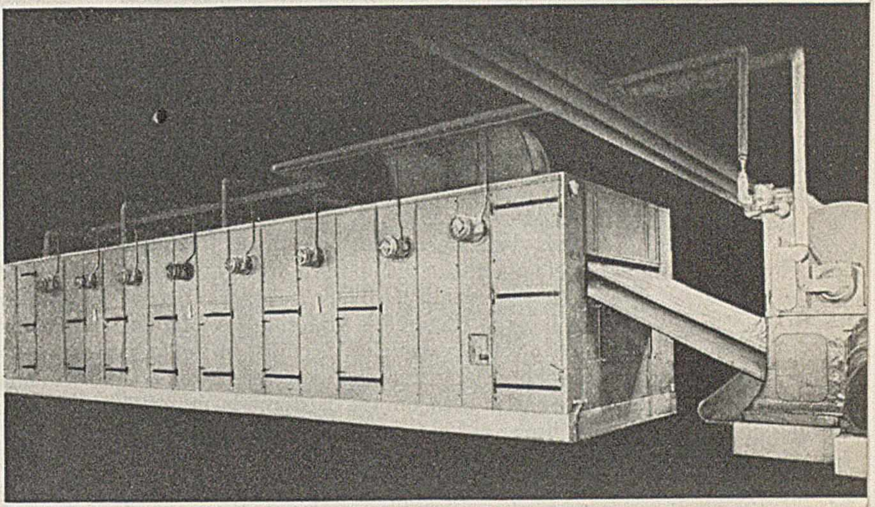
AFTER RAYON IS SPUN, IT IS DESULFURED, WASHED, AND THEN DRIED IN THE SEMIAUTOMATIC MODERN RAYON DRYER a similar material in another plant could be dried in the same time. Consequently, in order to obtain the most efficient machine for a particular plant, it is necessary to engineer the job from beginning to end. A careful study must be made covering the peculiarities of the material to be dried with relation to its sensitivity to heat, the rate at which it gives up moisture, the effect of drying under varying conditions on the color, feel, taste, and odor of the product, the amount of moisture to be removed, the capacity of dried material required, the most economical method of handling the material before and after drying in conjunction with the method of handling through the dryer, the character of heat and power supply, the value of material per pound, the permissible amount of labor at the existing cost, and a great many other details which must be analyzed before the type of machine which will be most efficient for that particular job can be decided.

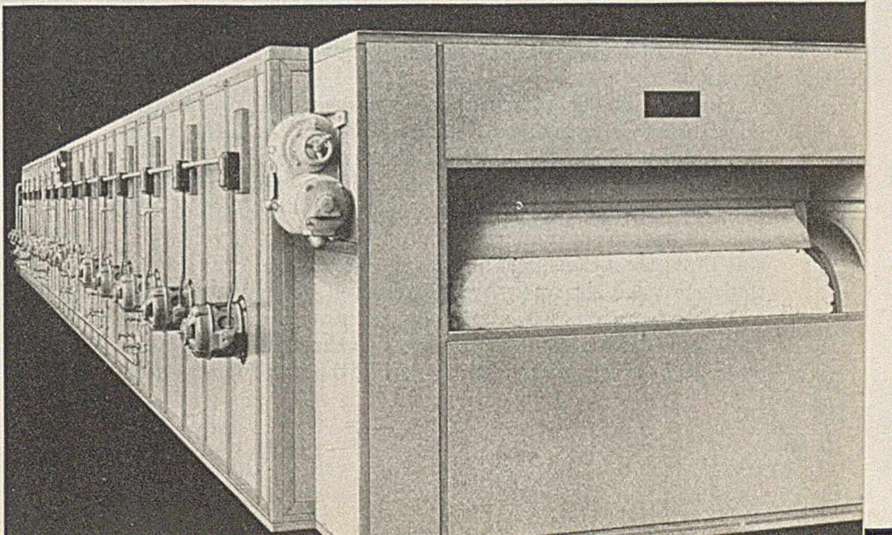
Drying machines are built of steel, stainless steel, aluminum, brass, copper, wood, brick, cement, and concrete. The type of material used for the construction can be determined only after a careful study of the conditions under which the machine is to be operated with regard to the effect of acids, moisture, etc., on the metals used and the contamination that might result from the effects of corrosion.

Drying machines must be well insulated to prevent loss of heat; otherwise steam consumption will be high and drying costs correspondingly high. The insulation utilized depends upon the temperature inside the dryer, the cost of heat used in the dryer, and the return on the investment represented by a saving in heat. Some machines are built without insulation, others are built with various forms of air-cell asbestos, others with rock wool or glass wool, some with cork, some with aluminum foil, and others with magnesium covering. A complete study of the factors surrounding the particular installation under consideration is necessary to deter-









(Reading from top to bottom)

Stick and Apron Tobacco Dryer for Drying and Conditioning Bundles of Tobacco Leaves before They Are Packed in Hogsheads

Hogsheads of tobacco are aged for 2 years.

Drying Rayon in Skeins in a Modern Automatic Dryer, with Controlled Temperature and Humidity

Automatic Type of Dryer Which Takes Hot Liquid Soap from the Kettle, Solidifies, Chips, and Dries It in 15 Minutes, Ready for Packaging

Automatic Type of Dryer for Handling Bleached Cellulose mine the most efficient type of insulation for the job. After a certain point is reached in insulation, the law of diminishing returns makes it unwise to spend money for additional insulation; likewise it is costly to try to save money by not having sufficient insulation.

Costs

The variables affecting drying costs are so diverse and numerous that it is difficult to present them in the form of a table. In general, the estimated cost is approximately 0.1 to 0.3 cent per pound of water evaporated, though there are many cases above and below these limits.

In the cost of drying must be included steam, power, labor, floor space, depreciation, maintenance, and interest on the investment. The expression of costs in terms of pounds of water evaporated is less variable than on the basis of pounds of material dried. For example, a thousand pounds of feathers requires a dryer with a much larger holding capacity than would be required for a similar weight of white lead. Therefore the cost of drying a pound of feathers would probably be much higher than that of drying a pound of white lead, but the cost of removing a pound of water from the feathers by a drying process might be less than for the lead. It is obvious also that the various factors entering into the total cost of drying vary from one plant to another. Depreciation, maintenance, and interest on investment will vary especially with the type of machine required for a particular job. As an example of an extreme case, clay pots used in production of glass may be cited. About 2 weeks are required to dry these clay pots in a mechanical dryer, and about 6 months are necessary if the pots are allowed to dry on the floor where they are molded. The necessity of carefully drying such pots to avoid cracking them contributes to the high drying costs. Another example is glue, which must be dried at low temperatures; the drying cost is therefore higher than is the case with the average material which may be dried in the neighborhood of 200° F.

Research and Preliminary Engineering

The building of modern and scientific drying machines is a complex engineering business, and a modern drying machinery company must of necessity maintain a large research department. In this department tests are made to determine the maximum temperature the material will stand without adversely affecting the quality. The exact percentage of moisture contained by the customer's material must be determined, and tests at various air velocities must be made to find the lowest possible drying time. This research department usually makes tests also on the customer's material under various conditions of air flow—first, through the material, both up and down, then across the material from right to left, from left to right, and, in some cases, over a combination of directions. In the case of loose materials the research department also makes various tests to determine the best thickness of loading the wet material to give the most efficient drying.

The research department then turns over to the preliminary engineering department a detailed report of the ideal conditions under which the material should be dried. The preliminary engineering department studies the customer's floor layout, his labor conditions, and the preceding and subsequent operations, and determines what type of dryer would suit these conditions best and would, at the same time, meet the conditions set forth by the research department under which the customer's material can be most efficiently dried.

In some cases a batch dryer, in which the material is placed on trays or trucks manually and left in the dryer for a stated period, is the type which best meets all conditions. In other cases a semiautomatic dryer, in which trucks of material are automatically progressed through a drying compartment, is needed. In the vast majority of cases, a completely automatic machine, in which the material is automatically fed to the dryer from some preceding operation, such as a rotary filter, automatic press, etc., and is conveyed on some form of conveyor through the drying compartment, is the type of dryer that gives the greatest economy and best quality.

After the preliminary engineering department has made a study of all the conditions, a preliminary plan is made showing the general type of dryer and its location in the customer's plant, with respect to other equipment preceding and following the drying operation. This preliminary layout is then discussed with the customer's engineers and production men, and any changes which seem desirable are then made.

Design of the Machine

After the preliminary plans have been approved, the data from the research department and from the preliminary engineering department are given to the production engineering department, and a machine is designed to fit the requirements exactly. At this point a long and varied experience in the design of drying machinery is essential. In order that a machine may be designed which will fill the customer's requirements exactly and at the same time be efficient and economical, it is necessary that the designing engineer be able to interpret commercially the findings of the research and preliminary engineers. A test in the laboratory is more or less an ideal situation which is seldom reached in practice. It is vitally important, therefore, that the engineer designing the machine shall have had sufficient experience to be able to transform the findings of these preliminary studies into a machine which will give the customer the capacity, the quality of drying, and the economy of operation and maintenance he wants. He must determine the best type of fans to use for the purpose, the number and size of fans, and their most efficient location and speed.

He must also determine the best type of heating medium, keeping in mind the source of heat supply. He must properly design all the mechanical parts of the machine so that there will be no undue wear or friction, and the conveying means must be such that the material being dried will not be damaged in its travel through the machine. He must also see that the heat generated by the heating medium is used with the greatest efficiency, and to do so he must determine the proper amount of air to exhaust from the dryer, the corresponding amount of intake fresh air, and the amount to be recirculated. He must design the framework of the machine in such a way that there will be no vibration and must make proper allowances for expansion and contraction; otherwise mechanical parts will be thrown out of line and wear unduly. Literally hundreds of other points too numerous to mention must be borne in mind when designing a drying machine if an efficient machine is to be produced, and the answers to all of these questions can be known only to those who have had years of experience in this kind of work.

Received April 21, 1938.

Correction. In our June issue some statistics were given in an editorial entitled "A Witness for the Defense." Through an oversight, the price quoted for sulfanilamide tablets failed to indicate the fact that this was for 1000 tablets. Correspondence indicates the desirability of giving this further information.

SYMPOSIUM ON DRYING AND AIR CONDITIONING[1]

Drying Commercial Solids

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University of Louisville, Louisville, Ky.

The air drying of commercial Prussian blue is believed to be typical of gelatinous solids that adhere firmly to the drying trays. The drying rate curves for this solid do not exhibit the normal constant- and falling-rate periods. A rate approaching zero is experienced during the last stage of the constant-rate period and just preceding the falling-rate period. This would lead to the belief that the capillary forces in the solid were controlling during that interval.

Drying in vacuum at lower temperatures and lower vacuum produced drying rate curves in which the zero-rate period was not so pronounced as in air drying. At higher temperatures and higher vacuum the zero rate period did not exist.

This type of solid should be dried on screens or in a rotary dryer. The drying curves show for the first time the relation between air and vacuum drying of solids.

MOST theoretical work on the mechanism of drying (*1*, *4*, *5*, *6*) has been confined to ideal solids. The drying of industrial materials is not necessarily identical with that of the perfect solids, and some investigators are broadening the accepted drying theory to include other than ideal solids. In this presentation a brief summary of semicommercial experiments performed over a period of years to test rigorously the accepted principles with a solid unlike any theoretical solid are discussed. A commercial paint pigment, Prussian blue, was dried under various conditions of humidity, temperature, and vacuum.

Method of Moisture Transfer

In drying a very wet solid, the first period corresponds to the evaporation of a saturated solution, and the rate of drying is largely affected by the solubility characteristics of the particular solid. Liquid is supplied both by that mechanically present on the surface and by diffusion from within the cake during this constant-rate period. Moisture transfer to the surface occurs by capillary action and diffusion of vapor through the pores of the material. The size of the capillaries, drying temperatures, and external pressure largely determine whether moisture transfer to the surface will be primarily by liquid or vapor movement or a combination of both.

Before drying commences, there are a large number of small voids on the surface that contain moisture. As these voids become exhausted after the start of the drying, a transfer of moisture to the surface is begun. As long as the supply of moisture and vapor to the surface is constant, the rate of drying remains constant. When liquid is no longer supplied to the surface in sufficient quantities to keep up the rate of evaporation, the constant-rate period ends. The critical moisture content depends on the factors affecting the diffusion rate. With low diffusional resistance and a slow rate of drying, the constant-rate period is prolonged and the critical moisture content is low; but with a high vaporization rate and large diffusional resistance, the drying rate falls off at high moisture contents (*7*). When heat is applied internally

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[1] Fourth Chemical Engineering Symposium held under the auspices of the Division of Industrial and Engineering Chemistry of the American Chemical Society at the University of Pennsylvania, Philadelphia, Pa., December 27 and 28, 1937. Previous papers in this symposium appeared on pages 384 and 388 of the April issue, on page 506 of the May issue, and on pages 993 to 1010 of the September issue.

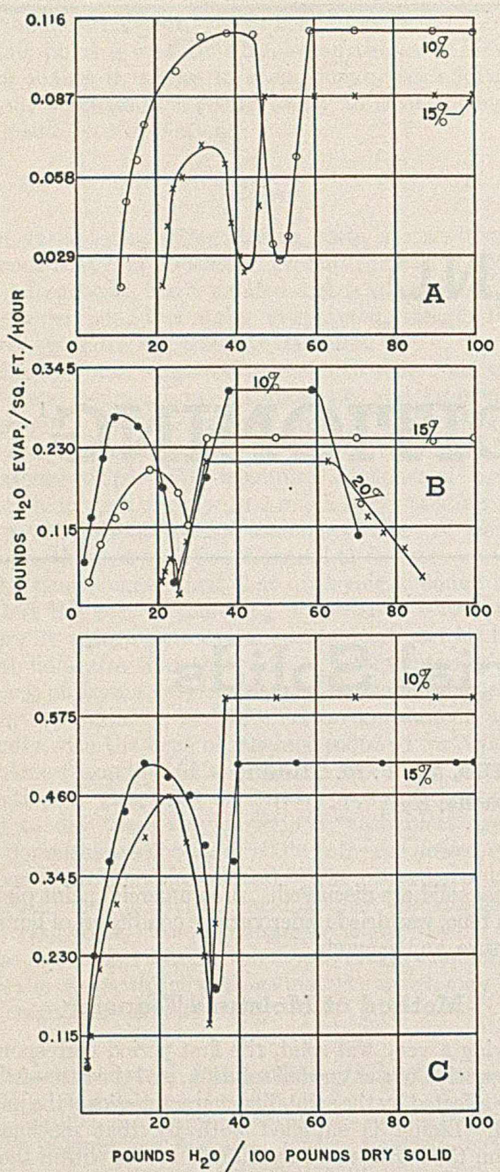

FIGURE 1. DRYING RATE CURVES

A. 140° F.; 10 and 15 per cent humidity
B. 160° F.; 10, 15, and 20 per cent humidity
C. 180° F.; 10 and 15 per cent humidity

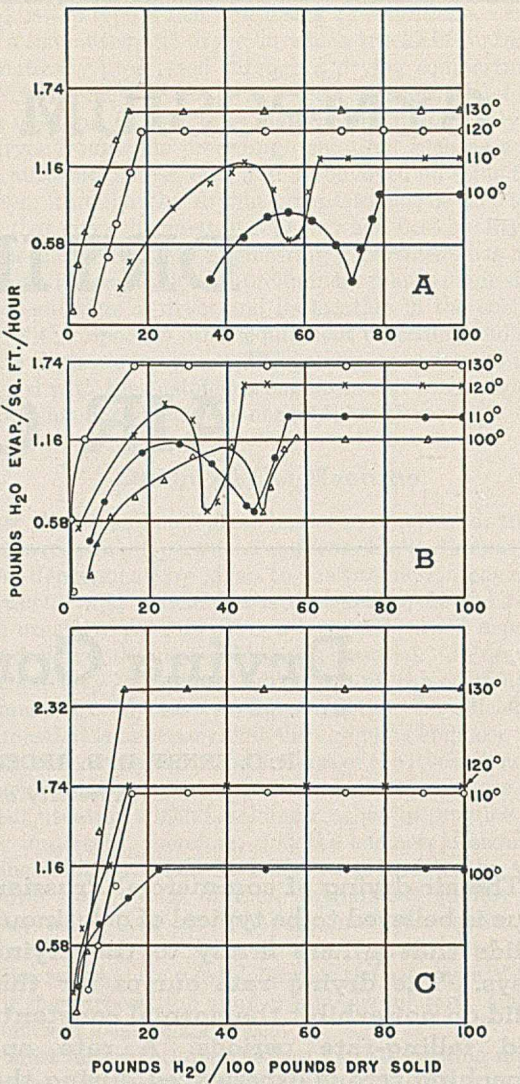

FIGURE 2. DRYING RATE CURVES AT A SHELF TEMPERATURE OF 100–130° C. (212–266° F.)

Vacuum: *A*, 18 inches; *B*, 22 inches; *C*, 26 inches

to the drying slab and the external pressure is lowered, increased diffusion results because of a greater pressure differential. This tends to lengthen the constant-rate period considerably, as will be shown later.

The type of capillaries have a large effect on the liquid diffusion. Solids with firm, closely packed structures have large capillary forces, but materials with loose, fibrous structure exert small tensions (*6*). The capillaries supply moisture to the surface as soon as vaporization begins, and as water is brought to the surface, it is necessarily replaced by air in the small passages. As water is brought to the exterior, it is necessarily replaced by air. As capillary rise varies inversely with the diameter, the liquid flows in the direction of capillaries having the smallest cross section. When the small internal reservoirs have been depleted, moisture continues coming to the surface until the external capillary diameters equal the internal diameters. Then water will be vaporized in the capillaries and the zone of evaporation will recede into the cake.

Some capillaries have large surface openings and small internal openings; others have their smallest openings in the surface. During the course of drying, the tubes with their smallest openings in the interior draw liquid inward, and then it is brought back to the surface (*3*). During the constant-rate period the inside of the cake is at a low temperature, and little evaporation occurs from the water receding into the cake. During the falling-rate period and in vacuum drying, considerable amounts of water may be vaporized internally.

Experimental Procedure

Commercial Prussian blue, a paint pigment furnished by the Kentucky Color and Chemical Company, was used in the experimental work. The blue was prepared by adding sulfuric acid and ammonium sulfate to ferrous sulfate and then precipitating with sodium ferrocyanide. The resulting precipitate was oxidized by sodium chlorate at temperatures ranging from 60° to 100° C. (140° to 212° F.). The pigment was washed by decantation over a period of 3 weeks and was then filtered in a plate-and-frame filter press. Semicommercial batches of 50 pounds containing about 50 per cent moisture were used in the air drying. In the vacuum drying, smaller batches of about 12 pounds were employed.

The air drying was carried out in a twelve-tray H-W conditioner. The air was heated by passing it over steam coils, and the humidity was controlled by steam injection and recirculation.

Temperature and humidity conditions of incoming and exhaust air were determined by means of wet- and dry-bulb thermometers.

The vacuum drying was effected in a vacuum shelf dryer consisting of a cast-iron shell with three steam-heated shelves. Copper-constantan thermocouples placed in the top, middle, and bottom of the cake were used to determine the cake temperatures.

Runs lasting 28 hours were made in the air drying at humidities ranging from 10 to 20 per cent and temperatures from 120° to 140° F. Vacuum drying runs lasted from 8 to 12 hours and were carried out at vacuums of 18 to 26 inches and at shelf temperatures of 100° to 130° C. (212° to 266° F.) The rate of drying curves were obtained by determining the slope of the moisture-time curves and plotting against moisture content.

Air Drying

The rate of drying curves of a few representative runs of Prussian blue are shown in Figure 1. The evaporation rate proceeded normally at first and at the end of the initial period suddenly decreased. The rate then rose sharply and fell off gradually as it would during the falling-rate period.

The blue was exceedingly wet at the beginning of the runs and firmly adhered to the drying trays. Drying proceeded normally at first while the surface moisture and internal reservoirs were being exhausted. When most of the cavities were emptied, the only moisture supplied to the surface was that held in the capillaries themselves. The liquid began to rise in the capillaries, and as the bottom of the cake adhered firmly to the tray, air was unable to enter the bottom openings. As the liquid rose, a vacuum was formed in the capillaries and liquid was unable to rise to the surface. With the supply of water diminished, the rate of drying immediately decreased. Some moisture vaporized in the capillaries and the rate never reached zero. The solid which had been shrinking and crumbling pulled away from the bottom of the tray, and air entered the capillaries. With a new supply of moisture at the surface, the drying rate rose immediately and drying proceeded normally (*2*).

From the suggested mechanism, the break in the curve would occur when the only moisture in the cake was held in the capillaries. This would occur after all the internal reservoirs had been exhausted at the end of the constant-rate period. This is supported by the rate curves as the diminished drying rates occur at the end of the constant-rate period.

If the resultant force caused by the vacuum seal could be lessened sufficiently, the break in the drying curve would not occur. It was proposed that in vacuum the effect of the vacuum seal would be minimized, and at high vacuums no discontinuity would occur.

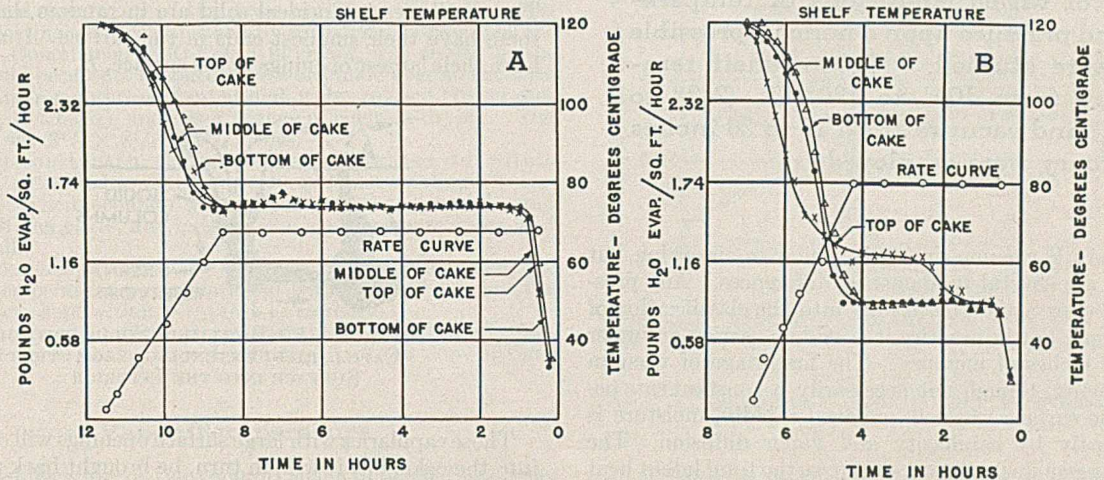

Figure 3. Drying Rate Curves and Cake Temperatures at a Shelf Temperature of 120° C. (248° F.)

Vacuum: *A*, 18 inches; *B*, 26 inches

Vacuum Drying

The drying rate curves of the pigment at varying vacuums and temperatures are plotted on Figure 2. At 18 and 22 inches of mercury there are noticeable breaks in the drying curves which are not so pronounced as in air drying. These discontinuities occur only at the lower shelf temperatures; and as the steam shelf temperature and rate of drying were increased, the shrinkage became much greater. The increasing shelf temperature must not be confused with increase in cake temperature, as the cake temperature depends only on the total pressure within the dryer and not on the shelf temperature during the constant-rate period. Increased shrinkage and crumbling by higher shelf temperature is a function only of the greater rate of moisture removal and not the shelf temperature. The greater shrinkage caused the cake to crumble and pull away from the tray more rapidly, and the dip in the curve was minimized with increasing temperature. At the highest shelf temperature no break occurred. It was only at 26 inches of mercury that no cessation of drying was noticed at the lower temperatures. This gives a conception of the magnitude of the vacuum caused by the solid's adhering to the drying trays.

The effect of applying heat internally to a drying slab is strikingly illustrated in the vacuum drying curves. In each case an increase in shelf temperature is accompanied by lengthened constant-rate period. At 130° C. (266° F.) it is remarkable that the constant-rate period extends over such a great moisture content. Similar results were obtained in the vacuum drying of Sil-O-Cel (*3*). The heat was supplied through the shelves to the bottom of the cake, and each increase in shelf temperature correspondingly increased the diffusion rate and the amount of water available for evaporation.

The variations of cake temperatures are shown on Figure 3. These two sets of curves are typical of the data obtained on the drying in vacuum. Temperatures were recorded at the top, middle, and bottom of the cake. At a shelf temperature of 120° C. (248° F.) and a vacuum of 18 inches of mercury in Figure 3*A* the cake temperature rose to a temperature corresponding to the boiling point of water at the total pressure on the dryer. At the end of the constant-rate period the temperature at the bottom and top of the cake rose before that at the middle of the slab. The temperature at the middle reached and passed the temperature at the top of the cake during the falling-rate period. There was good heat transfer through the bottom of the cake, and the temperature there rose first. The top was being heated by superheated vapor and radiation, and the surface temperature rose before the temperature at the middle. More heat was transferred from the bottom than from the top, and temperature at the middle reached and then passed that on the surface.

At the highest vacuum and temperature a different phenomenon was encountered. In Figure 3*B* temperature and rate curves at a shelf temperature of 120° C. and a vacuum of 26 inches of mercury are plotted. Similar results were obtained in runs at the same vacuum and at shelf temperatures of 130° C. The rate of evaporation was very rapid and the moisture was quickly depleted at the surface. Consequently the surface temperature rose, and a considerable amount of water was vaporized internally in addition to the upper surface evaporation. This result is similar to that experienced by Ernst, Ridgway, and Tiller (*3*) in the drying of Sil-O-Cel. The temperature at the middle and bottom of the cake surpassed the surface temperature during the falling-rate period.

Acknowledgment

The authors wish to acknowledge the fellowship assistance of the Louisville Oil, Paint, and Varnish Club as aid in carrying out this investigation, to the Kentucky Color and Chemical Company for supplying raw materials, and to S. Miller and E. Musterman for assistance in obtaining data.

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Practical Vacuum Drying

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During the past decade, many investigators have contributed to the theory of air drying; however, relatively little work has been reported on drying in vacuum (*3*). Experimental work was undertaken to determine the mechanism of drying at diminished pressure. The effects of varied conditions of temperature and pressure upon a noncompressible solid were studied. Steam shelf temperature from 100° to 130° C. (212° to 266° F.) and vacuum from 18 to 26 inches of mercury were employed.

BASICALLY vacuum drying is similar to air drying, but there are several fundamental differences. Any pressure below atmospheric falls into the classification of vacuum drying, but in practice it is seldom carried on under less than 18 inches of mercury. The first stage of vacuum drying is usually, though not necessarily, a constant rate period. As the surface water is removed rapidly, moisture is supplied mostly by capillarity and vapor diffusion. The rate of drying remains constant as long as the total latent heat of the available water is greater than the heat flow into the solid. By available water is meant any water that is free to vaporize, regardless of its position in the cake. The concept of available water is important since a large amount of water may evaporate internally during vacuum drying and diffuse to the surface as vapor. When the heat flow into the solid just balances the latent heat of evaporating moisture, the critical point is reached, and beyond this, the falling-rate period begins.

A drying solid may be considered as a complex system of capillaries extending from the surface into the interior of the solid and connecting small voids throughout the cake. Before the liquid reaches the surface, it may travel many times the thickness of the cake. The surface is connected with comparatively large cavities in the cake which act as liquid reservoirs. Figure 1 shows an idealized solid with capillaries extending from the surface into the interior. The flow of liquid is indicated by solid arrows and of vapor by dotted arrows. The capillaries in an ideal solid are in random distribution; some have their smallest ends in the surface, *A*, and others have their largest openings in the surface, *B*.

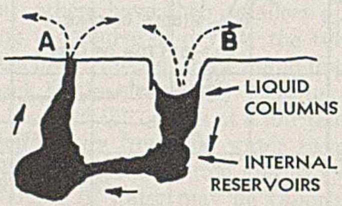

FIGURE 1. IDEALIZED SOLID WITH CAPILLARIES EXTENDING FROM THE SURFACE INTO THE INTERIOR

Those capillaries with large surface openings will draw water into the cake, but it will, in turn, be brought back to the surface by the capillaries with their smallest openings in the surface. The vapor pressure of the capillary water is lowered because of the concave liquid surface; and in air drying at atmospheric pressure there is little evaporation from the receding liquid columns. In vacuum drying at low pressure, however, there is considerably more vaporization from the receding capillaries with subsequent diffusion of vapor to the surface. Thus, in vacuum, drying is effected across the entire cross section of the solid and not primarily at the surface as in

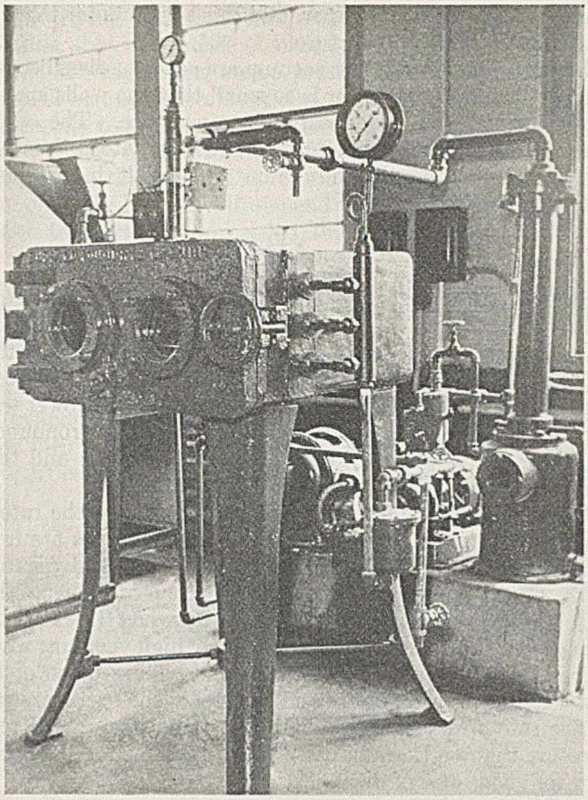

Figure 2. Three-Shelf Vacuum Dryer

air drying. Block (*1*) maintained this fact as far back as 1919, but he assumed that only vapor and no moisture was transferred through the solid.

Apparatus

Drying was carried on in an experimental three-shelf vacuum dryer provided with usual auxiliary equipment. The dryer (Figure 2) has three welded steel shelves, each 24 × 24 inches; the internal dimensions of the dryer are 25 × 25 × 11 inches high. Heating was accomplished by introducing steam into the shelves. Commercial Sil-O-Cel, a filter aid, was chosen as the drying solid because it is noncompressible, undergoes no chemical change, and remains consistent at high water content (70 per cent moisture, wet basis), and has a change of color on drying. The cake size was $8^1/_2 \times 8^1/_2 \times 1^1/_8$ inches.

Copper-constantan thermocouples calibrated to within ±0.5° C. were used to determine cake and vacuum chamber temperature. Thermocouples were placed in the top, middle, and bottom of the cakes, and in the steam shelf, vacuum space, and upper wall.

All experimental data were taken over a 12-hour period, the control temperature was maintained within ±0.5° C., and the vacuum was kept within $\pm ^1/_{16}$ inch of mercury.

Moisture content–time curves were plotted, and the instantaneous rates of drying were determined from the slope of these curves.

Vapor Temperature

The temperature of the vacuum space depended upon the temperature of the vapor passing through it and was necessarily at a higher temperature than the cake, as it received heat from the steam shelf directly above it. The temperature of the vapor, which was actually superheated steam, depended upon radiation, distance between shelves, and contact of the vapor with the shelf. High vapor temperature means a considerable loss of sensible heat. High vacuums give lower vapor temperatures and less loss of heat, but result in an increased load on the pump.

In Figure 3 the variation of the vacuum space temperature is plotted with cake temperature and drying rate curves to show the relation. This curve is typical of other runs and is the only one shown. The temperature of the internal vapor from the solid was at a higher temperature than the cake but did not become constant until nearly 30 per cent of the moisture had been removed about 2 hours after the start of the run. During the initial period 60 per cent of the total moisture was removed. When 9 per cent of the moisture had been removed during the falling-rate period, the vapor temperature began to rise and to approach the steam shelf temperature.

Cake Temperature

The general variation of cake temperature is shown in Figure 3. The cake reaches an equilibrium temperature in half an hour. At the start of drying, the top and bottom of the cake were heated slightly faster than the middle, indicating that heat was being transferred into the solid from both the bottom and the top. The temperature throughout the solid remained constant until 75 per cent of the water had been removed. At this point, which is about half way through the falling-rate period (on a moisture content–rate curve, rather than time-rate curve), the temperature at the top of the cake began to rise and indicated that the zone of evaporation was receding into the solid. This temperature rise followed that of the vapor. With the removal of an additional 7 per cent of water, the temperatures at the middle and bottom of the cake followed an upward trend simultaneously. As the temperature at the top of the cake rose sooner than at the middle or bottom, it is obvious that the flow of heat into the cake from the superheated vapor and by radiation exceeded the flow into the cake from the shelf on which the cake rested. Had the top thermocouple been subject to radiation, its temperature would have gradually risen from the start of drying instead of remaining constant as indicated in Figure 3. With solids, such as Prussian blue, that adhere more firmly to the drying trays than Sil-O-Cel, heat may be transferred more readily through the trays than from the vapor. Experimental data show this to be true (*1*). The cake temperature approached the steam shelf temperature.

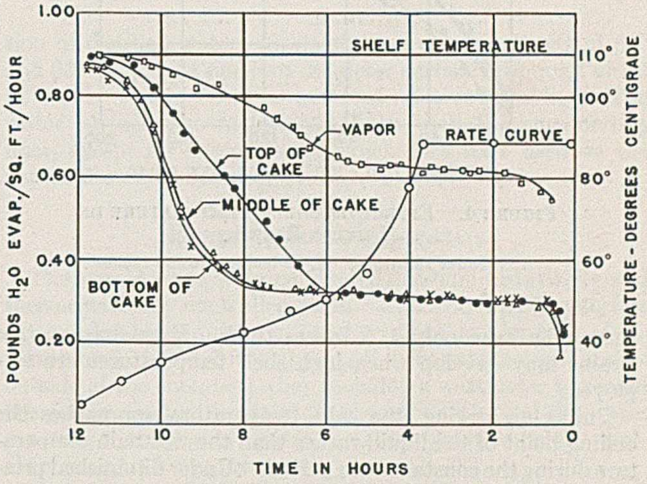

Figure 3. Drying Rate and Cake and Vapor Temperature Curves at 26-Inch Vacuum and Shelf Temperature of 110° C.

○, rate of drying; □, vapor temperature; ●, temperature of top of cake; △, temperature of middle of cake; ×, temperature of bottom of cake

It is particularly significant that temperature differences of more than 20° C. (36° F.) existed within the cake during the falling-rate period; this is a rather large temperature differ-

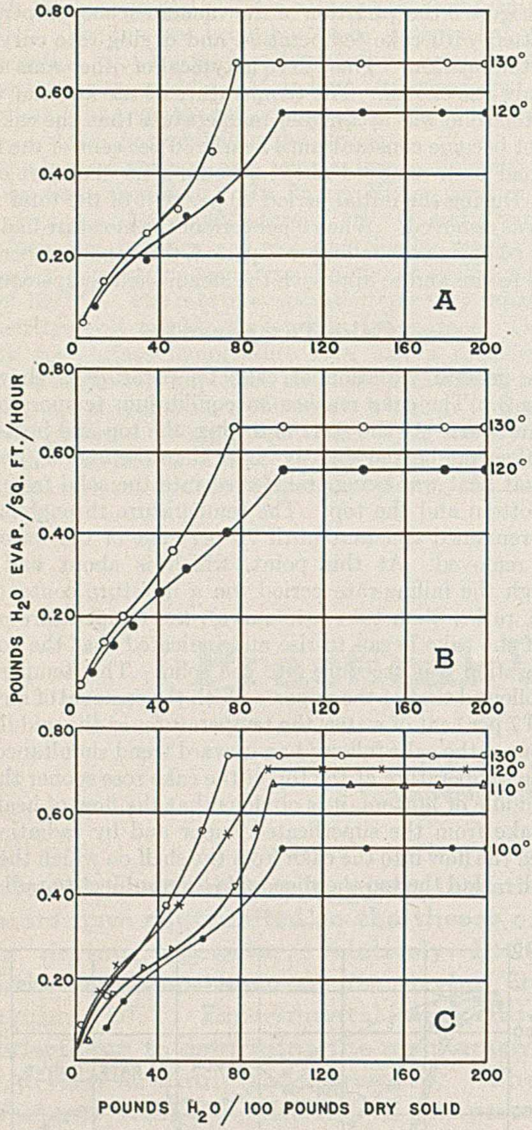

FIGURE 4. EFFECT OF SHELF TEMPERATURE ON DRYING RATE

A, vacuum 18 inches; *B*, 22 inches; *C*, 26 inches

ence for a cake only 1¹/₈ inches thick. Excessive internal strains may develop when high shelf temperatures are employed.

Unlike air drying, the cake temperature approaches the boiling point of the liquid rather than the wet-bulb temperature during the constant-rate period. Under diminished pressure the slab temperature remains constant during the first period, regardless of the steam shelf temperature. On the contrary, in air drying, where the liquid is usually below its boiling point, an increased temperature of the drying media results in higher cake temperatures.

Wall Temperature

Condensation must not occur on the walls because the dryer would act merely as a reflux, and no appreciable water removal would be effected. The temperature of the walls depends upon the heat conveyed to them by the water vapor, and remains low until moisture is vaporized at the start of drying. It is interesting to note that the wall temperature remained constant during the falling-rate period. Although the vapor temperature rose, there was a corresponding decrease in the amount of vapor, and this accounts for the constancy in the wall temperature.

Low temperatures at low vacuum are nearly useless because the heat given to the vapor is so small that the walls are not heated above the condensation temperature. The vapor must be heated enough to prevent condensation, but any temperature above this minimum will result in increased radiation and heat loss.

Rate of Drying

SHELF TEMPERATURE. The effect of shelf temperature upon the rate of drying is shown in Figure 4. The vacuum was constant in each case at 18, 22, and 26 inches of mercury. The rate of drying was increased approximately 15 per cent per 10° C. (18° F.) rise in shelf temperature at the lower temperatures. The increase in drying rate was less pronounced at higher temperatures. With increasing vacuum and temperature the constant-rate period was lengthened.

VACUUM. The effect of vacuum changes upon the rate of drying is shown in Figure 5. These drying curves are for a constant shelf temperature of 130° C. (266° F.) and vacuums of 18, 22, and 26 inches of mercury. The curves indicate that little variation results in the rate of drying when the vacuum is changed. This is true only for relatively high vacuums where there is a large difference between the boiling point of the water at the dryer pressure and the steam shelf temperature.

The rate of drying depends more on the steam shelf temperature than on the vacuum. High vacuums are not necessary for good rates of drying.

Conclusions

Vacuum drying is especially adapted to drying substances that decompose or undergo undesirable physical changes at high temperatures. The drying can be accomplished at a vacuum high enough to give a total pressure corresponding to a boiling point of water below the transition temperature.

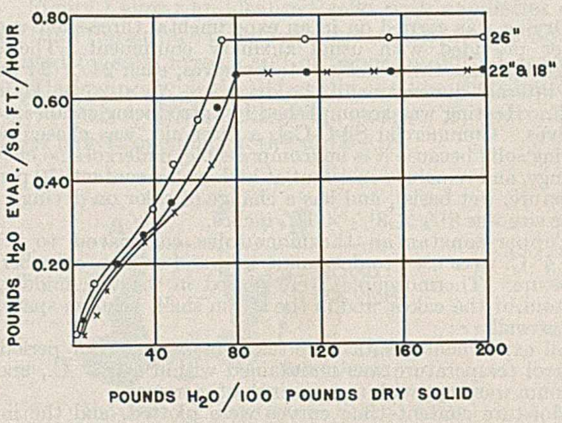

FIGURE 5. EFFECT OF VACUUM ON DRYING RATE CURVES AT A SHELF TEMPERATURE OF 130° C. AND VACUUM OF 18 TO 26 INCHES

Accurate control can easily be obtained by inserting a thermocouple in the top of the drying cake. Any steam pressure can be used. When the falling-rate period is reached and the cake temperature begins to rise, it is necessary to cut off the steam immediately, for the surface temperature rises rapidly (about 15° C. or 27° F. per hour in this investigation). From this point on, the drying must be completed by bleeding steam into the shelf, or better still, by the use of hot water. As the cake approaches the shelf temperature, the water can be used at the desired temperature.

For drying materials not affected by temperature, any vacuum above 18 inches of mercury will give a good drying rate. The higher the steam pressure, the greater the drying rate will be up to a certain point. The rate will increase with increasing temperature until the pump is unable to remove vapor as fast as it is formed. Pressure would then build up and reduce the rate. The maximum temperature that can economically be used will depend upon the individual pump. If this temperature is exceeded, the vapor will not be removed so rapidly as it is formed, and the rate of evaporation will be lowered as pressure builds up. In this investigation approximately 75 per cent of the water was removed in half the drying time.

The temperatures within the dryer are exceedingly important in determining the quality of product as well as the rate of evaporation and dryer efficiency. The method of heat flow into the solid is entirely dependent upon the physical properties of the solid. Excessive temperatures at the start of drying, although giving a high initial rate of drying, may cause surface hardening and subsequent lowered drying rates. Large temperature differences, usually occurring at the end of the constant-rate period, set up internal stresses and cause cracking. This is especially important when the constant-rate period extends over a long range of moisture, as the temperature may then rise rapidly with the sudden falling off of the rate of evaporation.

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Evaporation of Water into Quiet Air

From a One-Foot Diameter Surface

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The evaporation from a one-foot-diameter pan of distilled water into quiet air at 53 per cent humidity was measured for water temperatures between 63° and 93° F. The surface of the water was at the level of the surroundings. In the critical region, corresponding to a water temperature of 69.4° F., the buoyant effects of the mixture at the water surface and far away are equal. The unit evaporation rate above the critical region, in pounds/(square foot) (hour) may be expressed by the equation:

$$e = -0.024 + 65(c_{vw} - c_{v\infty})$$

Below the critical region the results may be expressed approximately by the equation:

$$e = 18.75\,(c_{vw} - c_{v\infty})$$

where c_{vw} is the concentration of water vapor on the gas side of the gas-liquid interface and $c_{v\infty}$ is the concentration of the water vapor in the atmosphere far from the pan, both in pounds per cubic foot.

A tentative correlation with thermal free convection data has been accomplished. The ratio $Nu/Nu' = 1.29$ for $10^6 < Gr' \times Pr$ (and $Gr' \times Pr'$) $< 10^8$ agrees fairly well with the results of Hilpert (*6*) determined for moist clay plates placed vertically. Acceptance of the thermal free convection–diffusional free convection analogy and generalization to other fluids is not urged until substantiated by further experimental results.

NUSSELT (*8*) suggested a detailed attack on the problem of diffusion. Heat transfer and diffusion phenomena obey similar field equations, and if the boundary conditions are similar, the solution of the steady-state thermal free-convection system of a particular geometrical configuration should yield a solution of the corresponding system involving diffusion. The purpose of this paper is to present data which will confirm the analogy for the case of evaporation of distilled water, within the temperature limits of 63° and 93° F., from a one-foot-diameter surface into quiet air at 71° ± 1° F. and 50 to 54 per cent relative humidity. The water surface was maintained flush with the surrounding floor, except for the cases for which rims were used on the pan as described below.

Evaporation Apparatus

The experiments were conducted in a humidistatically and thermostatically controlled room. The evaporation pan was surrounded by a quieting chamber, open at the top, of dimensions 5 × 5 × 7 feet high. All instruments were located outside of the chamber; they included a wattmeter to record the power required to maintain the temperature of the water constant, barograph, potentiometer, galvanometer, psychrometer, and evaporimeter.

EVAPORATION PAN. The tinned copper evaporation pan, 1 foot in diameter and 6 inches deep, is shown in Figure 1. The evaporation pan was contained within a pan 20 inches in diameter and 9 inches deep, the space between the two pans was packed with hair felt and 85 per cent magnesia. An electrical heating element placed below the evaporation pan supplied thermal energy to the water. Ten copper-constantan thermocouples were placed in the pan at various depths and diameters; the most important of them, for the purposes of this paper, were the two located at the surface of the water in such a manner as barely to deflect the water surface.

QUIETING CHAMBER. The evaporation pan was placed centrally in the floor of the quieting chamber (Figure 2). Air supply to the quieting chamber was provided for by placing the chamber upon blocks 1 inch high. The floor of the quieting chamber was 2 inches less in each dimension than the corresponding inside dimensions of the chamber, thus allowing air to enter vertically along the walls. The floor of the quieting chamber existed at the temperature of the air far away except for a narrow ring close to the pan which was a few degrees warmer. The top of the quieting chamber was open and the inside surface was covered with aluminum foil.

A traveling carriage was arranged across the top of the quieting chamber upon which copper-constantan thermocouples were mounted in such a fashion as to make possible a complete temperature exploration of the quieting chamber. For the purposes of this paper the mixture conditions outside of the quieting chamber were considered as the conditions far away.

EVAPORIMETER. The evaporimeter and accessory equipment are shown in Figure 3. The design permitted the determination of low evaporation rates in fairly short time intervals. The luminous output of a housed G. E., type G-1, "Sunlight" lamp (shown to the left in Figure 3) was filtered so that only the green lines were transmitted to the optical wedge. The standpipe, shown in the center of Figure 3, was connected to the side, 3 inches up from the bottom, of the evaporation pan through a $^1/_4$-inch o. d. copper pipe. Make-up water to the pan was supplied through this standpipe. Another standpipe, $2^3/_4$ inches in diameter and 12 inches high, separately connected to the evaporation pan and provided with leveling screws, contained the $2^1/_2$-inch-diameter brass float pan. A lever arm, L, 5.22 cm. long (2.039 inches), was pivoted on a knife edge in a grooved block located at the left edge of the standpipe. The other end of the lever arm, which carried a $^3/_4 \times {}^3/_8$ inch piece of plate glass, was actuated through a pivot point by a jewel bearing located in the center of the pan float. Across the top of the standpipe a larger piece of plate glass was placed bearing two etched lines, a distance (L_1) 0.4 inch apart. The grooved block was adjustable by means of two thumb screws. The error due to the difference in vertical temperature gradient existing in the pan and the standpipe may be shown to be negligible.

Green lines from the filtered light source were reflected downward by a piece of plate glass placed at 45° and above the standpipe. This beam impinged upon both elements of the optical wedge and produced interference bands, provided an angle existed between the elements of the wedge. The interference bands are observed through a telescope mounted so as to observe a limited field in a mirror placed above and parallel to the plate glass in the 45° position.

THEORY OF THE EVAPORIMETER. Figure 4 exhibits typical interference bands produced by the evaporimeter optical wedge. Figure 5 illustrates the significant variables required to relate the difference in level of the water with the number of interference bands (*11*).

(Reading from top to bottom)

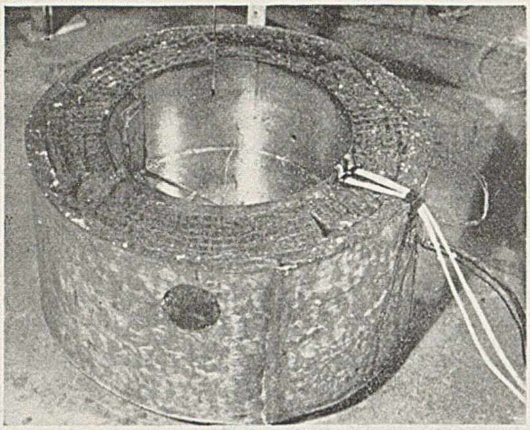

FIGURE 1. EVAPORATION PAN

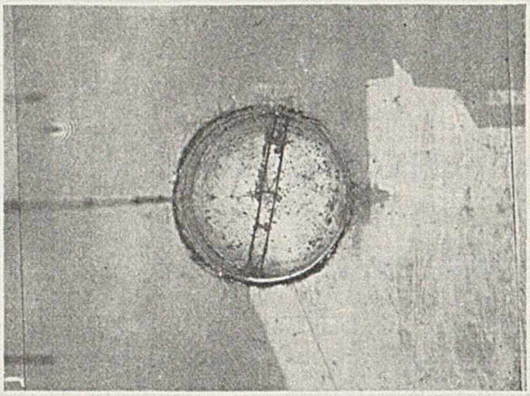

FIGURE 2. EVAPORATION PAN IN PLACE IN THE FLOOR OF THE QUIETING CHAMBER

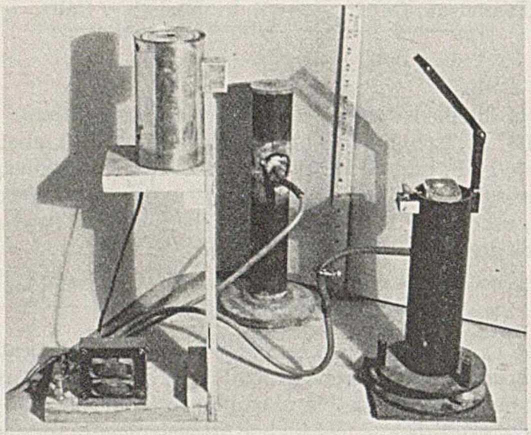

FIGURE 3. EVAPORIMETER AND ACCESSORY EQUIPMENT

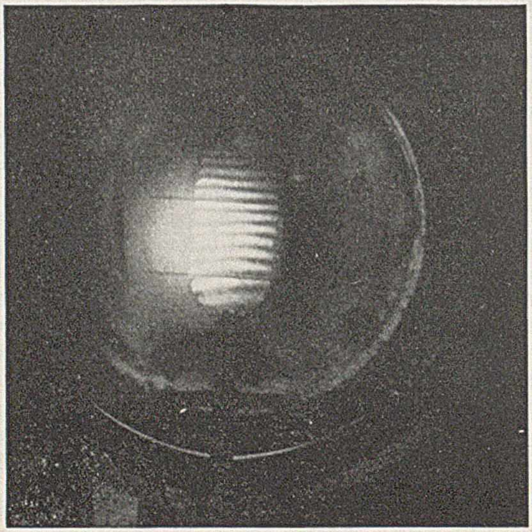

FIGURE 4. TYPICAL INTERFERENCE BANDS

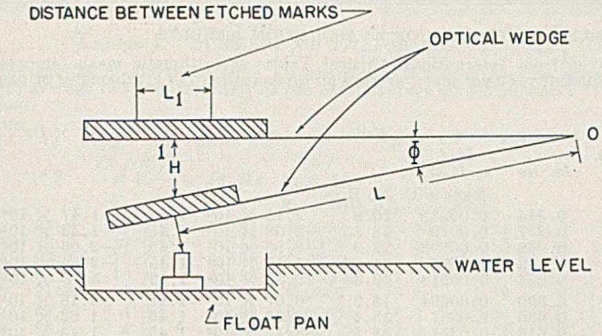

FIGURE 5. EVAPORIMETER FLOAT AND WEDGE

Interference will result if the distance, H, is a multiple of a half wave length; that is,

$$H = n_{01}\lambda/2$$

where n_{01} = number of interference bands between 0 and 1

A change of level of the pan, ΔH, will result in a change of the number of bands, Δn_{01}, included between 0 and 1, in accordance with the relation

$$\Delta H = \Delta n_{01}\lambda/2$$

obtained by differentiation. The change in the number of bands, Δn, in length L_1 is equal to $\Delta n_{01}L_1/L \cos \phi$. Substituting into the expression for ΔH yields:

$$\Delta H = \Delta n \frac{L}{L_1}\frac{\lambda}{2}$$

provided the angle ϕ is small. In these experiments, the wave length, λ, was equal to 5461 Å.

Experimental Technic

The water being evaporated was heated to a given temperature which was held constant by means of the electric element under the pan. When equilibrium had been established (determined by the constancy of water temperatures) barometric pressure, water temperatures, wet- and dry-bulb temperatures, power input, and the rate of evaporation were observed. The evaporation rate was measured by determining the rate of change of the interference bands produced at the evaporimeter. The lower or floating glass plate on the evaporimeter was usually slightly above the zero angle position at the start of a run, and as the water evaporated it would drop through the zero angle position (indicated by no interference bands) to slightly below this mid-position. A small amount of water would then be added through the filling standpipe and the process repeated; several observations were thus made at each water temperature.

It was found impossible to take observations with the present evaporimeter when the water temperature was above approximately 93° F., owing to the rapid rate of change of bands. On the other hand, it was found that accurate data on the rate of evaporation could not be obtained when the water surface was below approximately 63° F., as a result of the slow rate of change of interference bands.

Observations were taken of the evaporation rate under three conditions: (*a*) water surface flush with the floor of the quieting chamber, (*b*) water surface ½ inch below the floor level, and (*c*) water surface 1½ inches below the floor level. The latter two conditions were accomplished by attaching a sheet metal rim of the proper height to the evaporation pan and at the same time raising the floor an equal amount. By this procedure it was not necessary to disturb the thermocouples in the evaporation pan, and the change could be effected quickly. At all times the floor was flush with the top edge of the pan or rims, if the latter were being used at the time.

Unit Evaporation Rates

The results of the investigation are indicated in Table I and plotted on Figures 6 to 10.

The unit evaporation rates, e, are plotted for various water vapor concentration differences (approximately partial pressure differences) in Figure 6. The unit evaporation rate may

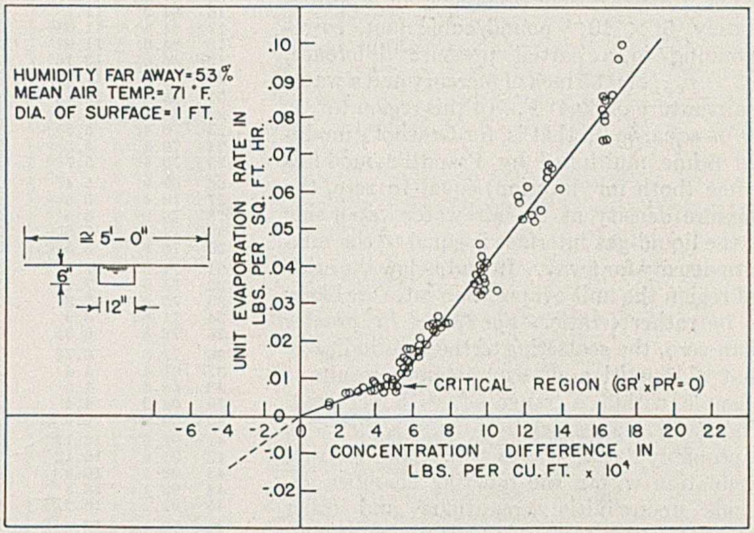

FIGURE 6. UNIT EVAPORATION RATE *vs.* CONCENTRATION DIFFERENCE AT THE SURFACE AND FAR AWAY

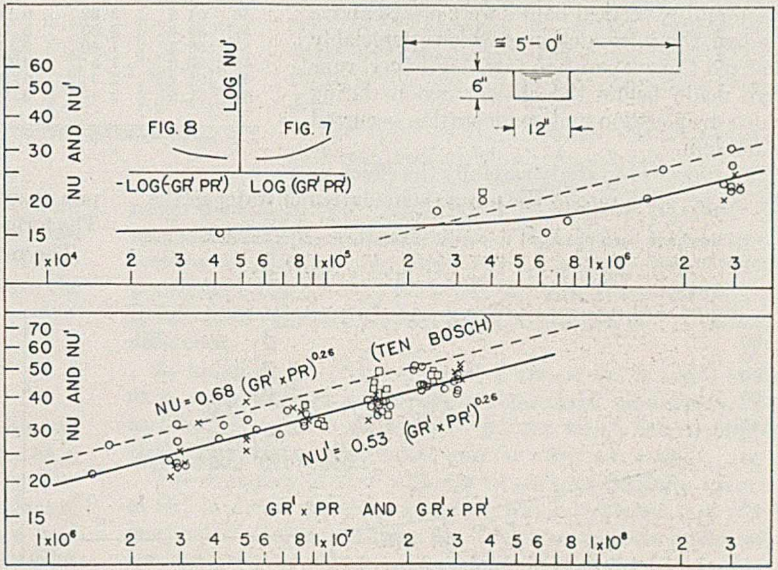

FIGURE 7. *Nu vs. Gr'Pr* AND *Nu' vs. Gr'Pr'* FOR HEAT TRANSFER AND EVAPORATION FROM HORIZONTAL CIRCULAR SURFACES

○ Evaporation, no rim
× Evaporation, 0.5-inch rim
□ Evaporation, 1.5-inch rim

be expressed by the following two equations:

$$e = -0.024 + 65\,(c_{vw} - c_{v\infty}) \quad \text{for } (c_{vw} - c_{v\infty}) \geq 5 \times 10^{-4} \text{ lb./cu. ft.} \qquad (1)$$

$$e = 18.75\,(c_{vw} - c_{v\infty}) \quad \text{for } (c_{vw} - c_{v\infty}) \leq 5 \times 10^{-4} \text{ lb./cu. ft.} \qquad (2)$$

In this investigation the partial pressure of the air in the gas side of the interface is approximately equal to the total pressure and is therefore substantially constant. For this reason the unit evaporation rate may be thought of as proportional to the concentration difference.

On the air-water vapor side of the liquid-gas interface a critical region exists at a water vapor concentration difference of approximately 5×10^{-4} pound/cubic foot, corresponding to a partial pressure difference, $p_{vw} - p_{v\infty}$, of 0.35 inch of mercury and a water temperature of 69.4° F. In this region $Gr' \times Pr'$ is equal to 0; that is, for Grashof's modulus prime multiplied by Prandtl's modulus prime (both for diffusion) equal to zero, the mixture density at the air-water vapor side of the liquid-gas interface is equal to the mixture density far away. In and below the critical region the unit evaporation rates are likely to be rather erratic. For $Gr' \times Pr'$ greater than zero, the scattering of the data indicates that a repetition of experimental results is possible within a range of ±15 per cent. The scattering, especially for $Gr' \times Pr' \leq 0$, is probably due to the fact that the mixture circulation within the quieting chamber depends upon initial conditions[1] and other variables which are beyond experimental control. In other words, the difference of water vapor concentration at the water surface and far away is not a true measure of the force causing evaporation because of intervening mixture currents. In order to substantiate this premise, vertical baffles were placed above the pan, the introduction of which appreciably changed the evaporation rate. Further, runs were made below the critical region during which evaporation and condensation occurred at random.

Table I. Summary of Evaporation Results

(Properties of air taken from International Critical Tables at arithmetic mean temperature; average relative humidity, 53 per cent; average air temperature, 71° F.; diameter of pan, 1 foot)

Run No.	t_w ° F.	$c_{vw} - c_{v\infty}$ Lb./cu. ft. $\times 10^4$	$p_w - p_\infty$ In. Hg	e Lb./sq. ft. hr.	Nu'	Gr'	Pr'	$Gr' \times Pr'$
				Runs with No Rim				
1	69.7	4.85	0.314	0.00985	20.9	2.13×10^6	1.45	1.47×10^6
2	68.0	4.32	0.277	0.0079	18.85	-2.08×10^6	1.45	-1.43×10^6
3	67.2	4.02	0.258	0.00895	22.9	-3.86×10^6	1.45	-2.66×10^6
4	66.8	3.92	0.249	0.0095	24.95	-4.15×10^6	1.45	-2.86×10^6
5	69.4	4.58	0.294	0.00913	20.38	5.36×10^5	1.45	3.70×10^5
6	68.9	4.66	0.300	0.00694	15.3	6.07×10^4	1.45	4.18×10^4
7	80.1	9.65	0.636	0.0367	38.4	2.36×10^7	1.46	1.62×10^7
8	79.4	9.3	0.616	0.0354	38.5	2.1×10^7	1.45	1.45×10^7
9	80.1	9.8	0.648	0.0356	36.5	2.14×10^7	1.45	1.475×10^7
10	80.2	9.6	0.633	0.0359	37.7	2.28×10^7	1.46	1.56×10^7
11	80.3	9.7	0.637	0.0359	37.5	2.28×10^7	1.46	1.56×10^7
12	80.3	9.7	0.637	0.0324	33.75	2.28×10^7	1.46	1.56×10^7
13	80.45	9.8	0.642	0.0370	38.2	2.45×10^7	1.46	1.68×10^7
14	80.6	9.9	0.659	0.0357	36.5	2.52×10^7	1.46	1.725×10^7
15	88.2	13.88	0.937	0.0608	42.3	4.07×10^7	1.49	2.73×10^7
16	84.2	11.7	0.783	0.0576	49.6	3.06×10^7	1.45	2.11×10^7
17	84.4	11.64	0.787	0.0592	51.0	3.06×10^7	1.45	2.11×10^7
18	84.6	11.91	0.800	0.0529	44.2	3.23×10^7	1.45	2.23×10^7
19	85.0	12.16	0.814	0.0616	50.7	3.27×10^7	1.45	2.26×10^7
20	85.2	12.38	0.828	0.0538	43.6	3.30×10^7	1.45	2.28×10^7
21	85.3	12.48	0.830	0.0520	41.7	3.27×10^7	1.45	2.26×10^7
22	86.1	12.83	0.860	0.0553	42.7	3.49×10^7	1.46	2.37×10^7
23	70.4	5.5	0.344	0.0144	26.6	2.42×10^6	1.45	1.67×10^6
24	70.3	5.5	0.351	0.0126	23.5	3.94×10^6	1.45	2.72×10^6
25	70.4	5.7	0.369	0.0124	22.4	4.54×10^6	1.45	3.13×10^6
26	69.9	5.4	0.342	0.0116	22.1	4.23×10^6	1.45	2.92×10^6
27	70.4	5.3	0.338	0.0143	27.6	4.28×10^6	1.46	2.93×10^6
28	70.9	5.5	0.357	0.0151	28.1	6.07×10^6	1.46	4.16×10^6
29	71.3	5.6	0.369	0.0148	31.6	4.20×10^6	1.45	2.90×10^6
30	70.8	5.5	0.356	0.0122	22.85	4.22×10^6	1.45	2.91×10^6
31	74.9	7.25	0.472	0.0223	31.35	1.22×10^7	1.45	8.42×10^6
32	74.9	7.1	0.467	0.0247	35.45	1.06×10^7	1.45	7.32×10^6
33	75.5	7.3	0.476	0.0247	34.3	1.257×10^7	1.45	8.67×10^6
34	71.85	5.9	0.380	0.0181	31.4	6.34×10^6	1.45	4.33×10^6
35	72.8	6.35	0.405	0.0189	30.4	8.32×10^6	1.46	5.7×10^6
36	73.5	6.78	0.434	0.0193	29.0	1.003×10^7	1.45	6.92×10^6
37	67.4	4.4	0.244	0.00615	24.3	-4.17×10^6	1.45	-2.88×10^6
38	66.6	4.5	0.242	0.0083	18.95	-4.17×10^6	1.45	-2.88×10^6
39	66.2	4.4	0.229	0.00753	17.7	-5.88×10^6	1.45	-4.06×10^6
40	65.9	4.7	0.240	0.00678	14.7	-5.88×10^6	1.45	-4.06×10^6
41	91.6	16.12	1.090	0.0823	45.6	4.77×10^7	1.61	3.01×10^7
42	91.6	16.12	1.090	0.0823	45.6	4.775×10^7	1.62	3.01×10^7
43	92.1	16.3	1.104	0.0805	45.1	4.77×10^7	1.62	2.99×10^7
44	92 1	16.3	1.105	0.0792	44.2	4.77×10^7	1.62	2.99×10^7
45	92.1	16.2	1.105	0.0740	41.5	4.77×10^7	1.62	2.99×10^7
46	92.1	16.4	1.128	0.0740	40.5	4.79×10^7	1.62	2.99×10^7
47	92.2	16.4	1.133	0.0740	40.5	4.79×10^7	1.62	2.99×10^7
48	69.0	4.9	0.308	0.00740	15.6	9.23×10^5	1.46	6.32×10^5
49	69.1	4.95	0.315	0.0082	17.1	11.04×10^5	1.46	7.57×10^5
50	68.9	4.82	0.303	0.00870	18.55	3.69×10^5	1.46	2.53×10^5
51	68.6	4.62	0.295	0.00705	15.75	-11.5×10^5	1.46	-7.88×10^5
52	66.3	4.2	0.265	0.00674	16.55	-4.54×10^6	1.46	-3.11×10^6
53	65.6	3.92	0.245	0.00688	23.2	-6.37×10^6	1.46	-4.36×10^6
54	65.6	3.80	0.235	0.00698	18.9	-6.83×10^6	1.46	-4.67×10^6
55	64.6	3.30	0.207	0.0074	23.25	-8.87×10^6	1.46	-6.07×10^6
56	64.5	3.32	0.204	0.0075	23.35	-7.5×10^6	1.46	-5.13×10^6
57	63.8	3.03	0.191	0.00653	22.3	-8.85×10^6	1.45	-6.06×10^6
58	56.3	1.50	0.0887	0.00326	22.8	-2.43×10^7	1.43	-1.695×10^7
59	57.0	1.5	0.0884	0.00361	25.2	-2.28×10^7	1.43	-1.59×10^7
60	61.7	2.6	0.164	0.00633	33.35	-1.39×10^7	1.43	-9.73×10^6
61	61.9	2.4	0.153	0.0060	25.95	-1.365×10^7	1.43	-9.53×10^6

It is proposed to study carefully the effect on the evaporation rate of the natural circulation of water in the pan as well as the effect of the extraneous mixture circulation. The former effect will probably be very small or negligible.

The rate of diffusion of water vapor through quiet air was calculated using the analogy (*4*) of the electrical energy flow from a disk to the earth (*5*). The computed diffusion rate was approximately one-tenth of the measured evaporation rate (below the critical), indicating the effect of the natural and extraneous circulation of the mixture in the quieting chamber. For $Gr' \times Pr' \geq 0$ the mixture will tend to rise vertically above the pan carrying water vapor with it. However for $Gr' \times Pr' \leq 0$, mixture from infinity will fall vertically toward the pan and move horizontally outward as it reaches the interface, carrying water vapor with it. The floor was maintained, as nearly as was possible, at the temperature of the mixture far away.

It is presumed that the condensation rate—

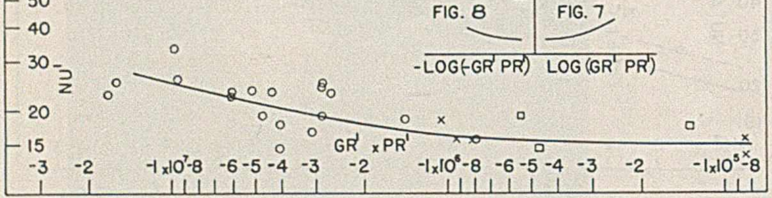

Figure 8. *Nu'* vs. *Gr'Pr'* for Evaporation from Horizontal Circular Surfaces

○ Evaporation, no rim
× Evaporation, 0.5-inch rim
□ Evaporation, 1.5-inch rim

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[1] Eddies have been observed to persist several hours after the door of the chamber has been closed.

Table I. Summary of Evaporation Results (*Continued*)

(Properties of air taken from International Critical Tables at arithmetic mean temperature; average relative humidity, 53 per cent; average air temperature, 71° F.; diameter of pan, 1 foot)

Run No.	t_w	$c_{vw} - c_{v\infty}$	$p_w - p_\infty$	e	Nu'	Gr'	Pr'	$Gr' \times Pr'$
	° *F.*	*Lb./cu. ft.* × 10^4	*In. Hg*	*Lb./sq. ft. hr.*				
				Runs with 0.5-Inch Rim				
62	92.8	17.2	1.164	0.0998	52.75	4.98×10^7	1.61	3.08×10^7
63	92.5	17.0	1.152	0.0962	51.35	4.93×10^7	1.595	3.09×10^7
64	92.2	16.7	1.135	0.0865	47.2	4.86×10^7	1.59	3.05×10^7
65	92.0	16.3	1.110	0.0850	47.2	4.80×10^7	1.58	3.04×10^7
66	91.8	16.2	1.101	0.0860	48.8	4.73×10^7	1.58	3.0×10^7
67	67.8	4.6	0.308	0.00833	18.6	-1.54×10^6	1.45	-1.06×10^6
68	68.0	4.8	0.292	0.00728	15.6	-1.17×10^6	1.45	-8.07×10^5
69	79.0	10.5	0.624	0.03395	32.63	2.09×10^7	1.45	1.44×10^7
70	78.95	9.5	0.620	0.0365	38.85	2.12×10^7	1.45	1.46×10^7
71	79.05	9.4	0.622	0.0365	39.25	2.16×10^7	1.45	1.49×10^7
72	79.4	9.5	0.631	0.0370	39 25	2.19×10^7	1.45	1.51×10^7
73	79.45	9.5	0.626	0.0367	40.2	2.19×10^7	1.45	1.51×10^7
74	79.5	9.5	0.624	0.0331	35.2	2.22×10^7	1.45	1.53×10^7
75	79.6	9.8	0.648	0.0334	34.25	2.25×10^7	1.45	1.55×10^7
76	68.0	4.7	0.300	0.00728	15.9	-1.35×10^6	1.45	-9.32×10^5
77	68.3	4.9	0.312	0.0065	13.65	-1.22×10^5	1.45	-8.42×10^4
78	68.5	4.9	0.314	0.00758	15.85	-1.22×10^5	1.45	-8.42×10^4
79	72.4	6.4	0.414	0.02095	38.5	7.58×10^6	1.45	5.23×10^6
80	72.5	6.4	0.414	0.01795	28.63	7.58×10^6	1.45	5.23×10^6
81	72.4	6.3	0.407	0.0174	28.2	7.58×10^6	1.45	5.23×10^6
82	72.4	6.3	0.406	0.0159	25.7	7.58×10^6	1.45	5.23×10^6
83	74.4	6.9	0.450	0.0246	36.3	1.11×10^7	1.44	7.62×10^6
84	74.7	7.0	0.459	0.0241	34.9	1.168×10^7	1.44	8.09×10^6
85	74.9	7.3	0.476	0.02295	31.95	1.20×10^7	1 44	8.34×10^6
86	75.1	7.4	0.478	0.0235	32.2	1.218×10^7	1.44	8.45×10^6
87	71.2	5.7	0.367	0.0181	32.4	5.04×10^6	1.44	3.5×10^6
88	71.1	5.8	0.367	0.0144	25.4	4.33×10^6	1.44	3.0×10^6
89	70.7	5.6	0.359	0.0124	22.63	4.15×10^6	1.44	2.88×10^6
90	70.9	5.8	0.369	0.0127	22.35	4.51×10^6	1.44	3.13×10^6
91	70.6	5.7	0.362	0.0114	20.5	3.97×10^6	1.44	2.76×10^6
				Runs with 1.5-Inch Rim				
92	87.9	13.3	0.903	0.0673	48.7	3.8×10^7	1.53	2.48×10^7
93	87.9	13.4	0.907	0.0668	47.9	3.82×10^7	1.53	2.50×10^7
94	87.7	13.2	0.897	0.0657	47.75	3.79×10^7	1.53	2.47×10^7
95	87.6	13.2	0.883	0.0638	46.95	3.79×10^7	1.515	2.50×10^7
96	68.5	4.9	0.315	0.00828	17.35	-1.935×10^5	1.46	-1.33×10^5
97	68.4	4.7	0.307	0.0067	14.65	-6.83×10^5	1.46	-4.68×10^5
98	80.5	9.6	0.641	0.0463	48.65	2.34×10^7	1.47	1.6×10^7
99	80.7	9.6	0.638	0.0387	40.5	2.44×10^7	1.47	1.67×10^7
100	80.8	9.7	0.644	0.0331	34.5	2.48×10^7	1.47	1.69×10^7
101	80.3	9.5	0.625	0.0331	35.15	2.35×10^7	1.47	1.61×10^7
102	80.9	9.6	0.635	0.0407	42.7	2.46×10^7	1.47	1.68×10^7
103	80.8	9.4	0.626	0.0378	40.5	2.40×10^7	1.47	1.64×10^7
104	68.7	4.8	0.315	0.00908	19.35	-7.82×10^5	1.44	-5.43×10^5
105	69.4	5.1	0.331	0.00683 0.00793	13.75 15.98	0	1.44	0
106	69.8	5.4	0.344	0.01145	21.7	5.375×10^5	1.44	3.73×10^5
107	74.4	7.3	0.475	0.0269	37.2	1.23×10^7	1.45	8.49×10^6
108	74.6	7.5	0.489	0.0237	32.2	1.40×10^7	1.45	9.67×10^6
109	75.3	7.8	0.507	0.0244	31.85	1.385×10^7	1.45	9.55×10^6
110	75.3	7.9	0.512	0.0248	31.95	1.43×10^7	1.45	9.87×10^6
111	79.4	9.6	0.632	0.0406	42.8	2.17×10^7	1.45	1.495×10^7
112	79.6	9.7	0.639	0.0428	44.6	2.22×10^7	1.45	1.53×10^7
113	79.9	9.8	0.644	0.0402	41.45	2.295×10^7	1.46	1.57×10^7

concentration difference curve will have a slope somewhere between the two unit-evaporation-rate lines. This portion of the curve is shown dotted on Figure 6, and no experimental data were available to the authors upon which to base the prediction.

Thermal Free Convection–Diffusional Free Convection Correlation

Figures 7 and 8 indicate the two boundary moduli, Nu and Nu', for heat transfer and evaporation, respectively, as a function of $Gr' \times Pr$ and $Gr' \times Pr'$, respectively. The physical constants which appear in these moduli were evaluated at the arithmetic mean temperature of the surface and far away. The coefficient of viscosity, μ, the specific heat at constant pressure, C_p, and the thermal conductivity, k, of dry air were used with a resultant error due to water vapor of approximately 1 per cent or less in each case. The density of the mixture was calculated as that of air with a 75 per cent relative humidity and at the arithmetic mean temperature. The diameter of the pan was chosen as the significant dimension. The function $\phi\ (Gr', Pr')$ was assumed to be of the form $\phi_1\ (Gr' \times Pr')$, implying that the inertia forces have been considered negligible compared with the viscous forces (*10*).

In the upper corner of Figures 7 and 8 a legend is shown indicating the portions of the curves which are being represented on the particular figure. The boundary modulus for evaporation, Nu', was computed from the experimental evaporation data. The heat-flow boundary modulus, Nu, was obtained by multiplying the experimental results presented by ten Bosch (*1*) for a vertical plate by 1.2 as recommended by the same author (*2*). This procedure does not conform with the suggestion of Wiese (*10*). He found that Nusselt's modulus for a free vertical plate was 20 per cent higher than for a free horizontal plate; heat transfer occurred on both sides, and the edges were also effective in heat transfer.

Figure 7 indicates that in a certain limited range the following empirical equations may be written:

Evaporation: $Nu' = 0.53\ (Gr' \times Pr')^{0.26}$ (3)
where $10^6 < Gr' \times Pr' < 10^8$
Heat flow: $Nu = 0.68\ (Gr' \times Pr)^{0.26}$ (4)
where $10^6 < Gr' \times Pr < 10^8$
and $Nu = 1.29\ Nu'$ (5)

The ratio of Nu/Nu' noted in Equation 5 may be compared with $Nu/Nu' = 1.06$ obtained by Hilpert (*6*) on vertical moist clay plates. The approximate equality of Nu and Nu' implies that the effective film thickness for heat transfer and evaporation are of the same order of magnitude.

Ten Bosch also presents experimental data which lie along a "theoretical line," the latter being some 20 per cent under the curve used in the computation of the coefficients and exponents of Equation 4. Should further experimentation indicate the lower curve to be correct, Nu will be but slightly higher than Nu'.

The upper curve of Figure 7 indicates that Nu' is approximately constant for $Gr' \times Pr' \leq 10^4$. The result indicates that within this range the weight film conductance, h', may be expected to vary inversely as the diameter of the pan. Further experimental data on this point will be sought. For a particular pan and $Gr' \times Pr' \leq 10^4$, the unit evaporation rate should then vary linearly and directly with the concentration difference.

As noted earlier in the discussion, $Gr' \times Pr'$ is equal to 0 at a water surface temperature determined experimentally as 69.4° F. (calculated as 68.7° F.) for which the densities of the mixtures at the surface and far away are equal.

The variation of Nu' with $Gr' \times Pr'$ for negative values of $Gr' \times Pr'$ is shown in Figure 8, which indicates that Nu' is approximately constant. The evaporation rates measured for water surface temperatures under 70° F. are somewhat uncertain, and the corresponding results are to be considered only as generally indicative of trends.

The dissimilarity of the processes of heat transfer and evaporation is shown graphically in Figure 9; pertinent variables for each process are plotted against the surface

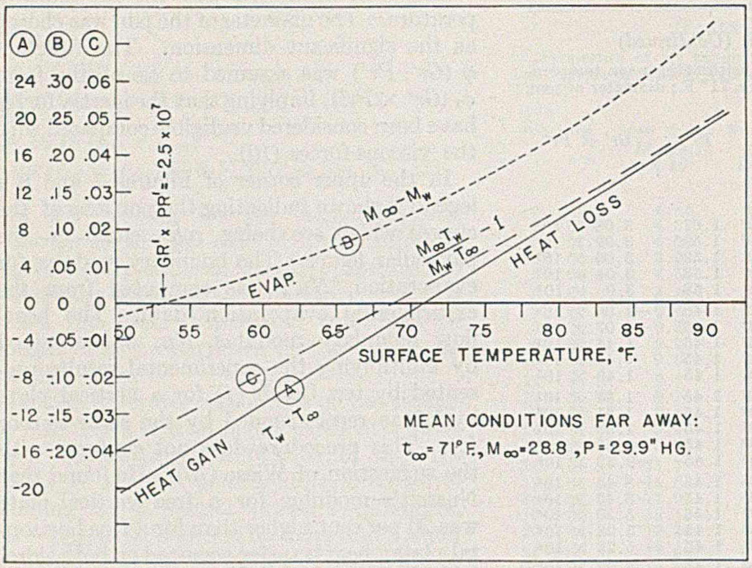

FIGURE 9. $(T_w - T_\infty)$, $(M_\infty - M_w)$, AND $\left(\frac{M_\infty T_w}{M_w T_\infty} - 1\right)$ *vs.* SURFACE TEMPERATURE (t_w)

temperature, t_w. For heat transfer alone *Gr* varies directly with $(T_w - T_\infty)$, *Gr'* varies directly with $(M_\infty - M_w)$ for isothermal evaporation, and *Gr'* varies directly with $\left(\frac{M_\infty T_w}{M_w T_\infty} - 1\right)$ for nonisothermal evaporation. For magnitudes of *Gr'* near or below 0 (t_w = 53° to 71° F. in Figure 9), heat transfer and diffusion occur in opposite directions with respect to the surface. For the experimental conditions of this investigation the change in direction of heat transfer alone occurs at 71° F.; that of isothermal evaporation occurs at 53° F. (the dew point). When both processes occur simultaneously, heat transfer and diffusion are in opposite directions for *Gr'* approximately between 0 and -2.5×10^7.

The weight film conductance per unit area for evaporation is plotted in Figure 10 against the dimensionless ratio $\left(\frac{M_\infty T_w}{M_w T_\infty} - 1\right)^{1/4}$. In a similar way, for only heat transfer by free convection the thermal film conductance per unit area is often plotted against the temperature difference to the quarter power.

Three additional incidental comments will be made. During preliminary tests a copper pan and distilled water were used. A scum, just visible to the eye, forming on the water surface would result in an evaporation rate double that obtained before the formation of the scum.

Several runs were made in which the rim height was changed to 0.5 and 1.5 inches. In both cases the lower boundary (floor) was kept at the level at the top of the rim and the water depth was kept constant. No appreciable changes in the evaporation rates were noted. This result is contrary to those reported by Stefan (*9*) for 0.64–6.16 mm. diameter tubes and large ratios of rim height to diameter. The transient evaporation rate was found by him to be inversely proportional to the depth (range, 0–44 mm.) of the fluid in the tube. It is proposed to repeat these runs and to increase the rim height by steps to one and a half times the pan diameter.

The experimental results cited in this paper are presented as tentative. Extraneous air motion due to temperature gradients across the quieting chamber and eddies at the open end caused increased evaporation rates over those which would result due to free evaporation only.

The foregoing discussion has been written in terms of the generalized variables (moduli) of heat transfer and diffusion. In many cases, however, reference has been made to the specific fluids, the diameter of the pan, humidity far away, and certain temperatures which obtained throughout the tests or which apply only to the system under observation. It is hoped that further experimentation with other fluids, with a variation of the humidity far away and other geometrical shapes, will indicate that the use of the generalized variables has been justified. Such generalization has proved satisfactory in the cases of forced convection and of forced convection and forced diffusion (*3*, *7*).

Acknowledgment

The authors wish to express thanks to G. H. Hickox for the design of the evaporimeter and the quieting chamber and for the preliminary organization of the project; to H. S. Gordon, C. W. Quentel, and W. Hand for their help in collecting data; to W. F. Pemberton for his assistance in constructing the apparatus; to V. H. Cherry for analytical guidance, to M. P. O'Brien for suggestions and encouragement; and to the Civil Engineering Department, C. Derleth, Jr., chairman, for the use of an air-conditioned room. NYA and WPA assistance was available for portions of the project.

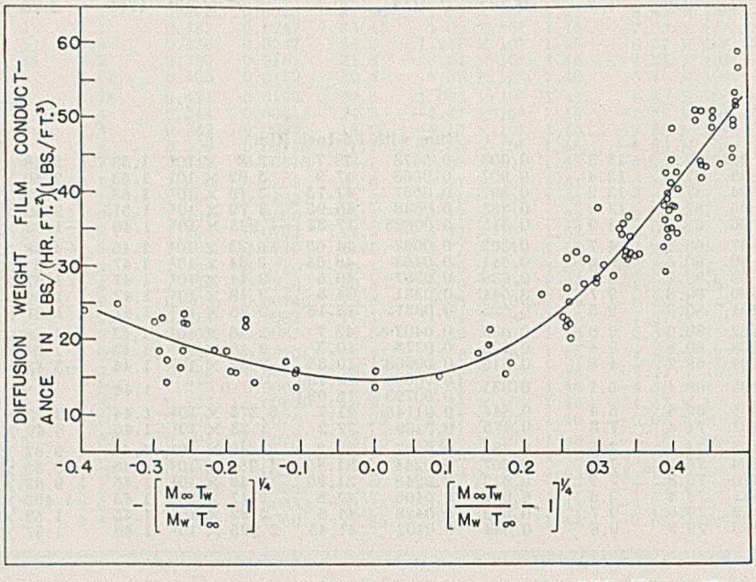

FIGURE 10. DIFFUSION WEIGHT FILM CONDUCTANCE *vs.* $\left[\frac{M_\infty T_w}{M_w T_\infty} - 1\right]^{1/4}$

Nomenclature

α = thermal diffusivity, ft. sq./hr. = $k/\rho C_p$
α' = diffusion coefficient, ft. sq./hr.
C_p = sp. heat at constant pressure, B. t. u./(lb.) (° F.)
ρ = weight density, lb./cu. ft.
c = concentration, lb./cu. ft.
D = diameter of pan, ft.
e = unit evaporation rate, lb./(sq. ft.) (hr.) = $h'(c_{vw} - c_{v\infty})$
g = gravitational constant, ft./hr.² = $32.2 \times 3600 \times 3600$
h = thermal film conductance per unit area, B. t. u./(hr.) (sq. ft.) (° F.)

h' = diffusion weight film conductance per unit area, $\frac{\text{lb.}}{[(\text{hr.})\ (\text{sq. ft.})]\ [\text{lb./cu. ft.}]}$
k = thermal conductivity, $\frac{\text{B. t. u.}}{[(\text{hr.})\ (\text{sq. ft.})]\ [^\circ\ \text{F./ft.}]}$
M = apparent mol. weight of air and water vapor mixture = $28.95 - 10.93\ p_v/P$
μ = coefficient of viscosity, lb./(hr.) (ft.) = for example, $0.43 \times 10^{-6} \times 32.2 \times 3600$
p_v = partial pressure due to water vapor, in. of Hg
P = total pressure of mixture, in. of Hg
T = absolute temp., ° F. abs.
Δt = temp. difference between air–water vapor side of gas-liquid interface and far away, ° F.

Subscripts:
w = surface of water in contact with water-mixture interface
∞ = mixture far away
v = water vapor

Generalized variables:
Gr = Grashof modulus, ensuring similarity of velocity fields in free convection = $\frac{D^3\rho^2 g}{\mu^2}\left[\frac{\Delta t}{T_\infty}\right]$
Gr' = Grashof modulus prime, applicable to diffusion = $\frac{D^3\rho^2 g}{\mu^2}\left[\frac{M_\infty\ T_w}{M_w\ T_\infty} - 1\right]$
Nu = Nusselt modulus, ensuring similarity of boundary conditions on the fluid side of a fluid-solid boundary = (hD/k)
Nu' = Nusselt modulus prime, applicable to diffusion = $(h'D/\alpha')$
Pr = Prandtl modulus = $C_p\mu/k = \mu/\alpha\rho$
Pr' = Prandtl modulus prime, applicable to diffusion = $\mu/\alpha'\rho$

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Rate of Evaporation from a Free Water Surface by a Perpendicular Air Stream

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Circular water surfaces of areas ranging from 0.05 to 0.37 square foot have been subjected to a perpendicular air stream having velocities from 3 to 15 feet per second [corresponding to mass velocities, G, of approximately 800–4000 pounds/(square foot) (hour)]. Tests at prevailing room temperature and humidity and at the lower velocities gave evaporation coefficients [k' = pounds evaporated/(square foot) (hour) (unit humidity difference)] which were about 50 per cent greater than the accepted coefficients for evaporation of water to an air stream flowing parallel to the surface. At the higher velocities the coefficients were about 10 per cent above those obtained with parallel flow by Lurie and Michailoff but 30 per cent below those obtained by Shepherd, Hadlock, and Brewer. No explanation of this anomalous situation at the higher velocities is offered.

The coefficients were found to fall on a line having the equation: $k' = 1.42\ G^{0.37}$. The heat transfer coefficient in this case of forced convection is given as $h_c = 0.37\ G^{0.37}$.

Tests with air streams at 125°, 175°, and 225° F. gave the same evaporation coefficients as the tests at room temperature. Coefficients in still air were only about 2 per cent of those at the lowest air velocity. In a limited number of drying tests on Celotex insulating board, the evaporation coefficients during the constant rate period were substantially the same as those for water under the same conditions.

THE drying of solids is usually considered as occurring in two major stages: (1) a constant rate period, followed by (2) a falling rate period. In the first period, during which evaporation of liquid takes place at the surface of the solid, the rate of drying is assumed to be limited by the rate of diffusion of vapor through a surface gas film into the main body of the gas. During the second period the rate of drying will be lowered as a result of the progressive decrease in wet area of solid exposed to the gas stream and of the resistance to diffusion of liquid or vapor from the interior to the surface. The fraction of the total drying time which is devoted to each of these periods varies over a wide range for different materials, depending upon such things as the porosity of the material being dried and the completeness with which the moisture can be removed by mechanical means previous to the drying operation. Inasmuch as the rate of vapor diffusion through a gas film is important as applied to the operation of drying, a number of studies have been made of the effect of certain variables on this rate. Many of these studies have, for convenience, involved evaporation from a free water surface, and it is generally assumed that the factors affecting the rate of evavoration in that case are very similar to those affecting the rate of drying of a surface completely wet with water. This assumption is supported by experiments reported by Sherwood (*14*) and by Shepherd, Hadlock, and Brewer (*13*) in which rates of evaporation from a water surface agreed well with rates of drying of various materials under comparable conditions.

One factor of great practical significance is the velocity of the gas stream parallel to the surface of the solid or the water surface, and recent summaries (*8, 15*) show reasonably satisfactory agreement in the results of a number of investigators concerned with vaporization from a free water surface. Another significant factor is the direction of the air stream relative to the surface at which evaporation is taking place. An early investigation of this factor by Carrier (*1*) was apparently intended to be applied to heat transfer to the wick of a wet-bulb thermometer. However, his results have often been interpreted as showing that the rate of drying by a stream of air striking a surface perpendicularly is somewhat more than double the rate obtainable with a parallel flow of the same velocity, other conditions being the same. Rates of the same order as those reported by Carrier have also been obtained by Coffey and Horne (*2*) in tests on a large slat-packed humidifying tower. Their tests have recently (*8*) been referred to as confirming Carrier's results, but on examination it appears that virtually all of the wetted surface of their tower was exposed to a parallel flow of air.

An effect of the magnitude indicated by Carrier's results is certainly of importance in the design of drying equipment, but until recently no drying experiments taking air direction as a major variable have been carried out. The recent work of Kamei, Mizuno, and Shioni (*7*), in which the effect of air direction on the rate of drying of clays was studied, showed that perpendicular flow was only slightly more effective than parallel flow. Their results will be discussed later in this paper. There are, however, several types of commercial dryers which employ air streams directed perpendicularly at the material being dried by means of jets. Veneer board, for example, is satisfactorily dried in this way. No data have been published comparing practical drying rates in such equipment with those obtained in equipment utilizing parallel air flow.

A stream of air approaching a surface perpendicularly can readily be visualized as being converted into a stream flowing essentially parallel to that surface as it reaches the surface. It is reasonable to expect a somewhat greater rate of evaporation than at the same velocity in purely parallel flow, because of the turbulence caused by the impact of the air stream; but the necessity that the flow must become parallel to the surface might well result in the rates of evaporation in perpendicular and in parallel flow being not greatly different. It appeared to the authors, therefore, that a set of experiments, involving evaporation from a free water surface by a stream of air striking perpendicularly, would permit a valuable comparison with the well-established results obtained when the air stream flows parallel to such a water surface. It was realized that the dimensions of the surface and the position with respect to the air stream affected the rate of evaporation, as shown by Himus (*5*) for water surfaces and by Powell and Griffiths (*11*) for cloth forms. The results in this paper, therefore, apply particularly to the case of a stream of air emerging from a duct of circular cross section and impinging on circular water surfaces of several sizes.

Apparatus

The experimental equipment (Figure 1) consisted of a vertical galvanized steel pipe, *B*, 6 inches in diameter and 17 feet long, at the upper end of which was attached a blower, *A*, capable of giving an average air velocity down the pipe as high as 15 feet per second. Electrical heating elements, *G*, were installed 4 feet from the upper end of the pipe, and 6 feet below this the pipe was packed with thin metal tubes, *H*, 2 inches in diameter and 2 feet long to act as straightening vanes. A laboratory watch glass, *C*, completely filled with water, was supported above a sensitive balance, *D*, by a rod 0.4 inch in diameter and 16 inches long, and placed so that the water surface was centered just 6 inches below the lower end of the pipe. Watch glasses 3 to 8.25 inches (7.5 to 21 cm.) in diameter were used in the tests. When the watch glasses were filled with water, surface tension raised the water surface slightly above the edge of the glass so as to make any edge effect practically negligible. The balance was protected from the air stream by a sheet metal shield having its apex 10 inches below the water surface.

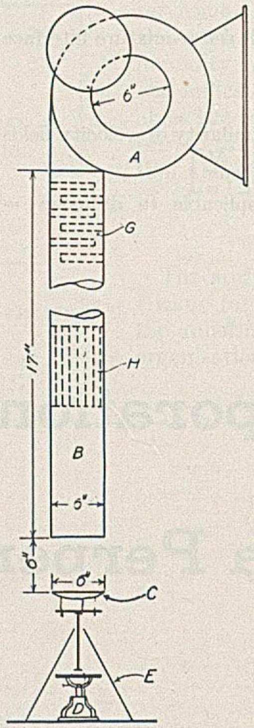


Figure 1. Evaporation Apparatus

The downward velocity of the air stream was controlled by an adjustable damper at the intake of the blower and was measured by a calibrated anemometer having a frame with an inside diameter the same as that of the pipe. This anemometer was checked at velocities up to 4 feet per second against a large commercial dry meter previously compared with a water-sealed gasholder. At higher velocities the experimental apparatus itself was used as a Thomas meter by measuring the electrical input and the temperature rise of the air stream. Comparing the results of these measurements with readings of the anemometer made at the same rate, but without electrical heat being supplied to the air stream, gave very satisfactory agreement with the results at lower velocities with the gas meter. It is believed that the air velocities, taken as an average over the cross section of the pipe, were measured with an error not exceeding 3 per cent.

Air temperature was measured by a shielded calibrated mercury-in-glass thermometer placed one foot above the lower end of the pipe. The humidity of the approaching air stream was determined by a sling psychrometer rotated in the vicinity of the blower intake and checked in the air stream at a high velocity before and after each run.

Procedure

Before beginning a run the full delivery of the blower was utilized while measurements of air humidity were made. The blower was then adjusted to give the desired air velocity. Measurements of the temperature of the water and air were then taken, the water temperature being found by immersing a calibrated thermometer. (At no time were variations in water temperature in different parts of the watch glass observed, although stirring of the water appeared to be very slight, even at the higher air velocities.) It was realized that the method did not reveal any possible difference between the temperature at the surface and the measured temperature of the main body of water. When air and water temperatures were constant, water at the same temperature as that in the watch glass was added to fill the watch glass completely. The time necessary for the evaporation of 1 to 5 grams of water, depending on the size of the watch glass being used, was then determined. A run at a given set of conditions was repeated at least once and sometimes several times until a satisfactory average value was obtained. For all runs with air at room temperature the measured rate of evaporation for an individual run showed deviations from the mean rate of that set of conditions amounting to 0.2–6.2 per cent, the average of these deviations being 2.6 per cent. At the higher air temperatures the observed times were shorter and conditions could be somewhat less closely controlled, making the deviations 0.2 to 17.0 per cent with an average of 4.0 per cent.

The partial pressure of water vapor in the air stream in any given run was not controlled but was that prevailing in the laboratory at the time. This was from 0.004 to 0.014 pound of water per pound of dry air (4.8 to 16.6 mm. partial pressure of water vapor), corresponding to 20–70 per cent of saturation at the average room temperature of 78° F. The air temperature was not controlled during the runs at room temperature, and ranged from 72° to 80° F.

Method of Calculation

MASS TRANSFER COEFFICIENT. The method of calculation can be illustrated by a typical test, No. 75. A watch glass 15 cm. (5.9 inches) in diameter was used, and the air velocity set at 9.35 feet per second as shown by the calibrated anemometer. The dry-bulb temperature of the air leaving the vertical pipe was 76.9° and its wet-bulb temperature 60.8° F., corresponding to a humidity of 0.0078 pound of water per pound of dry air. The water temperature during the run was 64.5° F., corresponding to a saturated humidity of 0.0130 pound per pound and making the humidity difference 0.0130 − 0.0078, or 0.0052 pound. The rate of evaporation was found to be 323 seconds per gram of water, equivalent to 0.129 pound evaporated per square foot per hour. Since this was accomplished with a driving force (here a humidity difference of 0.0052 pound of water per pound of dry air), the coefficient of evaporation or mass transfer, k', in the equation,

$$w = k'A\,(\Delta H) \tag{1}$$

where w = pounds of water evaporated per hour
k' = pounds of water evaporated per hour per square foot per unit of humidity difference
A = square feet of surface from which evaporation takes place
ΔH = humidity difference, pounds of water per pound of dry air

in this case equals 24.8 pounds/(hour) (square foot) (ΔH). (It should be pointed out that the humidity difference is somewhat more precisely expressed in terms of the partial pressures of water vapor. The use of the humidity unit introduces a small error when evaporation with a relatively large driving force is compared with evaporation with a small one. A comparison of the two extreme cases in the tests reported here shows that use of the humidity unit overstates the larger driving force relative to the smaller one by only 4 per cent. In all other cases the error is smaller; the use of the humidity unit was therefore considered sufficiently accurate for these experiments and expedited the calculations by permitting the use of an enlargement of a humidity chart, *19*.)

VELOCITY MEASUREMENT. It is well known that the velocity of a fluid flowing through a pipe of circular cross section is greatest at the axis of the pipe and decreases as the wall is approached. The average velocity of the air approaching the smallest of the watch glasses placed at the center of the air stream would therefore be appreciably greater than the average velocity of the air stream itself. In order to find the "effective" air velocity for each size of watch glass at a given average velocity for the 6-inch pipe as shown by the anemometer, velocity measurements were made at the end of the pipe, using a Pitot tube and a sensitive Wahlen micromanometer (*18*). Velocities were found at a number of points along two diameters at right angles. The average of the velocities for each set of four points at an equal distance from the pipe wall was then divided by the velocity at the axis; this ratio was plotted on a log-log scale against the ratio of distance from the pipe wall to the radius of the pipe, according to the method of Stanton (*16*). It was found that the velocity distribution at average air velocities of 6.1, 6.5, and 8.7 feet per second followed the line given by Stanton for the isothermal turbulent flow of air in a rough pipe, as shown by the anemometer. (Under the conditions of the experiment, turbulent flow would be expected at any velocity above 0.7 foot per second.) Similar runs at 15.9 and 17.9 feet per second conformed to the line given by Stanton for the isothermal turbulent flow of air in a smooth pipe. It was arbitrarily assumed that flows below 10 feet per second behaved as though the pipe were rough, and above this velocity as though the pipe were smooth. The velocities were then integrated over the area of each of the four watch glasses smaller than the pipe. For the velocities below 10 feet per second the effective velocity was found by multiplying the average velocity as shown by the anemometer by the resulting factors 1.23, 1.18, 1.14, and 1.01 for the 7.5-, 10-, 11.5-, and 15-cm. (2.95-, 3.9-, 4.53-, and 5.9-inch) watch glasses, respectively. Similarly, for velocities over 10 feet per second the corresponding factors were 1.15, 1.12, 1.096, and 1.01. (The uncertainty introduced by the assumption that the nature of the flow changed at about 10 feet per second is only 7 per cent for the 7.5-cm. watch glass, and less for all other sizes.) For the two watch glasses larger than the pipe diameter it was assumed that the descending air stream was distributed over their entire areas, giving factors of 0.644 and 0.527 for the 19- and 21-cm. (7.5- and 8.25-inch) watch glasses, respectively, for all rates of air flow.

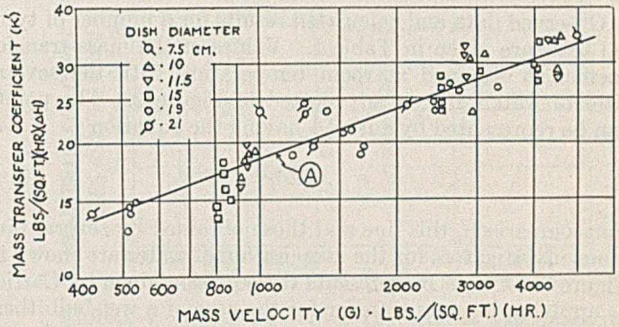


FIGURE 2. MASS TRANSFER FOR VARIOUS WATER SURFACES

By means of smoke tests, described later in this paper, it was found that there was little, if any, divergence of the air stream between the end of the pipe and the plane of evaporation. Such a divergence would have shifted the points in Figure 2 for the four sizes of watch glass smaller than the pipe to the left, relative to the points for the two larger sizes. The latter were presumably large enough to intercept the entire air stream. Figure 2 shows that if divergence occurred at all, its effect was within the over-all accuracy of the data, although an eightfold variation in evaporation surface was involved.

Applying the above method to the specimen calculation, in which the density of the air is 0.0735 pound per cubic foot and the average velocity 9.35 feet per second, gives a mass velocity of air approaching the 15-cm. watch glass as 9.35 × 3600 × 1.01 × 0.0735 or 2500 pounds per square foot per hour.

HEAT TRANSFER COEFFICIENT. The rate of vaporization of water can readily be used as a measure of the over-all

TABLE I. TYPICAL DATA AND RESULTS

Test No.	56	63	77	87	106	69	29	32	33	109	110	116
Watch glass diam., cm.	7.5	10	11.5	15	19	21	19	19	19	10[d]	19[d]	15[d]
Mass velocity of air, lb./(hr.)(sq. ft.)	4990	940	2870	4000	2500	2120	1430	1440	1440	4500	1620	790
Dry-bulb temp., ° F.	75.7	75.1	76.9	74.5	80.1	73.7	125.4	174.1	226.5	81.4	83.4	86.0
Wet-bulb temp., ° F.	55.9	55.5	60.9	54.3	59.5	55.15	77.9[c]	92.5[c]	101.0[c]	62.4	63.8	66.4
Water temp., ° F.	59.35	60.6	63.8	59.1	66.4	58.7	77.0	88.9	98.0	..[e]	..[e]	..[e]
Evaporation rate, sec./gram	877	912	530	231	186	170	137	94	61	400	176	380
Mass transfer coefficient k', lb./(hr.)(sq. ft.)(ΔH)[a]	34.6	17.5	27.4	29.6	24.5	23.6	18.2	17.5	16.4	..	..	..
Mass transfer coefficient k'', lb./(hr.)(sq. ft.)(ΔH)[b]	46.6	25.8	37.3	40.1	30.4	31.2	17.2	14.2	14.3	54.6	33.4	25.0
Temp. difference, ° F.	16.35	14.5	13.1	15.4	13.7	15.0	48.4	85.2	128.5	..	..	..
Over-all heat transfer coefficient h_t, B. t. u./(hr.)(sq. ft.)(° F.)	12.3	7.5	10.8	12.4	10.7	8.8	4.2	3.6	3.5	12.7[e]	8.0[e]	5.9[e]
Convection heat transfer coefficient h_c, B. t. u./(hr.)(sq. ft.)(° F.)	9.0	4.5	7.1	7.7	6.4	6.1	4.7	4.5	4.3			

[a] Based on measured water temperature.
[b] Assuming water at wet-bulb temperature.
[c] Calculated from psychrometer measurements at room temperature.
[d] Celotex disks.
[e] Surface assumed to be at wet-bulb temperature.

rate of heat transfer at the water surface according to the equation

$$w = \frac{h_t}{r_w} A(\Delta t) \qquad (2)$$

where h_t = over-all heat transfer coefficient, B. t. u./(sq. ft.) (hr.)(° F. temperature difference)
Δt = measured temperature difference between air stream and water, ° F.
r_w = latent heat of vaporization of water at the observed temperature of the water, B. t. u./lb.

The value of the over-all heat transfer coefficient, h_t, for the case being considered is $(0.129 \times 1055.7)/(76.9 - 64.5)$ or 11.0 B. t. u./(square foot) (hour) (° F.)

Mass Transfer Coefficients

Observed data and calculated results for a number of typical tests are given in Table I. Values of the mass transfer coefficient obtained at room temperature with the several sizes of watch glasses are plotted in Figure 2. The points can be represented by curve *A* having the equation

$$k' = 1.42\, G^{0.37} \qquad (3)$$

For comparison, this line and those obtained by several previous investigators for the evaporation of water are shown in Figure 3. Curve *B* represents the equation given by Carrier as applying to mass transfer for the case of a wet-bulb thermometer. While this curve was considered as applying to mass transfer under conditions of perpendicular air flow, it had not previously been tested. The present results indicate that it is reliable at the lower mass velocities but is about 50 per cent high at the higher mass velocities used in these experiments. Curves *C* and *D* illustrate the results obtained by Lurie and Michailoff (*8*) and Thiesenhusen (*17*) in the evaporation of water by air flowing parallel to a water surface. Curve *E* is recommended by Sherwood (*15*) for parallel air flow and is approximately the same as was found by Carrier for that case.

The most recent work in this field is that of Shepherd, Hadlock, and Brewer (*13*) who give curve *F* as a result of the correlation of their results on the drying of sand and the evaporation of water with parallel air flow with the results of a number of earlier investigators. This line shows the mass transfer coefficient as proportional to the 0.75 power of the mass velocity. This is close to the 0.8 power slope of curve *E* which is based on the assumption that the well-established variation of heat transfer coefficients with the 0.8 power of the mass velocity in similar circumstances should also apply to mass transfer coefficients. The data on evaporation of water represented by line *D* show the mass transfer coefficient as increasing only as the 0.5 power of the mass velocity.

There have been no previous experiments to determine the nature of the variation of mass transfer or heat transfer with mass velocity in perpendicular flow, but it appears that the slope may well be below the 0.8 value. A flow perpendicular to the axis of a cylinder may be considered as roughly equivalent to parallel flow on two sides and perpendicular flow on one face. Various cases of this sort showing lower powers could be cited. For example, Powell and Griffiths (*11*) found that evaporation from a cylinder was proportional to the 0.61 power of the mass velocity; Davis (*3*) found that heat was transferred from a wire in proportion to the 0.43 power of the mass velocity. McAdams (*9*) recommends the Reiher equation, in which the heat transfer coefficient is in proportion to the 0.56 power of the mass velocity, for the case of air flowing at right angles to a single cylinder. There appears, therefore, to be no reason to question the 0.37 power variation of mass transfer with mass velocity in perpendicular flow, as indicated by the results plotted in Figures 2 and 4.

There is uncertainty as to the variation of mass transfer coefficient with mass velocity in both parallel and perpendicular flow at mass velocities below 500 pounds/(hour) (square foot), corresponding to about 2 feet per second for air at ordinary conditions. Extrapolation of the equation given by Himus and Hinchley for evaporation in a current of air to zero velocity indicates a rate two-thirds as great as found at a mass velocity of 1000. Their equation for evaporation in "still" air, however, indicates a rate at zero velocity somewhat less than half as great as that at a mass velocity of 1000. In his later correlation of the same data, Himus gave an equation which, upon extrapolation to zero velocity, predicted a rate one-fourth as great as that at the above mass velocity. It has been suggested that free convection effects have a considerable influence on the rate of evaporation at the lower air velocities. Recently, careful work by Sharpley and Boelter (*12*) showed that the rate of evaporation to really still air is very small. Tests made by the authors with the 19-cm. watch glass in its usual position in a large laboratory without running the blower gave mass transfer coefficients ranging from 0.22 to 0.36 pound/(hour) (square foot) (ΔH). The average of the tests was 0.27, which was in good agreement with the value given by Sharpley and Boelter's Equation 1. This coefficient is about 2 per cent of those obtainable at the moderate mass velocity of 1000 with either parallel or perpendicular air flow; therefore free convection effects apparently cannot explain the appreciable rates of evaporation found at low air velocities.

A few drying experiments in which direction of air flow was varied have been reported by Kamei and co-workers (*7*). Mass transfer coefficients for these experiments cannot be calculated since the temperature at the surface of the clay being dried was not measured. However, a comparison of actual drying rates during the constant rate period indicates the effect of air direction. For example, in a series in which the mass velocity was 3500 pounds/(hour) (square foot), a test with air at 30° C. (86° F.) and 30 per cent relative humidity gave a 15 per cent higher rate with perpendicular flow than with parallel flow. Tests with air at 30° C. and 60 per cent relative humidity and 40° C. (104° F.) and 40 per cent relative humidity showed the drying rate to be 9 per cent greater with perpendicular flow. It was reported that some tests showed as much as a 30 per cent greater drying rate with perpendicular flow than with parallel flow under the same conditions.

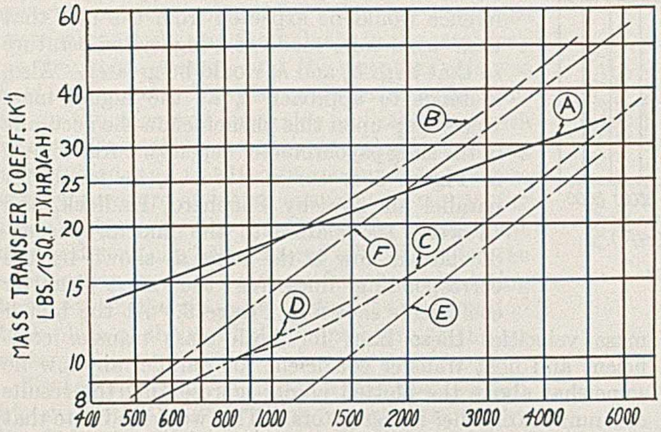


FIGURE 3. COMPARISON WITH RESULTS OF OTHERS

Kamei and co-workers suggested that the twofold difference between perpendicular and parallel flows to be expected from Carrier's experiments was not obtained by them because the porous clay surface held the water stationary, whereas different degrees of turbulence in a free water surface in the two cases might cause the difference to be more marked. However, the present experiments with water show at most a difference of only about 50 per cent at the lower air velocities, decreasing to about 10 per cent at the higher velocities, when compared with the results obtained with parallel flow by Lurie and Michailoff, for example. A comparison with the results obtained by Himus and Hinchley (*6*) and by Powell and Griffiths (*11*) could also be made, but as pointed out by Shepherd, Hadlock, and Brewer, such a comparison is of doubtful value. This is because in these two cases heat for vaporization of the water was supplied by submerged heating elements.

As shown in Figure 3, curve *A*, which represents results with perpendicular flow, actually crosses curve *F*, which represents the parallel flow results obtained both in drying sand and in evaporating water by Shepherd, Hadlock, and Brewer. A comparison of these two lines indicates that whereas perpendicular flow is about half again as effective as parallel flow at the lowest mass velocities, the former is only 70 per cent as effective as the latter at a mass velocity of 5000, for example. This anomalous situation at the higher mass velocities is not readily explainable, since a study of the data on which curves *A* and *F* are based does not reveal any reason for changing the position of either line. Results obtained in the drying of Celotex insulating board are reported later in the present paper, and they show that evaporation from a water surface or from a wet porous surface proceeds at practically the same rate.

It must therefore be concluded that the difference in drying rates, or mass transfer coefficients, between perpendicular flow and parallel flow conditions is not so great as has been thought. This is equivalent to saying that the Carrier equation (Figure 3, curve *B*) gives rates which are higher than those actually obtained over most of the range with perpendicular flow, whereas the Carrier equation for parallel flow, approximately the same as curve *E*, Figure 3, gives rates which are lower than those now accepted.

Mass Transfer Coefficients at Higher Temperature

Results of tests made at several air temperatures using the 19-cm. watch glass are plotted in Figure 4. The line shown has the equation

$$k' = 1.39\ G^{0.37} \tag{4}$$

which is practically the same as the line representing the results at room temperature shown in Figure 2. It would actually be expected that the coefficients obtained at the higher temperatures would be somewhat greater than those at room temperature, since the rate of vapor diffusion on a weight basis should be proportional to the square root of the absolute temperature of the fictive air film at the water surface. Assuming that this temperature is midway between that of the water and that of the air stream, the average film temperatures for tests at 75°, 125°, 175°, and 225° F. (Nos. 106, 29, 32, and 33 in Table I) are 73.2°, 101.2°, 131.5°, and 162.2° F. The square roots of the ratios of absolute temperatures thus indicate that the diffusion coefficient should be 2.6 per cent greater with the air stream at 125° than at 75° F. With the air stream at 175° F. the coefficient should be 5.3 per cent greater than at 75° F.; at 225° F. it should be 8.0 per cent greater than at 75° F. It is conceivable that the submerged thermometer bulb was affected by radiation from the heating element so as to show a higher temperature than that at the water surface. This error would have the effect of indicating a lower mass transfer coefficient than actually existed; it would account for the results at the higher temperature being somewhat lower than those at room temperature, rather than several per cent higher as might be expected. It cannot be claimed that the accuracy of the experiments is sufficient to establish that this small deviation from the expected results really exists.

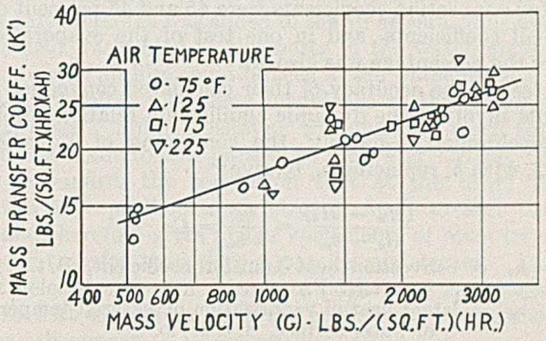


FIGURE 4. MASS TRANSFER AT VARIOUS TEMPERATURES

Heat Transfer Coefficients

Shepherd, Hadlock, and Brewer showed that results obtained in a number of investigations of the rate of evaporation of water and the drying of solids can be much better correlated by means of the convection heat transfer coefficient

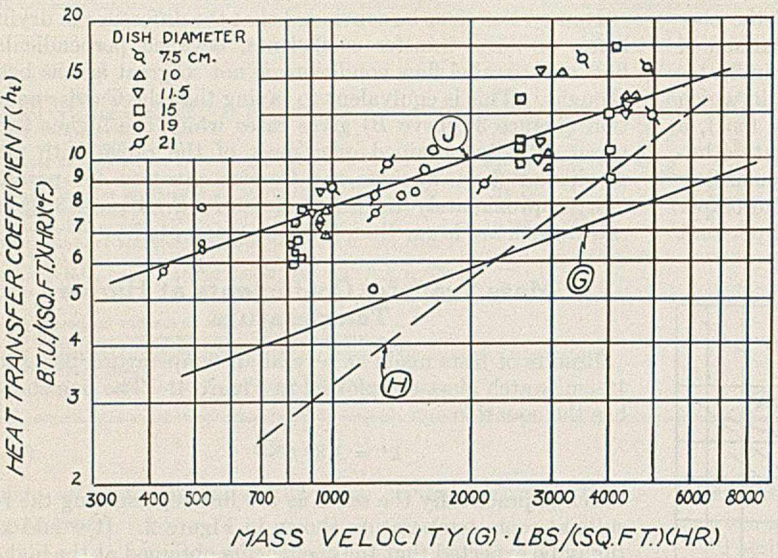


Figure 5. Heat Transfer for Various Water Surfaces

than by the usual mass transfer coefficient. They showed that a reliable convection heat transfer coefficient, h_c, can usually be obtained by deducting from h_t (the over-all coefficient) one coefficient, h_x, for heat transferred through the bottom and sides of the experimental vessel, and another, h_r, for the radiation of heat to or from the surface at which evaporation takes place. As would be expected, the difference between the over-all coefficients and the convection coefficient is particularly great when an uninsulated tray is used. In two such tests of the drying of sand their calculated convection coefficients were 45 and 46 per cent of the over-all coefficients, and in one test of the evaporation of water the percentage was also 45.

A test of the accuracy of their calculated convection coefficients involved the dynamic equilibrium relation employed in psychrometry—namely, the combining of Equations 1 and 2, with h_c replacing h_t, to give:

$$\frac{(H_w - H_a)}{(t_a - t_w)} = \frac{h_c}{k'r_w} = C \qquad (5)$$

where h_c = convection heat transfer coefficient, B. t. u. /(hr.) (sq. ft.) (° F.)

r_w = latent heat of vaporization of water at temperature of water surface, B. t. u. /lb.

Over fifty years ago the term C was shown by Ferrel (*4*) to be substantially constant, and the recent work of Mark (*10*) showed that h_c in B. t. u./(hour) (square foot) (° F.) divided by k' in pounds/(hour) (square foot) (humidity difference in pounds water per pound dry air), taking r_w as substantially constant over a considerable range of wet-bulb temperatures, is equal to 0.26. In almost all of the tests reported by Shepherd, Hadlock, and Brewer, the calculated values of h_c were such as to give very close to the expected value of this ratio when allowance was made for the different units used.

The over-all heat transfer coefficients obtained in the tests made by the present authors are shown in Figure 5. There appears to be a variation of this coefficient with the 0.33 power of the mass velocity. On the same figure curve G represents h_c so placed that at any given mass velocity the value is 0.26 times the corresponding value of the mass transfer coefficient k' shown by curve A in Figure 2. The equation for this curve is therefore:

$$h_c = 0.37\ G^{0.37} \qquad (6)$$

In view of the uncertainties involved in calculating h_c by deducting estimates of h_x and h_r from the observed over-all heat transfer coefficient in these experiments with uninsulated watch glasses, this method of basing h_c upon the observed values of the mass transfer coefficient is probably to be preferred.

In the room-temperature runs, h_c ranges from 56 to 60 per cent of h_t; these figures are slightly higher than those found by Shepherd, Hadlock, and Brewer with uninsulated trays. This difference would be expected from the fact that their tests were made at a higher temperature so that both h_x and h_r would be greater. Also, h_c tends to approach h_t at the higher mass velocities; upon this phenomenon the accuracy of the sling psychrometer depends. Also shown in Figure 5 is curve H for h_c as found for parallel air flow by Shepherd, Hadlock, and Brewer. Its relation to the line for perpendicular air flow is the same as shown by the corresponding lines for the mass transfer coefficients shown in Figure 3. At the higher mass velocities these lines for both mass transfer coefficient and heat transfer coefficient for parallel air flow lie somewhat above the plotted points representing the results of a number of other investigators. This would indicate that the difference in coefficients between perpendicular and parallel air flow at mass velocities of the order of 3000 and above is small. At a lower mass velocity perpendicular flow would be expected to give greater turbulence than parallel flow, making the difference between the coefficients such as shown in Figures 3 and 5. Evidence bearing on this point is given by Powell and Griffiths, who found that at a mass velocity of 1000 pounds/(hour) (square foot) the rate of evaporation from a cylinder was about 55 per cent greater than that from a plane of the same area with a parallel air flow. At a mass velocity of 3000 pounds/(hour) (square foot) the difference decreased to about 35 per cent.

Figure 6 shows the over-all heat transfer coefficients obtained with the 19-cm. watch glass at several temperatures. The value of this coefficient decreases with increasing air temperature, owing to the fact that the sum of h_x and h_r decreases and then becomes negative when heat is lost to the surroundings by convection from the unwetted surfaces and by radiation. With the air stream at 125° F. and a mass velocity of 5000 the temperature of the vessel of water is practically the same as that of the surroundings. Here h_t becomes equal to h_c. The intersection of the 125° F. line

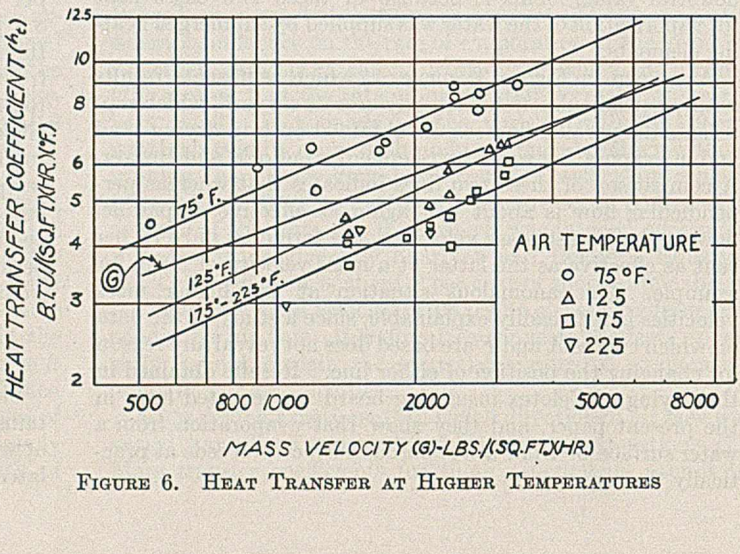
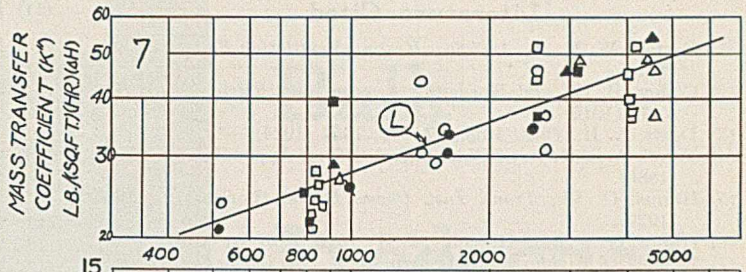


Figure 6. Heat Transfer at Higher Temperatures

at this point with curve G, representing the h_c calculated from the mass transfer coefficient, gives support to this method of calculation.



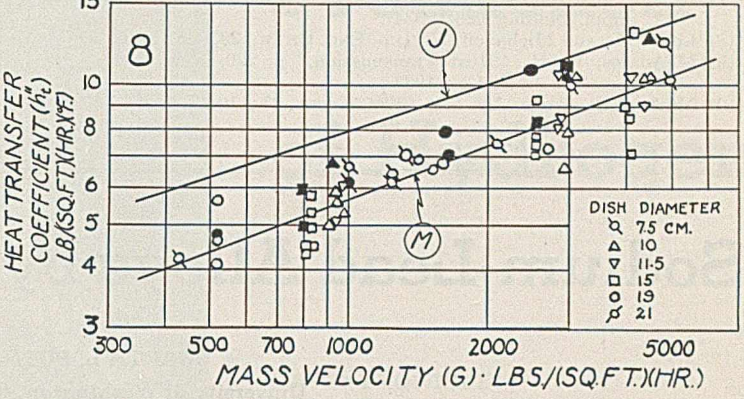


Figure 7. "Apparent" Mass Transfer for Water and Board

Figure 8. "Apparent" Heat Transfer for Water and Board

Drying of Insulating Board

The rate of drying of circular disks of Celotex (bagasse) insulating board of several sizes was also measured. This was done only at room temperature in the same way as was the rate of evaporation from a water surface, and data from several runs are included in Table I. The disks were supported over the balance in the same way as the watch glasses, and the smoother side was held uppermost. The disks were sealed with paraffin on the edge and lower side and saturated with water. Only the constant-rate period of drying was studied, and no attempt was made to measure the temperature at which evaporation was taking place. However, the mass transfer coefficients during drying can be compared with those for the evaporation from a water surface by calculating both sets on the assumption that the evaporation took place at the wet-bulb temperature of the air stream.

These "apparent" coefficients for water, termed k'', are plotted in Figure 7 and are represented by line L, having the equation

$$k'' = 2.17\ G^{0.37} \tag{7}$$

The black symbols represent the values of k'' obtained in the drying of the board. The agreement is sufficiently good, and it may be concluded, therefore, that substantially the same rates are found in the drying of insulating board and the evaporation of water by a perpendicular air stream. As previously mentioned, the drying rates of several materials by a stream of air flowing parallel to the surface have already been found to be of the same order as the rate for the evaporation of water.

A similar comparison can be made between the over-all heat transfer coefficients, again assuming that the evaporation took place at the wet-bulb temperature of the air stream. These apparent coefficients for the evaporation from a water surface, termed h_t'', are plotted in Figure 8, giving curve M. This plot also shows curve J, which represents the actual over-all heat transfer coefficient as found in Figure 5. The distance between these curves shows the extent to which the assumed temperature difference exceeds the one observed. As would be expected, the curves tend to approach each other at the higher air velocities. The black symbols in Figure 8 represent the apparent coefficients for the insulating board. These coefficients are substantially the same as those for water. However, at the higher air velocities they tend to approach the actual coefficients for water, indicating that the temperature at which water is evaporating from the board is closer to the wet-bulb temperature of the air stream than is the case for a free water surface. This would be expected in these room-temperature runs, since heat from the watch glass would be supplied through the water to the surface both by conduction and by convection, whereas the relatively low thermal conductivity of the insulating board would cause the heat flow through that material to be much smaller.

Nature of Air Flow

When this work was begun, it was assumed that a stream of air approaching a surface perpendicularly must be converted into a stream parallel to that surface. In the present experiments the air stream approaching the circular watch glasses or the circular disks of wallboard would be converted into a stream flow radially outward. A few qualitative experiments were made in which ammonia and hydrogen chloride were mixed in the air stream, and it was possible to observe the anticipated radial flow. Tests were also made in which only ammonia was added to the air stream while hydrochloric acid was added to the water in the watch glass. A slowly moving air film could be seen at the water surface, and this film exhibited increasing turbulence as the air velocity was increased. Similar behavior was observed when the air stream was made to flow parallel to the water surface. This tends to confirm the conclusion that at the lower mass velocities a perpendicular air stream causes greater turbulence and therefore gives higher coefficients of mass transfer and heat transfer than does a parallel air stream. At the higher velocities the turbulence in both cases is sufficiently great so that the difference in the coefficients becomes small and may disappear.

Conversion Factors

Coefficients for evaporation are expressed in the literature in a number of different units, and the following factors calculated to four significant figures are given for the use of those who need to make conversions from one unit to another. In using the humidity unit of driving force (pounds of water/pound of dry air) it is convenient, and usually sufficiently accurate, to take an average value for the partial pressure of air. A value of 750 mm. of mercury is used in calculating these factors. A coefficient of 1 pound/(hour) (square foot) (unit humidity difference in pounds water per pound air) is equivalent to a coefficient of

0.02106 lb./(hr.)(sq. ft.)(inch of mercury)
or 0.0008292 lb./(hr.)(sq. ft.)(mm. of mercury)
or 0.004048 kg./(hr.)(sq. m.)(mm. of mercury)
or 0.0_61125 g./(sec.)(sq. cm.)(mm. of mercury)
or 0.0004048 g./(hr.)(sq. cm.)(mm. of mercury)

Similarly, dry air under ordinary conditions (assume 25° C. and 760 mm. of mercury) having a mass velocity of 1 pound/(hour) (square foot) has a velocity of 0.003757 foot per second, or 0.001145 meter per second.

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Sodium-Lead Alloys by Carbon Reduction

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ALTHOUGH Castner (*3*) reported that the distillation of sodium (boiling point, 883° C.) from a sodium hydroxide–carbon mixture requires a temperature of 1000° C., Rossiter's patent (*6*) states that the reduction takes place at the surprisingly low temperature of 750° C., and that the sodium can be efficiently extracted from its solution in the melt. Halla and Tompa (*4*) showed that sodium reacts reversibly with sodium hydroxide to give a mixture of sodium hydride and sodium oxide.

Into wrought-iron crucibles, of 30-ml. capacity and with closely fitting covers, were placed charges consisting of 10 grams of lead, 10 grams of anhydrous sodium hydroxide, and 1.6 grams of pulverized petroleum coke (99.8 per cent carbon). Parallel experiments were made in which lead was omitted. The crucibles were heated to 750° C. in a calibrated electric resistance furnace until the evolution of hydrogen became negligible. The reduction proceeds according to the equation (*7*)

$$6NaOH + 2C \longrightarrow 2Na_2CO_3 + 2Na + 3H_2$$

As estimated by the relative sizes of the vigorously burning jets of hydrogen, lead did not lower the temperature of reduction. This was an unexpected result, since the heat of solution of one gram-atomic weight of sodium in an excess of lead is 39.1 kg.-cal. (*5*), a value greater than the heat of formation of an equivalent weight of water.

When the charge from which the lead had been omitted was dissolved in water, hydrogen was produced in volumes corresponding to a 3 per cent sodium content.

After being washed thoroughly with cold dilute nitric acid, the lead alloys were dissolved in 4 *N* nitric acid, evaporated to dryness, and analyzed for sodium by the zinc uranyl acetate method (*1*); it had previously been determined that large amounts of lead nitrate have little effect on the accuracy of the determination. Typical analyses were 4.31, 4.04, and 5.83 per cent sodium, corresponding to yields of about 50 per cent, based on the amount of sodium carbonate produced.

With 15-minute heating at 750° C., the conversion of sodium hydroxide to sodium carbonate was more than 90 per cent complete, as determined by phenolphthalein and methyl orange titrations. It is believed that the reason for the higher yields when lead was present was the exclusion of air from the alloy by the layer of molten sodium carbonate.

The carbonate of sodium was more difficultly reducible than the hydroxide. Uniform charges, consisting of 7.5 grams of anhydrous sodium carbonate, 2.5 grams of pulverized petroleum coke, and 25 grams of lead, were heated at 1000° C. The following results indicate that the reaction is a slow process:

Time of heating, hr.	0.25	1.0	4.0
Na found in alloy, %	0.01	0.38	0.79

With sodium carbonate, finely ground coke was a more efficient reducing agent than the coarse material. The reaction mixtures evolved small amounts of combustible gases when treated with water. These observations indicate that sodium can be held in solution at temperatures considerably above the boiling point of sodium and that the reaction proceeds in the stages (*a*) reduction of the carbonate and (*b*) combination of the alkali metal with lead.

All attempts to prepare alloys of the alkaline earth metals by carbon reduction of calcium oxide, barium carbonate, or strontium carbonate at 900° to 1100° C. were unsuccessful, the lead containing less than 0.01 per cent of the alkaline earth metal. However, potassium compounds were found more easily reducible than those of sodium.

Five to ten per cent sodium-lead alloys are used for the manufacture of tetraethyllead (*2*). As a simple method requiring a low capital investment, the Rossiter process might be found suitable for the production of sodium-lead alloys.

The author wishes to thank Kenneth A. Kobe for his very generous assistance and encouragement.

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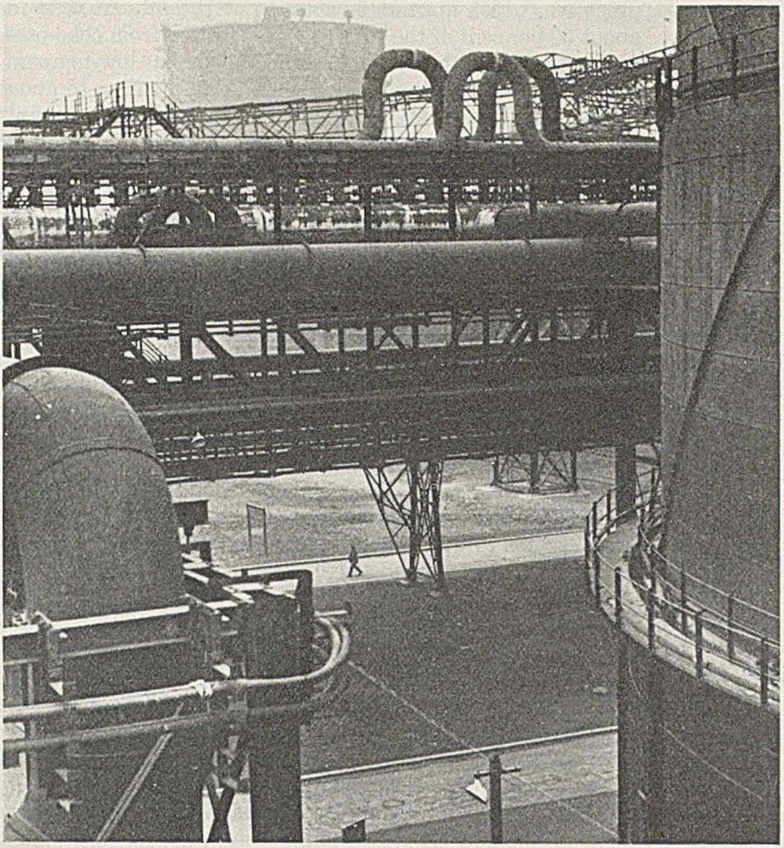

Billingham-on-Tees, Looking across Ammonia Avenue, with Gasholder for Water Gas in the Background

Bulk Production of Hydrogen

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BECAUSE of the vast developments in the synthetic nitrogen, hydrogenation, synthetic liquid fuel, soap and edible fat (margarine), methanol, and solvent industries, hydrogen has become, in recent years, one of the world's most important raw products. In this connection also the great advance of the synthetic ammonia process, the decline of the cyanamide process, the eclipse of electric arc methods, and the fact that the nitride process is not yet commercially feasible has had the result of increasing enormously the hydrogen demand for synthetic nitrogen. Probably also new commercial uses will be found, such as the operation of the internal combustion engine.

The following are the main reactions and methods that might theoretically be used for the production of hydrogen:

(1) Cold water and certain metals, such as sodium, potassium, and lithium:

$$2Na + 2H_2O = 2NaOH + H_2$$

(2) Cold water and a mixture of metallic sodium and aluminum silicide:

$$8Na + Al_2Si_4 + 18H_2O = 4Na_2SiO_3 + Al_2(OH)_6 + 15H_2$$

(3) Boiling water and the alkaline earth metals, magnesium, calcium, strontium, and barium:

$$Mg + 2H_2O = Mg(OH)_2 + H_2$$

(4) Boiling water and certain metals, such as zinc, covered with a film of copper (zinc-copper couple):

$$Zn + 2H_2O = Zn(OH)_2 + H_2$$

(5) Water at very high temperatures—for example, 572° F. (300° C.) or over—and finely divided iron, with the addition of catalysts if desired, although this is not necessary:

$$2Fe + 3H_2O = Fe_2O_3 + 3H_2$$

(6) Water at very high temperatures, 572–662° F. (300–350° C.), and finely divided carbon (coke), especially with the aid of catalysts:

$$C + 2H_2O = CO_2 + 2H_2$$

(7) Water on metallic hydrides, such as lithium and calcium:

$$Li_4H_2 + 4H_2O = 4LiOH + 3H_2 \text{ (Hydrolith process)}$$

(8) Steam and metals, or oxides of metals, at a high temperature such as iron borings heated to a bright red heat, over 1202° F. (650° C.):

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

(9) Steam and phosphorus (Liljenroth process):

$$P_2 + 5H_2O = P_2O_5 + 5H_2$$

(10) Highly superheated steam at about 1472° F. (800° C.) and sulfur vapor:

$$S + 2H_2O = SO_2 + 2H_2$$

(11) Steam, air, and metallic sulfides, such as zinc blende:

$$2ZnS + 4H_2O + O_2 = 2ZnO + 2SO_2 + 4H_2$$

(12) Dilute mineral acids and metals, such as sulfuric acid and zinc:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

(13) Boiling dilute sodium or potassium hydroxide solution and various metals, particularly aluminum, zinc, magnesium, and iron:

$$Zn + 2KOH = Zn(OK)_2 + H_2$$

(14) Boiling dilute sodium hydroxide solution and silicon or ferrosilica (Silicol process):

$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2$$

(15) Heating sodium hydroxide to a red heat with coal or coke:

$$4NaOH + C = Na_2CO_3 + Na_2O + 2H_2$$

(16) Heating alkaline salts of various organic acids, such as oxalic and formic:

$$Na_2C_2O_4 + 2NaOH = 2Na_2CO_3 + H_2$$

(17) Ignition of a mixture of powdered ferrosilicon and soda lime (Hydrogeint process of G. F. Jaubert, 1910):

$$Si + Ca(OH)_2 + 2NaOH = Na_2SiO_3.CaO + 2H_2$$

(18) Electrolysis of water, made acid or alkaline:

$$2H_2O = 2H_2 + O_2$$

(19) Complete gasification of carbonaceous material, such as coal, coke, and lignite, using a separate blast of steam and air, according to the water-gas reaction,

$$C + H_2O = CO + H_2$$
$$C + 2H_2O = CO_2 + 2H_2$$

or the producer-gas reaction, with the steam and air blast together, giving carbon monoxide and hydrogen mixed with nitrogen, and separating the hydrogen by various methods such as treatment of the water gas with steam and removal of the carbon dioxide:

$$CO + H_2O = CO_2 + H_2$$

(20) Separation of hydrogen by very low temperatures and moderate pressures to give fractional liquefaction from the complicated mixed gases obtained by the carbonization of coal, lignite, and other carbonaceous material, especially coke-oven gas, at low, high, or medium temperatures.

(21) Cracking of hydrocarbon gases, such as petroleum gases, natural gas, and carbonization gas, at very high temperatures, where the simple reaction is:

$$CH_4 = C + 2H_2$$

(22) Heating hydrocarbon gases, especially natural gas (mostly methane) mixed with steam, to high temperatures such as 932–1832° F. (500–1000° C.) in the presence of catalysts (such as nickel), with the formation of carbon dioxide and hydrogen. The main simple reaction is:

$$CH_4 + H_2O = CO + 3H_2$$

followed by

$$CO + H_2O = CO_2 + H_2$$

The carbon dioxide is then scrubbed out with water or dilute alkali under pressure or with organic amines in solution in water.

(23) Action of the electric spark on compressed acetylene:

$$C_2H_2 = 2C + H_2$$

(24) Electrolytic processes in which hydrogen is a by-product, such as the electrolysis of salt (sodium chloride) solution for the manufacture of bleaching powder.

(25) Bacteriological processes in which hydrogen is a by-product, such as the manufacture of acetone and butyl alcohol from starch jelly by the Fernbach bacteria, where the gases evolved are hydrogen, carbon dioxide, and a small proportion of nitrogen.

Obviously most of these reactions and methods are of no practical importance for the bulk production of hydrogen, chiefly because of the net cost of manufacture. Thus in many cases the raw products are too high in price or the hydrogen is so impure, as in the case of the action of acids upon metals, that an elaborate and expensive system of purification would be necessary.

Three methods are used for almost the entire world commercial production of hydrogen: (*a*) total gasification of coal, coke, and lignite by the water-gas and producer-gas processes, which appears to account at the present time for about 55 per cent of the total; (*b*) separation from coke-oven gas by the use of the Linde, Claude, and similar low-temperature compression liquefaction plants, corresponding to about 26 per cent of the total; and (*c*) electrolyis of water, amounting to about 16 per cent, leaving 3 per cent for all other methods. These include electrolysis of salt solution, fermentation, cracking of petroleum gases, natural gas, and coke-oven gas, and the action of steam on iron or iron oxide. Since 1925 there has been a decline in the production of hydrogen from water gas, a rapid rise in the production from coke-oven gas, and a slow increase in the use of electrolysis. About 1925 nearly 90 per cent of the total amount of hydrogen for all purposes came from water gas.

Several other processes, however, have valuable possibilities for the manufacture of hydrogen although they have not yet reached the stage of commercial success. For example, commencing about 1911, Friedrich Bergius studied the action of liquid water at 572–662° F. (300–350° C.) upon finely divided carbon or iron, using an autoclave. At 572° F. water begins to act rapidly upon carbon, forming carbon dioxide and hydrogen, and also upon iron:

$$2Fe + 3H_2O = Fe_2O_3 + 3H_2$$

The action is helped by catalysts, such as thallium chloride, a film of copper on the iron, ferrous chloride, and various copper, nickel, or platinum salts; the results obtained were very promising.

An interesting process for the synthetic nitrogen industry is the Liljenroth; steam acts on phosphorus to form very pure hydrogen, along with phosphorus pentoxide. The latter is dissolved in water to give phosphoric acid which is easily converted to phosphate fertilizers.

Equally interesting is the action of steam at 1472° F. (800° C.) on sulfur vapor. The sulfur dioxide is removed from the hydrogen by scrubbing with ammonia solution, forming ammonium sulfite; the latter is then oxidized to ammonium sulfate, ready for sale along with the synthetic ammonia.

Hydrogen from Water Gas

Water gas is generally made from coke, anthracite, bituminous coal, or lignite, using an alternate "blow" of about 2 minutes with air and a "run" of 5–6 minutes with steam. The endothermic water-gas reaction in the latter case is

$$C + H_2O = CO + H_2$$

but the temperature has to be maintained higher than about 1652° F. (900° C.) because below this point the reaction

$$C + 2H_2O = CO_2 + 2H_2$$

begins to predominate. Even at very high temperatures such as 2012° F. (1100° C.), there is always some formation of carbon dioxide according to the latter equation. For example, the following is the average composition of the water gas using coke at various temperatures in the fuel bed:

Temperature		Steam Decomposed	Compn. of Gas		
			H_2	CO	CO_2
° *F.*	° *C.*	%	%	%	%
1523	828	41.0	62.0	15.1	22.9
1751	954	70.2	53.5	39.7	6.8
1850	1010	94.0	48.8	49.7	1.5
2057	1125	99.4	50.9	48.5	0.6

After the blow with air, the bed is incandescent at about 1832–2012° F. (1000–1100° C.), but when the run with steam commences, the temperature immediately begins to drop. Consequently, after about 5–6 minutes it is necessary to stop the run before the figure falls lower than about 1742° F. (950° C.) and resume the blow with air for about 2 minutes to restore the temperature by combustion of part of the fuel bed:

$$C + O_2 = CO_2$$

The very hot blow gas, carbon dioxide and nitrogen with a small amount of carbon monoxide, is discharged separately.

The lower temperature reaction ($C + 2H_2O = CO_2 + 2H_2$) with simple removal of the carbon dioxide from the hydrogen by water scrubbing cannot be used on a commercial scale because the speed of the reaction is too slow. In the producer gas process the solid fuel is blown continuously with a mixture of air and steam, which means that all the nitrogen of the air remains in the producer gas and results in a much lower heating value. The approximate average composition of commercial water gas made from coke—that is, blue water gas—and producer gas made from bituminous coal is as follows:

Composition	Water Gas %	Producer Gas %
CO	43.00	24.00
H_2	47.70	13.00
Hydrocarbons, satd.	0.35	1.75
Hydrocarbons, unsatd.	0.00	0.25
Total combustibles	91.05	39.00
CO_2	3.75	5.50
O_2	0.35	0.35
N_2 (by difference)	4.85	55.15
Total	100.00	100.00
Heating value (gross) B. t. u./cu. ft.	300	155

When water gas is made from anthracite, bituminous coal, and lignite, the only difference as compared with coke is a slight increase of saturated hydrocarbons and the addition of a trace of unsaturated hydrocarbons. In preparing hydrogen from water gas the dust is removed, along with any small amount of sulfur, by means of iron oxide or by other methods, such as the Thylox process or activated carbon. Steam is then added and the gas heated to 752–932° F. (400–500° C.) and passed over a catalyst, such as iron with a promoter to convert all the carbon monoxide into carbon dioxide ($CO + H_2O = CO_2 + H_2$). The carbon dioxide is then removed by scrubbing with water and the result, after drying, is a gas containing approximately 97 per cent hydrogen, 2 per cent carbon monoxide, and 1 per cent nitrogen, which is pure enough for hydrogenation and most other processes. If required, traces of carbon monoxide and nitrogen can be removed by additional processes.

For example, according to the older methods the gas can be passed through concentrated sodium hydroxide at 500° F. (260° C.) under a pressure of 50 atmospheres, or through soda lime at 572° F. (300° C.) to eliminate carbon monoxide. Modern methods are the use of ammoniacal cuprous formate or conversion to methane by the reaction:

$$CO + 3H_2 = CH_4 + H_2O$$

Nitrogen can be removed by passing the gas over heated calcium chloride.

For ammonia synthesis this total gasification method is particularly suitable because the 1-3 nitrogen-hydrogen mixture can be made direct. Thus water gas and producer gas (containing over 55 per cent nitrogen) are mixed in the correct proportions, giving a product of about 35–40 per cent carbon monoxide, 33–36 per cent hydrogen, up to 1 per cent hydrocarbons, 3–5 per cent carbon dioxide, and 22–23 per cent nitrogen. This product is mixed with steam and passed over the iron catalyst, and the carbon dioxide is removed by water scrubbing; after drying, the correct 1-3 nitrogen-hydrogen proportion is left, and any remaining traces of impurities can be removed.

About 55 per cent of the world's hydrogen is believed to be produced by this total gasification method. It is used at the largest Haber-Bosch or similar synthetic ammonia installations—for example, at Oppau and Leuna in Germany (I. G. Farbenindustrie A.-G.) with lignite as the raw material, at the du Pont plant at Belle, W. Va., and the Allied Chemical and Dye plant at Hopewell, Va., and at Billingham-on-Tees, Great Britain (Imperial Chemical Industries, Ltd.). In the latter plant synthetic ammonia and methanol manufacture, as well as hydrogenation, using bituminous coal, creosote, and low-temperature tar, is operating.

One of the main advantages of the method is the low net cost of the hydrogen production which on the average is much cheaper than electrolysis. Comparison with the coke-oven gas method is complicated because of the difficulty of placing a correct value upon the latter gas. Approximately, however, under most conditions total-gasification hydrogen is cheaper than coke-oven-gas hydrogen only when very large consumptions are involved. An important advantage, however, as compared with coke-oven gas is that water gas is very simple in composition (nearly all carbon monoxide and hydrogen, with only traces of sulfur and hydrocarbons) so that the purification plant is not costly.

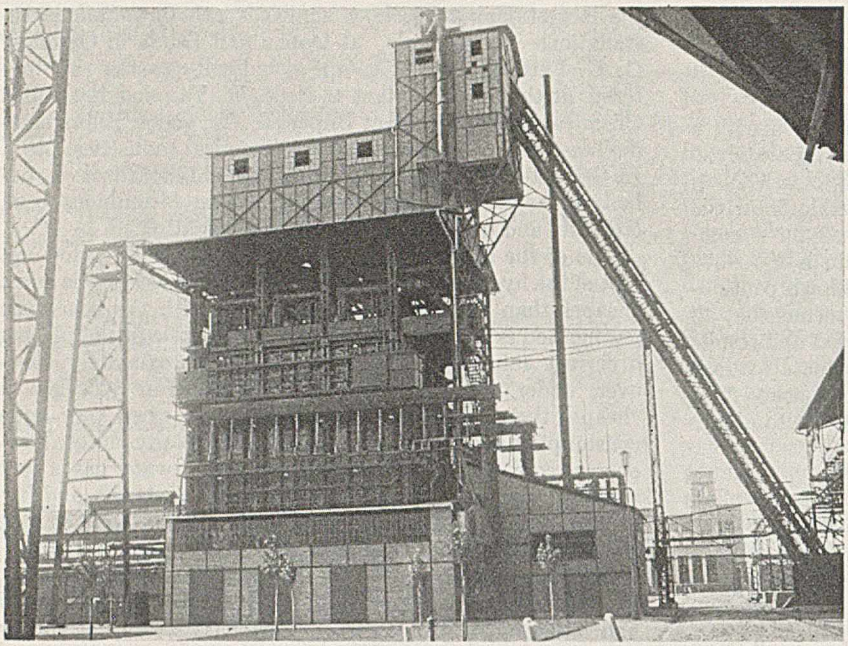
Total gasification also means that the hydrogenation, synthetic ammonia, or other plant is entirely self-contained and independent of outside or "external" sources of supply of the primary raw product—that is, hydrogen.

It is believed that some of the very large Winkler generators, which are used at the Leuna works in Germany for making water gas from roughly pulverized lignite for synthetic nitrogen, hydrogenation, and synthetic liquid fuel, are being operated with a blast of oxygen or of air enriched to a considerable degree with oxygen. Under these circumstances a continuous blast of steam and oxygen can be used; the result is water gas (carbon monoxide plus hydrogen) with a large admixture of carbon dioxide and some nitrogen, since the heat generated by the extra amount of oxygen, as compared with that in the atmosphere, is sufficient to maintain the temperature of the fuel bed without an alternate blow with air. The carbon dioxide can then be scrubbed out under pressure with water. In addition, the fuel bed of the generator, stated to be up to 18 feet wide, is relatively shallow (about 4.5 feet); and the oxygenated air and steam blast is supplied at very high pressure so that the particles of lignite are kept more or less in partial suspension and continual motion, resulting in a high rate of gasification. According to some reports these generators each have an output up to 35,300,000 cubic feet (1,000,000 cubic meters) of gas per 24 hours.

A new modification of total gasification now beginning to be used in Germany and other countries for the production of a high-hydrogen gas of the water-gas type is the Bubiag-Didier process. This has been developed by the Didier-Werke A.-G., of Berlin; the basic principle consists in the operation of vertical, continuous, externally heated chamber ovens carbonizing noncoking coal, lignite, or lignite briquets, with heavy continuous steaming of the charge by means of superheated steam. Also the main gas offtake is about halfway up the oven instead of at the top; this gives some degree of low-temperature carbonization in the upper part, with internal cracking of gases and vapors. In the lower part, however, up to 1832–2462° F. (1000–1350° C.) is obtained—that is, very high-temperature carbonization.

Steaming is carried out so that either complete gasification occurs, leaving only ash and clinker, or so that sufficient coke is left only for making the producer gas necessary to heat the chamber oven setting.

The Bubiag-Didier process may be described, therefore, in one sense as the water-gas process with a continuous run of steam and the heat necessary for maintaining the fuel bed at the required temperature of about 1832° F. (1000° C.) or



Bubiag-Didier Plant at Petfürdö, Hungary

Twelve chamber ovens are arranged in two rows of six ovens each, treating predried lignite

over; this heat is supplied from an external source instead of from an alternate blow with air and separation of the blow gas. The result is a gas containing about 33–35 per cent carbon monoxide and 50–52 per cent hydrogen, with less than 1.0 per cent saturated and unsaturated hydrocarbons because of the internal cracking. The composition of the gas can also be varied according to the exact method of operation which is very flexible; it depends, for example, upon whether the production of hydrogen, synthesis gas ($CO + 2H_2$), or towns gas is the object.

In 1935 a Bubiag-Didier hydrogen plant with twelve chamber ovens was erected by the Didier-Werke A.-G. at the synthetic nitrogen plant at Petfürdö, Hungary, belonging to the Hungarian Government; lignite from the Varpolota mine is dried down to about 19 per cent moisture by the special Fleissner predrying process.

The normal production of the original plant, using any desired method to eliminate the carbon monoxide such as oxidation to carbon dioxide by means of catalysts and scrubbing with water, was 2,648,000 cubic feet (75,000 cubic meters) of hydrogen per 24 hours. Since 1935, however, the plant has been enlarged, and it is believed that hydrogenation and synthetic liquid plants have also been erected.

A new method also used in Germany for the manufacture of hydrogen is the Pattenhausen process which consists in passing highly superheated steam (over 932° F. or 500° C.) continuously through carbonized lignite (char), presumably to give the reaction, $C + 2H_2O = CO_2 + 2H_2$. The carbon dioxide is removed by scrubbing, and apparently when a very reactive fuel such as carbonized lignite is used the action proceeds at a sufficient rate.

Hydrogen from Coke-Oven Gas

The coke-oven gas method for the production of hydrogen is of the utmost importance because full use can be made of an important and abundant by-product, not only in relation to the hydrogen content but also to other products. Any carbonization gas can be used in the same way. The world is carbonizing approximately 160,000,000 metric tons of coal per year in by-product recovery coke ovens, and the average yield per metric ton of coal is 11,000 cubic feet of rich coal gas with the following approximate average composition:

CO	6.0%
H_2	50.0
Hydrocarbons, satd.	27.0
Hydrocarbons, unsatd.	3.0
Total combustibles	86.0
CO_2	4.0
O_2	0.2
N_2 (by difference)	9.8
Total	100.0
Heating value (gross), B. t. u./cu. ft.	520

This analysis represents the gas taken over the whole period of carbonization, but the percentage of hydrogen varies according to the duration of the heating of the charge and is higher in the latter stages. In some cases up to 70 per cent hydrogen results towards the end; an ideal practice, not yet developed on a commercial scale, would be to separate the coke-oven gas into two or three portions according to the time the charge has been carbonized. For example, only the last 50 per cent would be used for hydrogen production.

The carbonization of 160 million metric tons of coal per year in by-product coke ovens means the production of 1760 billion cubic feet of coke-oven gas per year (11,000 cubic feet per ton).

Although a certain proportion of dual-fired or compound coke ovens are now operating (allowing for the settings being heated by blast furnace gas), nearly all the plants of the world are still heated by coke-oven gas. Detailed statistics are not available, but it is a fair assumption that throughout the world 55 per cent of the total production of coke-oven gas, or 6000 cubic feet of gas per ton of coal carbonized is used to heat the settings, although individual plants are much more efficient. The remaining 45 per cent, or 5000 cubic feet of gas per ton, is used in various ways, often on most uneconomical lines; in many cases it is actually blown to waste in the air. Thus part of the gas is burned in steam boilers and another part is sold to the manufactured towns gas industry, often at a price below the real value.

There is, however, no necessity for using coke-oven gas to heat the oven settings, since blast-furnace gas or producer gas made from coke breeze will do just as well. Since the annual world production of coke-oven gas is approximately 1760 billion cubic feet, this corresponds to a potential yield of 880 billion cubic feet of hydrogen (50 per cent). Unfortunately accurate figures for the annual world consumption of hydrogen are not available.

The general methods of separating hydrogen from coke-oven gas consist in scrubbing the gas with water, ammonia liquor, gas oil, and other products; if necessary, dust and tar particles are also separated. The gas is then subjected to pressure and extreme cooling on progressive lines in a liquefaction type of plant so that methane and other saturated hydrocarbons, ethylene and unsaturated hydrocarbons, carbon monoxide, and part of the nitrogen are liquefied. Hydrogen is then left in a very pure condition free from catalyst poisons, although it contains a small amount of nitrogen. The two main types of equipment used, as already indicated, are the Linde and the Claude; they differ only as regards the method of attaining the cooling effect.

The Linde or Linde-Bronn process originated about 1909 and was first used to obtain hydrogen from water gas. The Joule-Thomson effect is used for cooling; that is, the low temperature obtained by the evaporation of the liquid cools the incoming gas by means of special heat interchangers, so that gradually a large amount of gas is converted into liquid under the conditions of compression within the range of about 10–200 atmospheres pressure (142–2840 pounds per square inch).

In separating hydrogen from coke-oven gas by the Linde process in its earlier years of development, the gas was compressed to 10 atmospheres (142 pounds per square inch) and scrubbed with water. This removed nearly all the carbon dioxide, and any small amount of light oil left after the gas had passed through the gas oil scrubbers. The last traces of carbon dioxide were then eliminated by scrubbing with sodium hydroxide solution, and the gas was cooled by heat interchange with liquid gas. Following these steps, further cooling took place on the heat interchange principle from the evaporation of the liquid nitrogen. Under the pressure of 10 atmospheres, part of the nitrogen gas, as well as methane and other hydrocarbons in very small amount, separated in the liquid condition. The hydrogen gas, with some nitrogen, was finally sprayed with liquid nitrogen to complete the purification. For ammonia synthesis the necessary 1-3 nitrogen-hydrogen mixture was obtained by adding a further amount of nitrogen (by evaporation of the liquid).

In recent years, however, the Linde process has been altered in detail, and the coke-oven gas is first scrubbed with ammonia solution in water (to remove carbon dioxide), dilute sulfuric acid (to remove ammonia), and sodium hydroxide (to remove final traces of carbon dioxide).

Next a preliminary compression to 9 atmospheres (128 pounds per square inch) is given, followed by cooling with liquid, after which the coke-oven gas is warmed again to the temperature of the atmosphere and scrubbed with water. Then the gas is cooled to remove water, with further cooling and fractional liquefaction of all the gases except hydrogen. These include, as already indicated, nitrogen, carbon monoxide, methane, and other saturated hydrocarbons, and ethylene and other unsaturated hydrocarbons, which are made available for sale. Thus the unsaturated hydrocarbons can be separated and mixed with saturated hydrocarbons to give a liquid product in cylinders which, on evaporation, results in a gas of 1550–1600 B. t. u. per cubic foot. Average composition is about 30 per cent ethylene, 6 per cent propylene, 30 per cent methane, 30 per cent ethane, and small amounts of other hydrocarbons. Refractionation results in almost pure ethylene and propylene, available for the manufacture of products such as ethyl and propyl alcohol.

In the process of Georges Claude, developed in France by the Société l'Air Liquide, the cooling effect is obtained by causing the expanding gases, from a pressure of 30–40 atmospheres (426–569 pounds per square inch), to do external work—that is, drive an engine—which has the effect of causing a rapid drop in the temperature. The coke-oven gas from the by-product plant is compressed to 18–20 atmospheres (256–284 pounds per square inch) and scrubbed in succession with dilute ammonia (to remove carbon dioxide, hydrogen sulfide, and hydrogen cyanide), with water (to remove ammonia), with gas oil (to remove light oil), and with sodium hydroxide solution (to remove carbon dioxide), followed by drying with solid sodium hydroxide. The compressed gas then enters the liquefying apparatus and is progressively cooled by heat interchange from the extremely cold hydrogen as it ascends a liquefying column. Unsaturated hydrocarbons (including ethylene), saturated hydrocarbons (including methane), carbon monoxide, and most of the nitrogen are liquefied in turn; the hydrogen passes out at the top in a very pure condition. Also the design of the plant is such that the liquefied nitrogen scrubs the hydrogen gas, and the latter is then expanded to the final low temperature by being used to drive an engine.

As already indicated, the production of coke-oven-gas hydrogen is increasing rapidly at the expense of total-gasification hydrogen. For example, in 1926–27 about 86.5 per cent of the world's synthetic nitrogen products, operated on the principle of direct combination of nitrogen and hydrogen, used total-gasification hydrogen. In 1930–31, however, the total was 66.9 per cent, largely because of the increase in the use of coke-oven-gas hydrogen.

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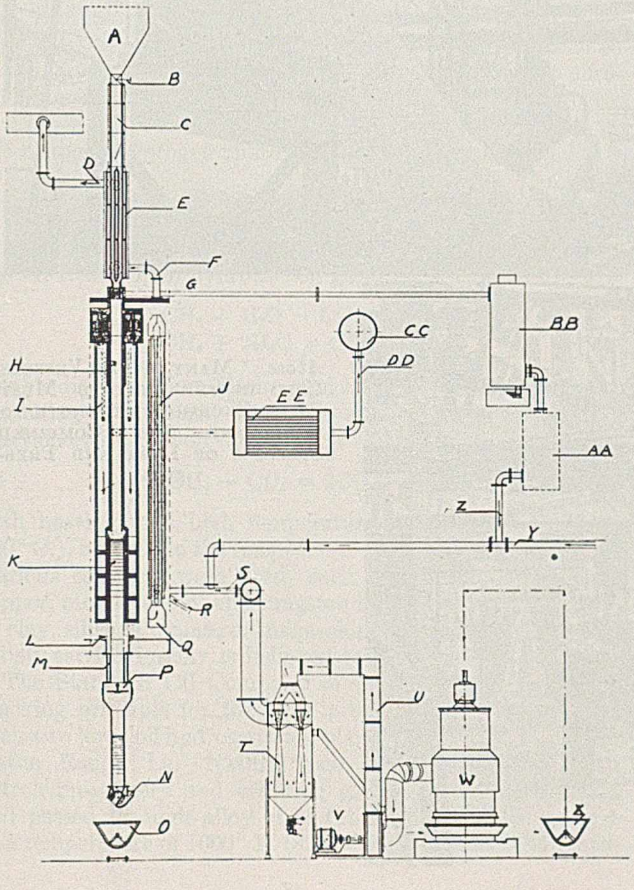
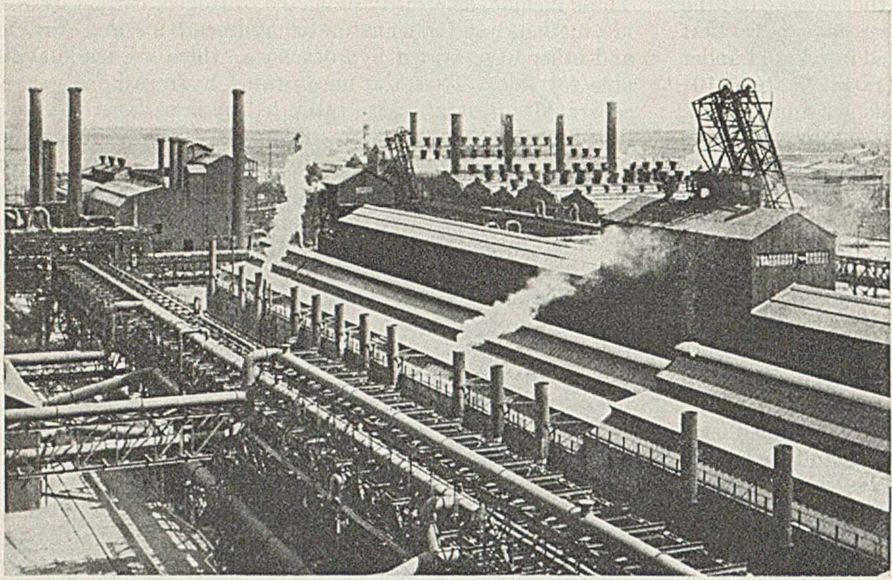


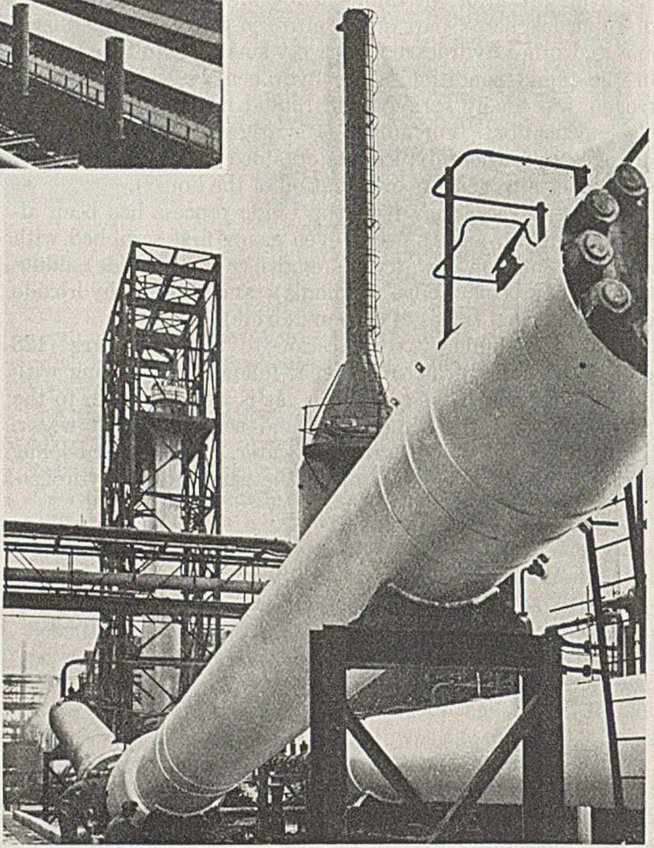
DIAGRAM OF THE PRODUCTION OF SYNTHESIS GAS BY THE BUBIAG-DIDIER PROCESS

A.	Coal bunker
B.	Valve
C.	Intermediate bunker
D.	Hot combustion gas outlet, 150–180° C.
E.	Predryer
F.	Hot combustion gas inlet, 550–600° C.
G.	Offtake pipe for low-temperature gas and oil vapors
H.	Reaction chamber
I.	Heating chamber at about 1350° C.
J.	Recuperators
K.	Water-gas zone
L.	Steam inlet, 350–400° C.
M.	Cooling jacket
N.	Water seal
O.	Residual coke
P.	Automatic discharge gear
Q.	Combustion gas inlet to recuperators 1050° C.
R.	Air for combustion
S.	Generator gas
T.	Dust dryer
U.	Hot gas
V.	Circulating fan (and motor)
W.	Generator
X.	Residual coke
Y.	Residual gas and synthesis gas
Z.	Oil-free low-temperature carbonization gas
AA.	Hydrogen sulfide separation, Alkazit process
BB.	Electrostatic tar separator
CC.	To the coolers and sulfur elimination plant
DD.	Synthesis gas
EE.	Waste heat boiler

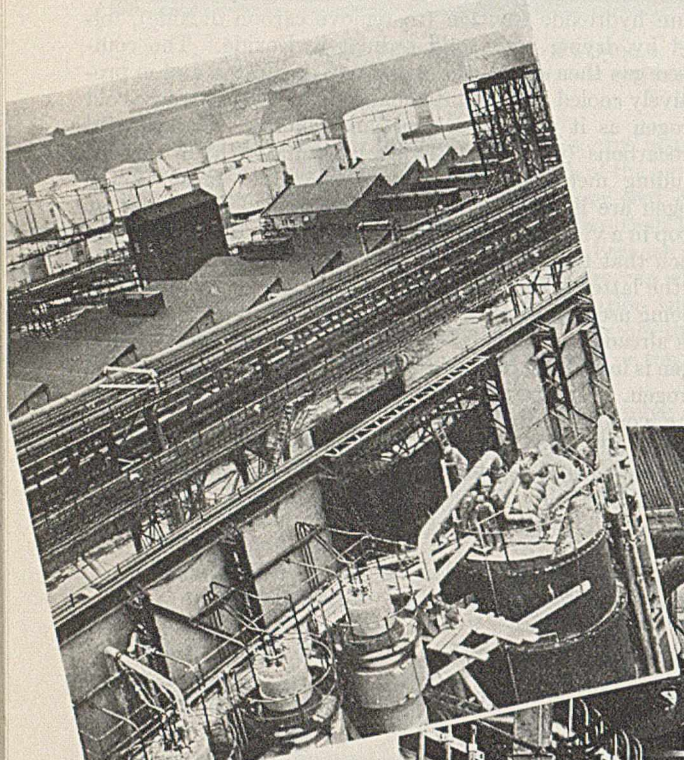
VIEWS TAKEN AT THE HYDROGENATION PLANT OF IMPERIAL CHEMICAL INDUSTRIES AT BILLINGHAM-ON-TEES, ENGLAND



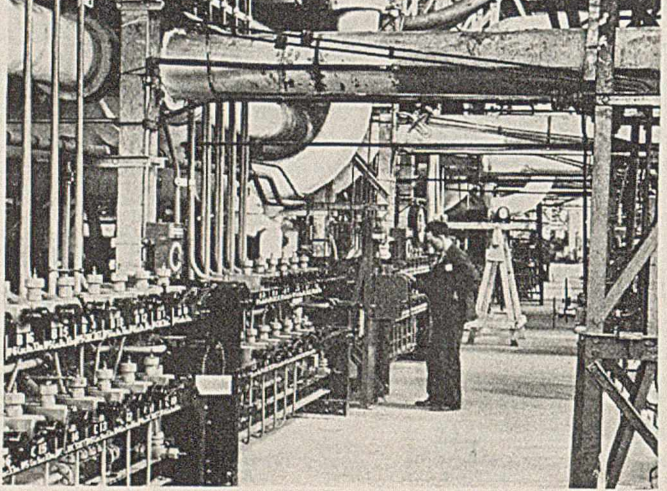
Left. WATER GAS PLANT WITH BOILER AND POWER PLANTS IN THE BACKGROUND



Above. MANY OF THE VESSELS USED IN THE PROCESS MUST BE OF ENORMOUS STRENGTH TO WITHSTAND THE COMBINED STRESSES OF HEAT AND PRESSURE



Above. TOP OF THE PLANT WITH TANK FARM IN THE BACKGROUND



Right. CONTROL INSTRUMENTS AND VALVES

One of the main advantages of this method is that full use is made of coke-oven gas, and the other liquefied products obtained, especially the hydrocarbons, are a valuable source of revenue. In general also, although it is difficult to place a fair value on coke-oven gas, hydrogen made from the latter is cheaper unless very large water-gas plants are operated. Consequently, for the Fischer-Tropsch and other synthetic liquid fuel plants which, unlike hydrogenation, can be of comparatively small size, and for synthetic nitrogen plants, such as the Claude, Casale, and Fauser which are also smaller in size than Haber-Bosch plants, coke-oven-gas hydrogen is, generally, cheaper and more convenient.

In these days also of successful long-distance pipe-line transmission of coke-oven gas, often extending to several hundred miles (as in Germany) and linking up many plants, the fact that the hydrogen is obtained from external sources is not now so objectionable as in the earlier days when pipeline length was limited. A difficulty, however, with coke-oven-gas hydrogen for ammonia synthesis is the indefinite and varying nitrogen content, generally within the range of 7.5–15.0 per cent, because of air leakage through the brick walls of the setting. Consequently the correct 1-3 nitrogen-hydrogen proportion is not always easy to obtain, but for hydrogenation and synthetic liquid fuel this is of no importance because all the nitrogen is removed.

A more recent and quite different development of the use of coke-oven gas as a source of hydrogen is cracking, mixing the gas with steam, and heating under pressure in stages to a very high temperature about 2372° F. (or 1300° C.) in alloy steel converters. The simple equation is

$$CH_4 + 2H_2O = CO_2 + 4H_2$$

although free carbon is formed and the carbon dioxide can be removed by pressure water sprays. For example, in Germany the Gesellschaft für Kohlentechnik, at Dortmund-Eving, makes the 1-3 nitrogen-hydrogen mixture for ammonia by cracking methane (or coke-oven gas) in the presence of steam and scrubbing out the carbon dioxide with water. The high-pressure converters used are stated to be constructed of an alloy composed of 55 per cent iron, 25 per cent chromium, and 20 per cent nickel. The similar Kuhlmann process in France uses coke-oven gas for making either hydrogen or the nitrogen-hydrogen mixture for ammonia synthesis.

Hydrogen from Petroleum Gases

Apart from coke-oven gas in particular, the action of superheated steam upon hydrocarbon gases

$$CH_4 + H_2O = CO + 3H_2$$
$$CH_4 + 2H_2O = CO_2 + 4H_2$$

was studied by Franz Fischer and Hans Tropsch in Germany beginning about 1928; they also studied the corresponding reactions with carbon dioxide,

$$CH_4 + CO_2 = 2CO + 2H_2$$

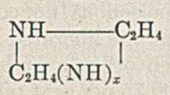
with heating to a high temperature, 1544–1688° F. (840–920° C.), but within the range of 932–1832° F. (500–1000° C.). Various catalysts were used, such as iron, cobalt, nickel, copper, molybdenum, and tungsten in a suitable carrier, such as clay, silica, alumina, or magnesium carbonate. Generally cobalt carried in clay is believed to give the best result.

The Standard Oil Company of New Jersey is using the cracking principle for the bulk production of hydrogen at their two large oil hydrogenation plants at Bayway, N. J., and Baton Rouge, La. Natural gas, if necessary along with petroleum-refinery and cracking gas, is mixed with steam and passed through alloy steel tubes filled with a catalyst at a temperature of 1600° F. (870° C.). (Details of the catalyst are not given but presumably it is of the nickel or cobalt composite type.) The methane interacts to form carbon monoxide and hydrogen, and the same general reaction takes place with other hydrocarbons present. The carbon monoxide–hydrogen mixture is then treated at 850° F. (455° C.) in the presence of another catalyst, presumably of the nickel variety, to convert the carbon monoxide into carbon dioxide, for easy removal. For this purpose pressure jets of water are used at the first plant (Bayway), but at the second plant (Baton Rouge), started in May, 1931, the carbon dioxide is scrubbed out with triethanolamine at 250 pounds per square inch pressure.

Carbon dioxide is rapidly absorbed, and a much smaller volume of liquid is required as compared with water. This general method of producing hydrogen, using natural gas as the raw product, is being used also at the United States Bureau of Mines experimental laboratory hydrogenation plant at Pittsburgh. According to Fieldner (*1*), natural gas is mixed with steam and heated to the high temperature in the presence of a nickel catalyst, the carbon monoxide present is converted to carbon dioxide by the addition of more steam and heating in the presence of a copper-cobalt catalyst, and the carbon dioxide is removed by scrubbing with a solution of amines in water.

The natural gas has the average composition of about 90 per cent methane, 8 per cent ethane, and 1.5 per cent nitrogen, along with traces of other gases, and is mixed 50 to 50 by volume with steam. This mixture is cracked in an apparatus consisting of two vertical concentric tubes of 25 per cent chromium–25 per cent nickel steel. Both tubes are 5 feet long; the outside diameter of the outer one is 7 inches and that of the inner, 5 inches. The annular space between is packed with the catalyst, made of nickel stampings, $^1/_4 \times {}^1/_4$ inch in size; and the temperature is maintained at about 1922° F. (1050° C.) as a 50-50 mixture of natural gas and steam passes through at the rate of 200 cubic feet per hour (normal temperature and pressure). The composition of the cracked gas is 75 per cent hydrogen, 21 per cent carbon monoxide, 1 per cent carbon dioxide, and 1 per cent methane, approximately. For conversion of the carbon monoxide to carbon dioxide, the gas, along with steam, is passed through a vertical 6-inch-diameter steel tube with a 2-inch copper rod at the center; eight plates or vanes are attached and project horizontally to form eight small compartments each carrying some of the copper-cobalt catalyst. Also the cracked gas is mixed in the proportion of 1 part by volume with 5 parts of steam, and the temperature is maintained at 572–662° F. (300–350° C.) by external heating. Next the excess steam is removed by a limited water spray and the carbon dioxide is scrubbed out with a solution of tetramine in water. This is a trade name for a mixture of polyethylene amines (stated to be chiefly diethylene triamine and triethylene tetramine) which has a boiling range of 5 per cent below 392° F. (200° C.) and 10 per cent over 572° F. (300° C.). The use of slightly alkaline polyethylene amines, dissolved in water, as an absorbent for mildly acidic gases such as carbon dioxide, as well as sulfur dioxide and hydrogen sulfide, was patented by Perkins (*3*).

These amines, which contain more atoms of carbon than of nitrogen, are made by the interaction of ethylene dichloride with ammonia followed by treatment with sodium hydroxide to liberate the free amine. They are of two kinds—open-chain amines of the general type $NH_2—C_2H_4—(C_2H_4NH)_x—NH_2$, and closed-chain or ring amines of the type



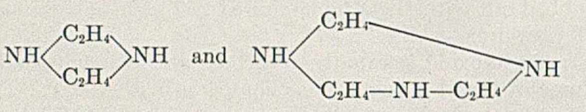
$$\begin{array}{l} NH\text{———}C_2H_4 \\ | \qquad\qquad\quad | \\ C_2H_4(NH)_x \end{array}$$

where x is a whole number.

Thus the composition of typical open-chain amines, (*a*) diethylene triamine, (*b*) triethylene tetramine, and (*c*) tetramethylene pentamine, is, respectively:

(*a*) $NH_2—C_2H_4—NH—C_2H_4—NH_2$
(*b*) $NH_2—C_2H_4—NH—C_2H_4—NH—C_2H_4—NH_2$
(*c*) $NH_2—C_2H_4—NH—C_2H_4—NH—C_2H_4—HN—C_2H_4—NH_2$

Of the second or ring series of amines, diethylene diamine and triethylene triamines are representative:



Polyethylene amines of this type usually have a boiling point within the range of 392–572° F. (200–300° C.) and are best used as a 50 per cent solution in cold water. For regeneration the solution is heated to about 212° F. (100° C.) when the carbon dioxide or other absorbed acid is driven off, leaving the solution ready for re-use on cooling.

Laboratory experimental work in connection with the use of these polyethylene amines for the removal of carbon dioxide was described by Hirst and Pinkel (*2*). Different amines and different solution strengths were used, such as 50 per cent diethanolamine, 50 per cent triethanolamine, and 5, 10, and 25 per cent Tetramine. Very good results, for example, were obtained with equal volumes of 50 per cent diethanolamine and 10 per cent Tetramine or with 10 per cent Tetramine alone. After treatment with the copper-cobalt catalyst, the cracked gas contains roughly about 80 per cent hydrogen and 20 per cent carbon dioxide, but traces of other gases, such as carbon monoxide, methane, and nitrogen, are present. After scrubbing with the amine solution, the resulting gas averages 96.0 per cent hydrogen with about 0.2 per cent carbon dioxide, 0.5 carbon monoxide, 0.2 oxygen, 1.2 methane, and 1.9 nitrogen. When more or less saturated, the amine solution is passed through a heat interchanger and regenerated by being heated in a boiling vessel operating with a distillation column; the carbon dioxide is driven off.

Hydrogen by Electrolysis

The manufacture of hydrogen by electrolysis, representing about 16 per cent of the world production, is obviously of great importance for countries generating cheap electricity by means of water power, such as the United States, Canada, Norway, Switzerland, and Russia, especially since the off-peak night load can be utilized to the fullest extent. Two general methods are used, electrolysis of a 20–30 per cent sulfuric acid solution, with lead electrodes, or a 10–20 per cent sodium hydroxide solution with iron electrodes.

During recent years the iron-alkali cell method has rapidly increased in favor, and is now generally regarded as superior to the lead-acid cell because there is less polarization and a lower voltage can be employed. The latter more than compensates for the lower conductivity.

In general, an electrolytic plant for making hydrogen consists of electrolytic cells, direct-current motor generators operating at the desired voltage, gas compressors, and gasholders.

All kinds of electrolytic cells have been designed generally according to one of four types: the tank type, the filter press type, and the partition type; the latter is made in two varieties, metal and nonpoisonous nonconductor types. The main object is to prevent the liberated hydrogen and oxygen from contaminating each other by admixture, so as to obtain hydrogen which is 99.75 per cent pure or more if possible.

Another principle developed in 1928 is electrolysis of water under high pressure up to 300 atmospheres (4266 pounds per square inch) with the claim that 99.9 per cent hydrogen and over 99 per cent oxygen are obtained, both under pressure.

An important factor in relation to the manufacture of hydrogen by electrolysis is the effective utilization of the oxygen. Thus about 5.0–8.0 cubic feet of hydrogen and 3.0–4.0 cubic feet of oxygen (normal temperature and pressure) are produced per kilowatt-hour, depending upon the conditions. One method of using the oxygen is for the total gasification of any solid carbonaceous material, such as coal, coke, and lignite, with a continuous blast of steam and oxygen or oxygenated air to obtain direct a gas of 300–335 B. t. u. per cubic foot.

An outstanding advantage of the principle is the high degree of purity of the hydrogen, and it is also convenient to operate; but in most nonwater-power countries the serious disadvantage is the high cost of production because of the price of current made from coal or other fuel.

A secondary source of hydrogen is the electrolysis of salt for the manufacture of chlorine and sodium hydroxide:

$$2NaCl = 2Na + Cl_2$$
$$2Na + 2H_2O = 2NaOH + H_2$$

Finally with regard to the less important methods in commercial use for the production of hydrogen, the action of steam on iron or iron ore, forming black oxide of iron, is still employed, especially for fat hardening. According to one method, a bed of iron ore is maintained at about 1000–1500° F. (540–815° C.). Steam is passed through for about 10 minutes, when approximately one-third is converted into hydrogen:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

Water gas is then passed through for about 20 minutes to reduce the black oxide to metallic iron or to the lower oxides of iron, after which the cycle is repeated, and so on.

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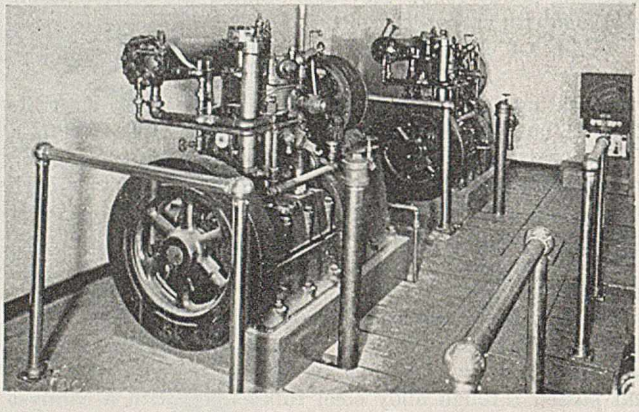

Helium and Hydrogen Compressors

Effect of Corrosion on the Durability of Paint Films

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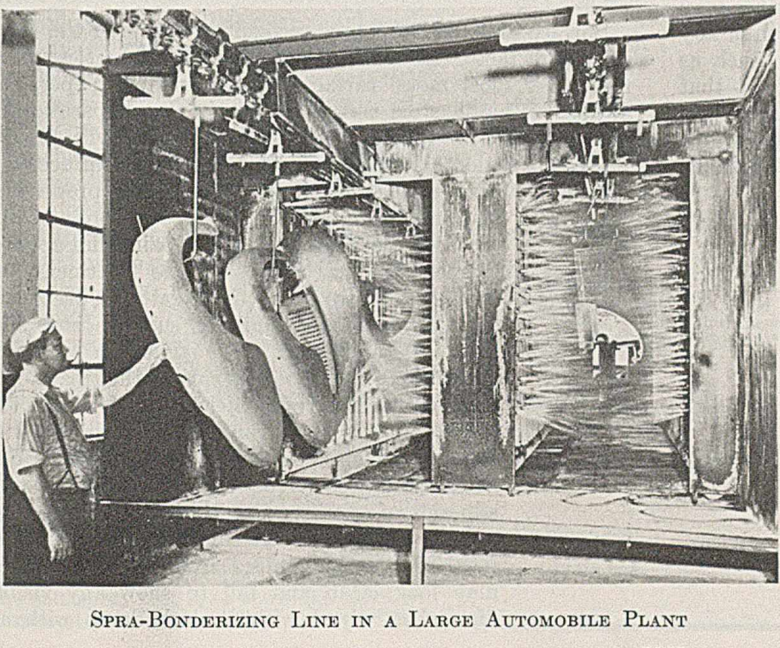
The durability of paint coatings applied over different metals depends to a great extent on the corrodibility of the base metal in the environment to which it is exposed. Chemical treatment of easily corrodible metals so as to convert their surfaces to a more stable and less reactive phosphate coating materially increases the durability of applied paint coatings. This treatment provides increased adhesion of paint films to the base metal and thus retards the peeling or chipping of the paint away from an abraded area.

Paint coatings containing a corrosion-inhibiting substance have greater durability than similar paint coatings without the corrosion-inhibiting compound. Most paint troubles have their beginning at the point of contact between the paint and the metal surface, and any recommended schedule for painting should not only include the composition of the paint but also specify the treatment of the metal prior to painting.

ONE of the oldest recognized factors in the painting of metal products and structures is the effect of corrosion on the durability of the paint film. It is obvious that many other factors, such as the composition and preparation of the base metal, the adherence and composition of the paint coating, as well as the conditions under which it was applied, influence the durability or serviceability of the paint film. So pronounced is the tendency of iron to rust that in practice very little bare iron or steel is employed, and nearly all such metal objects are painted either for protective or decorative purposes, and in either case the paint coating must remain as a continuous film over the base metal if it is to fulfill this requirement.

Throughout this discussion the word "durability" is used in the broad sense for referring to the serviceability or useful life of the paint film and is not to be construed as referring to the composition of the paint film itself or to its properties such as water resistance, flexibility, inertness, or similar characteristics. Indeed, the composition of the various paints employed in the test might well have been omitted from the report, since the investigation was undertaken primarily as a study of the effect of corrosion on the durability of paint films of the same composition applied over different metals and not a study of different paint formulations. That paint films differ widely in their protective value is well recognized, and for this reason the same paint coating must be used over metals of different corrosion resistance if the effect of corrosion is to be determined. However, for completeness, the paint formulas are included and any value they may serve should be considered purely supplemental.

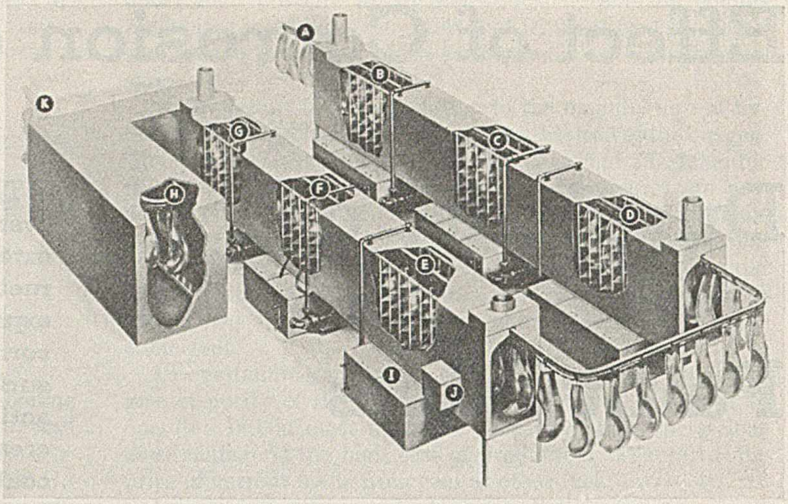
In view of the nature of this subject a brief description of the corrosion phenomenon is given; for a more detailed account, the reader is referred to some of the recent literature (*4*, *6*).



SPRA-BONDERIZING LINE IN A LARGE AUTOMOBILE PLANT

Corrosion Mechanism

The electrochemical theory of corrosion is generally accepted by authorities as the best method of explaining the corrosion process. In a broad sense, the term "corrosion" covers all reactions with the metals and their alloys. The ordinary corrosion or rusting of iron would cease under most conditions if moisture were excluded. No metal surface can be so homogeneous, both chemically and physically, that all points on its surface will exhibit exactly the same potential in contact with a liquid. Differences in chemical constitution and internal stresses serve to make some areas cathodic with respect to others as soon as the surface comes in contact with a corrosive medium. The corrosion reaction may be divided into two parts which may be called "anodic" or "cathodic" according to whether the electrodes absorb or give up electrons. Corrosion of most metals is largely produced by the flow of electric currents (that is, corrosion is electrochemical in nature instead of chemical) between the anodic and cathodic areas. The anodic part of the reaction is the dissolving of the base metal as metal ion which is accompanied by the giving up of electrons to the electrode. The cathodic part is the hydrogen ion going out of solution and becoming hydrogen gas with the absorption of electrons from the cathode. The combination of the two is the replacement of hydrogen in solution by metal, with corrosion of the metal and evolution of hydrogen gas either visibly or invisibly. If this hydrogen accumulating at the cathodic areas reacts with dissolved atmospheric oxygen, it permits corrosion to continue and the removal of hydrogen ions leaves an excess of hydroxyl ions; as a result the solution in the vicinity of the cathodic areas becomes alkaline (*3*). The formation of this alkali destroys the adhesion of any paint film over such areas, and the effect has been termed "alkaline peeling."



Equipment Utilized in the Bonderite Process

A. Production entering the cleaning section
B. Alkaline cleaning
C. Rinse
D. Rinse
E. Spra-Bonderizing section
F. Clear water rinse
G. Acidified rinse
H. Drying oven
I. Tank for Spra-Bonderizing solution
J. Tank for replenishing Spra-Bonderizing solution
K. Bonderized production leaving the drying oven, ready for the final finish

A great many factors influence the distribution or intensity of the corrosion reaction. Thus, if a certain metal forms a continuous film over its entire surface as soon as it is exposed to a certain medium, attack will be stifled at once. If, however, the film formed on the metal is not continuous, then attack may be initiated and continue indefinitely. The oxides of the metals are often nonconductors of electricity and insoluble in water, so that their presence or absence may have a vital effect on corrosion rates. The formation of any continuous nonmetallic coating on metal surfaces, such as their natural oxides, prevents corrosion to the extent that they exclude moisture and oxygen of the atmosphere contacting the base metal; since such coatings are nonconductors, they retard the flow of electric currents between the anodic and cathodic areas. The formation of nonmetallic phosphate coatings on metals by chemical treatment retards corrosion in a manner similar to the oxide coatings, except that the phosphate coatings are less cathodic and are thus more protective. Paint films had their evolution from oxide coatings and they afford protection to metal surfaces, either by mechanically excluding corrosive agents or by chemically inhibiting the corrosion reaction.

Metals Used in Test

Some of the metals employed in the test are included in Table I and were chosen on account of their wide difference in corrosion resistance and for their common use.

Surface Preparation Prior to Painting

Surface preparation is now recognized as one of the more important factors in securing durable and satisfactory paint films over most metal surfaces. In a previous paper, the author (*1*) emphasized certain factors in the preparation of iron and steel for painting; chemical treatment with a rustproofing solution (*7*) so as to convert the metal surface to a nonmetallic phosphate coating of the proper texture adapted to inhibiting corrosion and increasing the adherence of any paint film applied thereon was described. Surface treatment has been stressed by many investigators in preparing various metals for painting such as zinc surfaces (*5*), aluminum (*2*), magnesium and cadmium (*8*, *9*). Without exception, the treatments recommended have as their main objective the formation of a stable and nonreactive coating, chemically combined with the base metal, which not only retards corrosion but provides greater adhesion of applied paint films.

Table I. Metals Tested

Metal	Analysis C (max.)	Mn (max.)	P (max.)	S (max.)	Cr (max.)	Ni (max.)	Al (min.)	Zn Coating	Bonderite Coating
	%	%	%	%				*Oz./sq. ft.*	*G. P_2O_5/sq. ft.*
Steel[a]	0.20	0.60	0.045	0.055	..	...	...	...	....
Bonderized steel[b]	0.20	0.60	0.045	0.055	..	...	...	...	0.0850
Hot-dipped galvanized iron[c]	...	...	...	...	..	...	...	1.75	....
Bonderized galvanized iron	...	...	...	...	..	...	...	1.75	0.0850
Aluminum[d]	...	...	...	...	..	...	99.0	...	....
Coated aluminum[e]	...	...	...	...	..	...	99.0	...	....
18–8 stainless steel[f]	0.08	0.60	0.030	0.030	18	8	...	...	....

[a] SAE No. 1015.
[b] Chemical treatment with phosphate rustproofing solution.
[c] Class C; A. S. T. M. designation A 93-27.
[d] Half-hard bright finish.
[e] Chemical treatment in phosphate-fluoride bath.
[f] White pickled surface.

It is difficult to determine when bright surfaces such as galvanized iron are clean; they may look clean and fail to show any visible dirt when wiped with a cloth damp with an organic solvent, and yet paint will often show premature failure over such surfaces by peeling or chipping. The advantages of some foolproof method of preparing such metals for painting whereby a visible coating is produced on the surface is of tremendous practical importance.

Some estimate of the value of surface preparation prior to painting may be gained from the results obtained in this test. Four separate methods were used for preparing the steel panels for painting—namely, alkali cleaning, acid cleaning (phosphoric acid containing an organic solvent), sand blasting, and Bonderizing (a process which converts iron and zinc surfaces to a finely crystalline phosphate coating, *1*). Half the number of galvanized panels were solvent-cleaned only, and the remainder were solvent-cleaned and Bonderized. Half the number of aluminum panels were solvent-cleaned and sanded with No. 400 paper, and the remainder were solvent-cleaned and coated in a phosphate-fluoride solution. The stainless steel panels were all prepared by solvent cleaning. All steel panels were prepared from cold-rolled stock free of any mill scale. The alkali cleaning consisted in immersing the panels in a hot (212° F.) solution containing 4 ounces of alkali cleaner per gallon of water until all grease and foreign matter were removed and then rinsing in clean water to remove all traces of the cleaning solution before drying. The acid cleaning was carried out by scouring the panels with steel wool dipped in phosphoric acid (15 per cent) containing an organic solvent, followed by a thorough rinse in clean water and drying before painting. Preparation of the sandblasted panels consisted of removing all grease by alkali cleaning before sandblasting in the usual manner. The Bonderized panels were alkali-cleaned and then treated in a phosphate rustproofing solution for 2 minutes so as to convert the metal surface to a nonmetallic phosphate coating. The paint finishes used for preparing the samples are described in Table II.

Tests for Determining Durability of Paint Films

Development of new finishes, yearly model changes, and other circumstances often make it necessary to determine the durability of paint films over metal products in a short time, and for this purpose laboratory and outdoor exposure tests are used. As a rule, laboratory tests are accelerated; that is, some factors influencing the paint film are accentuated in the hope of producing in a relatively short time a result of some significance with respect to the durability of the paint film. Two laboratory tests (the salt spray and humidity tests) were employed for determining the durability of the paint films used in this investigation. Unfortunately no standardized procedure has been established for these tests, and the manner and purpose for which one laboratory makes use of the tests may differ widely from that of another; for this reason the procedure used in this investigation is briefly explained.

Salt Spray Test. The main purpose of the salt spray test is to show the effect of corrosion on the durability of paint films. Before the painted panels were placed in the salt spray cabinet, they were purposely scratched by means of a sharp instrument so as to expose a very thin section of the base metal. The test was graded at convenient intervals by measuring in inches the distance the paint film peeled or the distance of corrosion creepage under the paint film from this scratch. This procedure permits a definite numerical method of rating the degree of breakdown and thus practically eliminates the human element in evaluating the test data.

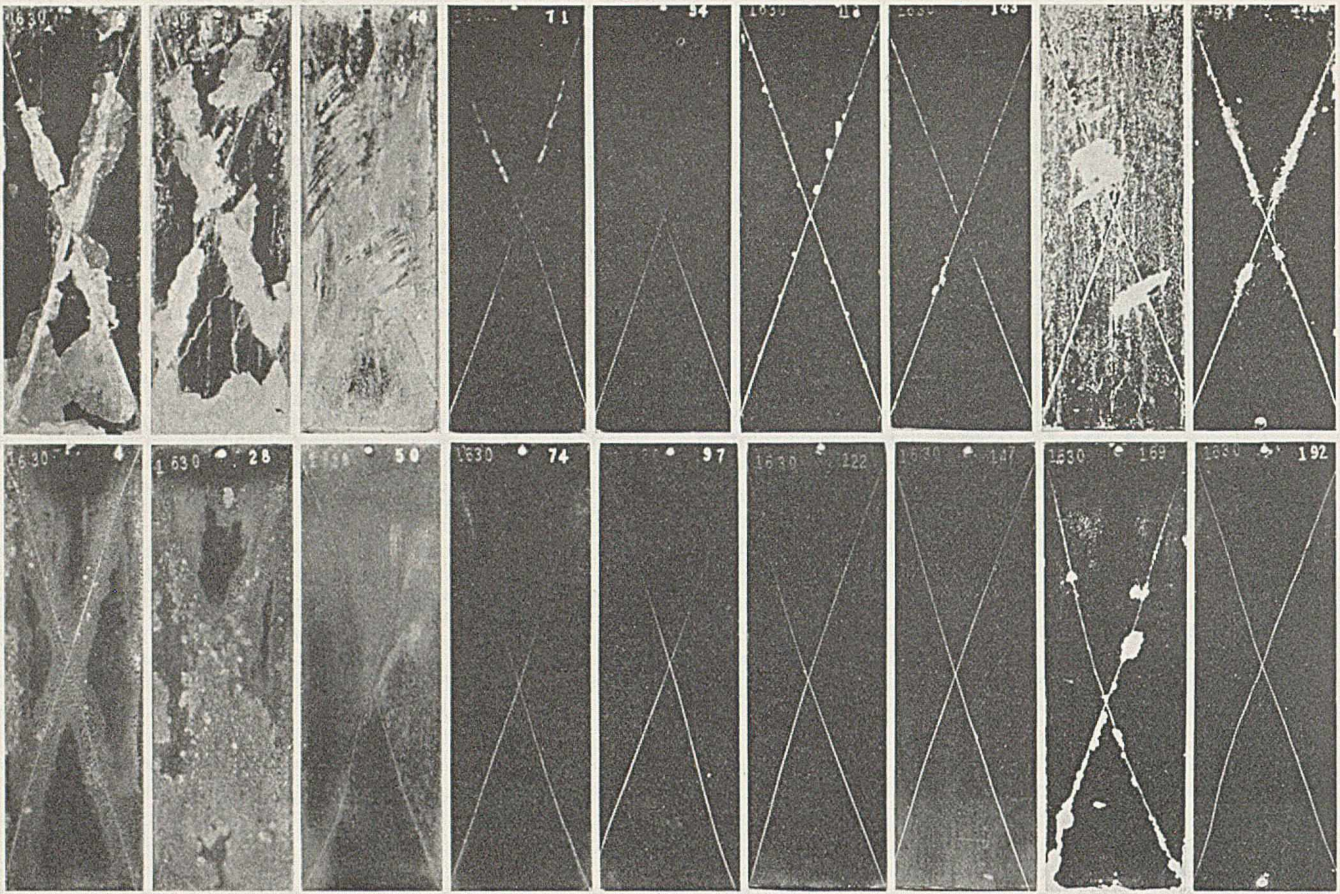
The amount of salt mist inside the cabinet was adequate and was maintained as uniform as possible. The temperature inside the test cabinet averaged 75° F. A 20 per cent salt solution prepared from high-purity sodium chloride was used in the cabinet; the solution was sprayed over and over again. A fresh salt solution was built up each week, and test specimens were inspected every other day.

Humidity Test. This test is generally used to show the effect of moisture on the durability of paint films and is graded in terms of paint blistering. The temperature inside the humidity cabinet was maintained at 100° to 110° F. with 96 to 100 per cent relative humidity. Moisture was caused to condense on the surface of the test specimens by having them rest on a suitable base through the inside of which cold water was passed. A difference was thus created in the temperature of the test specimens and the main cabinet.

Outdoor Exposure Test. Next to actual service tests, outdoor exposure tests are the most reliable for estimating the durability or useful life of paint films. They approximate as nearly as possible the actual service conditions in which the paint films are generally used. The painted panels exposed in this test were purposely scratched across their face side with a sharp instrument, exposing a very narrow section of the base metal and placed in

Table II. Paint Finishes Employed

Designation	Composition	Baking Schedule
Black enamel:		
Prime coat	Gilsonite, linseed oil, and synthetic resin	54 min., 390° F.
Finish coat	Asphalt, Gilsonite, and synthetic resin	45 min., 455° F.
Synthetic fender finish:		
1st finish coat	Carbon black, synthetic resins, and gums	Air-dried 5 min
2nd finish coat	Carbon black, synthetic resins, and gums	1 hr., 250° F.
Synthetic body finish:		
1st primer, surfacer coat	Iron oxide, fillers, linseed and tung oils	Air-dried 5 min.
2nd primer, surfacer coat	Iron oxide, fillers, linseed and tung oils	1 hr., 250° F.
1st finish coat	Carbon black, synthetic resins, and gums	1 hr., 250° F.
2nd finish coat	Carbon black, synthetic resins, and gums	1 hr., 250° F.
Lacquer body finish:		
Prime coat	Iron oxide, linseed and tung oils	1 hr., 250° F.
1st surfacer coat	Iron oxide, fillers, linseed and tung oils	Air-dried 5 min.
2nd surfacer coat	Iron oxide, fillers, linseed and tung oils	Air-dried 5 min.
2nd surfacer coat	Iron oxide, fillers, linseed and tung oils	1 hr., 250° F.
1st lacquer coat	Lamp black, nitrocellulose base	Air-dried
2nd lacquer coat	Lamp black, nitrocellulose base	Air-dried
Synthetic refrigerator finish (white):		
Primer	Pigment unknown, synthetic resins and gums	20 min., 425° F.
Finish enamel	Pigment unknown, synthetic resins and gums	1.5 hr., 285° F.
Exterior protective finish:		
Prime coat	Red lead, chromate, linseed and tung oils	Air-dried 48 hr.
1st finish coat	Titanium oxide, linseed and tung oils	Air-dried 24 hr.
2nd finish coat	Titanium oxide, linseed and tung oils	Air-dried 48 hr.



Alkali-cleaned steel | H_3PO_4-cleaned steel | Sand-blasted steel | Steel Bonderized | Stainless steel | Aluminum | Aluminum coated | Galvanized iron | Galvanized iron Bonderized

FIGURE 1. PAINTED SPECIMENS AFTER 780 HOURS IN SALT SPRAY (*above*) AND AFTER 18-MONTH EXPOSURE IN FLORIDA (*below*)

Miami, Fla., at 45° facing south in May, 1936. Monthly reports were made on the condition of the painted specimens.

A summary of the results obtained from the salt spray, humidity, and Florida exposure tests on the various metals and paint finishes are included in Table III.

Interpretation of Paint Test Results

Evaluation of results obtained from any accelerated method of testing the durability of paint films is often difficult and conclusions must be drawn with caution.

Throughout these experiments 4 × 12 inch panels were used for the painted specimens. The different methods used in preparing the panels for painting have been described elsewhere, and it will suffice to mention that extreme care was taken to assure that the surface of all panels was free of any substance which might have a deleterious effect on the paint film. In so far as was humanly possible, the same film thickness of the paint finishes was applied on all panels. Three panels of each base metal and of each cleaning treatment as well as the individual paint finishes were tested for durability by the separate accelerated and outdoor exposure tests.

The condition of the painted specimens is shown by Figure 1, and the relation between the results obtained by the salt spray test and Florida exposure of the different metals finished with two coats of baked black enamel is indicated in Figure 2. It is apparent that corrosion is the primary cause of the paint failure observed on the easily corrodible specimens shown in Figure 1, since the same paint finish was used on all the specimens. Improved adhesion of paint films applied over a roughened surface obtained by sandblasting did not materially improve the durability of the paint finish. Any recommended method of preparing easily corrodible surfaces for painting should tend to reduce or eliminate rather than increase the corrodible surface area underneath the paint film. Once moisture penetrates a paint film, its deleterious effect depends upon the amount of corrosion resulting from it. Chemical treatment of easily corrodible metal so as to provide a more stable and less reactive surface has been shown to be an effective method for increasing the durability of applied paint films. There is a fair relation between the results of the salt spray and Florida exposure tests at this date, and they reveal the influence of corrosion on the durability of the various paint finishes tested. (In previous experiments the writer observed a close relation between the results obtained from salt spray and Florida exposure tests for estimating the durability of various paint finishes.) Exposing a narrow section of the base metal by scratching the painted specimen with a sharp instrument before placing it in test approximates closely a condition which often occurs in actual service. Evaluating the breakdown of paint films from a given scratch on the face of the test specimen has proved more reliable as a means of predicting the durability of paint films in actual service than measuring the breakdown from the edges of the specimen. The uniformity in film thickness of the paint coating on the face as compared to the irregular and indefinite film thickness of the paint film on the edges of the specimen is believed responsible for this result.

Corrosion and its effect on the adherence of paint films over

Table III. Condition of Painted Panels after Various Tests

Metal	Treatment	After 780-Hr. Salt Spray Test[a]			After 1000-Hr. Humidity Test[b]			After 18-Mo. Fla. Exposure[a]		
		Black enamel finish[c]	Synthetic body finish	Synthetic fender finish[a]	Synthetic refrigerator	Lacquer finish	Synthetic fender finish	Synthetic body finish	Synthetic fender finish	Exterior protective finish
Steel	Alkali-cleaned	Failed 242 hr.	1/2	Failed 242 hr.	*vb*	*vbb*, 229 hr.	*vbb*, 63 hr.	1/8 at scratch & edges	1/4 at scratch & edges; rust pitting	1/16 at scratch; rust pitting
Steel	Acid-cleaned	Failed 242 hr.	3/8	Failed 342 hr.	*b*	*vbb*, 446 hr.	*vbb*, 540 hr.	1/16–3/16 at scratch & edges	1/4 at scratch & edges; definite rust pitting	1/16 at scratch; slight rust pitting
Steel	Sandblasted	Failed 461 hr.	3/8	Failed 780 hr.	*b*	*vbb*, 375 hr.	*vbb*, 63 hr.	1/16 at scratch & edges	3/16 at scratch, 80% of surface rust-pitted	1/32 at scratch; slight rust pitting
Steel	Bonderized	None	None	None	*vsb*	*vbb*, 710 hr.	*vb*	None	1/8 at scratch & edges	None
Aluminum	Solvent - cleaned & sanded (No. 400 paper)	1/8 in spots	1/32 in spots	1/16 in spots	*sb*	*vbb*, 494 hr.	*vbb* ,64 hr	None	None	None
Aluminum	Phosphate-fluoride	1/16 in spots	1/32 in spots	1/32 in spots	*vsb*	*b*	*vbb*, 63 hr.	None	None	None
Galvanized iron	Solvent-cleaned	Failed 173 hr.	3/16	Failed 508 hr.	*b*	*vbb*, 191 hr.	*vbb*, 167 hr.	95% of finish peeled off; zinc corroded	15% of finish peeled off	3/32–3/16 at scratch
Galvanized iron	Bonderized	1/8	1/16 in spots	1/16 in spots	*vsb*	*vbb*, 375 hr.	*vb*	None	None	None
Stainless steel	Solvent-cleaned	None	None	None	*b*	*vbb*, 717 hr.	*vbb*, 167 hr.	None	None	None

[a] Figures indicate average creepage in inches of paint film from scratch.

[b] Letters indicate degree of final blistering unless otherwise noted:

vsb = very slight blistering, a few scattered small blisters just recognizable with the aid of reflected artificial light held close to the surface.
sb = slight blistering, a stage where blisters are readily seen without the aid of reflected artificial light.
b = small blisters occurring generally over the area under observation.
vb = very blistered, large or small blisters generally distributed throughout paint film.
vbb = very badly blistered, large or small blisters distributed throughout entire paint film and rated as complete breakdown of finish.

[c] Failure rated as 0.75-inch creepage.

metal surfaces are clearly shown by the salt spray test; the test is therefore of considerable value in estimating the durability of paint coatings which are exposed to marine atmosphere or saline conditions. In sections of the country where ice conditions are severe, the deleterious effect of the salt used on the streets for removing the ice is a vital factor in the durability of finishes on automobiles. Its effect is often observed by the corrosion creepage under the paint finish from the edges of the fenders or from scratches and breaks in the paint film, and the resultant rust increases in volume until it forces the paint film from the metal.

Over bare steel and galvanized surfaces the durability of paint films as shown by 18-month Florida exposure was found to be directly proportional to the degree of blistering exhibited by the same finish tested in the humidity test here described. The durability of the paint films applied on aluminum and stainless steel are shown by 18-month Florida exposure not to be influenced by the degree of blistering they exhibited in the humidity test. Although the aluminum and stainless steel painted specimens rated "very badly blistered" in the humidity test in a short period, there is no sign of breakdown in the finish over these metals after 18-month Florida exposure. One may conclude from these results that the durability of paint films applied over easily corrodible metals is inversely proportional to the degree of blistering the paint films exhibited in the humidity test. The degree of blistering does not materially affect the durability of paint films

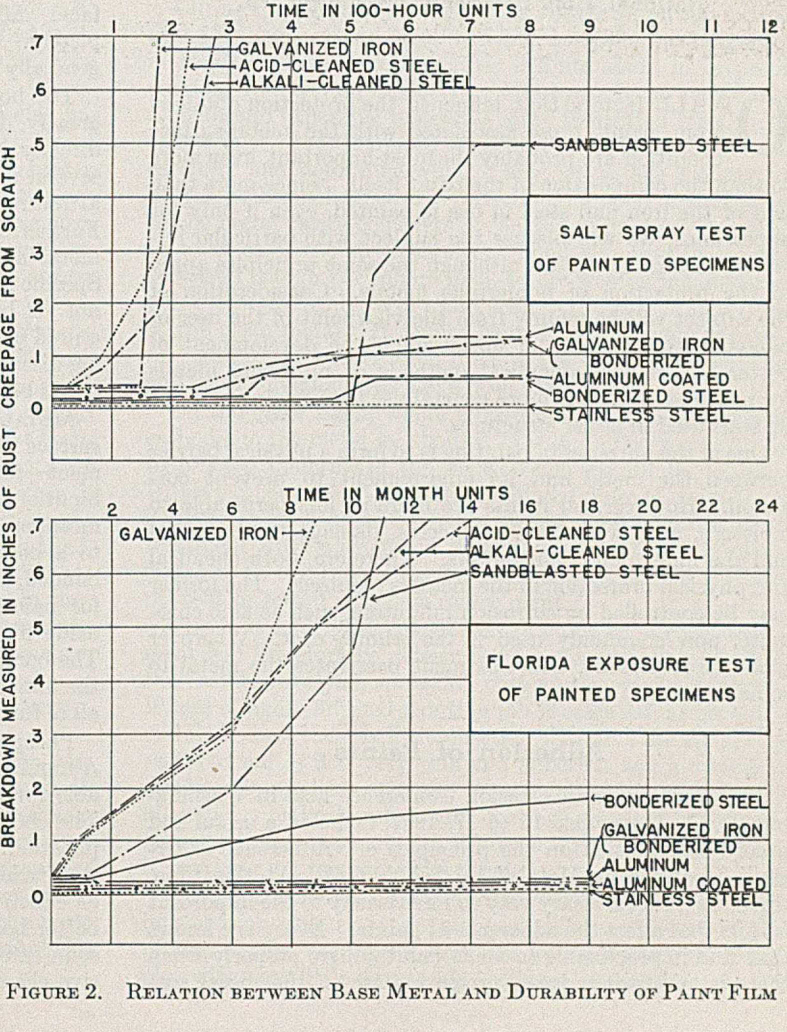


Figure 2. Relation between Base Metal and Durability of Paint Film

applied over almost noncorrodible metals. (Additional exposure of these specimens may alter this conclusion.)

It is believed that water penetration of the paint film is the main factor of all paint blistering. Assuming that a paint film was absolutely impervious to moisture and applied over clean metal (surface free of any active substance), it would not blister. Contrary to popular opinion, corrosion is a result of paint blistering and not a cause. Carefully cleaned glass specimens were painted and exposed in the humidity test; they were found to exhibit the same degree of blistering as steel specimens prepared in the same manner. Sandblasting or etching the glass with hydrofluoric acid so as to roughen its surface failed to prevent blistering when it was painted and tested as described. In general, the adhesion of the paint film to its supporting base influenced the size of the blisters but was found not to affect their number appreciably.. Increased adhesion of paint films to their base is conducive to preventing blisters from increasing in size and thereby to extending its useful life. Expressed by Wray and Van Vorst (*10*): "The permeability of the paint film to moisture is a fundamental property of practical importance. Moisture is necessary for the common types of corrosion; the exclusion of moisture by the paint film is an important function of a metal protective paint, and an understanding of the mechanism of moisture penetration and its measurement has become essential in modern paint technology."

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Pretreatment of Metal

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OF ALL factors that influence the protection obtained from paint, those associated with the metal-surface condition are probably the most important, even more so than the composition of the paint itself. Since more than half of the iron and steel in use is painted, even if only for appearance, we will discuss the subject with particular reference to ferrous metals, although the same principles apply to the protection of nonferrous metals. Consideration of the subject will be mainly from the viewpoint of the user of paints, with the hope of encouraging the development of better and more economical methods of preparing metals for painting, and their more general use in everyday practice on steel used in larger structures.

One of the purposes of painting is to form a physical barrier between the metal and its environment to prevent corrosion. However, all paints are more or less permeable to moisture, and, where it finds access, damage to the metal and the inner paint film follows. Therefore, both chemical and physical protection of the metal is required. The former may be controlled by corrosion inhibitors, such as zinc chromate, now commonly used in the priming coat. Wherever moisture is present, this treatment passivates the metal to some extent.

Adhesion of Paints

The Underground Corrosion Conference held in Washington, D. C., November 15 to 17, 1937, included a useful and timely contribution on the principles of "Adherence of Organic Coatings to Metals" by Schuh (*15*). At this time, therefore, it is necessary only to refer briefly to the important factors that affect the adherence of paints. Every one knows that it is impracticable to make paint adhere properly when there is moisture or loose foreign matter on the metal surface. All such unbonded matter should be removed completely. However, there are other factors that are not so generally recognized in preparing the surface for painting.

The bond between a paint film and the metal may vary greatly, depending upon several factors. The film should be directly in contact with the metal or so near (i. e., within several molecular layers) that it is within the close range of attractive forces at the interface between these materials. Furthermore, reactions sometimes take place between the metal and paint, which in some cases weaken the bond. Specific adhesion between paint and different materials cannot yet be measured. But for any one metal, all that is required is a reliable test for relative adhesion. In the following discussion of the principal factors that influence adhesion, it will be noticed that these are often interrelated.

Metal Surface Films. On all the common metals, surface films form by reaction of the metal with its environment—for example, the oxides, phosphates, or chromate combinations. In fact, oxide films form so rapidly in the atmosphere that it is doubtful whether paints are ever applied to a perfectly clean metal. Surface films that are tightly bonded, stable, and absorptive usually afford a better surface for painting than the metal itself. Evans (*4*) showed an oxide film to be blended into the metal surface structure. The bond of a surface film to metal, the cohesive strength of the film, and the adhesion between paint and surface film are all of fundamental importance in protection by paints.

Phosphated surfaces generally give good paint adherence. A number of processes based on this principle are now available for treating a wide variety of zinc and steel surfaces. The choice is based on service requirements and cost of application. Metallic phosphate combinations, as applied by the Parkerizing or Electrogranodine processes, are examples of effective but relatively expensive methods of making a better bond between paint and metal and of protecting it to some extent from corrosion. The influence of other less expensive chemical treatments on adhesion will be referred to later.

Roughness. Another important factor that materially improves adhesion is roughness, which increases the actual surface area. For instance, a metal surface that has been roughened by steel-grit blasting may have well over fifteen times the area of a smooth surface (*3*, *15*); even a very fine abrasive increases the surface area several times over a smoothly polished surface. The contour of the surface depends mainly on the particle size of the grit. Excessive roughness may invite corrosion, because of the thinner paint film that covers the high spots. Metal spray adheres mechanically to a sand-blasted metal surface but not to one that is smooth-machined. The surface area is also increased when a nonreactive stable film, such as iron phosphate, is formed on the warm metal surface (see the preceding paragraphs). This method of providing an enlarged inert surface for the reception of paint seems preferable in some ways to increasing the metallic surface, which is subject to corrosion. The weathering of hot-galvanized steel prior to painting is a well-known illustration of the beneficial effect of chemical roughening and metal surface films in improving adherence of paints.

Surfaces for Painting . . .

Dry Surface. Where the relative humidity is above 70, there is always the chance that an invisible adsorbed layer of moisture may be present on the metal, particularly when the metal temperature is below that of the air (*18*). Warming the metal sufficiently assures a dry surface and also improves the strength of bond to the coating.

Metal Composition. The composition of the metal is of some importance with respect to the properties of the surface film formed in air. For example, on account of the more adherent film on copper steel, paint holds better and lasts longer on this metal than on plain steel under most atmospheric conditions (*17*).

Chemical Action. Chemical action between the metal and the decomposition products of the paint vehicle may loosen the bond. For example, the adhesion of most oil paints to a new hot-galvanized surface weakens after a short time so that the paint tends to peel. This is thought to be due to the formation of zinc formate on the interface between the paint and the zinc (*23*). If the galvanized surface is previously roughened by chemical or physical means, or if a considerable amount of zinc dust is added to the paint, adhesion is much improved. The bond of asphalt coating applied hot over an asphaltic primer may be weakened in time by separation of an oil which fluxes the undercoat when the latter is very different in type or consistency from the outer coat. Therefore, it is not wise to conclude that adhesion of new coating combinations is good until so proved by a prolonged test under service conditions.

Changes in strength and ductility of the paint film also tend to destroy adhesion. Shrinkage, particularly in thick films, may overcome the adhesive bond. The composition, permeability to moisture, and aging properties of paints may have a marked effect on the initial adhesion or permanence of adhesion. When present in amounts over 25 per cent of the total pigment in the primer, inhibitors such as zinc chromate retard or prevent metal corrosion under paint that otherwise would destroy the bond between paint and metal.

Influence of Mill Scale on Durability of Paints

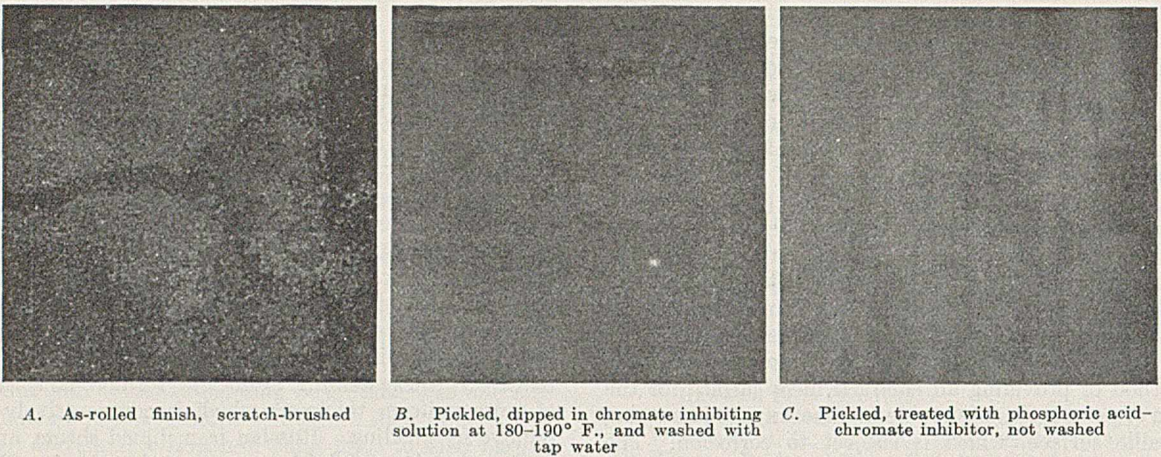
There has been much controversy on the question of whether or not mill scale should be completely removed before painting. An oxide layer builds up on the metal surface as it cools after the last pass of the rolling mill, and its composition and structure vary with the temperature at which the metal leaves the rolls. Therefore, there is considerable difference between mill scales, and their composition and adhesion cannot always be controlled in finishing steel products. About twenty years ago, a process was introduced by the National Tube Company to produce a uniform thin scale on pipe. The temperature was lowered to about 1650° F. before the finishing pass was entered in order to crack off the relatively thick welding scale and form a new thin scale of more uniform thickness which is comparatively easy to remove by pickling. Russian iron, blued sheets, and many of the colored metal finishes are examples of oxide films that provide considerable protection in some environments. However, the properties of mill scale on the larger steel products are not always under such control.

During the past two or three years, the corrosion committee of the British Iron and Steel Institute, and other investigators in England, have taken a rather definite stand in favor of removal of all mill scale (*7*). However, it is sometimes difficult and expensive to descale large fabricated steel units completely. It is therefore important to consider the matter carefully and determine what, if any, advantage is obtained by the additional expense involved. The bond of mill scale to the metal varies considerably on the same piece of steel. In some cases the strength of this bond amounts to several thousand pounds per square inch, before weathering, and the paint adheres firmly to dry mill scale surfaces just as it does to the clean metal. It cannot be denied that many successful painting jobs have been done where only the loose scale and other foreign matter have been removed.

On the other hand, where moisture is present the scale is cathodic to the metal by about 0.25 volt, and corrosion tends to proceed underneath the scale, which eventually loosens. If this happens after the steel is painted, failure of the coating is likely to be hastened. Later in this paper metal surface treatment will be discussed that may be applied to a clean metal or to one that is partly covered with a tight scale to prevent or retard corrosion under paint.

The best and most economical practice of surface treatment will therefore be determined by consideration of all of the factors involved, including cost and service conditions. Where a highly finished painting job is essential, as on automobile bodies, there is little question that all scale should be removed unless it is very thin and adherent and a corrosion inhibitor is applied. On the other hand, when the thicker bituminous or Portland cement coatings are used as for protection of pipe underground, it does not pay to spend much, if anything, on removing tight scale.

The National Bureau of Standards' tests (*10*) of bare pipe in corrosive soils show no material difference between the pitting of pipe carrying a standard mill scale and the same pipe with very little or no scale. General conclusions cannot



A. As-rolled finish, scratch-brushed

B. Pickled, dipped in chromate inhibiting solution at 180–190° F., and washed with tap water

C. Pickled, treated with phosphoric acid–chromate inhibitor, not washed

FIGURE 1. STEEL PANELS GIVEN TWO COATS OF LINSEED-TUNG OIL LACQUER AFTER PRETREATMENTS NOTED ABOVE, AND EXPOSED 53 WEEKS ON THE ROOF IN PITTSBURGH'S SEMI-INDUSTRIAL ATMOSPHERE

be drawn from these tests because metal underground is subjected to local differences of potential due to variations in the soil and water in contact with the pipe, which are often in excess of the potential generated between mill scale and metal.

Methods of Cleaning the Metal Surface

There are various ways of cleaning the surface before it is painted. Where desirable, most of the mill scale can be removed or loosened by exposure to a corrosive atmosphere for several months. The percentage of scale removed depends mainly upon the corrosiveness of the air and the period of exposure. For instance, a few purchasers of pipe for gas and oil pipe lines order the material shipped without any coating because they find that after being weathered in transit, the pipe is easier to clean by sand, steel-grit blasting, or other means. Sandblasting is one of the most effective means for removing mill scale. Under some conditions, however, it is objectionable on account of the dust problem, the cost, and the difficulty of application. The air used in the blast should be fairly dry; otherwise, when it expands, moisture may be deposited on the clean metal. No matter how the surface is cleaned, in corrosive air it should receive a rust-inhibitive priming paint immediately after cleaning.

A method of hydraulic sandblasting is being developed that may have some advantages particularly in preventing dust in foundries.

Mechanical impact appliances have proved effective for cleaning steel, particularly after the mill scale has been loosened by weathering. Cleaning machines of this type have been devised that remove mill scale and rust from the pipe, and also roughen the surface.

Power-driven wire brushes in the hands of reliable operators can be used most effectively in reconditioning old structures that require repainting.

Pickling in hot dilute acid and rinsing in hot water are often less expensive and more satisfactory than sand or steel-grit blasting.

One of the latest methods is to pickle the metal free from scale in 5 per cent sulfuric acid at 160° F. (*6*). After being rinsed in hot water, it is immersed in a 2 per cent free phosphoric acid bath containing approximately 0.5 per cent of iron in solution at 185° F. for about 3 or 4 minutes. On removal from the phosphoric acid bath the pipe is allowed to dry without washing and is painted while warm. Phosphoric acid gives an iron phosphate inhibitive finish well adapted to hold paint, as pointed out before. Where practicable, this treatment is favorable to good painting. Even scrubbing with a water-alcohol solution of phosphoric acid is reported to be useful in preparing the surface for painting.

If there is any suspicion that a film of moisture is present on the surface of a metal, it may be wiped with a clean gas flame immediately before the paint is applied. (Wet metal should not be dried in this way.)

Application of Inhibitors to Metal Surfaces

It is well known that the electrochemical process of corrosion is retarded or prevented under certain conditions when the electrolyte contains a certain amount of an inhibitor, such as sodium chromate. This is apparently due to the polarization of anodic areas by the formation of self-healing films (*5*, *14*, *19*).

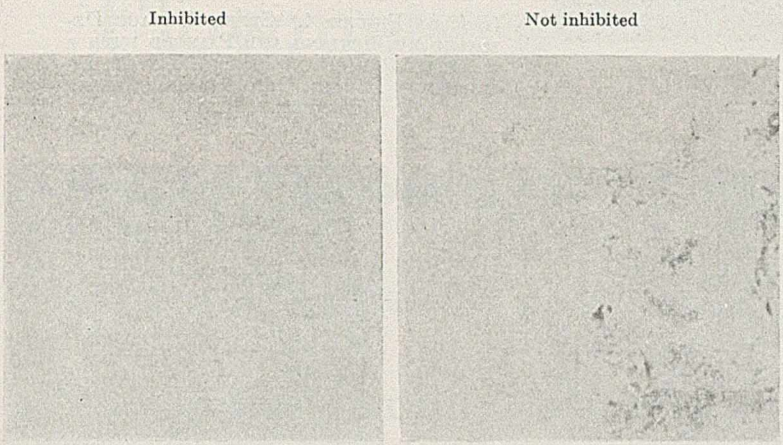
The potential of a metal to water is that of the natural metal surface film and is materially affected by the composition of applied paint coatings. Time-potential curves indicate that the chemical protective effect is just as important as physical protection of paints on metals (*2*).

The use of a slightly soluble zinc chromate in the priming coat of paints is now generally recognized as good practice. Red and blue lead are mild inhibitors of corrosion but are much improved when used with more than 25 per cent of zinc chromate. The general use of red lead as priming paint on the as-rolled surface of iron or steel probably accounts for the comparatively little trouble experienced in painting over tightly attached mill scale. Apparently the metal is rendered more or less passive by a small amount of inhibitor dissolved by moisture which finds access through defects in the paint. Addition of the sodium chromates to water greatly retards or stops the galvanic action between mill scale and steel. The amount required to do this depends upon the composition of the water. Based on qualitative tests in Pittsburgh city water, only a trace of corrosion is found on steel carrying mill scale when the dichromate concentration is about 800 p. p. m. In the absence of mill scale, about 300 p. p. m. of dichromate will be sufficient to prevent corrosion under these conditions. The normal chromate (pH 8.5) is still more effective. It would seem to be only one step further to apply a chromate inhibitor to the metal before painting. The phosphated film formed by reaction between iron and phosphoric acid acts as a milder inhibitor and serves a useful purpose in improving adherence of paint. Combination of these materials has proved useful in preventing or retarding corrosion in industrial water.

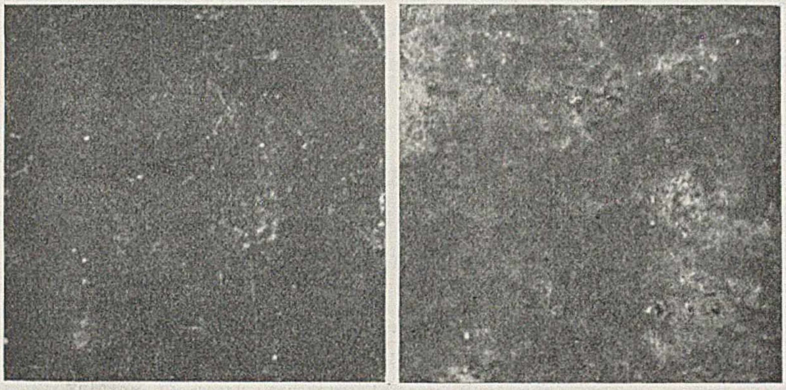
Within the past few years, a number of water-inhibitive solutions have appeared on the market for pretreatment of metal surfaces on a large scale, prior to painting, to improve adhesion and retard corrosion under the paint. These contain essentially orthophosphoric acid or chromic acid. At least one contains both phosphoric acid and chromium salts with other proprietary oil-dispersing ingredients.

The effect of these inhibitors depends upon their proper application and somewhat upon conditions of exposure. For instance, in industrial air and in the salt-spray chamber, a marked improvement was found in the resistance of a paint film on steel test panels that had received a wash of orthophosphoric acid–chromate solution (Figures 1 and 2). In warm Florida salt air there was some improvement although much less, as would be expected, probably as a result of the presence of chloride ions. When applied to steel panels prior to painting for tests underwater, the same inhibitor showed a material reduction in size and number of blisters (Figures 3 and 4):

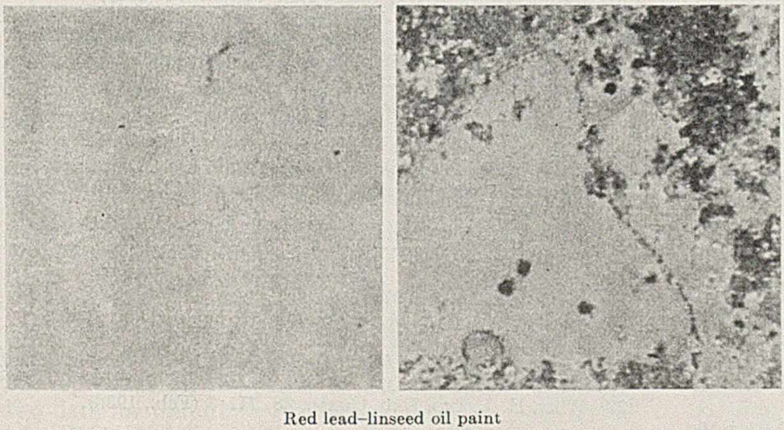
> In preparing these test panels, the inhibitor was applied after they were thoroughly cleaned, surplus solution drained off, surface dried, and paint brushed on indoors at about 70° F. The best procedure for practical application remains to be developed in detail, according to operating conditions. To secure the most satisfactory results, the steel surface should be preferably descaled but at least free from unbonded mill scale, rust, and dirt; the temperature of the treated metal and atmosphere should not be below 60° F. to ensure completion of reaction; excess inhibiting solution should be removed, and the surface completely dried before painting. In practical application it may prove advisable, especially on surfaces that have not been completely descaled, to wash with water after the inhibitor has reacted, before drying. If applied when the temperature is too low, the reaction between the solution and the metal may be incomplete, leaving unused acid on the metal. When painted, this acid may be trapped in and later react, destroying the paint film.



Basic lead chromate primer



Zinc chromate–iron oxide paint



Red lead–linseed oil paint

FIGURE 2. STEEL PANELS, AS ROLLED, WITH AND WITHOUT PHOSPHORIC ACID–CHROMATE INHIBITOR AND ONE COAT OF PAINT; EACH PAIR EXPOSED IN THE SALT-SPRAY CHAMBER AT THE SAME TIME FOR THE SAME PERIOD

Courtesy, American Bridge Company Laboratory

The adherent films that these inhibitors form on the metal increase the surface available for contact with the paint and at the same time have a passivating effect that may be quite useful in neutralizing local potentials such as those due to mill scale or rust.

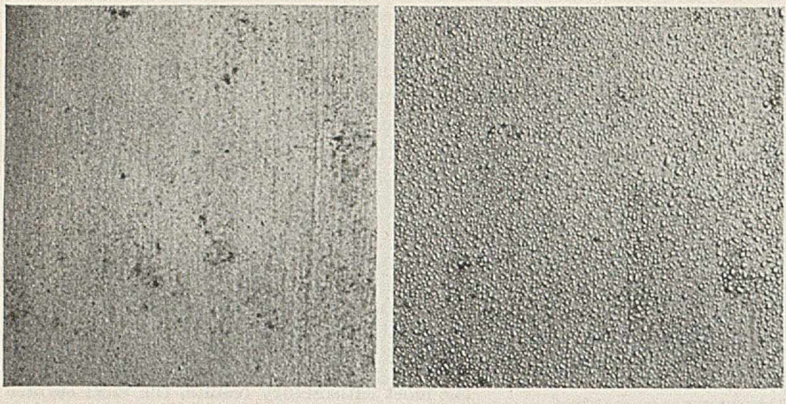
These inhibiting materials have not been applied in practice on a large scale long enough to develop fully all necessary precautions in application and determine the degree of protection that can be depended upon under various service conditions. However, much the same principle has been employed for some time in various forms (in hot solutions) for the preparation of highly finished steel for painting, such as for automobile body parts.

Chromate inhibitors would probably not be effective in an atmosphere that was decidedly acid, since acidity dissolves the film and increases corrosion. The addition of a basic pigment or zinc dust should be helpful in the priming coat, under such conditions.

The amount of moisture that can penetrate a good paint film is quite limited, so that a very small amount of soluble chromate should give the concentration necessary to passivate the metal. The solubility of zinc chromate in water is about 800 p. p. m.

Summary and Conclusion

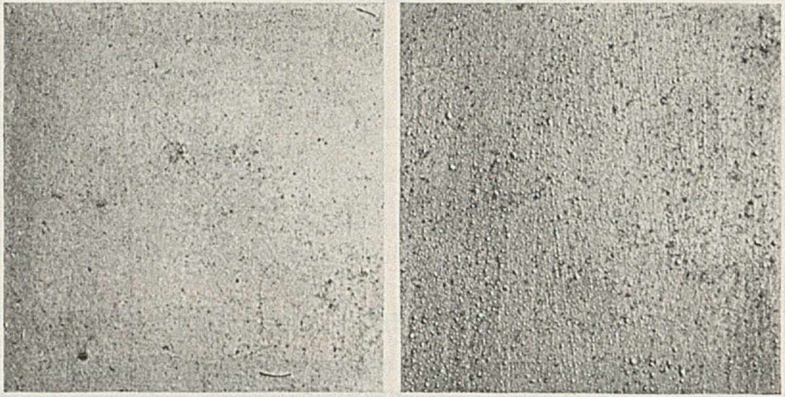
It is evident that metal corrosion and the paint problem are intimately related. To obtain the best protection of iron and steel by paint, proper preparation of the surface is of fundamental importance. This includes, at least, removal of all foreign matter not tightly bonded to the metal or



Surface inhibited with phosphoric acid-chromate solution before painting

Surface not inhibited before painting

(*Left*) Figure 3. Steel Surface Well Weathered, Scratch-Brushed, and Painted with a Phenolic Primer Containing 50 Per Cent Zinc Chromate and a Phenolic Finishing Coat; Immersed in Lorain, Ohio, Harbor Water for About 8 Months



Surface inhibited with Bakelite primer and finishing coat before painting

Surface not inhibited before painting

(*Below*) Figure 4. Steel Surface Descaled by Pickling and Painted with a Bakelite Primer and Finishing Coat; Immersed in Lorain, Ohio, Harbor Water for About 8 Months

unsuitable as a base for paint. Various methods for removing mill scale under different conditions of service have been discussed. The surface should be actually dry, preferably warm, and free from reactive substances when paint is applied.

Water solutions of inhibitors applicable at normal or higher temperatures are being developed that react with the metal to form inhibitive films. The rate of this reaction decreases with the temperature so that precautions must be taken to ensure either the completion of the reaction or the removal of all soluble material that has not reacted before the surface is dried prior to painting.[1] Properly applied, this treatment in certain cases has been found to improve paint adhesion; it tends to polarize the iron mill-scale couple, and to reduce local differences in potential. The advantage of an efficient inhibitive pigment in the priming coat is now generally recognized. The combination of an inhibitor properly applied to the metal and in the priming paint tends to reduce further the chance of destruction of the bond between paint and metal by corrosion. However, the practical value of these low-cost water inhibitors to fabricated or structural steel has not been fully demonstrated by long-time tests in service. The remarkable developments in paints and painting technic in recent years have been accomplished gradually by testing and experience. The successful application of water-soluble inhibitors to the metal on a large scale will probably have to go through a similar process of development. Where better and more expensive paints are to be applied, it seems still more important that all necessary precautions be taken in the preparation of the surface.[1]

Recent tests and experience indicate that, as a rule, when carried out with all necessary precautions, the most desirable preparation of steel surfaces for painting (particularly for underwater service) is complete descaling, followed by phosphating or similar chemical treatment.

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[1] After this paper was written, the American Society for Testing Materials set up a new subcommittee (XXIX of Committee D-1) on Preparation of Iron and Steel for Painting. This subcommittee should be a good medium for testing all factors having to do with preparation of the metal surfaces for painting.

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Discharge Rates from Gas Flowmeters

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Proper Temperature and Pressure Corrections

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EQUATIONS, well tested by experiment, are available for flow of gases through primary devices such as the plate or nozzle orifice or the Venturi tube. These involve a difference of pressure across the constriction, usually expressed as differential manometer reading. By the use of the equation it is possible to calculate the flow, as volume (or weight) per unit time, which will be discharged through the instrument at any given differential pressure manometer reading; the inlet temperature and pressure must be specified. The converse, the manometer reading for a given discharge, is similarly calculable.

Less well developed but equally well proved are the equations for discharge from an instrument of the same type in which the pressure-reducing constriction is a long piece of capillary tubing. Calculations of discharge rate, at specified conditions, may be made for any manometer reading.

If it is desired to draw a line of discharge rate *vs.* manometer reading for any of the above instruments, the conditions at which this line applies must be specified. For any other conditions it is necessary to draw another line. An infinite number of lines is therefore required to provide for all the operating conditions possible.

The purpose of this paper is to show that, by a rearrangement of the terms of the known equations, plots of discharge flow rates may be recorded in such a manner that a single line represents all conditions of temperature and pressure. The data for the drawing of this original plot may be calculated at specified conditions, or measurements of actual discharge rates (i. e., calibration of the instrument) may be employed. Examples of lines drawn by each of these methods are given in Figures 3 and 4.

The proposed methods provide a much speedier way of using the instruments than calculation by the equation. The author knows of no other single-line method, universal for all pressures and temperatures, of correctly recording flow rate data through such instruments, although two incorrect methods are known to be practiced. The first admits its error but fails to do anything to remedy it. The meter is calibrated at one time of year and recalibrated when seasonal changes result in widely different average room temperatures. No effect of pressure variation is ever included. The second method is probably the more insidious, since it involves a supposed "correction" which does not actually effect a true correction. The volume flowing per unit time is measured, corrected to standard conditions, and plotted against the reading of the differential manometer (*2*). This is obviously equivalent to a plot of weight rate (or molal rate) against R. The equations developed here prove that this is not a correct method for weight rate plots in any of the meters discussed. Since the volume rate at standard conditions, V_s, is equal to

$$V(T_s/T)(p/p_s) = V(p/T)(\text{a constant})$$

it will be apparent from the equations presented here that this constitutes an incorrect method for volume flow rate plots as well, for none of the derived plot ordinates is of this form.

A new method is proposed of plotting discharge flow rates, for instruments of the Venturi and orifice type, against the differential manometer reading. The groups to be plotted are so calculated that one line on such a plot will be universal for varying values of inlet pressure and temperature. The groups are derived by rearrangement of the terms of well-known equations.

Types of instruments included in the discussion are plate and nozzle orifices, Venturi tubes, and long-tube capillary orifices. The last are studied in both viscous and turbulent flow ranges for the gas in the capillary. For each of the types of meter, a sample discharge rate plot is shown, as recommended.

Alignment charts are also given as a convenient method of calculating the groups found to be necessary in the new type of plot.

If V_s is plotted against R, subsequent use of the plot will result in the following errors for a temperature change of 10° C. and barometric change of 20 mm. of mercury in the opposite direction (i. e., temperature rise and barometric fall, or vice versa): for plate or nozzle orifices or Venturi tubes, 3 per cent on either weight or volume rate plots; for capillary meters, 2.3 per cent on volume rate plots and 12 per cent on weight rate plots.

Assumptions and Limitations

In all subsequent work it is assumed that the simple gas laws apply. No cases in which Δp is large as compared to p_A (not to exceed 10 per cent at the most) were considered. High pressure drops require the use of more complicated equations of discharge and invalidate the simplifying assumptions made in relating ΔH to R. The situation may be avoided by the proper selection of the size of the line in which the throttling constriction is placed.

Plate Orifices, Nozzle Orifices, and Venturis

APPARATUS. Meters considered in this section consist of two parts: (*a*) the primary device, orifice or Venturi, and (*b*) the differential manometer connected to show the pressure drop across the constriction of the primary device. Illustrations of plate orifices, nozzle orifices, and Venturis are available in the literature (*1, 3*). The capillary orifice is not included in this section.

PRESENT EQUATIONS. Years of research by mechanical and gas engineers have resulted in the following equations for the devices of this group (*1*):

$$V_A(\text{cu. ft./sec. at } p_A, T_A) = 140.6\,\overline{K}Y_A D_B^2 \sqrt{\frac{T_A}{p_A G y}}\ \sqrt{R'} \tag{1}$$

where D is in feet, p_A in pounds per square foot, and T_A in ° K. For the Venturi a preferable equation exists with substitutions for $\overline{K}$ and Y_A. Since these terms are to be eliminated, the presentation of both equations is unnecessary.

If we consider only one instrument and only one gas at a time, and if we assume the ratio p_b/p_A to be nearly unity so that Y_A is essentially unity, and the simple gas laws to apply so that y is unity, considerable simplification will result:

$$V_A = C_1'\sqrt{R}\sqrt{\frac{T_A}{p_A}} \tag{2}$$

It is apparent that the value of C_1' may also include a term to correct the units of V to cubic feet per minute or per hour. It is also apparent that with small values of Δp it is reasonable to drop the subscripts on V, T, and p.

Rearranged, Equation 2 gives

$$V_A\sqrt{\frac{p_A}{T_A}} = C_1'\sqrt{R} \tag{3}$$

Equation 3 now indicates that a plot of $V_A\sqrt{p_A/T_A}$ as ordinate against $\sqrt{R}$ as abscissa should result in a curve which is universal for all values of p_A and T_A. If V_A alone is plotted against $\sqrt{R}$, a different line will result for every set of pressure and temperature values, as indicated by Equation 1.

It is often more desirable to know a weight rate than a volume rate. The weight rate is obtained by multiplying both sides of Equation 1 or 2 by ρ_A. Then, since

$$V_A\rho_A = W$$

$$W = C_1'\rho_A\sqrt{\frac{T_A}{p_A}}\sqrt{R} \tag{4}$$

From the A. S. M. E. report on fluid meters (*1*),

$$\rho_A = 0.01042\ p_A G y/T_A \tag{5}$$

Simplifying by the same assumptions used to produce Equation 2 from 1, the y may be dropped and G regarded as another constant. Then, substituting Equation 5 in 4,

$$W = C_2'\frac{p_A}{T_A}\sqrt{\frac{T_A}{p_A}}\sqrt{R} = C_2'\sqrt{\frac{p_A}{T_A}}\sqrt{R}$$

By rearrangement this becomes:

$$W\sqrt{T_A/p_A} = C_2'\sqrt{R} \tag{6}$$

Therefore, the universal plot to be used should be $W\sqrt{T_A/p_A}$ as ordinate against $\sqrt{R}$ as abscissa.

The results of Equations 3 and 6 may be obtained by a different method; the equation for liquids flowing through orifices or Venturi tubes (*3, 5*) is used as the basis. This equation is given as

$$\sqrt{u_B^2 - u_A^2} = C\sqrt{2g\Delta H} \tag{7}$$

In order to employ this equation for gases, it is necessary to make the same assumptions used in simplifying Equation 1. Then, for any instrument, u_B may be expressed in terms of u_A, u_A may be expressed in terms of volume flow rate, V, or weight flow rate, W, and the following equations may be derived:

$$V = C_1\sqrt{\Delta H} \tag{8}$$

$$W = C_1\rho\sqrt{\Delta H} \tag{9}$$

In Equations 8 and 9,

$$C_1 = A_A C\sqrt{2g}\sqrt{\frac{A_B^2}{A_A^2 - A_B^2}} \tag{9A}$$

By the simple gas laws,

$$\rho = pM/BT \tag{10}$$

and Equation 9 may be written

$$W = C_2\frac{p}{T}\sqrt{\Delta H};\quad C_2 = C_1 M/B \tag{11}$$

Although Equations 8 and 11 may be used to specify universal plots with ΔH as abscissa, they will be more useful normally if ΔH is replaced by R:

$$\Delta H = \frac{R(\rho_L - \rho_G)}{\rho_G} = R\left(\frac{d_L}{d_G} - 1\right) \tag{12}$$

where d_L and d_G are specific gravities referred to the same standard. Equation 12 is simplified by the assumption that one is negligible in comparison with d_L/d_G, which amounts to neglecting the weight of gas on top of the liquid in the manometer.

With an air-water manometer, if the temperature of each phase is 20° C. and the air is at a pressure as high as 30 pounds per square inch gage, d_L/d_G is approximately 276; the assumption that one is negligible in comparison with this figure involves an error of slightly less than 0.4 per cent. For heavier gases or lighter liquids in the manometer arms, the error under the same conditions is magnified. In general, the error increases with increase of pressure and decrease of temperature.

For normal conditions it is therefore reasonable to write

$$\Delta H = R\,d_L/d_G \tag{13}$$

where $d_G = \dfrac{d_s T_s}{T}\dfrac{p}{p_s}$

since d_G is dependent upon conditions. Since d_s, T_s, p_s, and d_L are all constants, Equation 13 becomes:

$$\Delta H = aRT/p;\quad a = d_L p_s/d_s T_s \tag{14}$$

By substituting Equation 14 in 8 and 11, the following are obtained:

$$V\sqrt{p/T} = C_1'\sqrt{R} \tag{15}$$

$$W\sqrt{T/p} = C_2'\sqrt{R} \tag{16}$$

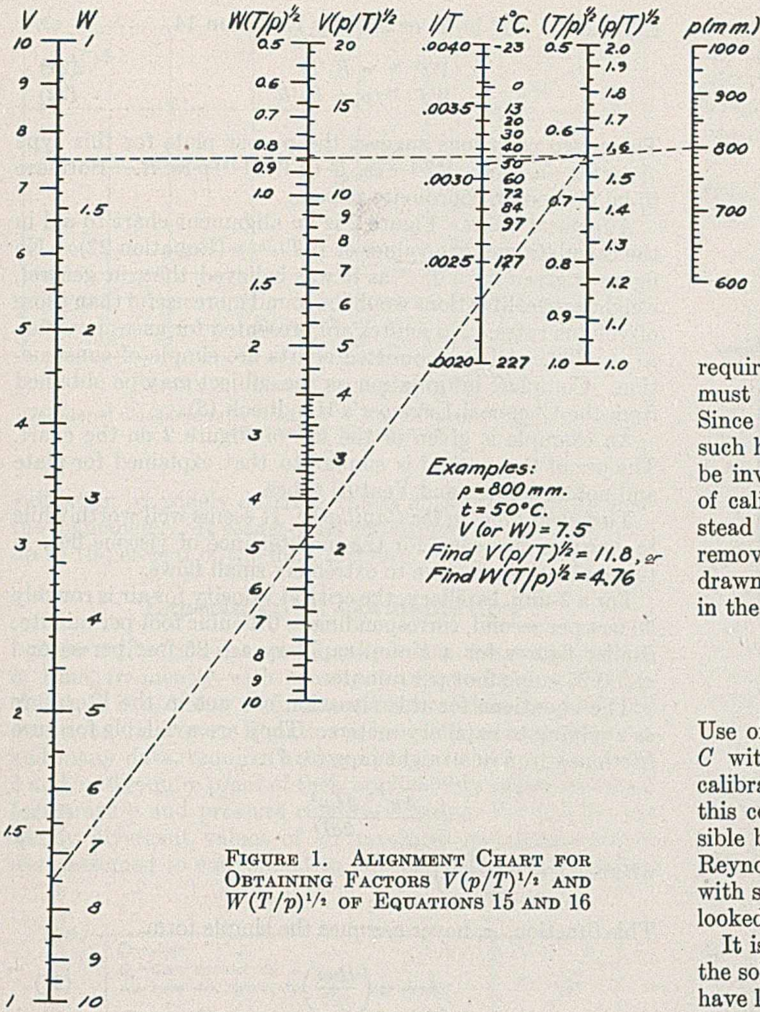

FIGURE 1. ALIGNMENT CHART FOR OBTAINING FACTORS $V(p/T)^{1/2}$ AND $W(T/p)^{1/2}$ OF EQUATIONS 15 AND 16

These results are the same as those obtained with the A. S. M. E. equation as a starting point (compare Equations 3 and 6).

In the recommended plots the intercept on log-log paper (the slope on coördinate paper) may be calculated if values of C, the discharge coefficient, are known (see subsequent paragraphs on the variable value of C); the values of C_1' and C_2' are known for any instrument and any gas (Equations 8, 9*A*, 11, and 14). These should be of principal use in predicting a calibration line as a check on the accuracy of the data taken.

ALIGNMENT CHART. An alignment chart is presented in Figure 1 for the rapid calculation of values of $V(p/T)^{1/2}$ or $W(T/p)^{1/2}$. The method of use is illustrated in Figure 1. The line $(T/p)^{1/2}$, $(p/T)^{1/2}$ is essentially a reference line; the units are not essential to the solution of the groups desired.

EXAMPLE OF METHOD. Data are available for volume discharge rates *vs.* manometer readings for a Venturi tube; the pressure and temperature conditions are known at each rate of discharge. Since it has been assumed that p_b/p_A approaches 1, outlet conditions may be substituted for inlet T and p if desired, although accuracy is decreased thereby.

At each discharge rate, calculate $V(p/T)^{1/2}$, utilizing Figure 1 if desired. Plot these values against R on log-log paper. Draw a line through the points.

At some subsequent time a definite flow rate, V, is desired. The pressure and temperature at which the instrument is to operate are determined and $V(p/T)^{1/2}$ is calculated. The manometer reading to be set is then read from the plot of $V(p/T)^{1/2}$ against R. If the converse, the flow rate for a definite recorded value of R, had been desired, $V(p/T)^{1/2}$ would have been read from the chart at this known R, and V would have been calculated by the aid of Figure 1 or by direct calculation, using the recorded values of p and T.

POSSIBILITY OF VARIABLE VALUE OF C. When the equations on orifice plates and Venturi tubes are plotted on appropriate graph paper, they will produce straight lines only if coefficient C is constant over the range at which readings are required. This means that the rate of flow in the main tube must be of a Reynolds number greater than 10,000 (*1*, *3*). Since it is not always feasible to design a low Δp orifice of such high flows, it is entirely possible that a varying C may be involved. The methods recommended for the recording of calibration curves will, in such cases, produce curves instead of straight lines. If desired, this variable C may be removed from the group of constants (e. g., C may be withdrawn from the constant, C_1, of Equation 9A) and included in the variables. Equations 15 and 16 would then appear as

$$(V/C)(p/T)^{0.5} = C_1''\sqrt{R} \qquad (15A)$$

$$(W/C)(T/p)^{0.5} = C_2''\sqrt{R} \qquad (16A)$$

Use of plots would require a knowledge of the variation of C with u, or $Du\rho/\mu$, which would be obtainable from the calibration. The use of the calibration is complicated by this correction factor and should be avoided whenever possible by design of the orifice to provide the proper range of Reynolds numbers. Since this becomes increasingly difficult with smaller pipe sizes, it is a point which must not be overlooked.

It is probable, atmospheric temperature and pressure being the sole variations, that variation of Reynolds number will have little effect upon C because of the small range covered. For most accurate work, however, the effect should be investigated unless all Reynolds numbers are in the range of 10,000 and greater when constancy of C is well assured.

Capillary Tube Orifices

METER TYPE. The meter consists of a differential pressure manometer connected across a primary device in which the pressure-throttling constriction is a long tube of smaller diameter than the main gas line. This type of device is usually employed in glass equipment, the throttling constriction being a piece of capillary glass tubing. The validity of the following equations is dependent upon the design of the instrument so that Δp from friction shall present the major resistance, Δp from expansion and contraction at entrance to, and exit from, the capillary being negligible in comparison. If any doubts occur in a particular case as to the fulfillment of such conditions, the situation may be assured by using small tapered contraction and diffusion tubes at the inlet and outlet of the capillary.

PRESENT EQUATIONS AND THEIR REFORMATION. *Viscous Flow in the Capillary.* The equation for this type of meter, with the gas in viscous flow in the capillary, was presented by Benton (*2*) in 1919. It is Poiseuille's equation for pressure drop for fluids in viscous flow:

$$V = K\frac{D^4\Delta p}{\mu L} = K\frac{\rho D^4 \Delta H}{\mu L};\ K = \frac{\pi g}{8} \qquad (17)$$

If this equation is to be used in a manner similar to that recommended for plate or nozzle orifices and Venturi tubes, μ and ρ must be expressed in terms of pressure and tempera-

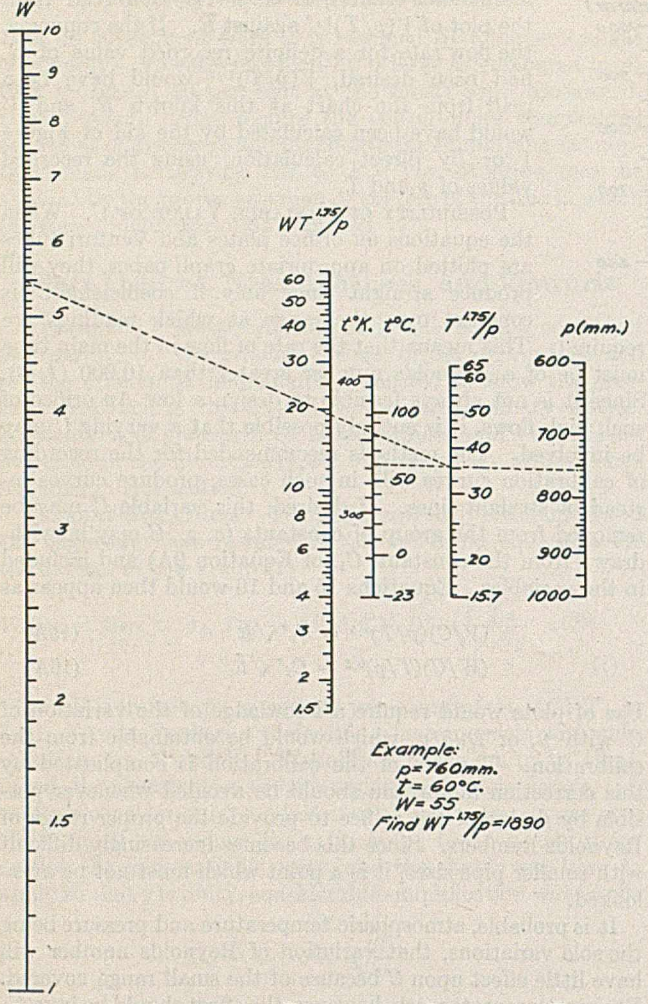

FIGURE 2. ALIGNMENT CHART FOR OBTAINING FACTOR $WT^{1.75}/p$ OF EQUATION 22

ture. For gases ρ has already been expressed in terms of p and T (Equation 10). It may be said that μ is independent of pressure over normal ranges; its dependence upon temperature is given by

$$\mu = \alpha T^{0.75} \tag{18}$$

Theoretically this relation will be found expressed as

$$\mu = \alpha\sqrt{T}$$

The author's investigation of the data on many common gases has led to the conclusion that the use of the 0.75 power of T is consistent with the data without resort to more complicated equations, such as Sutherland's (3), in the range of 0° to 100° C. The gases for which this has been found to be nearly true are air, oxygen, nitrogen, carbon monoxide, nitric oxide, hydrogen, and ethane. Certain others (ammonia, carbon dioxide, and methane) have viscosities which appear to vary with the 0.9 power of the absolute temperature. For these gases the temperature powers in the subsequent equations must, of necessity, be changed. Examples of this will be shown. The data from which these powers of the temperature have been derived were obtained from the Chemical Engineers' Handbook (3).

Substituting Equations 10 and 18, 17 becomes

$$V = K_1\, p\, \Delta H/T^{1.75} \tag{19}$$
$$W = K_2 p^2\, \Delta H/T^{2.75} \tag{20}$$

Eliminating ΔH in favor of R by Equation 14,

$$VT^{0.75} = K_1'R \tag{21}$$
$$WT^{1.75}/p = K_2'R \tag{22}$$

These two equations suggest the proper plots for this type of meter—namely, $VT^{0.75}$ *vs.* R or $WT^{1.75}/p$ *vs.* R. Both are to be plotted on coördinate paper.

Alignment Chart. Figure 2 is an alignment chart to aid in the calculation of the values of $WT^{1.75}/p$ (Equation 22). No figure is given for $VT^{0.75}$ as it was believed that, in general, weight rate calibrations would be found more useful than those of volume rates. No figures are presented for gases in which $\mu = \alpha T^{0.9}$. All such omitted charts are simple of construction. Complete information on the subject may be obtained from the Chemical Engineer's Handbook (3).

An example is given of the use of Figure 2 on the chart. The use of the method is similar to that explained for plate and nozzle orifices and Venturi tubes.

Turbulent Flow in the Capillary. It seems well worth while to consider this case, for the maintenance of viscous flow in the capillary limits one to extremely small flows.

For a 2-mm. capillary, the critical velocity for air is roughly 50 feet per second, corresponding to 0.1 cubic foot per minute; similar figures for a 4-mm. capillary are 25 feet per second and 0.25 cubic foot per minute.

The equations for this situation are not in the literature as applying to capillary meters. They are available for pure frictional drop in straight pipe (3, 5):

$$\frac{\Delta p}{\rho} = \frac{fLu^2}{2gD} \tag{23}$$

where $f = \varphi\left(\frac{Du\rho}{\mu}\right)$

This function, φ, never assumes the simple form,

$$f = a\left(\frac{Du\rho}{\mu}\right)^n \tag{24}$$

but it can be so considered over short ranges of $Du\rho/\mu$. The larger the range, the greater the error involved. For the case of $Du\rho/\mu$ from 2500 to 20,000, an average value of the slope of the f *vs.* $Du\rho/\mu$ line shows $n = -0.28$, from which the following equations result:

$$\Delta H = \frac{\varphi(Du\rho/\mu)Lu^2}{2gD} = b\left(\frac{\mu}{u\rho}\right)^{0.28} u^2$$

Substituting Equations 10 and 18,

$$\Delta H = b'\left(\frac{T^{0.75}\,T}{up}\right)^{0.28} u^2 = b'\left(\frac{T^{1.75}}{p}\right)^{0.28} u^{1.72}$$

Since $\Delta H = aRT/p$ (Equation 14),

$$R = b_1 \frac{T^{0.49}}{p^{0.28}} \frac{p}{T} u^{1.72}$$
$$b_2R = \frac{p^{0.72}}{T^{0.51}} V^{1.72}$$
$$b_3R^{0.58} = \frac{p^{0.42}}{T^{0.30}} V \tag{25}$$

A log-log plot of $V(p^{0.42}/T^{0.30})$ *vs.* R should thus produce a slight curve of average slope equal to 0.58.

It should be noted that these equations are developed from the assumption that the coefficient of viscosity of the gas varies with the 0.75 power of T. If this is not true for the gas being metered, the powers of T will change throughout the derivation. For those gases for which $\mu = \alpha T^{0.9}$, the power of T in Equation 25 becomes 0.27.

Design of the meter should be such that Δp may not become so high that the relation $\Delta H = aRT/p$ is in danger of in-

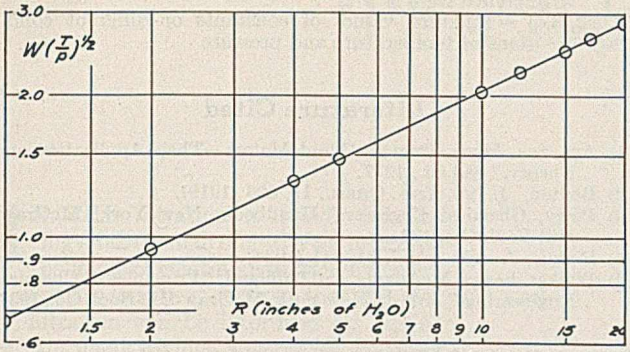

FIGURE 3. NEW DISCHARGE RATE PLOT

Calculated discharge rates from a 4 × 2 inch Venturi tube, replotted as suggested by Equation 16

validation by widely differing values of ρ in the two arms of the manometer. It seems quite satisfactory to use Δp values up to 10 per cent of the inlet pressure.

Experimental Confirmation

Since calibration data are usually taken over a short period of time, frequently with constancy of conditions a definite object, it is not easy to find experimental data to check the equations. However, Equation 1, based upon long experience and many data, requires no experimental check. Equations 3 and/or 6 require proof of their applicability under universal temperature and pressure conditions only. For this reason widely divergent values of air pressures and temperatures were assumed to correspond to varying readings of a differential manometer connected to a 4 × 2 inch Venturi tube. From these assumed values the discharge weight rate was calculated (Equations 1 and 5). As indicated by Equation 6, these weight rates were multiplied by $(T/p)^{1/2}$. All values are given in the following table:

Manometer Reading, R *Inches* H_2O	t_A °*C.*	p_A *Inches Hg*	$W_{\text{calcd.}}$ *Lb./sec.*	$W\left(\frac{T}{p}\right)^{1/2}$
1	20	29.92	0.113	0.678
2	20	30	0.162	0.971
4	25	40	0.256	1.35
5	60	40	0.272	1.50
10	25	20	0.281	2.10
12	40	20	0.302	2.30
15	100	30	0.380	2.57
17	20	30	0.456	2.73
20	40	48	0.606	2.96

The values of $W(T/p)^{1/2}$ are plotted on log-log paper against R in Figure 3. This shows the perfect straight line obtainable at high Reynolds numbers.

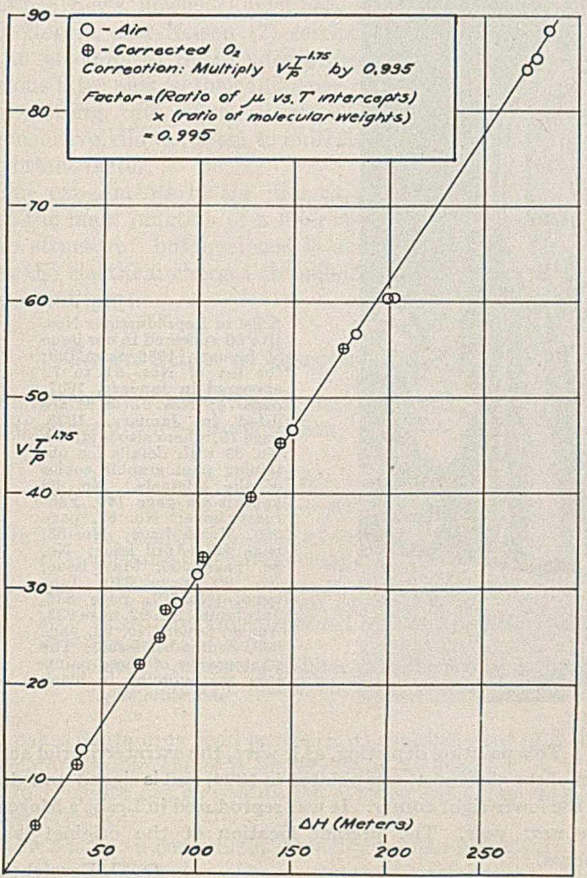

FIGURE 4. NEW DISCHARGE RATE PLOT

Pinkus' data (4) replotted as suggested by Equation 19

Pinkus (4) presented very accurate data for the calibration of a capillary meter, operating in the viscous flow range, with air and oxygen. Conditions with air varied to include pressures from 775 to 830 mm. of mercury and temperatures from 3.9° to 19.5° C. These data were recalculated and plotted as suggested by Equation 19; the 1.75 power of T was used, since the coefficients of viscosity of both air and oxygen were found to be dependent upon the 0.75 power of T. This work is presented in Figure 4.

"Corrected" points will be noted for the oxygen line. The corrections are theoretical, made by determining the relative values of K_1 for oxygen and air in Equation 19. The factors involved in the correction are the molecular weights of the two gases and the α values in the expression:

$$\mu = \alpha T^{0.75}$$

Since the factor is 0.995, the lower points are inappreciably affected. The single line for the two gases indicates that it should be possible to use an instrument of this type, calibrated with one gas, for any other gas whose coefficient of viscosity varies with the same power of the absolute temperature.

Acknowledgment

The author wishes to express his appreciation of the valuable advice and suggestions offered by J. C. Elgin, Princeton University, and T. H. Chilton, the du Pont Company.

Nomenclature

Consistent units are used throughout.

a = constant = $d_L p_s / d_s T_s$
b = constant
d = specific gravity, dimensionless
f = friction factor, dimensionless
g = gravitational constant
p = absolute pressure
t = normal scale temperature (Centigrade or Fahrenheit)
u = mean linear velocity
y = supercompressibility factor (1)
A = cross-sectional area
B = gas law constant in $pV = nBT$, where n is the number of moles of gas in a volume V
C = constant in orifice or Venturi equation
D = diameter
G = specific gravity of any gas referred to (air = 1)
H = static head, units of length
$\overline{K}$ = constant in A. S. M. E. orifice-Venturi equation
K = constant in capillary meter equation
L = length of capillary
M = molecular weight of gas
R = differential manometer reading
R' = differential manometer reading, corrected to inches of water at 60° F.
T = absolute temperature

V = volume rate of flow
W = weight rate of flow
Y = expansion factor (*1*)

α = constant
Δ = difference, applied to ΔH or Δp
φ = function
μ = coefficient of viscosity
ρ = density

Subscripts:
A = upstream pressure tap position, differential pressure producing device
B = constriction, differential pressure producing device
G = gas
L = liquid
b = downstream pressure tap position, differential pressure producing device
s = reference state
1, 2, 3, 4 = different values of constants or different conditions of temperature and pressure

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THE LOVE FILTRE

By Edgar Bundy

A list of Reproductions Nos. 1 to 60 appeared in our issue of January, 1936, page 129; the list of Nos. 61 to 72 appeared in January, 1937, page 74; Nos. 73 to 84 are listed in January, 1938, page 70, where also is shown No. 85 with details for obtaining photographic copies of the originals. No. 86 appears on page 145, February issue; No. 87, page 269, March issue; No. 88, page 427, April issue; No. 89, page 500, May issue; No. 90, page 630, June issue; No. 91, page 834, July issue; No. 92, page 933, August issue; No. 93, page 992, September issue. The photographs of these paintings are supplied in black and white only.

With this, No. 94 in the Berolzheimer series of Alchemical and Historical Reproductions, we add a new artist to the series.

Edgar Bundy, A. R. A., was born in Brighton, England, in 1862, and spent most of his life in London. His work, mostly historical and realistic genre paintings, was exhibited at the Royal Academy, commencing in 1881, and from 1907 on at the Paris Salon. He died in 1922.

This painting depicting, as it were, the extraterritorial activities of the alchemist, was painted in 1894, and is signed and dated in the lower right corner. It was reproduced in Leshe's Magazine the next year. The present location of the original is not known.

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New York, N. Y.

The Action of Filter Aids

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University College, London

Although filter aids such as kieselguhr are widely used to assist in difficult filtrations, it is not generally realized that a filter aid is properly effective only if correctly proportioned in the filter cake. This study is concerned with the effect of the proportion of filter aid and of the pressure of filtration on the permeability of filter cakes. Filter aids give cakes of more open texture, which allow higher rates of flow, greater rigidity, and higher pressures of filtration. If too much filter aid is used, the increased thickness of cake tends to counterbalance these advantages. The properties of filter aids are discussed.

IN THE filtration of liquids containing a fairly small quantity of unwanted colloidal or gelatinous matter in suspension, it has long been realized that the rate of filtration can be improved by adding certain finely divided substances generally known as filter aids (*1*). Brick dust, precipitated calcium carbonate, paper pulp, and many other materials are utilized, but most generally efficient and most widely used is diatomaceous earth or kieselguhr (*2*). Despite the wide use of filter aids, little attention has been paid to their mode of action. Addition of solids to a suspension might be expected to decrease the rate of filtration, and normally this would be the case. A filter aid has the reverse effect, apparently because it can build up a rigid skeleton which is sufficiently porous to accommodate all the gelatinous particles and to leave channels for filtrate to pass through freely. In support of this point of view it is found that the most efficient types of kieselguhr contain particles of a shape adapted to lock together to form a tough bulky cake, in which the pores occupy over 70 per cent of the total volume.

Other views, however, have been advanced. Olin, Morrison, Rogers, and Nelson (*7*) carried out a few experiments in an attempt to relate adsorption of malachite green by various filter aids to their influence on the filtration rate and the settling rate of suspensions. Their results, though inconclusive, did not seem to indicate that adsorption was an important factor.

The experiments in the present paper support the view that the main function of a filter aid is to provide a porous cake structure; but evidence is also given which suggests that the electrical charges on colloidal particles can play an important part.

Calculation of Specific Resistance

As shown by Walker, Lewis, and McAdams (*10*), rates of filtration are given by the equation,

$$\frac{dV}{d\theta} = \frac{PA^2}{rvV + \rho A} \tag{1}$$

where V = cc. of filtrate in time θ (seconds)
P = pressure difference across cake and cloth, grams/sq. cm.
A = area of filtering surface, sq. cm.
v = cc. of filter cake deposited by 1 cc. of filtrate
ρ = resistance of cloth
r = specific resistance of filter cake, or resistance of unit thickness on unit area—i. e., of unit cube

For cakes containing rigid particles, r is independent of P, but for compressible cakes it is necessary to insert $r = r'P^s$, where r' and s are constants for a given cake but vary for different cakes.

Now v is not a convenient quantity to measure accurately, owing to the difficulty of measuring cake thickness. Gilse, Ginneken, and Waterman (*6*) therefore suggested that the specific resistance be referred to unit weight of cake per unit area. Then instead of v, the proportional quantity, c, is used where c is the dry weight of cake (in grams) deposited by 1 cc. of filtrate. To determine c, a known volume of slurry is measured out, evaporated, and ignited to constant weight. In the case of fairly thick slurries, as Ruth (*8*) pointed out, it is necessary to take account of the difference between volume of filtrate and volume of slurry—i. e., of volume of cake—and he has given complete rules for this correction. For the present work this correction was deemed unnecessary, as the highest values of c, used for kieselguhr, were 0.02 gram per cc.; for less easily filtered materials they extended down to 0.005 gram per cc.

The writer also showed that it is permissible to introduce a term for viscosity, η, in analogy with Poiseuille's law, so that the modified filtration equation becomes

$$\frac{dV}{d\theta} = \frac{PA^2}{\eta(r_1cV + \rho A)} \tag{2}$$

where η = viscosity of filtrate, poises
r_1 = specific resistance in the sense of being the resistance of unit dry weight of cake solids per unit area

For compressible cakes,

$$r_1 = r_1'P^s$$

If filtration is carried out at constant pressure, r_1 and ρ are both constant, so that the time-discharge curve is given by

$$\theta = \frac{\eta r_1 c}{2PA^2}V^2 + \frac{\eta\rho}{PA}V \tag{3}$$

and is therefore a parabola. The best method of rectifying this curve is that given by Underwood (*9*)—namely, to plot θ/V against V. Incidentally, to obtain the best results, V and θ should be measured from the moment that P reaches

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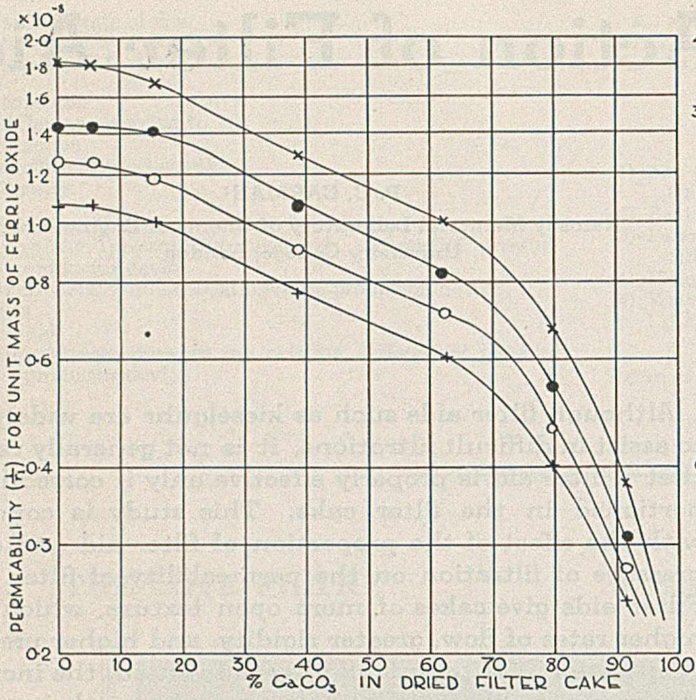
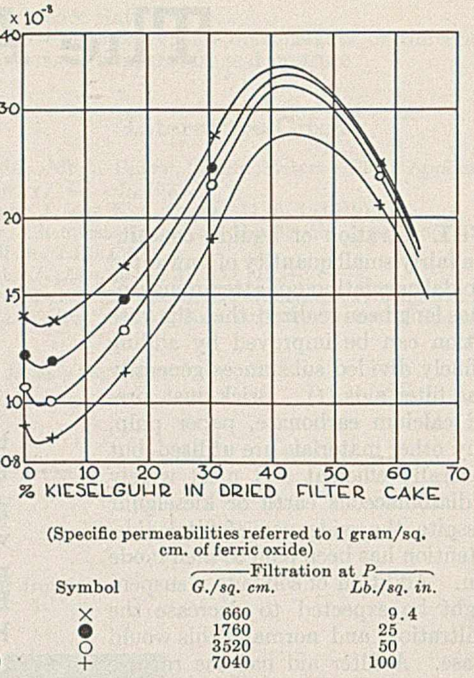




(Specific permeabilities referred to 1 gram/sq. cm. of ferric oxide)

Symbol	Filtration at P G./sq. cm.	Filtration at P Lb./sq. in.
×	660	9.4
●	1760	25
○	3520	50
+	7040	100

FIGURE 1 (*Left*). FILTRATION OF MIXTURES OF FERRIC OXIDE AND CALCIUM CARBONATE

FIGURE 2 (*Right*). FILTRATION OF MIXTURES OF FERRIC OXIDE AND KIESELGUHR

its constant value and not from the beginning of the filtration. The gradient, b, of the straight line obtained is thus given by

$$b = \frac{\eta r_1 c}{2PA^2}$$

Conversely, r_1 is obtained by substitution in

$$r_1 = \frac{2bPA^2}{\eta c} \tag{4}$$

In general, r_1 denotes the specific resistance for unit weight of total cake solids. In cases where filter aids are added to a slurry, however, it is proposed to use it in a somewhat modified way. Suppose it is necessary to filter a slurry containing concentration, c_1, of ferric oxide, and that to effect rapid filtration, a concentration, c_2, of kieselguhr is added. If the results are to be truly comparable, r_1 should correspond in both cases to 1 gram of ferric oxide per sq. cm. Therefore, in calculating r_1 from Equation 4, the value inserted for c should be the concentration of ferric oxide, c_1, and not the total concentration of cake solids, $c_1 + c_2$. For instance, if cake solids contain 99 per cent kieselguhr, it is less important to know that the resistance of unit weight of cake solids approximates that of unit weight of kieselguhr, than that the resistance per unit weight of ferric oxide approximates that of 99 grams of kieselguhr. As the proportion of kieselguhr rises to 100 per cent, r_1 rises to infinity.

Actually, in plotting the curves given in the present paper, reciprocals of r_1, or specific permeabilities, were used, since these correspond to rates of flow and thereby enable more ready interpretation of the curves by the practical engineer. These reciprocals can be converted to practical units if multiplied by the factor, 1.06×10^{10}. They then correspond to rate of flow in Imperial gallons per hour per square foot of filtering surface given by a liquid of 1 centipoise viscosity (e. g., water at 20° C.), at a filtration pressure of 1 pound per square inch when the cake contains 1 pound per square foot of the reference solid—e. g., ferric oxide in the preceding paragraph. As $1/r_1$ varies with P, it would be more correct to state that P/r_1 corresponds to rate of filtration at a filtration pressure of P pounds per square inch.

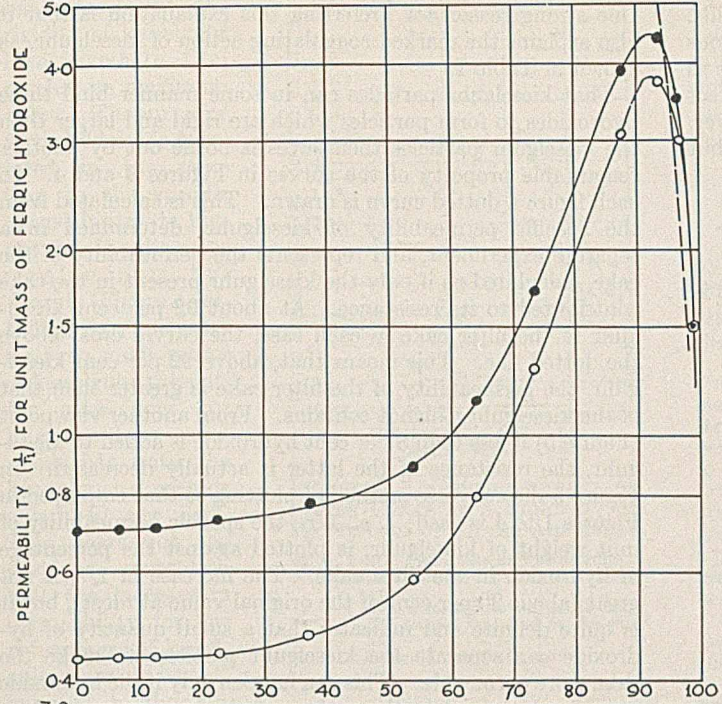
In order to show the relative values of $1/r_1$ most clearly in Figures 1 to 4, the ordinates were plotted on a logarithmic scale, since a constant ratio between two values of $1/r_1$ is then represented by a constant length, independent of their absolute values.

Preparation of Reproducible Slurries

The apparatus used for the present work was a small filter with a filtering surface of 34.2 sq. cm., which was carefully designed to give accurate reproducibility of this filtering area in successive runs. During an experiment the slurry was kept agitated in order to prevent sedimentation. Full details of apparatus and technic were published elsewhere (*3*).

The calcium carbonate used was the material known as levigated whitening, the ferric oxide was a finely ground product used as a pigment, and the kieselguhr was the grade sold under the name of Filter-Cel. Each of these was stirred with several successive quantities of distilled water, followed by settling and decantation after each stage in order to remove all traces of all soluble matter, especially soluble electrolytes. During this process the coarsest fractions from ferric oxide and kieselguhr were discarded, as these would tend to settle out during filtration and thus make reproducibility difficult. Finally, each material was made up into a concentrated stock suspension in distilled water. The concentration was measured so that, to prepare any concentration of slurry for filtering, it was necessary merely to shake the stock slurry and to pipet 25 cc., 50 cc., 100 cc., etc., into 2 liters of distilled water. Since dilution was with distilled water and the stock contained no soluble matter, it was possible to attain a high degree of consistency and reproducibility. Tests showed that the stocks did not change when kept for 2 or 3 months.

To obtain reproducible slurries of the two metallic hydroxides was a more difficult matter. These substances were precipitated with sodium hydroxide from concentrated solutions of the corresponding salts. They were then subjected to a long series of washings and decantations with distilled water to remove all soluble electrolytes. As this



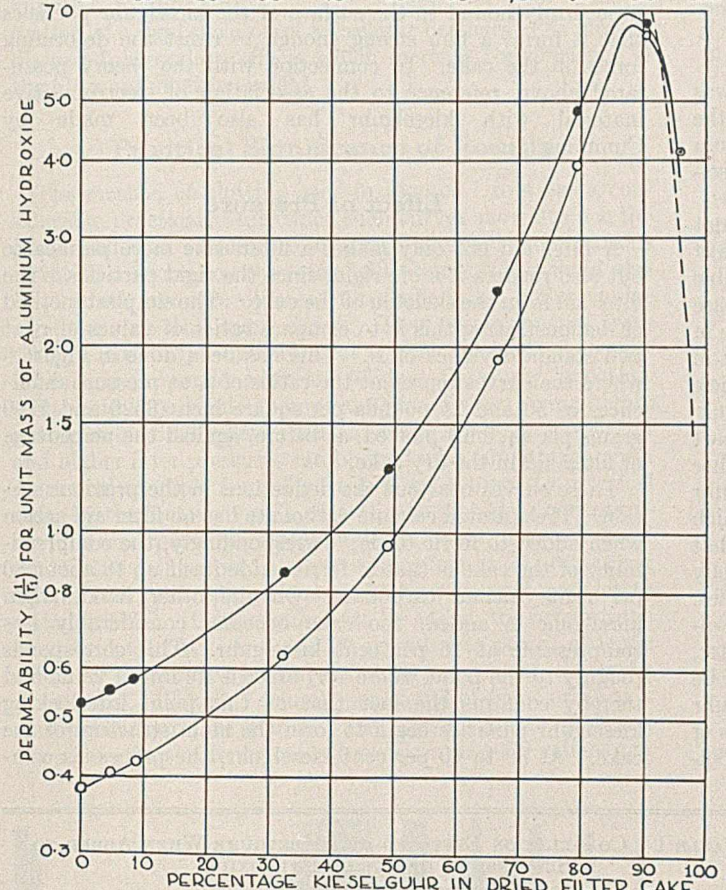


Figure 3 (*Above*). Filtration of Mixtures of Ferric Hydroxide and Kieselguhr

(Specific permeabilities referred to 1 gram/sq. cm. ferric oxide)

Figure 4 (*Below*). Filtration of Mixtures of Aluminum Hydroxide and Kieselguhr

(Specific permeabilities referred to 1 gram/sq. cm. alumina)

Symbol	Filtration at P G./sq. cm	Filtration at P Lb./sq. in.
●	1760	25
○	3520	50

approached completion, fairly extensive peptization took place and settling became very slow. Consequently, in the final stages decantation was carried out in a centrifuge. The thick slurry in distilled water which was finally obtained for each hydroxide was passed twice through a small hand emulsifier to disintegrate all large aggregates and, after aging for a few days, was ready for use. Experimental slurries were prepared as before by dilution with distilled water; for the same reasons they gave consistent and reproducible data. This result has not been achieved with similar types of slurry in any previous investigation; as published elsewhere (*3*), these stock slurries were used to test Equation 2, and they provided the first experimental confirmation for systematic variation of c and of A for highly compressible cakes. The stock slurries changed slowly in filtering properties when kept (about 10 per cent in 2 months); but since in the former series of experiments (*3*) and also in the present series only 2 weeks elapsed between the first and the last experiment, this variation need not be taken into account.

The concentration of all stock slurries was determined by pipetting out 50 cc. into an evaporating dish, evaporating, and heating strongly to constant weight. Thus, the concentrations of the hydroxides are expressed as grams per cc. of ferric oxide and of alumina, respectively.

Effect of Proportion of Filter Aid

In the following experiments the plot of θ/V against V was always linear, showing that Equation 2 and its integrated form at constant pressure (Equation 3) are as true for mixtures of gelatinous and rigid particles as for either alone. As further confirmation, for any given proportion of filter aid to total filter cake, r_1 was shown to have the same value for two different values of c (one double the other), provided P was the same in both experiments.

In Figures 1 to 4, values of $1/r_1$ on a logarithmic scale are plotted against the percentage weight of filter aid in the dry cake. Each curve corresponds to a different value of P, as shown.

Figure 1 illustrates the effect of adding precipitated calcium carbonate to suspensions of finely ground ferric oxide. Although precipitated calcium carbonate is often used unwisely as a filter aid, in this particular case it does not behave as a filter aid at all. The values of $1/r_1$ decrease steadily to the final value of zero at 100 per cent calcium carbonate. As already noted, this final value must be given by all filter aids since for 100 per cent calcium carbonate, unit weight of ferric oxide corresponds to a cake of infinite thickness.

In Figure 2 the curves are given for the addition of kieselguhr to another sample of finely ground ferric oxide. At first, when the kieselguhr particles are few and scattered through the bulk of the cake, they serve merely to increase cake thickness without giving the cake a more porous texture. Consequently, the value of $1/r_1$ falls at first, but as kieselguhr becomes present in sufficient amount to form a porous cake structure, $1/r_1$ begins to rise rapidly until it reaches about twice its original value. This represents a maximum value, since $1/r_1$ must finally fall to zero at 100 per cent kieselguhr in the filter cake. These curves emphasize that, although kieselguhr does behave as a filter aid, it does so only for proportions between 10 and 80 per cent of the filter cake.

Ferric oxide, however, does not provide the type of suspension which would normally be treated with filter aids. Figure 3 shows the effect of adding kieselguhr to gelatinous ferric hydroxide. The curves are of the same general type as in Figure 2, but as would be expected, the beneficial effect of adding kieselguhr is much more marked. However, for small additions of kieselguhr, $1/r_1$ does not decrease but remains constant.

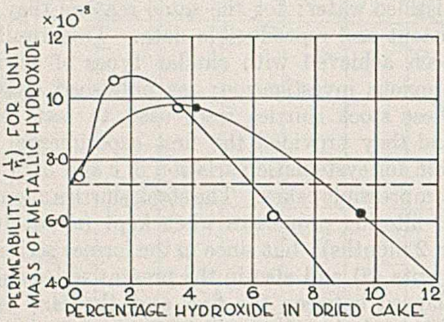


FIGURE 5. EFFECT OF SMALL ADDITIONS OF METALLIC HYDROXIDES TO KIESELGUHR

(Specific permeabilities referred to 1 gram/sq. cm. of kieselguhr)

● = Ferric hydroxide and kieselguhr
○ = Aluminum hydroxide and kieselguhr
(In both curves, P = 1760 gram/sq. cm., i. e., 25 lb./sq. in.)

In a further series of experiments (Figure 4) kieselguhr was added to gelatinous aluminum hydroxide. The trend of the curves is similar, except that $1/r_1$ rises towards its maximum value on addition of even the smallest proportion of kieselguhr.

Figures 3 and 4 suggest that the action of kieselguhr is not always limited to its mechanical influence on the structure of the filter cake. It seems reasonable that the only possible effect of adding a small proportion of kieselguhr is to increase the bulk of the cake and hence its resistance, as is the case in Figure 2. The apparent contradiction to this statement in the above cases would be explicable if a kieselguhr particle were able to bind some of the hydroxide in its vicinity firmly to its surface. This would be equivalent to removal of part of the gelatinous part of the cake and thus lead to a higher permeability than would normally be expected. Kieselguhr consists of skeletons of diatoms, the structure of which abounds in crevices and pores. It is possible, therefore, that the soft hydroxide is forced into these pores and thereby becomes an integral part of the rigid kieselguhr particles.

The writer, however, favors a different suggestion. Colloidal silica bears a negative electrical charge in pure water, and it seems probable that a negative charge will also be found on any silica surface, such as that of the kieselguhr particle. In fact, the negative charge on certain particles of diatomaceous earth was demonstrated by White (*2*). Colloidal sols of ferric and aluminum hydroxides contain positively charged particles. In the present suspensions of these hydroxides in distilled water, it was observed that a considerable part of the hydroxide seemed to be in colloidal suspension, since it did not settle on standing. Owing to the high specific surface of kieselguhr, therefore, the effect of a small addition would be considerable, if it attracted some of the positive colloid particles to its surface where they would remain firmly bound. This effect would be especially noteworthy when it is remembered that the colloidal part of the suspension creates most of the resistance to filtration. One strong reason for preferring this explanation is that it also explains the marked coagulating action of kieselguhr, as shown in Table I.

That kieselguhr particles can in some manner bind these hydroxides to form particles which are rigid and larger than the kieselguhr particles themselves is borne out by another remarkable property of the curves in Figures 3 and 4. In each figure a dotted curve is drawn. This is calculated from the specific permeability of kieselguhr, determined in a separate experiment, and represents the permeability of the cake, calculated as if only the kieselguhr present in the cake contributed to its resistance. At about 92 per cent kieselguhr in the filter cake in each case, the curves cross above the dotted line. This means that, above 92 per cent kieselguhr, the permeability of the filter cake is greater than that of the kieselguhr which it contains. From another viewpoint (Figure 5) if less than 8 per cent hydroxide is added to kieselguhr, the resistance of the latter is actually decreased. In Figure 5 the converse method of plotting to that employed in Figures 1 to 4 is used; i. e., $1/r_1$, the specific permeability of unit weight of kieselguhr, is plotted against the percentage of hydroxide in the filter cake. The increase in $1/r_1$ is not great (about 20 per cent of the original value at most), but it is quite definite and indicates that a small quantity of hydroxide can separate the kieselguhr particles to make the cake more permeable. This can happen only if the hydroxide is so firmly bound to the surface of the kieselguhr particles that it forms a film strong enough to resist the deforming forces in the cake. In connection with the theory postulated above, reference to the association of electropositive material with kieselguhr has also been made by Cummins (*5*).

Effect of Pressure

A filter aid not only makes a filter cake more permeable but also renders it more rigid, since the rigid particles of the filter aid form the skeleton of the cake. The simplest method of demonstrating this is to compare ratios of values of r_1 at two standard values of P. This has been done in Figure 6 where the curves represent the ratios of r_1 at pressure differences of 50 and 25 pounds per square inch (3520 and 1760 grams per sq. cm.) plotted, as before, against the percentage of filter aid in the dry cake.

These curves bear out the deductions in the previous section. Precipitated calcium carbonate has no filter aid action when added to ferric oxide; correspondingly, the compressibility of the cake is that of ferric oxide itself up to about 80 per cent calcium carbonate. On the other hand, when kieselguhr is added, the cake becomes considerably less compressible at 16 per cent kieselguhr. This corresponds roughly to the point where $1/r_1$ exceeds its initial value and thereby confirms the fact that at this point interlocking kieselguhr particles begin to form the main structure of the cake. At 30 to 40 per cent kieselguhr, the process is com-

TABLE I. COAGULATION EFFECTED BY KIESELGUHR WHEN ADDED TO SUSPENSIONS OF FERRIC HYDROXIDE

% Kieselguhr	Effect
0.0	Hardly any sediment in 30 min.; suspension dark brown
6.8	Considerable coagulation; loose flocs settle rapidly, leaving dark brown supernatant liquid
22.7	Much more coagulation; supernatant liquid definitely lighter in color
54.0	Practically whole of solids settled in less than 1 min.; light yellow supernatant liquid
98.6	Actually settles faster than kieselguhr; clear supernatant liquid

plete; the cake then has practically the rigidity of kieselguhr itself, while $1/r_1$ reaches its maximum value. The curve for ferric hydroxide is related in the same way to the specific permeabilities in Figure 3. In the case of aluminum hydroxide (Figure 4) although $1/r_1$ increases for even small values of kieselguhr present, the cake does not become less compressible until the kieselguhr exceeds about 40 per cent. This bears out the previous contention that the increase in permeability for low percentages of kieselguhr cannot be attributed to the formation of a rigid skeleton of kieselguhr particles. As already discussed, secondary effects which increase the efficiency of the filter aid must be sought.

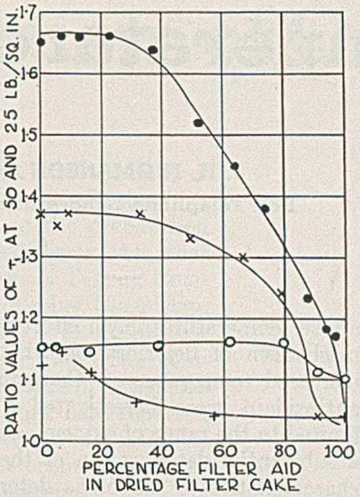


FIGURE 6. COMPRESSIBILITY OF FILTER CAKES AS A FUNCTION OF PROPORTION OF FILTER AID ADDED

● = Ferric hydroxide and kieselguhr
× = Aluminum hydroxide and kieselguhr
○ = Calcium carbonate and ferric oxide, the former intended as the filter aid
\+ = Kieselguhr and ferric oxide

Practical Significance of Results

The method of plotting used in Figures 1 to 4 has a considerable practical value, since such curves show at once the relative effect of various proportions of filter aid and of various filtration pressures on the rate of filtration. They could also be used to compare different filter aids tested under similar conditions on the same slurry. Two points emerge from the present study—namely, that a filter aid is efficient only if properly proportioned to the solids in the slurry, and that a filter aid is particularly important for slurries giving highly compressible filter cakes, since the cakes are made more rigid and higher filter pressures can be used with advantage. As a numerical example from Figure 3, if we convert to practical units by the factor given in an earlier section, a cake containing 1 pound per square foot of ferric oxide gives a rate of flow of 187 gallons per hour per square foot at 25 pounds per square inch, and 228 gallons at 50 pounds, with respect to water at 20° C. If kieselguhr is to be added, the proportions must be kept between 3 and 20 pounds per pound of ferric oxide—i. e., between 75 and about 96 per cent of kieselguhr in the cake. Taking 7 pounds per pound of ferric oxide as a reasonable figure, we find that the rates of flow for 1 pound per square foot of ferric oxide have risen to 1030 gallons per hour per square foot at 25 pounds per square inch and to 1590 gallons at 50 pounds, respectively. Not only has the rate of filtration been increased enormously, but it is also now well worth while to use the higher pressure. It is not intended here to work out the most economical quantity of kieselguhr to use, since this has already been done in some detail elsewhere (*4*).

Summary and Conclusions

The behavior of filter aids has been studied experimentally by determining the specific permeability of various typical slurries for various proportions of filter aid and at different filtration pressures. These are in agreement with the theory that:

1. The action of a filter aid such as kieselguhr is mainly mechanical; i. e., its function is to provide a rigid filter cake structure of high porosity. When kieselguhr is added to suspensions of finely ground ferric oxide, this conception is sufficient to explain the results.
2. However, when kieselguhr is added to suspensions which are partly in the colloidal state, the kieselguhr proves to have a greater efficiency than is to be expected from its action in forming a porous cake. Since colloidal particles of the metallic hydroxides used have positive electrical charges, it is suggested that these become firmly bound to negatively charged kieselguhr particles.
3. An interesting corollary of the foregoing observation is the fact that a small addition of the metallic hydroxide to kieselguhr actually increases the permeability of the latter.
4. The mode of calculating and plotting the data in the present paper has made clear that (*a*) filter aids are effective only if correctly proportioned in the cake, and (*b*) they are best applied to highly compressible cakes, since the improvement in rigidity of the cake enables higher filtration pressures to be used.

Acknowledgments

The author expresses his thanks to M. B. Donald for useful criticism in the course of the above work, and to the trustees of the Leverhulme Studentships in Chemical Engineering for the grant of a studentship, which made the work possible.

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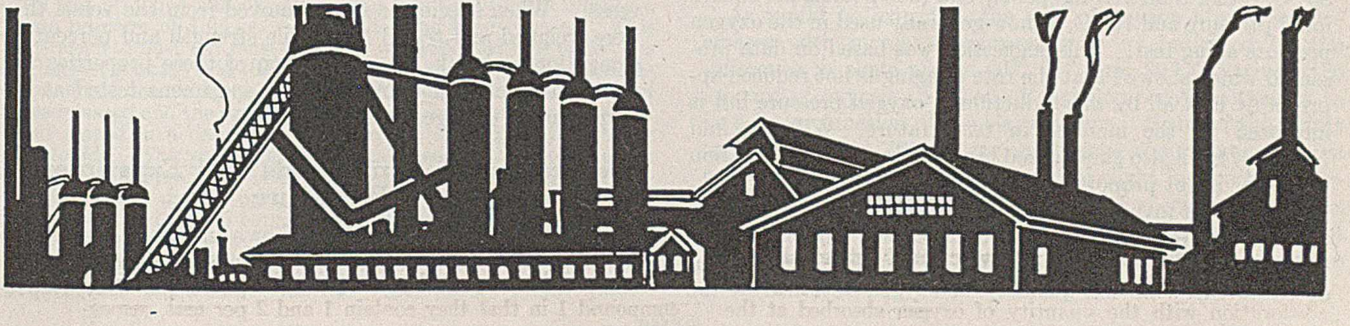

Effect of Temperature on the

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The effect of temperature on the rate of oxidation of vulcanized rubber has been determined at 60°, 70°, and 80° C. This investigation was confined to the oxidation range which accounts for a substantial deterioration of physical properties. Physical deterioration was correlated with quantity of oxygen absorbed.

It was found that the quantity of oxygen absorbed was a linear function of the time of aging at each of the three test temperatures, and that tensile strength and elongation at break decreased as linear functions of the quantity of oxygen absorbed following an initial induction period. Additions of antioxidant to the compound reduce the rate of oxidation which remains a linear function of time.

The temperature coefficient of oxidation or physical deterioration was calculated to be 2.38 for each 10° C. increase in temperature over the range investigated. This is equivalent to an 8° C. rise in temperature to double the rate of oxidation, which is in good agreement with the results of other investigators.

IT IS NOW generally recognized that the primary agent usually responsible for the deterioration of rubber is oxygen which is absorbed from the atmosphere. Accelerated aging tests devised to increase the rate of oxygen absorption are in general use for comparing and predicting the probable life of rubber compounds and rubber goods. In these tests acceleration of oxygen absorption is usually effected by increasing the oxygen concentration above atmospheric, by increasing the temperature, or by a combination of both. The present tendency of accelerated aging tests is in the direction of using moderate increases in oxygen concentration over atmospheric conditions and temperatures higher than 60° or 70° C. which have been considered as standard for the purpose for some years. In an earlier paper (*9*) the present authors suggested the use of an oxygen pressure of 3.5 kg. per sq. cm. (50 pounds per square inch) and a temperature of 80° C. rather than 21.1 kg. per sq. cm. (300 pounds per square inch) pressure and 70° C. as now generally used in the oxygen pressure aging test. This suggestion was based on data presented which showed that the rate of aging is not reduced appreciably if at all by this reduction in oxygen pressure but is increased by the increase in temperature. Williams and Neal (*13*) have also emphasized the fact that rate of oxidation of rubber is not proportional to oxygen pressure.

The present investigation was undertaken to determine the comparative rates at which soft vulcanized rubber absorbs oxygen at 60°, 70°, and 80° C. and to correlate the physical deterioration with the quantity of oxygen absorbed at the above temperatures in an effort to detect any differences in mechanism of deterioration which might be attributed to increased temperatures. Compounds with and without an antioxidant were investigated. These studies have been limited to the range of oxygen absorption which accounts for a substantial deterioration of the usually accepted physical characteristics of rubber as determined by tensile strength measurements.

Only recently has it been recognized that complete deterioration of the useful physical properties of rubber occurs as the result of the absorption of only a small amount of the total oxygen which the rubber may ultimately absorb. In his studies relating oxygen absorption to natural aging at constant pressure at 80° C., Kohman (*11*) reported that the deterioration of well-cured rubber may be considered as directly proportional to the amount of oxygen absorbed so long as the rubber retains sufficient strength to be of practical use, and that the absorption of as little as 0.5 per cent of oxygen may result in substantial decreases in tensile strength.

Dufraisse and Etienne (*8*) recently studied the effect of vulcanization on the rate of oxidation at 80° C. in relation to deterioration of tensile strength and elongation at break. Cramer, Sjothun, and Oneacre (*5*) determined by analysis the amount of oxygen absorbed by rubber and rubber compounds as a result of milling and accelerated aging. They also correlated oxygen found by analysis with deterioration in tensile strength. Milligan and Shaw (*12*) showed that decay of tensile strength of rubber compounds is proportional to the amount of oxygen absorbed from the air at 82.22° C. (180° F.).

In discussing the determination of oxygen absorbed by rubber, Dufraisse (*6*) lists three processes which are applicable: analytical, gravimetric, and volumetric methods. In his work, Kohman used a volumetric method at constant pressure. Dufraisse and his co-workers have also contributed greatly to the development of this method. Cramer, Sjothun, and Oneacre preferred the analytical method because of its applicability to determination of oxygen content of rubber already aged.

The work here reported was carried out by employing both gravimetric and volumetric methods. Standard tensile specimens of vulcanized rubber after drying and weighing were suspended in a small pressure vessel under an original oxygen pressure of about 2 atmospheres absolute for various periods of time at 60°, 70°, and 80° C. As oxidation progressed, the decrease in oxygen pressure was followed by means of a recording pressure gage attached to the pressure vessel. When specimens were removed from the vessel they were weighed and tested for tensile strength and percentage elongation at break. A comparison of these properties was made with those of unoxidized dry specimens tested at the same time as the aged specimens.

Preparation of Compounds and Experimental Procedure

The three rubber compounds shown in Table I were used for the work here reported. Compounds 2 and 3 differ from compound 1 in that they contain 1 and 2 per cent, respec-

Mechanism of Oxidation of Rubber

tively, based on the crude rubber content of an antioxidant, phenyl-α-naphthylamine.

The procedure followed in the preparation of compounds and molded sheets was that recommended by the Physical Testing Committee of the Division of Rubber Chemistry, AMERICAN CHEMICAL SOCIETY (*1*). Sufficient quantities of crude rubber and other compounding materials for the entire investigation were set aside when the work here reported was undertaken in order to avoid variations in the rubber which might occur as a result of using different lots of materials.

The compounds were cured in the form of sheets about 15.2 cm. square and 0.19 cm. thick in a mold for exactly 40 minutes at 142° C. The time of cure was selected to give slightly less than maximum tensile strength. For test purposes standard tensile specimens were cut using a die having an over-all length of 13.4 cm. (5.375 inches) and a constricted area identical with the A. S. T. M. type C die (*2*). The average tensile strength and percentage elongation at break were calculated in accordance with A. S. T. M. standard procedure for evaluating aging effects (*3*).

Aging tests were carried out in a steel pressure vessel having a capacity of about 500 cc. designed and used generally for determining "potential gum" in gasoline. Connections were made through the screw top of the vessel to an oxygen supply tank and to a recording pressure gage having a chart range of 0 to 1.40 kg. per sq. cm. (0 to 20 pounds per square inch) and scale divisions of 0.014 kg. (0.2 pound) permitting estimations to less than 0.007 kg. (0.1 pound) pressure. The pressure vessel was immersed in a water bath maintained at the test temperature with a possible variation of ±1° C. The temperature during the tests showed less than this possible variation, however. Figure 1 is a schematic drawing of the apparatus used.

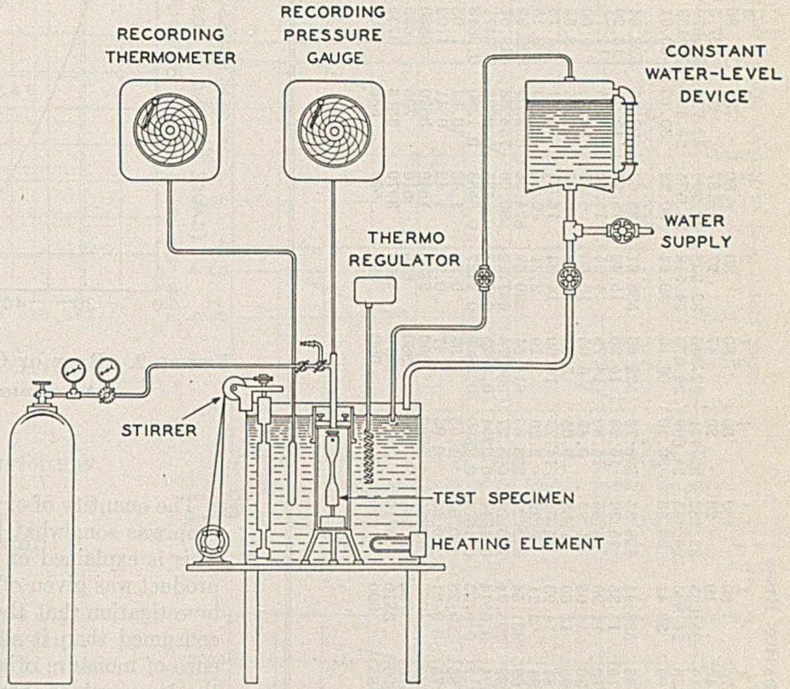

FIGURE 1. DIAGRAM OF AGING APPARATUS

TABLE I. COMPOSITION OF RUBBER COMPOUNDS

Material	Compound 1	2	3
Smoked sheets	100.00	100.00	100.00
Zinc oxide	20.00	20.00	20.00
Sulfur	3.00	3.00	3.00
Di-*o*-tolylguanidine	0.75	0.75	0.75
Phenyl-α-naphthylamine	...	1.00	2.00
	123.75	124.75	125.75

Tensile specimens cut from molded sheets of the compound were strung six on a supporting pin, which was the number used for each aging charge, and dried in the dark at room temperature over phosphorus pentoxide. When dried to constant weight, the six specimens supported on a pin were removed from the desiccator and quickly placed in the pressure vessel which had previously been warmed to the desired aging temperature. The screw top was attached and oxygen passed into the vessel at once to a gage pressure of 1.05 kg. (15 pounds) and then released. This operation to flush out most of the air was repeated four times, the aging test starting with the fifth charge of oxygen. At the termination of the desired aging period, the residual oxygen in the vessel was released and the aged specimens were removed from the vessel and placed in a desiccator again in the dark over phosphorus pentoxide. The specimens were again weighed all together on the mounting pin to determine weight gain. They were then replaced in the desiccator and tested for tensile properties after resting for at least 16 hours along with control specimens which had been kept in the desiccator during the aging period. Weight gain at the end of this drying period was found to be practically identical with that previously determined.

Details of the various oxidation runs are given in Table II. Although the volume corrections applied are smaller than the pressure indicated by one scale division on the pressure gage, their application appears to be justified since gage readings were estimated between scale division marks.

Effect of Temperature on the Rate of Oxygen Absorption

Test specimens of compound 1 were aged under the conditions described for periods of time varying from 72 to 234 hours at 60° C., 24 to 145 hours at 70° C., and 10 to 47 hours at 80° C. Figure 2 shows the course of oxygen pressure reductions as indicated on the pressure gage for all these runs. While the reduction in pressure was apparently not an exact linear function of time in each case, it was sufficiently close to a straight-line function to be considered as such for present purposes. It is recognized that the mechanism of oxidation of rubber is autocatalytic in nature, but it appears that over the short range of oxidation investigated and under the conditions selected, the autocatalytic effect is negligible. The end quantities of oxygen absorbed in each run as indicated by weight gains and pressure reductions at the various temperatures are plotted in Figure 3.

As would be expected, the rate of oxygen absorption increases with increased temperature. As indicated by the difference in slope of the 60°, 70°, and 80° C. curves, the amount of oxygen absorbed at each temperature appears to be a linear function of the elapsed time. Some of the points on the 60° and 70° C. curves diverge somewhat. This is accounted for on the basis of possible slight inadvertent variations in the degree of vulcanization of specimens. As has been shown by Dufraisse and Etienne, the rate of oxidation of rubber will vary widely with only small variations in degree of vulcanization.

TABLE II. DETAILS OF OXIDATION RUNS

Compound No.	1	1	1	1	1	1	1	1	1	1	1	1	2	2	2	3	3	3
Temperature, ° C.	60	60	60	60	70	70	70	70	80	80	80	80	80	80	80	80	80	80
Time, hours	72	143	192	234	24	75	98	145	10	20	29	47	97	187	47	167.5	95	240
Charge, grams of rubber compound	33.093	33.949	33.061	34.646	32.800	32.819	33.517	33.719	33.093	33.182	32.751	32.845	32.928	32.909	32.778	32.679	32.869	32.740
Rubber hydrocarbon, grams	24.866	25.590	24.84	25.282	24.646	24.661	25.185	25.336	24.866	24.933	24.609	24.679	24.548	24.534	24.436	24.169	24.310	24.215
Vol. of rubber compound, cc.	30.32	31.20	30.39	30.92	30.15	30.17	30.81	30.99	30.41	30.50	30.10	30.19	30.24	30.22	30.10	30.01	30.18	30.06
Vol. of system without rubber, cc.	558.85	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
Vol. of system with rubber, cc.	528.53	527.65	528.46	527.93	528.70	528.18	528.04	527.86	528.44	528.35	528.75	528.66	528.61	528.63	528.75	528.84	528.67	528.79
Initial gage reading, lb. per sq. in.[a]	15.05	15.15	15.2	15.5	15.15	15.1	15.55	15.15	15.35	15.30	15.25	15.20	15.40	15.25	15.20	15.20	15.15	15.25
Cor. initial gage reading. lb. per sq. in.[a]	14.6	14.7	14.75	15.05	14.70	14.65	15.1	14.70	14.90	14.85	14.80	14.75	14.95	14.80	14.75	14.75	14.70	14.80
Final gage reading, lb. per sq. in.[a]	13.25	11.1	8.7	6.9	13.3	7.80	6.90	4.30	14.05	11.95	9.45	6.05	10.60	6.50	12.70	9.00	11.30	6.50
Cor. final gage reading, lb. per sq. in.[a]	12.8	10.7	8.3	6.5	12.85	7.40	6.50	3.90	13.60	11.55	9.05	5.65	10.17	6.05	12.25	8.55	10.90	6.10
Barometric pressure, lb. per sq. in.[a]	14.56	14.93	14.88	14.92	14.70	14.72	14.75	14.84	14.93	14.65	14.73	14.60	14.83	14.76	14.94	14.75	14.82	14.73
Oxygen solubility (calcd.), cc.	3.29	3.43	3.34	3.44	2.74	2.73	2.84	2.83	2.24	2.22	2.20	2.19	2.21	2.14	2.19	2.15	2.17	2.16
Vol. of O_2 at start (std. cond.), cc.	862.81	875.35	876.60	885.82	844.34	843.43	856.26	847.09	831.54	822.22	823.65	818.51	830.39	824.24	828.09	822.92	823.24	823.66
Vol. of O_2 at end (std. cond.), cc.	809.57	757.19	685.77	633.12	791.20	635.25	609.56	537.39	795.74	730.24	663.27	564.74	697.12	580.26	758.38	649.97	717.26	581.01
Weight of O_2 absorbed, gram	0.076	0.1689	0.2726	0.3613	0.0759	0.2974	0.3525	0.4424	0.0514	0.1314	0.2294	0.3625	0.1898	0.3485	0.0996	0.2471	0.1513	0.3467
Gain in weight of specimens, gram	0.0829	0.1919	0.3023	0.3946	0.0879	0.3215	0.3605	0.4717	0.0703	0.1574	0.2600	0.3869	0.2127	0.3583	0.1280	0.2618	0.1760	0.3741
Weight gain, per cent	0.33	0.75	1.21	1.56	0.36	1.30	1.43	1.86	0.28	0.63	1.05	1.57	0.86	1.46	0.52	1.08	0.72	1.54
O_2 absorbed by vol. per cent	0.31	0.66	1.10	1.43	0.31	1.21	1.39	1.75	0.21	0.53	0.93	1.47	0.77	1.42	0.41	1.02	0.62	1.43
T. S. of aged specimens, lb. per sq. in.[a]	3815	3100	1975	1595	3970	1645	1410	550	4060	2880	2080	890	2855	1540	3630	2880	2865	1760
Elongation of aged specimens, per cent	675	685	630	595	700	620	600	475	735	685	660	580	675	610	705	655	680	635
T. S. of control specimens, lb. per sq. in.[a]	4085	3890	3810	3510	3880	3955	3505	3890	3810	3810	3810	3810	4005	3970	3815	3735	3795	3910
Elongation of control specimens, per cent	715	685	690	640	660	675	655	685	690	690	690	690	695	690	685	690	710	710

[a] Lb. per sq. in. × 0.0703 = kg. per sq. cm.

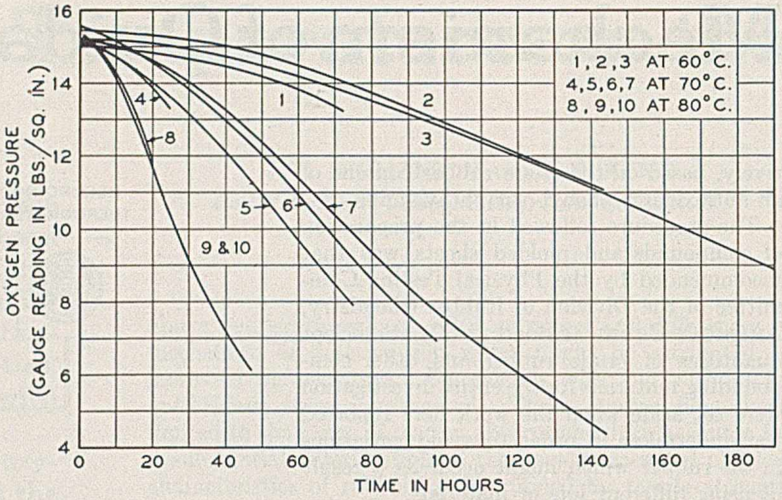

FIGURE 2. RATE OF OXIDATION OF COMPOUND 1 AT 60°, 70°, AND 80° C.

As indicated by oxygen pressure reduction (gage readings)

The quantity of oxygen absorbed in each run as determined by pressure drop was somewhat less than the quantity determined by weight gain. This is explained on the basis that a small quantity of volatile oxidation product was given off by the rubber. Milligan and Shaw found in their investigation that the residual pressure was greater when all oxygen was consumed than it should have been. They attributed this to the presence of moisture originally in the specimens. The authors believe that the lower values obtained by the pressure-reduction method are probably due largely to the presence of water split off from the rubber following oxidation, since the test specimens were dry originally.

On the basis of the investigations of Dufraisse and Etienne, and Cramer and co-workers, it is to be expected that the rate curves shown in Figure 3 would be inclined to the right if the rubber had been vulcanized less or if the compound had contained an antioxidant. Other accelerator combinations giving better aging compounds might also be expected to reduce the rate of oxidation and incline the curves in the direction of the abscissa. Overcures would be expected to move the curves in the direction of the ordinate. It is believed, however, that the oxidation rates for this compound at the three temperatures investigated would remain propor-

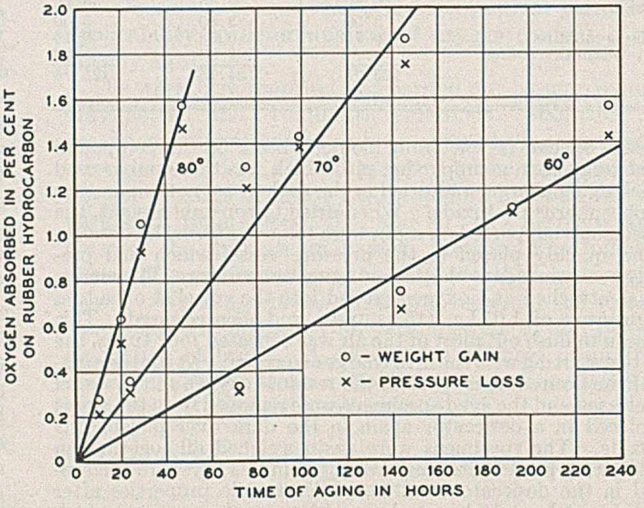

FIGURE 3. RATE OF OXIDATION OF COMPOUND 1 AT 60°, 70°, AND 80° C.

As determined by weight gain and decrease in oxygen pressure

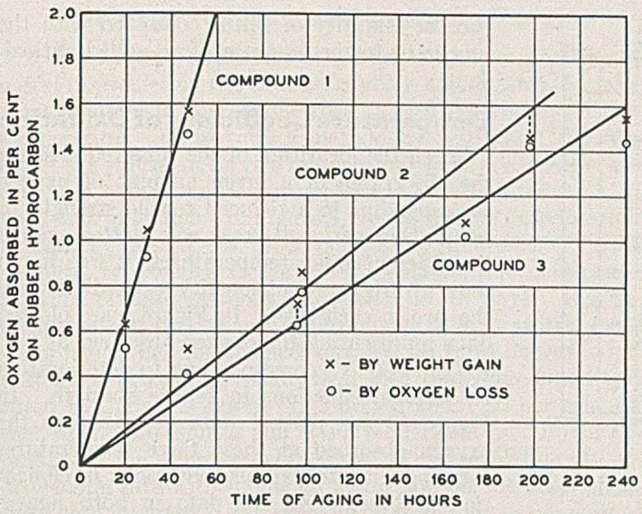

Figure 4. Effect of an Antioxidant on Rate of Oxygen Absorption at 80° C.

tional to each other despite shifts in either direction for any of the enumerated reasons.

Effect of Antioxidants on Rate of Oxygen Absorption

Specimens of compounds 2 and 3 containing 1 and 2 per cent, respectively, on the rubber content of phenyl-α-naphthylamine were aged under conditions described at 80° C. for periods of time varying from 48 to 240 hours. As was expected, the rate of oxidation was reduced over that of the specimens containing no antioxidant. The oxidation rate curves as obtained for compounds 2 and 3 at 80° C. are given in Figure 4 in comparison with the rate for compound 1 containing no antioxidant.

The curves show that the compound containing no antioxidant requires 30 hours to absorb 1 per cent of oxygen, as compared with 125 hours for the compound containing 1 part of antioxidant and 160 hours for the compound containing 2 parts of antioxidant. Under the conditions of this investigation the presence of the particular antioxidant employed causes a retardation in the rate of oxidation but does not appear to change the type of linear relationship which exists between quantity of oxygen absorbed and time. Further increases in antioxidant content would be expected to effect further decreases in rate of oxygen absorption, but the effect would be less marked.

Effect of Oxygen Absorbed on Tensile Strength and Elongation

During the initial stages of oxygen absorption or oxidation, in some cases there was an increase of tensile strength and elongation at break. This was very likely due to further curing of the samples at the aging temperature. Following the initial oxidation period, it was found that tensile strength and elongation at break decreased as a linear function of the quantity of oxygen absorbed. In Figure 5 are plotted the tensile strength values determined on specimens of compound 1 which had absorbed various quantities of oxygen at 60°, 70°, and 80° C. Figure 6 shows the change in tensile strength of compounds 2 and 3 with progressive absorption of oxygen. These figures showing proportionality between tensile strength and quantity of oxygen absorbed are drawn with respect to points representing weight gains rather than pressure losses because it is believed that the former are the more accurate for the reasons given above.

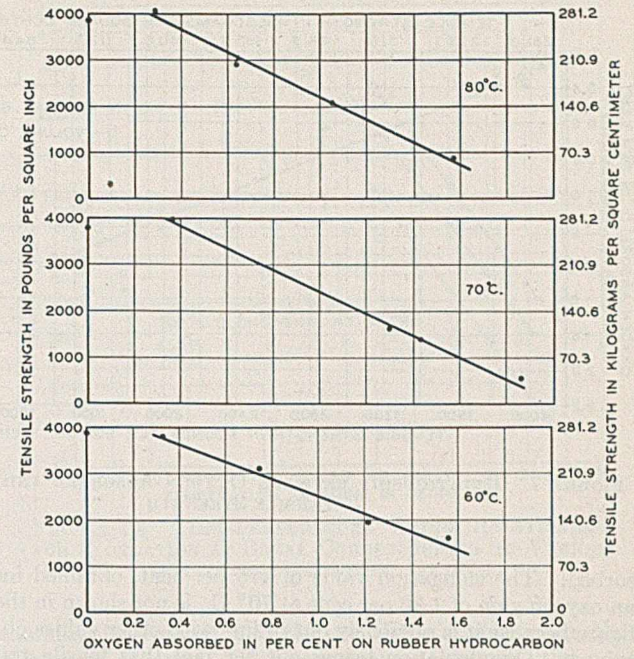

Figure 5. Effect of Oxygen Absorbed on Tensile Strength of Compound 1

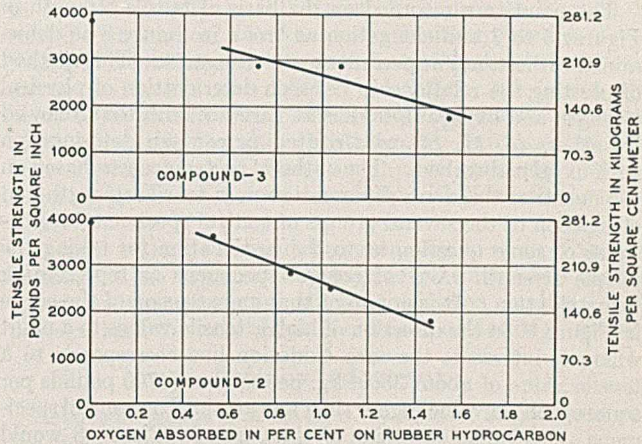

Figure 6. Effect of Oxygen Absorbed at 80° C. on Tensile Strength

As indicated by a comparison of the data plotted in Figure 5, the extent of physical deterioration corresponding to a given quantity of oxygen absorbed appears to increase slightly as the temperature of oxidation is increased. This apparent difference may be due to the loss of a greater quantity of the volatile oxidation product with increased temperatures of oxidation.

A comparison of the data plotted in Figures 5 and 6 indicates that additions of antioxidant to the compound reduce the physical deterioration which corresponds to a given oxygen absorption, the larger quantity of antioxidant having a correspondingly greater effect. This can be explained on the basis that the antioxidant consumes some of the oxygen in the process.

In Figure 7 all the weight gain and oxygen pressure loss values for compounds with and without antioxidant aged at the three test temperatures are plotted against corresponding tensile strength values found. Similar data for oxygen absorption and elongation at break are shown in Figure 8, except that weight gains alone are used to represent oxygen ab-

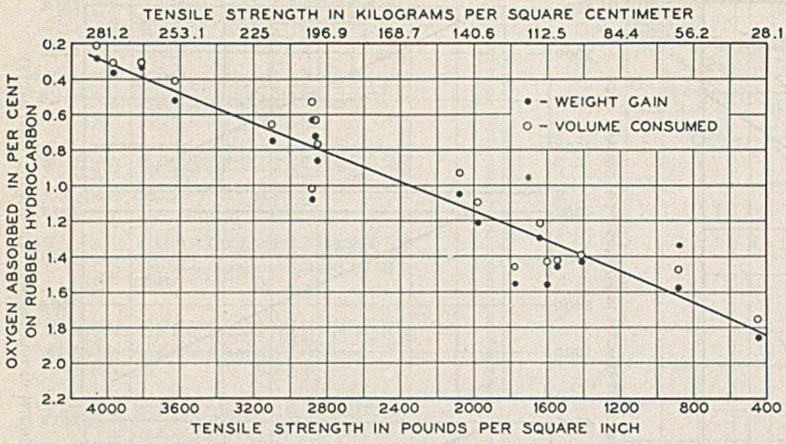

Figure 7. Relationship between Oxygen Absorbed and Decrease in Tensile Strength

sorbed. The elongation value of 475 per cent, obtained for an oxygen gain of 1.86 per cent at 70° C., is not shown in the figure because it is obviously out of line with other values obtained. This deviation brings out the fact that tensile and elongation tests are subject to considerable error when made on specimens which have been aged to an oxygen content approaching 2 per cent.

The points are recorded on the basis of tensile strength in Figures 5 to 7 and elongation at break in Figure 8 as determined rather than as percentage deterioration. This method of plotting the relationship between deterioration of physical strength and oxygen uptake is at variance with that followed by others (*5*, *11*, *12*) who related percentage deterioration with oxygen absorbed. The authors' preference was based on the fact that there was some variation in tensile strength and elongation of the several groups of control specimens and because of some question as to the justification for taking the tensile strength value of control specimens as representing zero oxidation. It is apparent that an extension of the curve in Figure 10 in the direction of higher tensile values to a point where it intersects the zero oxidation line corresponds to a tensile value of about 330.4 kg. per sq. cm. (4700 pounds per square inch), a value higher than any attained on control specimens. A similar extension of the curve in Figure 8 would indicate a value for elongation at break of about 770 per cent, which is also higher than was obtained on any controls.

Using the data in Figure 7 to relate approximate percentage deterioration in tensile strength with oxygen absorbed as was done by others we find an oxygen absorption of about 1.2 per cent on the rubber hydrocarbon corresponding to a 50 per cent decrease in tensile strength. This compares with about 0.5 per cent on hydrocarbon content reported by Kohman, and 1.2 per cent on the rubber content reported by Cramer, Sjothun, and Oneacre. Kohman obviously did not infer that the absorption of a definite quantity of oxygen would always result in a definite deterioration with various compounds and various degrees of cure. His data referred to one particular compound which was vulcanized to a state where most of the sulfur content was probably combined with the rubber. If Kohman's data are plotted on the same scale as Figure 7, they can be represented by a straight line above but parallel to that representing the data here reported. It is the authors' opinion that in the case of an overcured stock a lower oxygen addition will correspond to a given deterioration than with a normally cured or an undercured stock. On this basis, probably none of the reported values for quantity of oxygen absorbed corresponding to a given physical deterioration are necessarily in error but vary because of a difference in state of cure or quantity of sulfur combined with the rubber or to the presence of an added antioxidant.

Temperature Coefficient of Oxidation

When the logarithm of the time required for the absorption of a given amount of oxygen corresponding to a reduced tensile strength or reduced elongation at break was plotted against the different aging temperatures, it was found that a direct proportionality existed between the two in each case. In Figure 9 are plotted data representing the oxygen absorbed at 60°, 70°, and 80° C. corresponding to deterioration to various reductions in tensile strength. In Figure 10 are plotted data representing the oxygen absorbed at these three temperatures corresponding to various reductions in elongation at break. All the data in both figures conform to families of straight parallel lines. The experimental results so plotted may be expressed by the following equation:

$$\frac{t_1}{t_2} = \frac{D_2}{D_1} = 2^{\frac{T_2 - T_1}{8.00}}$$

or $$\log t_1 - \log t_2 = \log D_2 - \log D_1 = 0.0376\ (T_2 - T_1)$$

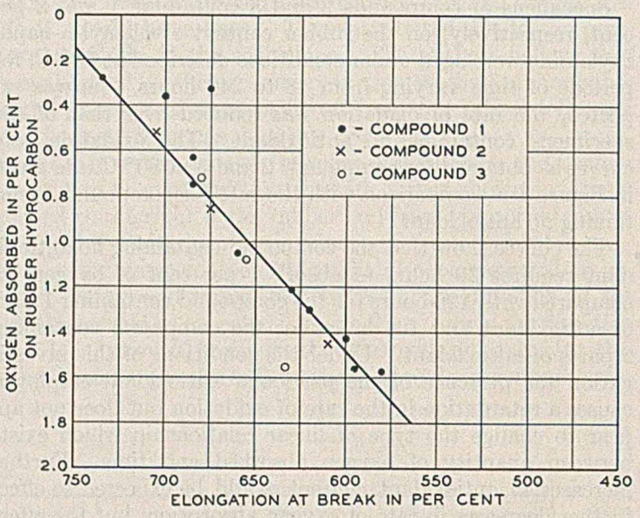

Figure 8. Relationship between Oxygen Absorbed and Decrease in Elongation at Break

where t_1, D_1 and T_1 and t_2, D_2 and T_2 are, respectively, a first and second set of values of time of aging, degree of oxidation or deterioration, and temperature in degrees Centigrade. The equation is similar to that used for expressing coefficient of vulcanization and the procedure followed in calculating the temperature coefficient of oxidation parallels that followed in calculating temperature coefficient of vulcanization (*10*).

The temperature coefficient of a reaction is most frequently expressed as a factor by which the rate may be multiplied when the temperature is raised 10° C. So expressed, the temperature coefficient of oxidation or deterioration under the conditions of this investigation was found to be 2.38, corresponding to 8.00° C. (14.4° F.) to double the rate of aging. Bierer and Davis (*4*) found that the aging rate doubles for an 8.3° rise in temperature and Williams and Neal (*13*) have reported that the rate of oxygen absorption doubles for each 7° to 10° C. rise in temperature up to about 80° C.

Relation to Accelerated Aging Tests

A temperature coefficient of oxidation as here reported is useful in predicting the time for a given deterioration to take place at other temperatures when the time is known for one temperature. It provides a method for predicting ultimate life of the rubber at service temperature when life at some accelerated aging temperature is known. It is interesting to note that when line 4 in Figure 9, representing a deterioration to 140.6 kg. per sq. cm. (2000 pounds per square inch) tensile strength, is extended to the 25° C. ordinate, the corresponding time of aging is about 4500 hours or 187 days. In a coöperative test carried out by a number of laboratories some years ago under the auspices of the A. S. T. M. it was found that a compound almost identical with that represented and cured to the same extent deteriorated about 20 per cent on shelf-aging in 6 months and about 50 per cent on outdoor exposure for the same period of time. This correlation of outdoor aging rate with predicted aging rate on the basis of results here reported is certainly of interest though possibly of little significance.

Judging from the work here reported and the work of others to which reference has been made, it would appear that the decay of physical properties of vulcanized rubber, particularly tensile strength and elongation at break, is linear with increased oxygen absorption following a preliminary induction period. During this so-called induction period, the tensile strength and elongation at break may actually increase if a substantial amount of the sulfur present is not combined. If the rubber is overcured there may be no apparent induction period.

The use of an accelerated aging test has been suggested (*7*, *12*) in which the extent of deterioration is evaluated by measuring the consumption of oxygen volumetrically. Such a test has advantages for factory control testing and research investigations, since the apparatus is simple, only small samples are required, and the use of the volumetric method eliminates the need for tensile tests. However, the volumetric method has certain disadvantages for specification testing by consumers. For example, since the rubber content of the compound is not always known, it is not possible to base the absorption of oxygen on a definite amount of rubber hydrocarbon. Furthermore, the interpretation of the results is complicated by the fact that rubber resins, antioxidants, and other nonrubber hydrocarbon substances are likely to be present which will absorb appreciable quantities of oxygen during the test. Furthermore, Dufraisse and Etienne showed that the change in physical properties with a given oxygen absorption varies widely with time of vulcanization.

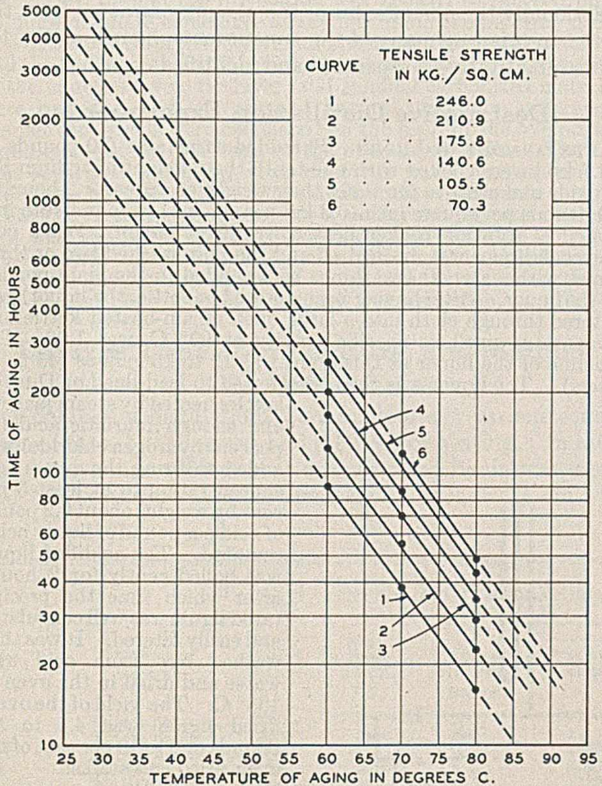

FIGURE 9. TIME-TEMPERATURE AGING RELATIONSHIP FOR TENSILE STRENGTH CORRESPONDING TO VARIOUS QUANTITIES OF ABSORBED OXYGEN

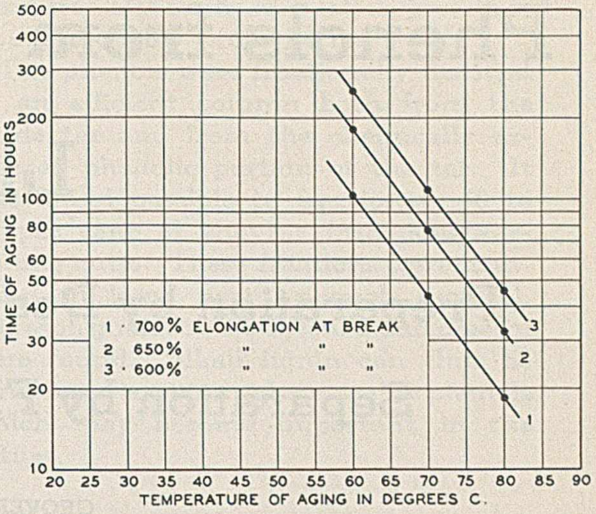

FIGURE 10. TIME-TEMPERATURE AGING RELATIONSHIP FOR ELONGATION AT BREAK CORRESPONDING TO VARIOUS QUANTITIES OF ABSORBED OXYGEN

It must be borne in mind, however, that in spite of the deficiencies of the oxygen absorption method for use as a general aging test it remains a valuable method when combined with physical tests to study the mechanism of oxidation of rubber.

Acknowledgment

Acknowledgment is made to G. S. Mueller for carrying out the experimental work involved in this investigation.

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Phenols from Cornstalk Alkali Lignin

Preparation by Destructive Distillation and Separation by Fractional Distillation

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THE destructive distillation of lignin isolated from wood by the fuming hydrochloric acid and 72 per cent sulfuric acid methods has been studied by many investigators (*5, 7*). Lignin prepared from sources other than wood and by other methods has been largely neglected in destructive distillation studies. The only experiments of this kind on alkali lignin are those of Phillips (*7*) who prepared his lignin from corncobs. He compared the yields of products from the destructive distillation at atmospheric pressure of corncob lignin isolated by three methods—namely, the fuming hydrochloric acid, the 72 per cent sulfuric acid, and the alkali methods.

Of particular interest is the oil or tar obtained as one of the products from the destructive distillation of lignin. This tar amounts to 8–14 per cent (basis lignin) in the case of the fuming hydrochloric acid and 72 per cent sulfuric acid lignin, and 17–28 per cent in the case of the alkali lignin. Phillips obtained 7.5 per cent of tar (basis lignin) from the corncob fuming hydrochloric acid lignin, 7.8 per cent from the corncob 72 per cent sulfuric acid lignin, and 17.7 per cent from the corncob alkali lignin. Comparing these yields on the basis of the original corncobs, the order is reversed: for the hydrochloric acid lignin the yield is 1.9 per cent; for the 72 per cent sulfuric acid lignin, 1.5 per cent; and for the alkali lignin, 0.88 per cent. The yield of the tar is dependent on the pressure at which the distillation is carried out; for example, by distilling alkali lignin from corncobs at a pressure of 25 mm. of mercury in an atmosphere of carbon dioxide, Phillips and Goss (*8*) obtained a yield of 28.3 per cent of tar (basis lignin).

The oil or tar from all kinds of lignin contains a certain amount of material which is insoluble in sodium bicarbonate solution but which is soluble in sodium hydroxide solution and is therefore phenolic in nature. The amount of this phenolic fraction is from 20 to 35 per cent (basis tar) in the case of the fuming hydrochloric acid and 72 per cent sulfuric acid methods of isolation, and much higher (80 to 90 per cent) in the case of the alkali method of isolation. The only previous investigation of the nature of the phenolic fraction of the tar is that of Phillips and Goss, who used chemical methods to separate several phenols from the tar. They identified phenol, *o*-cresol, guaiacol, *n*-propyl guaiacol, creosol, and 1-vinyl-3-methoxy-4-hydroxybenzene in the phenolic portion of the tar. The fraction of the tar from which these compounds were isolated amounted to only 15 per cent of the crude tar, however, and no estimation of the amounts of the several compounds could be made by the methods of separation used.

In the present study the conditions of the destructive distillation of cornstalk alkali lignin for obtaining high yields of phenols were determined. It was found possible to distill fractionally the phenolic tar or the phenols extracted from the tar. In this way many of the constituent phenols of the tar were quantitatively separated and identified.

Destructive Distillation Experiments

PREPARATION OF LIGNIN. Shredded cornstalks (50 pounds or 22.7 kg.) were cooked with one-tenth their weight of sodium hydroxide and eight to ten times their weight of water for 2 hours at 90 pounds per square inch (6.3 kg. per sq. cm.) gage pressure in a spherical rotating cooker heated by direct steam. When cool the cook liquor was drained off and the pulp washed two or three times with water, the washings being added to the main portion of the liquor. After having been allowed to settle, the liquor) was filtered through cloth into a large open steam-heated kettle and evaporated until its specific gravity at 90° C. was 1.06. The volume of the liquor at this point was 12 to 15 gallons (45 to 57 liters). The liquor was then transferred to lead-lined or Duriron kettles heated by steam jackets, and enough muriatic acid (25 per cent hydrogen chloride), was added to bring the excess acid concentration to at least 3 per cent by weight, about 0.2 pound of acid per pound of liquor being required. The acidified liquor was boiled gently for 2 hours, after which time the precipitated lignin was well coagulated and easily filtered. It was then washed free from acid with water and dried in the oven at 105° C. The yield of the oven-dried lignin was 4.5 to 5.0 pounds or 9 to 10 per cent of the oven-dried cornstalks.

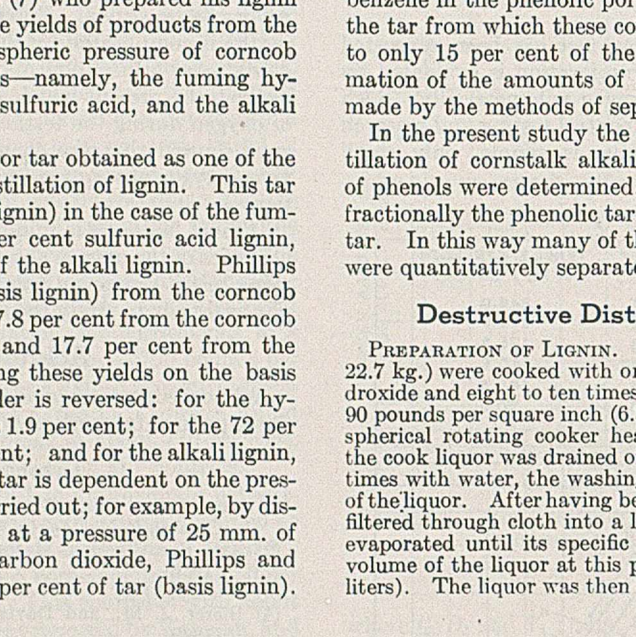

FIGURE 1. SMALL-SCALE DESTRUCTIVE DISTILLATION APPARATUS

APPARATUS AND PROCEDURE. For small-scale destructive distillations, a cast-iron retort, *A*,

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Alkali lignin from cornstalks has been destructively distilled under varying conditions of time, temperature, method of heating, and pressure. The conditions for optimum phenolic tar yield at an absolute pressure of 5.5 inches of mercury are (*a*) a final retort temperature of at least 400° C.; (*b*) a time of heating sufficient to allow all the distillate to come over, the rate of heating not being important; (*c*) any convenient means of heating the retort, a direct flame giving as good results as a heating bath. The optimum pressure found for production of phenols was 2.2 inches of mercury absolute, although still lower pressures would probably prove better.

The phenols were fractionally distilled in an efficient column both from the crude tar and from the chemically extracted phenolic portion of the tar. It was found possible to fractionate 40 to 55 per cent of the tar into constant-boiling cuts. These fractions were identified in large part; phenol, *o*-cresol, *p*-cresol, guaiacol, 3,5-xylenol, and creosol were found. Alkali lignin can thus be considered a potential source of phenols which may become important in the future.

about 180 cubic inches (3 liters) in capacity was used (Figure 1). The retort was heated either by a direct gas flame or by a suitable bath which was in turn gas-heated. A tightly fitting cover was held in place by a yoke and small clamps, an asbestos composition gasket being used. The cover was fitted with a thermometer well which extended to within 0.25 inch (0.635 cm.) of the bottom of the retort. The temperature was determined either by a thermometer or an iron-constantan thermocouple connected to a suitable pyrometer. The vapor line through which the distillates passed led directly to a receiving flask, *B*, which was cooled in a water bath, *C*. Above this was a Liebig condenser, *D*, which further cooled the lighter constituents. The vapors were finally led through an ice-cooled trap, *E*, and thence to a small rotary vacuum pump, *F*, which maintained the system at the desired pressure.

In making the distillations, the lignin was charged into the retort, and the system was tightly closed. When the desired pressure had been attained, the ring burner which supplied the heat was turned on and the distillation was allowed to proceed until no more distillate came over at the maximum temperature used. The distillates from the receiver and from the trap were combined and the two layers separated in a separatory funnel. The weights of the aqueous layer, tar layer, and residual carbonized material were recorded, and the gas and loss calculated by difference; the per cent yields were calculated on the basis of the oven-dried lignin and also on the basis of the oven-dried stalks. The tar thus separated contained some dissolved water, the amount of which was not determined in the small-scale experiments.

For the large-scale experiments a similar system was used except that the retort consisted of a horizontal iron pipe, 8 inches (20.3 cm.) in diameter and 14 inches (35.6 cm.) in length. One end of the pipe was fitted with a flange and the other was closed by a circular piece of sheet iron which was welded on.

Effect of Time, Temperature, and Method of Heating

A number of distillations were made under various conditions of time, temperature, and methods of heating. In each run 0.441 pound (200 grams) of oven-dried lignin was used, and the pressure was maintained at 5.5 inches (14 cm.) of mercury absolute (23.5 inches vacuum). The retort was heated by baths of lubricating oil, sodium nitrate, and molten lead, and by direct flame.

The results are shown in Table I. The maximum retort temperature is the maximum temperature inside the retort as shown by the thermocouple in the well. The time of heating is the total time between the firing of the retort and the time when the fire was cut off. For the first three runs in Table I (II, IV, and VII) in which direct flame heating was used, the temperature inside the retort is an important factor in the yield of tar; at 300° C. the yield is much smaller than at 395° and 500° C. This fact is further borne out by run III, in which the lignin was heated no higher than 235° C. for 4.3 hours, after which time practically no distillate had been obtained. It was then heated an additional 4.5 hours at temperatures no higher than 360° C. The yields of tar were almost as great as those in the direct-flame heating runs. It can be concluded that the greater part of the distillate came over between about 250° and 400° C. Phillips (*7*) stated that 400° C. is the best temperature for the destructive distillation of alkali lignin from corncobs, which checks the present findings well.

The total time and rate of heating seemed relatively unimportant. For example, runs V and VI were both made with a heating bath of molten lead, the maximum temperature being about the same in each case. Although the time of run V is over twice that of run VI, the yields of tar and aqueous distillate are identical. This fact was also observed in other experiments.

It was thought that by heating the lignin more uniformly, overheating at the surface of the retort would be prevented and better yields of distillates might be obtained. Consequently, the several runs (III, V, and VI) using liquid heat-

Table I. Effect of Temperature, Time, and Method of Heating on Yields

Run No.	Method of Heating	Max. Retort Temp.	Max. Bath Temp.	Time of Heating	Per Cent Yield of Products							
					Basis Oven-Dried Lignin				Basis Oven-Dried Stalks			
					Aqueous dist.	Tar	Carbon residue	Gas and loss	Aqueous dist.	Tar	Carbon residue	Gas and loss
		° C.	° C.	Hours								
II	Direct flame	300	...	2.0	7.0	14.2	67.0	11.8	0.70	1.42	6.70	1.18
IV	Direct flame	395	...	3.2	11.1	17.7	57.5	13.7	1.11	1.77	5.75	1.37
VII	Direct flame	500	...	2.75	14.5	17.5	52.0	16.0	1.45	1.75	5.20	1.60
III	Oil bath	235	290	4.3	Slight	Slight	..	Slight	Slight	Slight	..	Slight
	$NaNO_3$ bath	360	420	4.5	7.5	14.4	60.5	17.6	0.75	1.44	6.05	1.76
VI	Lead bath	420	490	2.0	10.6	17.6	51.2	20.6	1.06	1.76	5.12	2.06
V	Lead bath	390	490	4.25	10.6	17.7	56.6	15.1	1.06	1.77	5.66	1.51

ing baths were made. However, in no case were the yields of distillates better than those obtained by direct flame heating. It must then be concluded that the method of heating has no effect on the yields of distillates if the retort temperature is high enough.

It may be concluded from the above experiments, therefore, that the optimum conditions for the production of tar by destructive distillation of alkali lignin under 5.5 inches (14 cm.) of mercury absolute pressure are: (*a*) a final retort temperature of at least 400° C., (*b*) a time of heating sufficient to drive over all the distillate (the rate of heating is not very important), and (*c*) any convenient means of heating the retort (the method of heating is relatively unimportant, and a direct flame gives as good results as a heating bath).

Effect of Pressures Lower than Atmospheric

Once the above conditions (for 5.5 inches of mercury) were established, a number of distillations were carried out at varying pressures below atmospheric in order to observe the effect on the yield of the products. 0.441 pound (200 grams) of oven-dried lignin was used in each distillation. Direct flame heating was used, the maximum retort temperature being 400° to 500° C. The pressures were kept constant within 0.5 inch (1.27 cm.) of mercury. The absolute pressures recorded were based on a 29.0-inch (73.7-cm.) barometer reading. The time of heating was about 3 hours in all runs.

The results are given in Table II and shown graphically in Figure 2. At an absolute pressure of about 5 inches (12.7 cm.) of mercury the yield of total distillate and tar reached a distinct maximum. On the other hand, the aqueous distillate was sensibly constant throughout the entire range of pressure except in the very low range, where it dropped. Another interesting feature of Figure 2 is the abrupt increase in tar yield and consequently in total distillate yield when a very slight vacuum was maintained on the retort. The carbonized residue curve is roughly the inverse of the tar and total distillate curves.

TABLE II. EFFECT OF LOW PRESSURES ON YIELDS

		Per Cent Yield of Products							
		Basis Oven-Dried Lignin				Basis Oven-Dried Stalks			
Run No.	Abs. Pressure, In. Hg	Aqueous dist.	Tar	Carbon residue	Gas and loss	Aqueous dist.	Tar	Carbon residue	Gas and loss
XIV	2.2	8.2	16.1	59.8	15.9	0.82	1.61	5.98	1.59
XV	2.2	11.0	15.7	57.0	16.3	1.10	1.57	5.70	1.63
XVI	2.2	14.7	15.5	56.0	13.8	1.47	1.55	5.60	1.38
XIII	4.0	13.8	17.1	53.7	15.4	1.38	1.71	5.37	1.54
XII	5.0	11.8	19.5	57.0	11.7	1.18	1.95	5.70	1.17
IV	5.5	11.1	17.7	57.5	13.7	1.11	1.77	5.75	1.37
VII	5.5	14.5	17.5	52.0	16.0	1.45	1.75	5.20	1.60
IX	17.0	14.4	14.6	54.5	16.5	1.44	1.46	5.45	1.65
XI	17.0	16.1	14.7	57.0	12.2	1.61	1.47	5.70	1.22
X	28.0	15.0	14.0	56.5	14.5	1.50	1.40	5.65	1.45
VIII	29.0 (atm.)	15.0	11.6	59.2	14.2	1.50	1.16	5.92	1.42

Reducing the pressure in the retort might be expected to produce two major effects: (*a*) an increased rate of removal from the retort of the vaporized decomposition products and (*b*) lowering of the boiling points of the products and thus the temperature at which they would be vaporized. Both of these factors should increase the yield of distillate because of the smaller chance for complete decomposition of the intermediates into carbon or its oxides.

The abrupt increase in tar yield when the pressure was reduced to 1 inch of mercury below atmospheric may be explained by assuming that the first-mentioned factor was the determining one in this range. The increase in yield of tar due to the better removal of the vapors would certainly be more pronounced than that caused by the lowering of boiling point at this slight vacuum. The gradual increase in distillate resulting from a further decrease in pressure may be supposed to result from the lowered boiling points and, to some extent, from the increased speed of vapor removal. The reason for the decreasing yield after the pressure had been reduced below 5 inches is rather hard to explain on this basis, however.

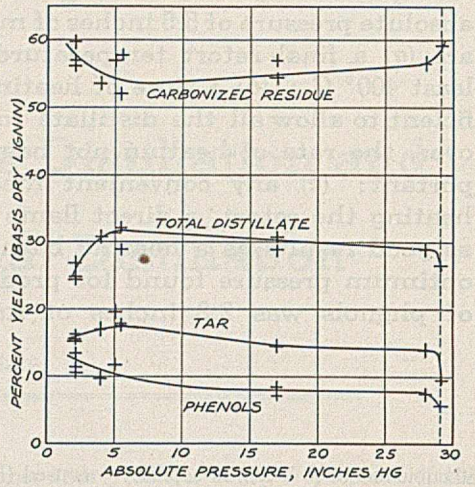

FIGURE 2. YIELDS OF LIGNIN DISTILLATES AT LOW PRESSURES

It is interesting to compare the yields of tar obtained in the present study with those of Phillips (*7*). The best yield of wet tar obtained in the present experiments was 17.7 per cent (basis oven-dried lignin); Phillips and Goss obtained 28.3 per cent from corncob alkali lignin at 25 mm. of mercury absolute pressure. However, the lignin used in the present experiments represented 10 per cent of the cornstalks, whereas that of Phillips represented only 5 per cent of the corncobs because of milder conditions of extraction. The yields of tar, based on the original raw material, are thus 1.77 per cent (basis oven-dried cornstalks) in the present study and 1.41 per cent (basis corncobs) in Phillips' experiments. The fact that the yields are so different when based on the lignin seems to indicate that the lignin of the raw material which requires more drastic conditions for its removal is considerably different from that which comes out with relatively mild extraction conditions. This was also shown by Phillips (*6*) in experiments on the fractional extraction of lignin from corncobs.

Composition of Tar

The separation of the tar into its major classes of compounds was accomplished by previous lignin investigators by successive extractions with sodium bicarbonate and sodium hydroxide solutions which were supposed to dissolve the acidic and phenolic portions, respectively. The acids and phenols were recovered by acidification of these solutions, and the insoluble tar remaining from the above extractions was classed as neutral tar. This method of analysis gave in some cases very high percentages of phenols; Phillips (*7*), for example, found that 84 per cent of the tar from his destructive distillation experiments at atmospheric pressure was insoluble in sodium bicarbonate solution but soluble in sodium hydroxide solutions. He thus reported that the tar contained 84 per cent of phenols.

In studying tar from the low-temperature carbonization of coal, Morgan (*3*) found that sodium hydroxide extractions of the tar dissolved not only the phenols but also considerable amounts of other classes of compounds which, when separated from the phenols, were entirely insoluble in caustic solution. He found that one of the best methods of separating these phenate-soluble compounds was by the use of caustic soda saturated with salt, a reagent which extracts only the phenols, instead of the ordinary aqueous solution of sodium hydroxide. The phenate-soluble materials then remained behind with the neutral oils, and the phenols were thus selectively extracted.

This method of separation was tried on some of the tars from the first six runs, and it was found that they behaved similarly to the coal tar studied by Morgan. When aqueous 10 per cent sodium hydroxide was used to extract some of the lignin tar which had previously been extracted with sodium bicarbonate, about 90 per cent of it dissolved. When 10 per cent sodium hydroxide saturated with salt was used, however, only about 60 per cent of it dissolved. The tar which was insoluble in the caustic-brine extraction was now also insoluble in the ordinary 10 per cent sodium hydroxide solution. As a result of these tests the following method of separation and estimation, which is similar to that used by Morgan, was adopted:

1. The tar from each run, about 30 to 35 grams in quantity, was extracted with 50 ml. of 10 per cent sodium bicarbonate. Its loss in weight was recorded as acids.
2. The insoluble tar from the first step was dissolved in an equal volume of benzene and extracted with two 25-ml. portions of the caustic-brine reagent. After having been shaken with this reagent and allowed to stand, the mixture separated into three layers: the lower layer consisted of the alkaline solution of the phenols, the middle layer consisted of precipitated neutral tar, and the top layer consisted of a solution of the benzene-soluble tar. The benzene was necessary for good separation of the neutral tar and the phenate solution; unless it was present a suspension formed which was very difficult to break up. The phenol solution was separated, acidified, and the resulting phenols were separated and weighed.
3. The neutral tar was calculated by difference, no attempt being made to estimate the quantities of the benzene-soluble and benzene-insoluble neutral tar because of the difficulty of separating them quantitatively.

The tar from each of runs VII to XVI, inclusive, was analyzed by the above procedure, and the results are recorded in Table III. The per cent composition of the tar was calculated both on the basis of the crude wet tar and on that of the original oven-dried lignin. The tar in each case contained some water, but this was not determined in the small-scale runs. The percentage of phenols increases with decreasing pressure, the percentage of neutral tar first increases and then falls off with decreasing pressure, and the percentage of acids remains sensibly constant. From the standpoint of phenol production it appears advantageous to decrease the pressure as much as possible, because the yield of phenols continues to increase at very low pressures, despite the drop in total tar yield. The yield of phenols is also shown graphically in Figure 2.

TABLE III. EFFECT OF LOW PRESSURES ON TAR COMPOSITION

		Per Cent Composition of Tar					
		Basis Crude Tar (Wet)			Basis Oven-Dried Lignin		
Run No.	Abs. Pressure, In. Hg	Acids	Phenols	Neutral tar	Acids	Phenols	Neutral tar
XIV	2.2	7.1	64.5	28.4	1.1	10.4	4.6
XV	2.2	8.9	72.0	19.1	1.4	11.3	3.0
XVI	2.2	5.5	86.9	7.6	0.9	13.4	1.2
XIII	4.0	8.8	57.2	34.0	1.5	9.8	5.8
XII	5.0	4.6	60.0	35.4	0.9	11.7	6.9
IX	17.0	10.0	49.0	41.0	1.4	7.1	5.9
XI	17.0	11.2	57.0	31.8	1.6	8.4	4.7
X	28.0	10.7	53.2	36.1	1.5	7.5	5.0
VIII	29.0 (atm.)	12.9	49.2	37.9	1.5	5.7	4.4

In view of the rather large difference between the amount of phenols observed when the caustic-brine reagent is substituted for the usual aqueous caustic solution, it is probable that most of the values for the yield of phenols in the literature are considerably higher than the true values. The amounts found in the present study are large enough to make lignin an attractive potential source of phenols, however.

Fractionation of Distillates

APPARATUS AND METHOD. The fractionating column was constructed of 0.39-inch (10-mm.) inside-diameter Pyrex tubing. It was packed with 0.126-inch (3.2-mm.) inside-diameter single-turn glass helices (*1*), the packed section being 100 cm. in height. Around the packed section was a 0.55-inch (14-mm.) inside-diameter Pyrex tube on which was wound 50 feet (15.2 meters) of Nichrome resistance wire to provide side heating, and this was in turn enclosed in a 1.26-inch (32-mm.) inside-diameter Pyrex tube which served as further insulation. The kettle consisted of a 500-ml. flask which was heated by an electrical heater. Reflux was furnished by a total condenser at the top of the column.

The fractionations were carried out using 150- to 250-ml. charges. A high reflux ratio (20–30 to 1) was maintained at all times and the still was operated at as high a boiling rate as possible without flooding. Adiabatic conditions were maintained in the column by close control of the side heat. Fractions were collected corresponding as nearly as possible to the constant-boiling portions of the fractionation curves. All fractionations were conducted at atmospheric pressure.

Fractionation of Tar

The tar from the large-scale destructive distillations was fractionated after various pretreatments. This tar was wet, containing 13 per cent water (wet basis) as determined in the following fractionations, and represented 14 per cent of the oven-dried lignin; the dry tar thus represented 12.2 per cent of the oven-dried lignin. In fractionation *A* the tar was given no pretreatment. In fractionation *B* the tar was predistilled in an ordinary distilling flask before being fractionated. For fractionation *C* the phenols were extracted from the crude tar as follows: 204 grams of the crude wet tar were dissolved in an equal volume of benzene and extracted successively with 10 per cent hydrochloric acid, 10 per cent sodium bicarbonate, 10 per cent sodium hydroxide saturated with sodium chloride, and 10 per cent sodium hydroxide. The hydrochloric acid and sodium bicarbonate extracts were washed with benzene, and these washings were added to the residual solution of tar before the alkaline extractions. The alkaline extracts were combined and the phenols were recovered by acidification with 25 per cent sulfuric acid. The crude phenols thus obtained were distilled without fractionation before being charged into the fractionating column. The hydrochloric acid extract was made alkaline with sodium hydroxide solution, and a precipitate formed which was filtered, washed, and dried. It was a dark purple amorphous powder weighing 0.4 gram which partially dissolved in water to give a deep purple solution. This material was not further investigated; it probably consisted of a mixture of basic nitrogenous compounds, since it had a characteristic odor and evolved ammonia when boiled with sodium hydroxide solution. For purposes of comparison a fractionation of a com-

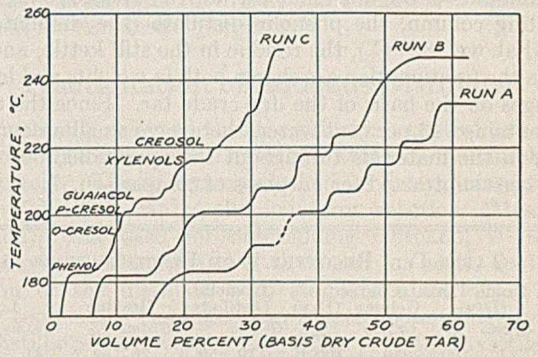

FIGURE 3. FRACTIONATION OF LIGNIN TARS

mercial cresylic acid was made; this is designated as fractionation *D*.

The fractionations were carried out until decomposition of the material in the kettle set in, as evidenced by liberation of white fumes and lowering of the vapor temperature. The fractions from the lignin tar were in all cases colorless or very light shades of pink or yellow. On standing several days, however, they turned dark red or black. The fractions from fractionation *C* (extracted phenols) showed less tendency than the others to discolor, but after several weeks they were also dark in color. The fractions from the commercial cresylic acid remained light in color, however.

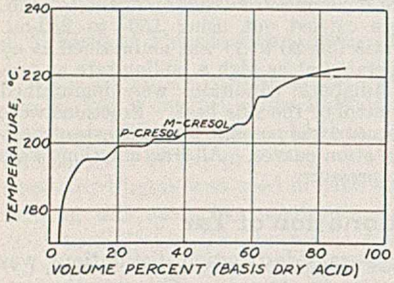

FIGURE 4. FRACTIONATION OF COMMERCIAL CRESYLIC ACID (RUN *D*)

The results of the fractionations are shown in Figures 3 and 4, where the cumulative volume per cent of distillate (basis dry crude tar) is plotted against the vapor temperature in the top of the column. Sharp fractions were obtained in most cases. The material boiling below 182° C., the lower limit of the phenolic temperature range, consisted entirely of water and in a few cases of a small amount of methanol; there was no evidence of light oils or other material of any kind. A summary of the recovery of material is shown in Table IV. The amounts of the dry crude tar, the dry charge to the fractionating column, the phenolic distillate (the distillate obtained above 182° C.), the residue in the still kettle, and the loss in the fractionation are shown both in weights and in percentages on the basis of the dry crude tar. Since the crude tar contained 13 per cent water, there were small amounts of water in the materials throughout the operations, but these have been subtracted for purposes of comparison.

TABLE IV. RECOVERY FROM FRACTIONATIONS

Run No.	Crude Tar (Dry)		Charge to Column (Dry)		Phenolic Distillate		Residue		Loss	
	Grams	%[a]	*Grams*	%[a]	*Grams*	%[a]	*Grams*	%[a]	*Grams*	%[a]
A	236	100	236	100.0	119	50.5	76	32.2	41	17.3
B	125	100	104	83.2	69	55.2	11	8.8	24	19.2
C	178	100	88.5	49.6	58	32.6	15	8.4	15.5	17.5
D	199	100	199	100.0	171	85.9	12	6.0	16	8.1

[a] All per cents are on the basis of the dry crude tar.

The predistillation without fractionation (fractionation *B*) increased the yield of the phenolic distillate by almost 5 per cent (basis dry crude tar). Figure 3 shows that this is due in large part to the fact that decomposition set in earlier in the fractionation of the crude tar (fractionation *A*) than in that of the predistilled tar (fractionation *B*). The crude tar began to decompose at a vapor temperature of 233° and a kettle temperature of 312° C., whereas the predistilled tar began to decompose at a vapor temperature of 248° and a kettle temperature of 330° C. The recovery of phenolic distillate from the extracted and predistilled phenols (fractionation *C*) was somewhat poorer than that of the first two fractionations. This may be explained in part by the greater loss of material due to incomplete extraction, mechanical losses, etc. It is also possible that the phenolic distillates of fractionations *A* and *B* contained substances other than phenols, but this seems unlikely because of the similarity in properties of the fractions of the extracted phenols and crude tar. Furthermore, rough experiments on the neutral portions of the tar indicated that they contained very little material boiling in the phenolic range. The losses were rather large because the material held up in the column packing after the fractionation was not removed but was included in the losses.

These results on the recovery of total phenols from the tar check the analyses made by the caustic-brine extraction method quite well. Table III shows that at a pressure of 28 inches of mercury absolute (the pressure of the large-scale runs) the tar contains about 53 per cent phenols (wet basis) or 61 per cent phenols (dry basis). The recovery of phenolic distillate in fractionations *A* and *B* was 50.5 and 55.2 per cent, respectively. Thus over 80 per cent of the total phenols (as estimated by the caustic-brine method) were recovered in fractionation *A*, and 91 per cent in fractionation *B*. The recovery of the crude predistilled phenols in fractionation *C* was 49.6 per cent of the dry crude tar which contained 61 per cent total phenols (dry basis); this recovery amounted to 81 per cent of the total phenols. The recovery of fractionated phenols in this run was 32.6 per cent of the dry crude tar, or 53 per cent of the total phenols. The smaller recovery in fractionation *C* may be attributed to the fact that the amount of charge was smaller than in the other fractionations which would magnify the percentage loss in the column holdup, and also to the fact that the residue in this fractionation consisted entirely of phenols whereas in fractionations *A* and *B* it was probably largely composed of neutral and acidic compounds.

Identification of Phenols

The yields of the various fractions from the three runs are shown in Table V. The boiling points and refractive indices are those of the material at the flat portions of the curves. The amounts of the various fractions were ascertained by drawing vertical lines through the mid-points of the transitions between the various fractions and recording the differences in abscissas between these lines. This method, of course, will include any compounds which may have been present in amounts too small to be fractionated out distinctly, but the sharp breaks in the curves indicate that few such compounds were present in appreciable amounts in the majority of cases. All of the fractions were cooled to −20° C. in an attempt to freeze them, but in most cases a glass or very viscous mass was obtained which could not be crystallized. For comparison, Table VI shows the boiling points and refractive indices of the more common phenols in the boiling range studied (*2*).

Since the fractions from run *C* (extracted phenols) seemed more pure than those of runs *A* and *B*, they were used exclusively for the chemical identification work; the details are as follows:

The fraction boiling at 183° C. was solid at room temperature and showed the characteristic crystal structure of phenol. It melted at 35° C. A nitro derivative was prepared according to Mulliken's procedure (*4*) which melted at 121.5–122.5° C. (melting point of picric acid, 122.5° C.). The fraction was therefore phenol.

The fraction boiling at 191° C. was small and therefore not very pure. A picrate was prepared which melted at 87–88° C. (melting point of the picrate of *o*-cresol, 88° C.). The fraction therefore contained *o*-cresol.

The fraction boiling at 201° C. gave an aryloxyacetic acid melting at 130–132° C. (melting point of the aryloxyacetic acid of *p*-cresol, 134–136° C.). The fraction therefore consisted chiefly of *p*-cresol.

The fraction boiling at 205° C. yielded a 3,5-dinitrobenzoyl ester which melted at 140–141° C. (melting point of the 3,5-dinitrobenzoyl ester of guaiacol, 141° C.). It also gave a picrate melting at 87–88° C. (melting point of the picrate of guaiacol, 86° C.). The fraction was therefore guaiacol.

TABLE V. FRACTIONATION OF TARS

Fraction Boiling at, ° C.	Refractive Index, n_D^{20}	Per Cent Yield			Chief Constituent
		Basis dry tar	Basis oven-dried lignin	Basis oven-dried stalks	
		Crude Lignin Tar (Run *A*)			
183	1.5405	14.9	1.82	0.182	Phenol
191	1.5275	6.7	0.83	0.083	*o*-Cresol
201	1.5195	6.4	0.78	0.078	*p*-Cresol
207	1.5210	5.1	0.62	0.062	Guaiacol
215	1.5230	5.5	0.67	0.067	Xylenols
222	1.5198	4.7	0.57	0.057	Creosol
233	1.5175	7.2	0.88	0.088	....
Total yield		50.5	6.17	0.617	....
		Predistilled Lignin Tar (Run *B*)			
182	1.5422	9.6	1.18	0.118	Phenol
189	1.5402	4.0	0.49	0.049	*o*-Cresol
201	1.5400	10.4	1.27	0.127	*p*-Cresol
208	1.5290	6.4	0.78	0.078	Guaiacol
218	1.5310	5.6	0.68	0.068	Xylenols
225	1.5290	7.2	0.88	0.088	....
248	1.5468	12.0	1.46	0.146	....
Total yield		55.2	6.74	0.674	....
		Crude Predistilled Phenols from Lignin Tar (Run *C*)			
183	Solid	6.8	0.84	0.084	Phenol
191	1.5407	1.1	0.13	0.013	*o*-Cresol
201	1.5378	2.8	0.34	0.034	*p*-Cresol
205	1.5392	4.3	0.52	0.052	Guaiacol
208	1.5345	1.4	0.17	0.017	....
216	1.5320	5.6	0.68	0.068	3,5-Xylenol
220	1.5300	1.7	0.21	0.021	Creosol
225	1.5299	2.8	0.34	0.034	....
231	1.5330	2.8	0.34	0.034	....
240	....	1.1	0.13	0.013	....
249	1.5412	2.2	0.27	0.027	....
Total yield		32.6	3.97	0.397	

The fraction boiling at 208° C. had a refractive index of 1.5345; it was small in amount and probably not very pure. An aryloxyacetic acid of this fraction melted sharply at 93° C. after recrystallization from water and petroleum ether. The fraction was not further identified.

The fraction boiling at 216° C. probably contained more than one compound. No sharp-melting 3,5-dinitrobenzoyl ester could be obtained, its melting point increasing from 98° to 126° C. on repeated recrystallization from ethanol, petroleum ether, and methanol. However, a small amount of a bromo derivative was isolated which melted sharply at 160° C.; this indicates that 3,5-xylenol was present (melting point of the tribromo derivative of 3,5-xylenol, 162.5° C.). The other constituent or constituents of this fraction were probably other isomeric xylenols, since there are several such compounds boiling in this region.

The small fraction boiling at 220° C. contained creosol since an aryloxyacetic acid prepared from it melted sharply at 86° C. (melting point of the aryloxyacetic acid of creosol is 84–85° C.) and a picrate melted at 97° C. (melting point of the picrate of creosol is 96.8° C.).

The fraction boiling at 231° C. yielded an aryloxyacetic acid melting at 74–76° C. It was not further identified.

The fraction boiling at 249° C. yielded a 2,4-dinitrophenyl ether which melted at 162–163° C. after repeated recrystallization. A 3,5-dinitrobenzoyl ester melted at 157–160° C. No known phenol could be found which yielded derivatives of these characteristics, and the fraction was not further identified.

The yields of the various fractions for the three fractionations are given in Table V. The yields are calculated on the basis of the dry crude tar, the oven-dried lignin, and the oven-dried cornstalks, using a yield of 14 per cent of wet tar from the lignin and a yield of 10 per cent oven-dried lignin from the oven-dried cornstalks. These figures are for a distillation pressure of 28 inches of mercury absolute, and the yield of tar and phenols would be considerably higher from a high-vacuum distillation (Table III).

Comparing these results with those of Phillips and Goss (*8*) who identified several phenols in lignin tar, it is observed that all of the compounds which they found, with the exception of *n*-propylguaiacol and 1-vinyl-3-methoxy-4-hydroxybenzene, were found in the present study. Phillips and Goss separated the phenolic compounds from the tar by alkaline extraction, steam distillation of the crude phenols, separation of the steam-volatile portion into solid and liquid potassium phenolates, and finally fractionation of the recovered phenols in a three-bulb fractionating column. Their recovery of the steam-volatile phenols was 15 per cent of the tar, and that of the total fractionated phenols was 9.1 per cent of the tar. Because of the relatively inefficient fractionation and because of the incomplete recovery of the phenols, no quantitative estimation of the amounts of the various compounds was possible. As a result of the present study it is believed that Table V gives a fairly accurate quantitative account of the distillable components of the lignin tar. The yields of phenol and *o*-cresol seem unusually high in fractionation *A;* poor fractionation was obtained in this region due to flooding, however, and they are probably too high. The yields of the other fractions in fractionations *A* and *B* agree fairly well. The yields in fractionation *C* are all smaller than those in fractionations *A* and *B*, and in some cases are in different proportions. This may be the result of incomplete extraction of some of the more difficultly alkali-soluble phenols.

Fractionation *D* (Figure 4), in which a commercial cresylic acid was used, indicates the similarity between coal-tar phenolic distillates and the lignin-tar phenols. In addition to *m*- and *p*-cresols, a number of other compounds were present as indicated by the numerous plateaus. The separation of *m*- and *p*-cresol (at 201° and 203° C.), although probably not complete, is an indication that the column was sufficiently efficient for the present purposes.

Fractionation of Aqueous Distillates

It is usually assumed that the principal constituents of the aqueous distillate from lignin are acetone, methanol, and acetic acid. The customary method for determining acetone in the distillate is by the iodoform reaction (Messinger method), that used for determining methanol is usually methoxyl determination, and that used for acetic acid is titration of the distillate with standard alkali (*7*). These three compounds have not been isolated quantitatively from the distillates, however, by any of the previous investigators. The usual yield of acetone reported in the literature ranges

TABLE VI. PHENOLIC COMPOUNDS ARRANGED IN ORDER OF INCREASING BOILING POINT

	B. P., ° C.	Refractive Index, n_D^{20}
Phenol	182	1.5425 (41° C.)
2-Methylphenol (*o*-cresol)	190.8	1.547
4-Methylphenol (*p*-cresol)	201.1	1.540
3-Methylphenol (*m*-cresol)	202.8	1.540
2-Methoxyphenol (guaiacol)	205.1	....
o-Ethylphenol	207.5	....
2,4-Dimethylphenol (xylenol)	211.5	....
2,5-Dimethylphenol (xylenol)	211.5	....
2,6-Dimethylphenol (xylenol)	212	....
m-Ethylphenol	214	....
2,3-Dimethylphenol (xylenol)	218	....
p-Ethylphenol	219	....
3,5-Dimethylphenol (xylenol)	219.5	....
2-Methoxy-4-methylphenol (creosol)	221.8	1.537
3,4-Dimethylphenol (xylenol)	225.1	....
1-Methyl-6-isopropylphenol	226	1.5218
4-Methyl-6-isopropylphenol	229	1.5234
2-Methyl-6-isopropylphenol (thymol)	231.8	....
1-Methyl-5-isopropylphenol (carvacrol)	237.9	1.524
1,2-Dihydroxybenzene (catechol)	245	....
1-Hydroxy-4-methylphenol (homocatechol)	252	1.5425 (74° C.)
Eugenol	253	1.5439 (14° C.)
Isoeugenol	267.5	1.5680

from 0.10 to 0.20 per cent (basis lignin) for both alkali and fuming hydrochloric acid lignin, although Phillips (7) found as high as 1.0 per cent for 72 per cent sulfuric acid lignin. For methanol, 0.07 to 1.9 per cent (basis lignin) have been reported, 0.90 per cent being an average figure for alkali, 72 per cent sulfuric acid, and fuming hydrochloric acid lignin. The yield of acetic acid ranges from 0.05 to 0.30 per cent for alkali lignin and 0.9 to 1.3 per cent for the fuming hydrochloric acid and 72 per cent sulfuric acid lignins.

In order to compare the present aqueous distillates with those of previous investigators, the aqueous distillates from four of the large-scale distillations were analyzed using the customary methods previously mentioned. The results of the analyses are: acetone, 0.285 per cent; methanol, 0.28 per cent; and acetic acid, 0.432 per cent.

These figures were somewhat different from those reported in the literature; therefore a quantitative separation of the constituents by fractional distillation was attempted. The combined aqueous distillates from three large-scale runs were divided into two portions and fractionated in the column, one without any pretreatment and the other after it had been made alkaline with sodium hydroxide. In order to obtain a check on the efficiency of the column for such a separation, a control fractionation was made of a solution of acetone, methanol, and water in amounts corresponding to 0.10 and 0.79 per cent (basis lignin) for the acetone and methanol, respectively.

The results are shown in Figure 5. Good separation of the methanol was obtained, and the average yield from both fractionations is 0.84 per cent (basis oven-dried lignin). A separation of the acetone was not accomplished, however, and on the basis of comparison with the control fractionation, it can be concluded that there was less than 0.10 per cent (basis lignin) present, since the initial boiling points and the first parts of the fractionation curves lie considerably higher than that for the control run. After the water had all been removed in the first fractionation (no pretreatment of distillate) such a small amount of material remained in the kettle that it could not be fractionated further; the acetic acid (boiling point 118° C.) could therefore not be separated in this way.

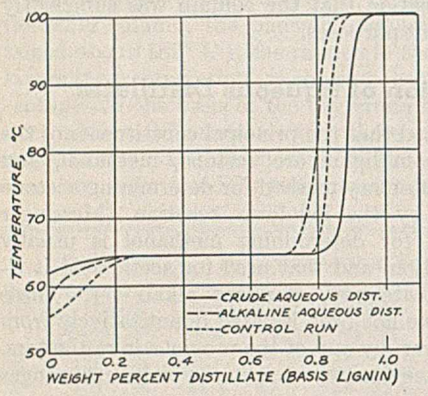

FIGURE 5. FRACTIONATION OF LIGNIN AQUEOUS DISTILLATE

In order to separate the acetic acid, the alkaline residue from the second fractionation was saturated with carbon dioxide and the liberated phenols were removed by filtration and ether extraction. The solution was then acidified with sulfuric acid, and the free acids were separated from the solution by four ether extractions. The ether solution was concentrated by distillation of the extract until the vapor temperature was 50° C. The total amount of oil remaining after the ether had been removed was only 0.1 per cent (basis lignin). It was distilled in a small flask; the temperature rose steadily from 50° to 255° C., almost all of the oil being distillable. It may be concluded that the amount of acetic acid (boiling point 118° C.) present was very small; the value (0.432 per cent) obtained by the usual titration method is therefore much too high.

It may be concluded that the values obtained by the customary methods of analysis for acetone, methanol, and acetic acid may lead to considerable error when applied to the aqueous distillates from lignin. This is doubtless due to the presence of materials other than these three constituents which interfere with the reactions. It is likely that many of the values recorded in the literature are in error because of this fact.

Neutral Tar and Carbonized Residue

The neutral tar as separated by the caustic extraction method consisted of a benzene-soluble portion and a benzene-insoluble portion. The latter was a light brown soft mass, which settled to the bottom of the benzene solution. These two fractions were entirely soluble in benzene in the presence of the phenols, as is evident from the method of separation used. No attempt was made to identify these materials.

The carbonized residue was a light, porous material which had about twice the volume of the original lignin. It was of a granular texture and was not sooty.

Discussion

In comparison to coal tar, wood tar, and other natural sources of phenols, the tar from alkali lignin has a far greater phenol content. The yield of the tar from the lignin is also larger than that of the tar from coal and wood destructive distillations. As a source of phenols, therefore, alkali lignin would be far superior to the present-day sources with respect to the yield. Offsetting this advantage, however, is the higher cost of production of the lignin and the difficulty of using the lignin carbonized residue as a substitute for coke and charcoal. The first of these disadvantages would be overcome by the development of a cheap method of recovering the lignin from soda and sulfate wood pulp liquors or of a cheap method of separating lignin from agricultural by-product materials. The second disadvantage would be overcome either by development of new uses for the carbonized residue sufficient to absorb its production or by modification of it in such a manner as to make it acceptable as a substitute for coke or charcoal. Preliminary tests indicate that good activated carbon may be made from it. By briquetting the carbonized residue it could be used for fuel and for many other purposes. In view of the increasing demand for phenolic compounds, lignin should thus be considered a potential source of phenols which may become important in the future.

Acknowledgment

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Relation of Soil Properties to Corrosion of Buried Steel

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Studies were made of the relation of the soil volume–water content, the soil pH, and the soil electrical resistivity to the corrosion of buried steel pipe. Data were developed from laboratory tests to show the importance of each of these factors. The results were extended to field measurements of soil resistivities and pH values *vs.* actual corrosion rates to show the correlation between the field and laboratory results. It was found that while both the electrical resistivity and the pH of soils have some effect on the soil corrosion rate, the governing factor is the soil volume–water content.

THE subject of the corrosion of buried steel pipe is of great interest to the oil, gas, and water industries and has received considerable attention during the past 20 years. The importance of this subject to the oil industry is indicated by the fact that there are 201,170 km. (125,000 miles) of pipe ranging in size from 10.16 to 50.8 cm. (4 to 20 inches) used to transport petroleum and its products (*11*). Among the first in the United States to be concerned with the problem of underground corrosion was Logan (*7*). His attention was first directed to this subject through corrosion of city water and gas pipes caused by leakage of direct currents from street railway systems. The results of these studies showed that factors other than stray current leakage could be responsible for corrosion of buried pipes and that these factors arose from contact of the pipes with soils. This work led to the well-known tests of the National Bureau of Standards (*6–9*), where duplicate sets of ferrous pipe materials were buried in each of a number of test soil locations scattered over the United States. The American Petroleum Institute later recognized the problem of underground corrosion by forming a subcommittee in 1928 to foster investigations of this subject. The American Gas Association has likewise fostered a study of soil corrosion with particular reference to the formulation of pipe coatings. A great deal of the work has been done from the standpoint of investigating and developing methods for reducing the rate of attack; this has led to the development of numerous pipe coating systems and to the use of cathodic protection. Other students of the soil corrosion problem have attempted to correlate soil corrosion rates with soil properties. In this work different investigators have attempted to show that several soil factors can be used to predetermine soil corrosion rates. Denison (*1*) presented data to show that the total acidity and the pH of soils were closely related to the actual corrosion experienced by a pipe line. He also found that the pitting factor of a soil is influenced by certain of its mechanical properties, such as the percentage of the total volume of moist soil occupied by air, the ratio of the moisture for saturation to the moisture equivalent, and the dispersibility of silt and clay. Weidner and Davis (*16*) concluded that there is some correlation between long line currents and soil corrosion, and that there is considerable correlation between soil resistivity and pit depth. Gill and Rogers (*4*) made a thorough investigation of several miles of pipe to test the theory that either the soil electrical resistivity or long line currents might be used to determine corrosive areas. Their results were that the accumulation or discharge of long line currents is without practical bearing upon the subject of soil corrosion, and that there is a slight correlation between corrosion and soil resistivity but the relation is too general to possess practical importance. Shepard (*15*), however, in agreement with Weidner and Davis, found that the measurement of long line currents and soil resistivity could be used as an aid in locating corrosive soils. Although McGary (*10*) indicated that soils containing oxidizing agents such as nitrates give rise to severe corrosion, and Richards (*12*) reported that the quantity of sulfur present in the soil can be used as the corrosion index, the majority of the argument in soil corrosion studies has revolved around the measurement of soil acidity, pH, electrical resistivity, and long line currents. The latter measurement is applicable only where the line is in place and is not a method for predetermining the soil corrosion rate.

Adaptation of Electrochemical Theory to Soil Corrosion

In studying soil corrosion the factors encountered are not only the numerous ones found in cases of atmospheric corrosion but also those which result from the peculiar physical and chemical properties of soils.

The properties of soils which also contribute to the condition of atmospheric corrosion are:

1. The presence of water.
2. The presence of soluble salts. These may be either easily soluble and leachable materials such as sodium chloride or sparsely soluble soil complexes. These soluble materials give rise to the soil electrical resistivity, the pH, the total acidity, the buffer capacity, etc.
3. The presence of gases such as air, together with the usual or changed proportions of oxygen, carbon dioxide, nitrogen, hydrogen sulfide, etc.
4. The corrosion product, which may be protective or not, depending upon the method of formation.
5. Temperatures between the annual maximum and minimum.
6. Alternate wetting and drying conditions or negligible water velocity in the case of submersion.

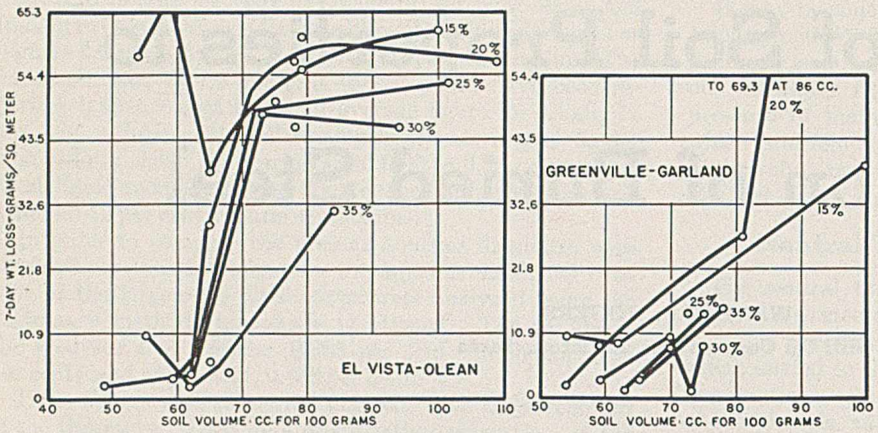

Figure 1. Relation of Soil Volume and Water Content to Corrosion

The properties which are more or less peculiar to soil corrosion deal with physical as well as chemical factors. These result from the complexity of the soil particle. Soils vary in composition from pure sands which possess little or no soil colloids, to clays which are made up almost entirely of colloidal particles. Between these limits are all possible intermediate conditions. Pure sands are comparatively easy to evaluate in regard to chemical and physical properties. They usually possess little or no soluble salts and are but slightly buffered. The addition of moisture to a sand does not cause any change in its particle size. The main effect of the moisture is simply that of filling the soil pores and replacing the soil air. The majority of soils, however, contain more or less colloidal particles. These colloids are complexes of iron, silica, or alumina, and the addition of water to such soils allows the colloidal properties to be brought into play. Instead of moisture replacing the soil air, it is utilized by the soil colloids to develop the properties of absorption, swelling or contraction, gelation, plasticity, etc. Any description of these soil colloids is outside the scope of this paper, and authoritative texts may be consulted (*2*). It is sufficient here to point out these properties and to indicate how they may affect the corrosion reaction. For instance, clay soils are known to possess a greater porosity than do sands. Clay soil air, however, as a result of the more tortuous passages of the soil, does not easily move to enter into the corrosion reaction. The addition of a small quantity of moisture to such a clay soil might result in such swelling that all the soil air would be displaced or so bound that the permeability of the soil would approach zero and the corrosion rate would be greatly reduced. The addition of an equal quantity of moisture to a sand (if less than the saturation value) might increase the corrosion rate because the water would not be absorbed by the soil particles but would be available for the corrosion reaction.

Laboratory Test Procedure

Studies were made in the laboratory on several typical soils to determine the effect of the variation of each of several factors on the soil corrosion rate. For purposes of test three soils were used. One of these was known to be corrosive to steel; the second was known to be noncorrosive; and the third which was a coarse river sand was chosen because of its high resistivity, low buffer action, lack of colloids, and high permeability.

The first tests were made to determine the effect of variations of the soil air for fixed moisture concentrations. In this series of tests the pH was kept constant. The soil resistivity varied with the water content. The object was to determine how the corrosion rate would vary for a soil as water evaporated, leaving more and more air in the soil pores.

The second tests were made to determine the effect of variations of the electrical resistivity of the soil. In these tests the soil water content, the soil air content, and the pH were kept constant; the electrical resistivity was the only variable.

The third tests were made to determine the effect of the soil pH. In these tests all factors were again kept constant except the variable, hydrogen-ion concentration.

The soil to be tested was first dried at 105° C. for 6 hours. It was then ground in a ball mill until the soil particles would pass through a 20-mesh screen. One hundred grams of dried soil were taken for each test. The test specimens were 0.092-cm. (20-gage) cold rolled steel cut in 2.54-cm. squares. These specimens were pickled in acid to remove all mill scale, numbered, cleaned in sodium hydroxide and zinc mixture (*3*), washed, dried, and kept in a desiccator until ready for use. The required quantity of water, either as distilled water or buffered for pH or electrical resistivity as desired, was added to the soil, and the mixture was ground with a large spoon until the soil and water were thoroughly mixed. About half of the soil was placed in the glass jar and tamped with a porcelain bar. The metal specimen was laid on top of this soil and the remainder of the soil placed over the specimen. This soil was then tamped until the required degree of packing was obtained.

About four dozen 138-cc. (4-ounce) glass containers were used to hold the specimens. A representative number were gaged and were found to have a capacity of 138 ± 2.0 cc. The average depth was 6.9 cm. The soil depth was measured to the nearest 0.079 cm. ($^1/_{32}$ inch) using a steel rule calibrated to this accuracy. A deviation of 0.079 cm. in height would amount to 1.58-cc. variation in soil volume. The 100 grams of soil were weighed to the nearest gram which, with a specific gravity of 2.7, would amount to a variation of 0.37 cc. This variation would result in a small change in corrosion for some of the tests and a rather large change for others. Its value cannot be given as a definite figure but can be approximated from the moisture-volume curves. The vapor space left in the glass jar depended upon the depth to which the soil was packed. In all cases, however, there was ample oxygen present to allow for a greater weight loss than was obtained. After the soils were packed to the required depth, the test jars were left at room temperature for 7 days. At the end of this time the jars were opened and the metal specimens were removed, cleaned in hot sodium hydroxide and zinc solution, and reweighed. The weight loss was calculated as grams per square meter for the 7-day period of test. These data have been taken as indicative of the true soil corrosion rate under the conditions of the test.

Effect of Variations in Soil Water and Air

The three soils which were used for this and the other tests, together with some of their physical and chemical properties, are given in Table I.

Table I. Properties of Laboratory Test Soils

Soil	Corrosion Rate per Year *Mm.*	*In.*	Sand %	Silt %	Clay %	Colloids %	pH	Resistivity at Satn. *Ohm-cm.*
Kalmia	...	...	100	..	..	..	7.4	10,100
Garland-Greenville 69-3	0.127	0.005	22	20	58	64	7.0	504
El Vista–Olean 31.60	1.02	0.040	...	..	..	57	5.5	401

El Vista–Olean 31.60. This soil possesses an acid pH and a low resistivity. It is a corrosive soil since it gives rise to rust holes in 5 years. Because of the high colloidal content of this soil the water requirements were large, a maximum of 35 per cent being necessary for saturation. For the various tests the water content was reduced in quantities of 5 per cent

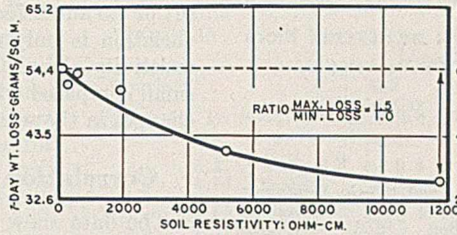

FIGURE 2. EFFECT OF SOIL RESISTIVITY ON CORROSION OF KALMIA SAND–SODIUM CHLORIDE SOLUTIONS

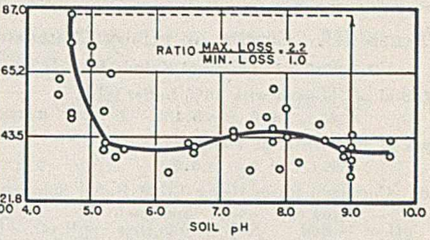

FIGURE 3. EFFECT OF SOIL pH ON CORROSION OF KALMIA SAND–BUFFER SOLUTION MIXTURES

each. The data are shown at the left of Figure 1. Examination of the figure shows that for 15 per cent water, the minimum used, the soil gives large corrosion rates regardless of the air content. For the other water concentrations, particularly those where the soil was closely packed (possessing a volume of 48 to 62 cc.), evidently the soil pores were filled with water to the exclusion of oxygen and little corrosion occurred. Increasing the soil volume over 62 cc., which is the same as increasing the quantity of oxygen present, greatly increased the corrosion rate. Figure 1 shows that 35 per cent water gives the minimum corrosion rate and indicates that the soil has a scarcity of oxygen and a low air permeability while in this condition. The maximum variation in corrosion rate was from 67.7 to 1.9 grams per square meter, a variation of 31 to 1.

GREENVILLE-GARLAND 69-3. This soil possesses a neutral pH and a low resistivity when wetted with distilled water. The soil is known to be noncorrosive in the field. The soil possesses a high colloidal content, and 35 per cent water was required for saturation. The data are shown at the right of Figure 1. For the 15 and 20 per cent moisture concentrations when the soil was loosely packed, high corrosion rates were obtained. For the values of 25, 30, and 35 per cent moisture and for the 15 and 20 per cent concentrations when the packing was below 80 cc., the corrosion rate was very low. Thus for most moisture contents this soil would be noncorrosive. Only when this soil is in a very loose condition and has a small water content is it corrosive. The maximum variation in corrosion rate was from 1.1 to 62.2 grams per square meter, a variation of 56.5 to 1.

Effect of Soil Resistivity

Of the three soils in this test group only one, the Kalmia sand, possessed a sufficiently high resistivity to allow of any downward variation. While it is possible that continued washing of soluble salts from the other soils might have increased their resistance, it was not considered advisable to do this because the losses of colloidal materials through the washing might result in an altered soil physical condition which would give rise to untrue corrosion rates. Tests were made using the Kalmia sand to determine the effect of variation in electrical resistivity on the soil corrosion rate. In this test the soil volume–water content and the pH were kept constant. The resistivity alone was varied. In order to obtain a weight loss high enough for differences in resistivity to manifest themselves, the soil water-air content chosen was that which conforms to a packing of 50.7 cc. and 13 per cent moisture. A series of solutions of varying resistivity were made up, consisting of chemically pure sodium chloride dissolved in distilled water. The resistivity of these solutions varied from 10.1 ohm-cm. in the lowest case to 4560 ohm-cm. in the highest. Three sets of tests were run. Each test included duplicate samples for check, giving a total of six measurements for each value of resistivity. When the test specimens were made up, samples of the soil–sodium chloride solution were packed in a one-inch cube conductivity cell, and the resistance of the soil-moisture mixture was determined. The resistivity measurements were made with a Leeds & Northrup ohmmeter (serial number 129,717) operated by alternating current. At the conclusion of the tests pH check determinations were made on a representative number of the soils. These checks were made by mixing samples of the soil with distilled water in the percentage of two parts of water to one of soil. This mixture was well shaken and allowed to stand 24 hours. The pH of the soil water was then determined colorimetrically using La Motte[1] color standards. The data obtained in these tests are given in Table II and Figure 2.

The soil resistance varied from 94 to 11,750 ohm-cm. This caused a variation in corrosion rate from 54.7 to 36.1 grams per square meter, which is a ratio of 1.5 to 1. Thus, although the soil resistivity does influence the soil corrosion rate, Figure 1, which shows the variation caused by soil water-air values, indicates that this latter function is of much greater importance than the effect of the soil resistivity.

TABLE II. EFFECT OF ELECTRICAL RESISTIVITY ON CORROSION BY KALMIA SAND

Soil, water, air volume, cc.	50.7
Weight dry soil, grams	100
Moisture, %	13.0
pH	6.4–7.0
Container size, cc.	138

Resistivity Range *Ohm-cm.*	Av. Resistivity *Ohm-cm.*	Weight Loss[a] *Grams/sq. meter*
94–104	99	54.7
246–260	253	52.0
490–570	530	54.1
1,610–2,200	1,905	51.5
4,500–5,700	5,150	41.0
10,800–12,700	11,750	36.1

[a] Each weight loss measurement is the average of six individual specimens.

Effect of Soil pH on Soil Corrosion

The effect of the soil pH on the corrosion rate of Kalmia sand was next determined. In this case the soil volume–water proportion and the electrical resistivity were kept constant and the only variation was the pH of the soil. In this case only the Kalmia sand was used because the other soils possessed such high buffer capacities that no variation in pH was obtained when a 0.1 *M* buffer solution was added. The water content and the soil volume values were taken as 13 per cent and 50.7 cc. packing, respectively, as were used for the soil resistivity tests. It was found that even the Kalmia sand possessed a slight buffering action. The buffer solutions were made up to a strength of 0.1 and 0.5 *M* according to the data given by Kolthoff and Furman (*5*). The pH of the buffer solutions was checked colorimetrically by La Motte color standards and also with a Beckman[2] glass electrode. To determine the buffer capacity of the Kalmia sand, tests were made using only the buffer solution–soil mixture but without the metal specimen. The tests were allowed to stand the regular time of 7 days. The pH of the mixture before and after test was determined by means of a glass electrode. The data are given in Table III. There is a slight shift in the alkaline direction, varying from 0 to 0.5 pH.

Three series of tests were made to determine the effect of pH on corrosion. In these tests the electrical resistivity of the mixture was determined at the time of preparation of the test

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[1] La Motte Chemical Company, Baltimore, Md.

[2] National Technical Laboratories, Pasadena, Calif.

Table III. Effect of pH on Corrosion by Kalmia Sand

A. Buffer Capacity of Kalmia Sand to 0.5 *M* Buffer Solutions

Initial pH of sand with 13% buffer soln.:	4.3	4.6	5.1	6.8	6.6	8.0	8.4
pH of mixture after 7-day contact:	4.7	4.9	5.5	...	6.9	8.0	8.9

B. Corrosion Rates Using 0.1 *M* Buffer Solutions and 138-Cc. Container

pH of Buffer Soln.	pH of Soil after 7 Days	Soil Resistivity *Ohm-cm.*	Specimen Wt. Loss after 7 Days *G./sq. m.*	pH of Buffer Soln.	pH of Soil after 7 Days	Soil Resistivity *Ohm-cm.*	Specimen Wt. Loss after 7 Days *G./sq. m.*
4.0	6.5	2132	42.7	10.0	9.0	1778	43.5
4.0	6.2	2235	32.2	10.0	9.0	1625	35.9
8.0	7.4	2032	32.3				
8.0	7.4	2006	47.5				

C. Corrosion Rates Using 0.5 *M* Buffer Solutions and 138-Cc. Container

pH of Buffer Soln.	pH of Soil after 7 Days	Soil Resistivity *Ohm-cm.*	Specimen Wt. Loss after 7 Days *G./sq. m.*	pH of Buffer Soln.	pH of Soil after 7 Days	Soil Resistivity *Ohm-cm.*	Specimen Wt. Loss after 7 Days *G./sq. m.*
4.0	4.7	748	86.5	8.0	8.0	580	44.0
4.0	4.7	622	75.5	8.0	8.0	580	53.4
5.0	5.2	646	39.0	9.0	7.8	464	46.7
5.0	6.6	642	41.5	9.0	8.9	382	37.8
6.0	6.6	496	40.0	9.0	8.9	434	40.1
6.0	6.6	568	40.0	10.0	9.0	523	30.0
6.2	7.2	584	45.5	10.0	9.6	470	42.7
8.0	7.8	432	42.8	10.0	9.6	386	37.1

D. Corrosion Rates Using 0.5 *M* Buffer Solutions and 276-Cc. Container

pH of Buffer Soln.	pH of Soil after 7 Days	Soil Resistivity *Ohm-cm.*	Specimen Wt. Loss after 7 Days *G./sq. m.*	pH of Buffer Soln.	pH of Soil after 7 Days	Soil Resistivity *Ohm-cm.*	Specimen Wt. Loss after 7 Days *G./sq. m.*
3.8	4.5	610	57.5	4.8	5.5	510	39.3
2.9	4.5	456	62.5	8.0	7.4	410	44.6
3.8	4.7	610	49.7	8.0	7.7	410	50.0
3.8	4.7	610	51.2	6.0	7.8	500	59.7
4.0	5.0	660	74.7	5.7	7.9	480	33.8
4.0	5.0	660	68.3	5.7	8.2	480	35.1
4.8	5.2	510	53.0	9.4	8.5	510	47.6
5.0	5.3	550	65.7	9.4	8.6	510	42.5
4.8	5.4	510	37.4	5.7	9.0	480	40.3

cell. The pH of the test soil was determined at the start and close of the test. These pH determinations were made colorimetrically, as the glass electrode was not available at that time. The data are presented in Figure 3. The resistivities of these tests were rather high, lying in the range 1600 to 2200 ohm-cm. For the 0.5 *M* buffer solutions the electrical resistivity varied between 400 and 660 ohm-cm. The data are rather scattered, particularly in the range 7.5 to 8.5. In this range the factor of chance seemed to exercise an important part in causing such a wide dispersion in the data. It is evident, however, that pH does exert an influence on the soil corrosion rate. Apparently above 5.5, variations in pH are of little importance. Below 5.5 the soil pH causes an increase in the corrosion rate. The maximum difference between the pH of 4.5 and 9.75 is not large, the ratio being 2.2 to 1. This variation is only slightly larger than the variation due to resistivity alone. Here again, however, these variations are small compared with the variations which may be caused by changes in the water-air volumes.

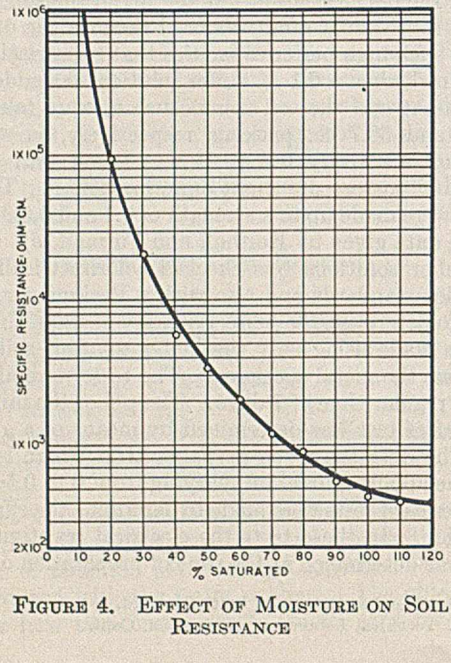


Figure 4. Effect of Moisture on Soil Resistance

Correlation of Laboratory with Field Data

The data show that, while variations in the electrical resistivity or the pH of a soil may result in some slight variation in the soil corrosion rate, the most important function of a soil is its water-air content. It remained, therefore, to determine whether or not these data could be applied to field corrosion rates. In order to obtain definitely the pitting rates of soils in the field, pit depth measurements were made on several pipe lines when they were uncovered for repairs. These lines were located on the Texas Gulf Coast. Two sections of pipe lines were taken for this study, and the soils from these lines were used from time to time to obtain data on any particular factor that was to be checked. The first line was the Almeda-Lynchburg 15.2-cm. (6-inch) line between mile poles 25.82 and 23.90. This line was laid in 1920 and was uncovered in 1931 after 10.3-year burial. At the time the line was uncovered, pit depth measurements were made each 20 feet along the 2 miles exposed. The second line was the Delphine–El Vista No. 2, 25.4 cm. (10 inches) between mile poles 28.90 to 31.27. This line was laid in 1927 and was taken up for repairs in 1933 after 5.9-year burial. The deepest pit each 10 feet of this pipe was recorded.

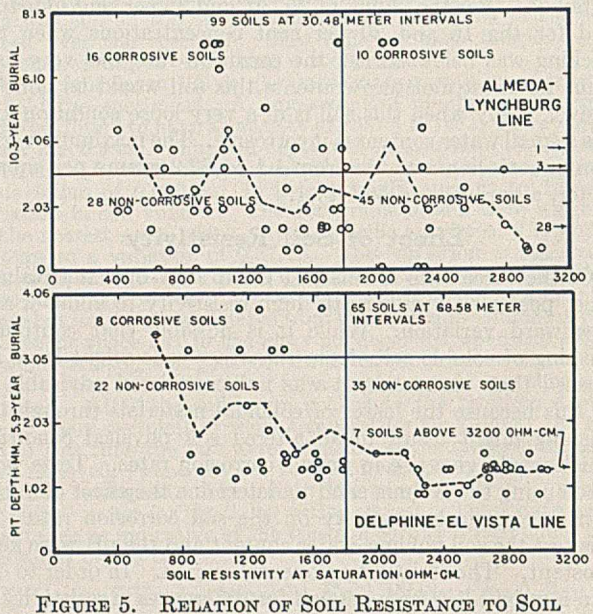


Figure 5. Relation of Soil Resistance to Soil Corrosion

Soil Resistivity as Corrosion Index

Variation of Resistivity with Moisture Content. The electrical resistivity of soils has been used by a number of investigators (*15, 16*) to differentiate between corrosive and noncorrosive areas. The electrical resistivity may be measured in the field at pipe depth, or the soils may be brought into the laboratory and the measurement made under water-saturated conditions. The latter method has the advantage that it leads to a determination of the minimum resistance of the soil and is a reproducible figure. Soil resistivity measurements made in the field are likely to vary widely, depending upon the season of the year at which the measurements are made. To illustrate this point, measurements were made in the laboratory to show the effect of the water content of a soil on its electrical resistivity. The results of one of these typical tests are shown in Figure 4, where the data are listed as resistivity *vs.* percentage of water for saturation. The resistivity varied from 100,000 to 375 ohm-cm. as the water content increased from 20 to 120 per cent saturation.

These data show that, if any correlation is to be obtained between the soil resistance and corrosion, the resistivity must be obtained under defined moisture conditions. For this reason the comparisons which are made here use the soil resistivity at the moisture-saturated condition.

ALMEDA-LYNCHBURG LINE. When this line was repaired, ninety-nine soils at 30.48-meter (100-foot) intervals were sampled, and the deepest pit within 3.05 meters was noted. The soil resistivities at saturation *vs.* the pit depths are listed in Table IV and plotted in the upper half of Figure 5. For purposes of comparison the soils are split into four groups. The first two groups are classed according to resistance. One of these includes the soils below 1800 ohm-cm., and the second group, those higher than 1800. The third and fourth groupings are made on the basis of corrosion rate. All soils which gave rise to a pipe pit depth greater than 3.04 mm. (0.120 inch) are considered corrosive; pit depths below this are considered noncorrosive. In addition, a curve was drawn to show the average variation in pit depth with soil resistivity. Below 1800 ohm-cm. there were sixteen corrosive and twenty-eight noncorrosive soils. Above 1800 ohm-cm. there were ten corrosive and forty-five noncorrosive soils. Thus if all the pipe in soils with less than 1800 ohm-cm. resistivity had been coated, 44/99 or 44.5 per cent of the pipe would have been coated. Of this amount 16.1 per cent would have required coating whereas 28.4 per cent would not. In addition, 10.1 per cent of the soils which should have been coated would have been left bare. A trend exists between soil resistance and corrosion, but it is not sufficiently defined to be used as an index value.

TABLE IV. SOIL PROPERTIES AND PIT DEPTH DATA FOR THE ALMEDA-LYNCHBURG LINE[a]

Sample Location No.	Pit Depth		Soil Resistivity at Satn.	pH	Sample Location No.	Pit Depth		Soil Resistivity at Satn.	pH
	Mm.	*In.*	*Ohm-cm.*			*Mm.*	*In.*	*Ohm-cm.*	
1	3.81	0.150	1,780	...	54	1.90	0.075	1,220	6.3
2	4.44	0.175	406	7.2	55	1.90	0.075	2,320	4.5
3	3.17	0.125	1,810	5.9	56	1.27	0.050	3,680	4.4
4	5.08	0.200	1,320	6.2	57	7.11	Hole	2,110	5.0
5	7.11	0.280	1,015	7.2	58	0.63	0.025	11,450	4.7
6	3.81	0.150	4,440	6.9	59	1.90	0.075	4,820	4.9
7	3.81	0.150	1,500	6.1	60	1.90	0.075	407	5.7
8	3.81	0.150	1,060	5.3	61	0.63	0.025	1,520	5.6
9	..	No	2,260	5.4	62	1.27	0.050	1,675	5.1
10	1.27	0.050	2,370	5.5	63	1.27	0.050	1,320	4.8
11	..	No	3,430	...	64	..	No	10,150	4.9
12	1.27	0.050	1,780	...	65	..	No	9,650	4.8
13	0.63	0.025	5,080	5.8	66	0.63	0.025	738	5.7
14	..	No	5,080	5.0	67	1.27	0.050	610	5.7
15	..	No	6,350	5.3	68	0.63	0.025	1,470	5.1
16	7.11	0.280	940	5.7	69	..	No	3,810	5.3
17	1.90	0.075	965	5.9	70	..	No	4,060	4.9
18	3.17	0.125	1,065	5.6	71	0.63	0.025	3,040	5.4
19	1.27	0.050	1,675	5.4	72	1.27	0.050	2,990	5.3
20	0.63	0.025	2,920	5.3	73	..	No	2,030	5.8
21	1.90	0.075	....	5.8	74	..	No	2,290	5.5
22	3.17	0.125	2,790	5.6	75	0.63	0.025	....	6.0
23	0.63	0.025	3,300	5.4	76	0.63	0.025	2,920	5.3
24	..	No	9,140	5.1	77	2.54	0.100	2,540	4.5
25	1.27	0.050	1,420	5.9	78	2.54	0.100	888	6.3
26	2.54	0.100	1,450	6.4	79	1.90	0.075	1,780	5.9
27	..	No	1,295	5.9	80	3.81	0.150	660	5.8
28	..	No	....	4.9	81	3.17	0.125	698	5.7
29	..	No	8,890	5.3	82	1.27	0.050	1,830	5.3
30	..	No	6,100	...	83	1.90	0.075	1,070	5.8
31	..	No	5,840	5.0	84	1.90	0.075	2,540	6.1
32	..	No	11,450	4.8	85	3.81	0.150	....	5.4
33	6.35	0.250	1,040	7.2	86	4.44	0.175	2,290	5.1
34	4.44	0.175	1,092	6.3	87	1.27	0.050	8,620	4.8
35	3.81	0.150	750	6.9	88	0.63	0.025	....	5.7
36	3.17	0.125	6,350	4.3	89	3.17	0.125	....	...
37	7.11	0.280	2,050	5.4	90	2.54	0.100	737	...
38	1.90	0.075	1,575	5.5	91	1.90	0.075	5,340	5.9
39	0.63	0.025	11,450	4.5	92	1.90	0.075	2,790	5.4
40	..	No	660	7.4	93	1.90	0.075	4,440	5.3
41	0.63	0.025	889	5.7	94	1.27	0.050	7,620	5.3
42	..	No	890	5.9	95	2.54	0.100	8,640	5.3
43	1.90	0.075	470	6.2	96	0.63	0.025	7,370	5.6
44	0.63	0.025	....	...	97	0.63	0.025	8,890	5.3
45	1.25	0.050	1,550	4.8	98	3.17	0.125	6,600	5.0
46	2.54	0.100	4,450	5.5	99	2.54	0.100	1,675	...
47	3.81	0.150	1,675	5.8	100	1.90	0.075	2,180	5.2
48	7.11	0.280	1,775	6.0	101	1.27	0.050	10,400	...
49	3.17	0.125	2,290	5.9	102	0.63	0.025	5,580	...
50	0.63	0.025	7,870	5.0	103	1.27	0.050	4,820	...
51	1.90	0.075	1,730	5.4	104	5.08	0.200	....	...
52	1.90	0.075	890	6.1	105	2.54	0.100	4,700	...
53	1.27	0.050	1,680	6.2	106	7.11	0.280	1,015	...

[a] Measurements made 30.48 meters (100 feet) apart; 10.3-year burial.

DELPHINE–EL VISTA LINE. When this line was repaired, sixty-eight soils at 68.58-meter (225-foot) intervals were sampled, and the deepest pit within 3.05 meters of the soil sample was obtained. The data showing the relation between soil resistivity and pit depth are listed in Table V and shown in the lower half of Figure 5. Again the soils were split into the four groups. Eight of the sixty-eight soils were corrosive. All of these fell in the resistivity interval below 1800 ohm-cm. In addition, however, twenty-two noncorrosive soils also fell in this same resistance group. Thus if soil resistance were made the basis for coating this line, thirty of the sixty-five soils or 46.2 per cent would have been coated. Of these thirty soils, only eight or 12.3 per cent required coating, whereas the other 23.9 per cent did not. The remaining thirty-five soils above 1800 ohm-cm. were uniformly noncorrosive. A curve was also drawn to show the relation between the average pit depth and soil resistivity. The average pit depth decreases with increase in soil resistivity.

The data obtained from a study of the relation of soil resistance to pit depth measurements on these two lines show that, while in general there is a tendency for the soils of lower resistance to give rise to the more rapid corrosion rates, the tendency is not sufficiently marked to be used as an index to determine soil corrosion in rates. It can only be said that, if a survey of a line shows that all the soils have a resistance at saturation greater than 1800 ohm-cm., there will be very few corrosive soils among them. However, few areas will be found for which the soil resistivities will, in general, be above 1800 ohm-cm.

Relation of Soil pH to Corrosion

ALMEDA-LYNCHBURG LINE. Ninety-nine soils taken at 30 48-meter (100-foot) intervals along this line were brought to the laboratory for determination of the pH values. A Beckman glass electrode was used to make these measurements. Distilled water was added to each soil until it became plastic enough to allow the glass electrode to be inserted. These moisture contents approached the saturation point but rarely, if ever, exceeded it. Thus these soils were wetted to a condition which approaches their normal condition during the wet season of the year. The pH measurements are given

Table V. Soil Properties and Pit Depth Data on the Delphine–El Vista Line[a]

Pole	Pit Depth		Soil Resistivity at Satn.	pH
	Mm.	In.	Ohm-cm.	
1	1.27	0.050	..	...
2	1.27	0.050	5080	...
3	1.27	0.050	4320	...
4	1.27	0.050	2790	...
5	1.27	0.050	2415	...
6	1.27	0.050	3305	...
7	1.27	0.050	1675	...
8	1.27	0.050	2240	...
9	1.27	0.050	3050	...
10	1.27	0.050	2670	...
11	1.27	0.050	2690	...
12	1.27	0.050	2670	...
13	1.27	0.050	2790	...
14	1.27	0.050	5080	...
15	1.27	0.050	2440	...
16	1.27	0.050	2730	...
17	1.02	0.040	2540	...
18	0.88	0.035	2980	...
19	0.88	0.035	2600	...
20	0.88	0.035	2415	...
21	0.88	0.035	2340	...
22	1.02	0.040	3175	...
23	0.88	0.035	3690	...
24	0.88	0.035	2290	6.2
25	0.88	0.035	2490	5.3
26	0.88	0.035	1525	5.1
27	0.88	0.035	3460	5.0
28	0.88	0.035	2790	5.3
29	0.88	0.035	3430	5.6
30	1.52	0.060	2670	4.9
31	1.40	0.055	..	6.4
32	1.52	0.060	1425	6.3
33	1.52	0.060	2160	5.2
34	1.40	0.055	1780	5.2
35	1.40	0.055	1625	5.9
36	1.40	0.055	1270	5.2
37	1.40	0.055	1435	6.1
38	1.40	0.055	..	6.0
39	1.27	0.050	1295	4.7
40	1.27	0.050	1005	5.1
41	1.27	0.050	2860	4.3
42	1.27	0.050	2790	6.7
43	1.27	0.050	1780	6.8
44	1.52	0.060	1475	5.9
45	1.52	0.060	1425	6.0
46	2.29	0.090	1195	5.3
47	1.27	0.050	1525	5.3
48	1.27	0.050	1590	4.6
49	1.52	0.060	1980	5.2
50	1.14	0.045	1625	7.0
51	1.14	0.045	1120	7.9
52	1.27	0.050	1195	4.9
53	1.14	0.045	2670	5.8
54	1.52	0.060	2920	6.7
55	1.52	0.060	1610	7.2
56	1.27	0.050	915	5.2
57	1.02	0.040	2290	6.0
58	1.52	0.060	840	6.0
59	1.90	0.075	1320	7.4
60	3.17	0.125	635	6.5
61	3.81	0.150	1145	5.0
62	3.43	0.135	1780	5.9
63	3.17	0.125	1420	6.3
64	3.17	0.125	825	6.4
65	3.81	0.150	1650	5.8
66	3.81	0.150	1270	5.0
67	3.17	0.125	1345	6.1
68	3.17	0.125	1145	5.3

[a] Measurements at poles 68.58 meters (225 feet) apart; 5.9-year burial.

in Table IV. These are plotted against the corresponding pit depth in the upper half of Figure 6. In making the comparison between pH and corrosion, all soils which gave rise to a pit depth greater than 3.04 mm. (0.120 inch) are considered corrosive. In general these ninety-three soils possessed a wide range in pH value. Twenty-four of them were corrosive and varied in pH from 4.3 to 7.1. Sixty-nine were noncorrosive and varied in pH from 4.4 to 7.4. This shows that both corrosive and noncorrosive soils varied over identical pH ranges and that there is no relation between these values and the soil corrosion rate.

Delphine–El Vista Line. Forty-six soils were taken at 68.58-meter (225-foot) intervals along the Delphine–El Vista line and brought to the laboratory for pH measurements. The technic and method of making the measurement were the same as for the Almeda-Lynchburg soils. This line was of unusual interest in that the soils were noncorrosive until the last half mile was reached, when they became highly corrosive. The data obtained are listed in Table V and shown in the lower half of Figure 6. Again the soils were split into corrosive and noncorrosive groups. They varied widely in pH. The nine corrosive soils varied between pH values of 5.0 to 6.5. The thirty-seven noncorrosive soils varied between pH values of 4.3 to 7.9. Certain of the noncorrosive soils were even more acid than were the corrosive soils. Here again there fails to be demonstrated even the slightest correlation between soil pH and soil corrosion.

The data from these two lines show that, although many soils of acid character were encountered, the severe pitting which occurred was not related to the pH value. Although the laboratory tests show that variation of soil pH only exerts an influence over the corrosion rate, in the field the variation of other factors and particularly the soil volume–water content are of such great importance that the effect of the pH is obscured. It is concluded that this factor cannot be used as an index of the soil corrosion rate.

Influence of Artificial Factors on Soil Corrosion

Effect of Trench Backfill. One of the interesting features of soil corrosion which has been pointed out by Scott (*14*) is the fact that the pitting rate of a soil may decrease with time. These data have been shown to be true not only for the Bureau of Standards soil corrosion tests but also in this investigation. Scott points out that this decrease of corrosion rate with time is probably due to many factors, among which the enlargement with time of the anodic or cathodic areas and the protective effect of the corrosion products which accumulate on the pipe are important. In addition to these two factors, it is believed that the data of this report show that the changing soil conditions which arise through settling of the backfill are also of great importance. This follows from the important effect variations in the soil volume–water content have on the corrosion rate. The test data show that a loose soil is more corrosive for any given quantity of water below the saturation point than is a tightly packed soil under the same moisture content. Thus the high initial corrosion rates of buried pipe can be explained on the basis of the high porosity and permeability of soils immediately after backfilling. Inasmuch as several years are usually required for a soil to settle completely, during this time the soil is in an accelerated rate as regards its normal corrosive action. Thus soils which slowly pack back to normal show annual decreases in corrosion losses. It is believed that this variation in soil porosity is more responsible for the decrease in corrosion rate than is the protective effect of the corrosion product, although the development of this latter undoubtedly aids in decreasing the corrosion rate. Evidence

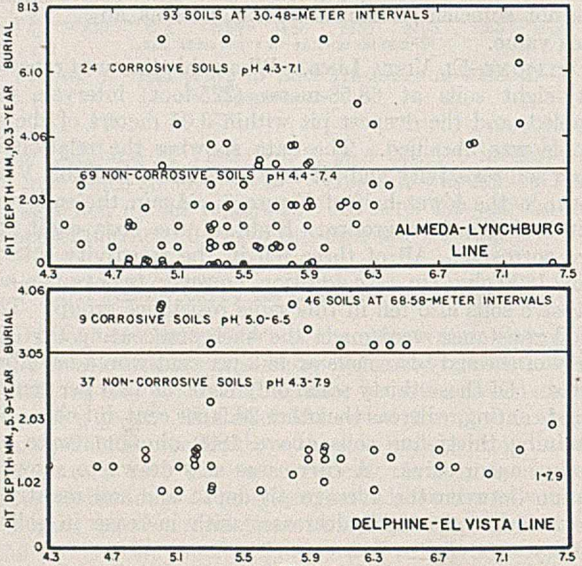
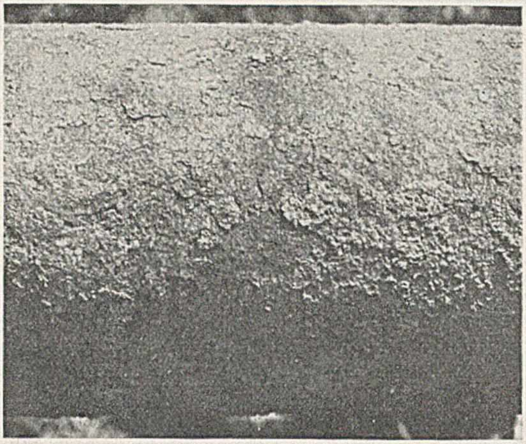


Figure 6. Relation of Soil pH to Soil Corrosion



(*Reading from top to bottom*)

FIGURE 7. THICK IRON OXIDE CORROSION PRODUCT DEVELOPED IN 5 YEARS

FIGURE 8. THIN IRON OXIDE CORROSION PRODUCT AFTER 12-YEAR BURIAL

FIGURE 9. CORROSIVE SOIL AREA CAUSED BY OIL LEAK

(Soil kept soft and mucky by oil on soil particles)

that at least thickness of the corrosion product is no guide to the protection afforded by it is shown by Figures 7 and 8. Figure 7 is a very thick iron oxide scale developed on a pipe during 5 years, and in this time penetration of the wall occurred. This may be contrasted with Figure 8 which shows a thin scale found on a pipe after 12-year burial; during that time the initial corrosion rate had probably decreased materially. It follows that high initial corrosion rates of soils can be prevented in some measure by tightly packing the soils at the time of backfill. This, of course, is impractical in any extensive pipe-line job.

EFFECT OF OILY SOILS. Rogers (*13*) showed that soils which become admixed with oil are frequently highly corrosive to the buried pipe. Figure 9 shows the appearance of the usual type of oily ground in which these high corrosion rates are found. Although the fact was not fully appreciated at the time the original data were presented, such soils are almost always quite loose and nonconsolidated. When the soil particles become coated with oil, they do not coalesce easily but remain in the abnormal condition of being loosely packed and possessing a high porosity. The effect of oil thus changes what may be normally a noncorrosive soil to a soil in a condition susceptible of producing rapid corrosion rates of buried steel pipe.

Discussion of Results

The most important conclusions which may be drawn from these tests deal with their practical value. It has been shown that the physical condition of a soil as regards its soil volume–water content controls its corrosion rate. By artificially or naturally controlling the soil volume–water content, any soil can be put in a condition which will allow corrosion to occur. In order to determine in the field whether or not a soil could be considered as corrosive, a seasonal study of its variation in moisture-air values would have to be made. Such a study would show definitely the corrosive action of the soil. Although this type of investigation is applicable to a study of a few soils, it cannot be made at present along an extensive right of way because of the mass of labor involved. The method cannot, therefore, be recommended for field use at present where a simple inexpensive test is desired.

Certain conclusions can also be drawn regarding the value of these studies in protective pipe coatings. The data show that the physical condition of the soil controls the corrosion rate. Suppose that a permanent wrapping material without the use of any coating between the pipe and the wrapper were put around the pipe. This wrapper might allow free water to leak through the lap of the wrapper and to the pipe, but the effect of the soil physical property would be removed. The pipe would then suffer such corrosion as is experienced under slow conditions of wetting and drying. Although this may be fairly rapid under some conditions, in all probability the corrosion rate would be much less than if the pipe were exposed to the soil. If a coating were placed between the pipe and the wrapper, the corrosion rate would be further reduced. It is believed that the use of a permanent nonrotting wrapper for a pipe is the most important part of any protective coating system and can alone be relied upon to prevent the majority of the soil corrosion which would otherwise occur.

Conclusions

From the laboratory and field studies which have been made of soil corrosion of buried pipe it is concluded that:

1. The controlling factor in soil corrosion of buried steel is the effect of variations in the soil water-air proportions. Laboratory variations of these factors allowed variations in corrosion rates of 31.1–1 to 56.5–1 to occur.
2. The electrical resistivity of a soil exerts an influence on its corrosion rate. Variations in this factor in the laboratory for Kalmia sand over the range 12,000 to 94 ohm-cm. resulted in a variation in corrosion rate between 1.5 and 1.
3. The pH of a soil exerts an influence on its corrosion rate. Laboratory tests show that varying the pH of Kalmia sand between 4.5 and 9.75 resulted in a variation in corrosion rate between 2.2 and 1.
4. Comparison of soil resistivity measurements at saturation with the corresponding pipe pit depth show that there is a definite trend between resistivity and corrosion. The trend is not sufficiently accurate, however, to be used as an index of soil corrosion. It can only be said that very few corrosive soils

have resistivity values greater than 1800 ohm-cm. The majority of soils, however, possess values of resistivity less than this.

5. Comparison of soil pH values with field corrosion rates indicate a complete lack of any correlation between these quantities. The method cannot be used as a field index of soil corrosion.

6. The corrosion rate of a soil in the field may be determined by following its seasonal variation in water-air volumes and checking again a laboratory index test.

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SEPARATION PROCESSES

Analysis of Unit Sections

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The equipment used in separation processes can be thought of as composed of relatively simple units which may be combined in a number of ways. The molal property *vs.* mole fraction diagrams for a number of such simple unit parts are presented, and the combination of these unit parts into the design diagram for a complete unit is illustrated. Special consideration has been given to column sections with inefficient plates and column sections operating with entrainment.

In a previous paper (*3*) the general methods of analysis of separation processes were discussed. The method was illustrated by an analysis of an ideal contactor section, a nonadiabatic simple section, and a feed or withdrawal unit. In general, the apparatus for any complicated process may be broken down into several standard units which may be combined to make up the apparatus of the complete process. The graphical analysis of such standard units of equipment and process is always the same, and we may obtain the analysis of the complete apparatus and process by combining the analyses of the unit sections.

Conjugate Phases

In the previous paper it was indicated that in the countercurrent contactor the compositions of *A* and *B* phases leaving the same contact unit (e. g., liquid and vapor leaving the same plate) are determined by a contact condition. In general this condition will involve diffusion rates, rates of flow of *A* and *B* streams, degree of intimateness of contact, and the compositions of all four streams associated with the unit, as controlling factors. In the simplest case the *A* and *B* phase streams leaving the unit will be at equilibrium.

The molal heat content of a boiling liquid of any definite composition has a definite value, and the boiling liquids are, in general, represented by points on a single curve. Similarly the saturated vapors are represented by points on the vapor curve. In solvent extraction, saturated solvent-rich phase is represented by one curve and saturated solvent-poor phase by another.

To each particular composition of boiling liquid there corresponds only one composition of saturated vapor which can be in equilibrium with the liquid. To each point on the curve of boiling liquid there corresponds only one point on the saturated vapor curve which represents vapor that can be in equilibrium with the given boiling liquid. It is customary to represent this equilibrium condition by joining the two equilibrium phases by an equilibrium tie line. The points at the end of an equilibrium tie line are called "conjugate points" in the diagram.

The equilibrium condition may be represented in other less cumbersome ways than by the use of tie lines. For instance, we may locate on the *B* phase curve (Figure 1) points conjugate to points on the *A* phase curve which represent round mole fractions of light component. Each of these points is labeled with the mole fraction of light component in the conjugate A phase. When we wish to locate a point representing liquid in equilibrium with a given saturated vapor, we read a value from this equilibrium scale at the point representing the vapor and locate a point on the liquid curve which has this value as its mole fraction of light component.

Caustic Curves. If we draw in the tie lines and extend them past the equilibrium phase curves, we find that in general they are tangent to a curve. The tie lines possess an envelope or caustic curve (E and F, Figure 2). We may use this caustic curve to locate tie lines. To find the points on the B phase curve corresponding to given A phase points, we draw a straight line from A phase curve tangent to the caustic curve. The intersection of this tangent line with the B phase curve will represent the conjugate (equilibrium) B phase corresponding to the given A phase. The caustic curves are particularly useful for interpolation between the points experimentally determined.

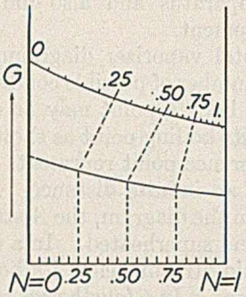


Figure 1. Conjugate Phases

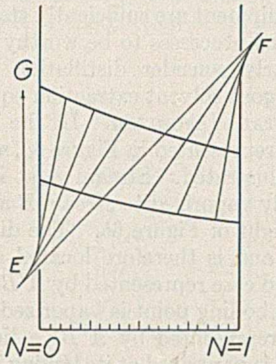


Figure 2. Caustic Curve of Tie Lines in Conjugate Phases

Ideal Simple Distilling Column Section

When equilibrium is established in each contact unit and the equilibrium diagram takes the simple form of Figure 3, as it does for distillation processes, the design method reduces to that of Ponchon (*2*) for an ideal simple section. As shown in Figure 3, the A points must lie on the A phase curve and the B points on the B phase curve, since the streams leaving any one contact unit (i. e., A_ν and $B_{\nu+1}$) must be at equilibrium and lie at the ends of a tie line on the equilibrium curves. In no other case is this so. The method of Ponchon (*2*) is applicable only to an ideal column which is adiabatic, with negligible or constant holdup, and which effects complete equilibrium on the plates.

Nonequilibrium Contact

Failure to establish equilibrium may be due to failure to reach the proper composition, failure to reach the right temperature, or both. In the first case the A and B phase points will all lie on the equilibrium curves, but the contact phases will not lie at the ends of an equilibrium tie line. In this case in going from B_ν to $B_{\nu+1}$, we will advance only a fraction of the distance towards the point we should reach for equilibrium with A_ν. This fraction of the equilibrium distance is what Murphree (*1*) has designated as the efficiency of a bubble plate, in connection with the design method of McCabe and Thiele. It is the ratio of change in mole fraction of the vapor stream effected by the plate to that which it should accomplish at equilibrium. Figure 4 represents a plate which is approximately 60 per cent efficient.

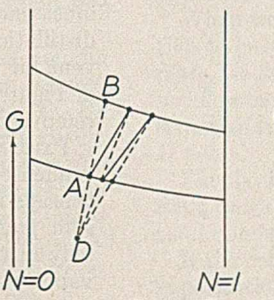


Figure 3. Ideal Simple Column Section Unit

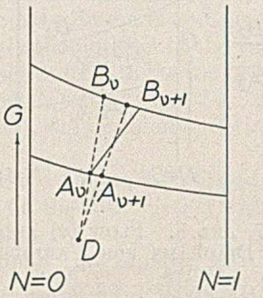


Figure 4. Nonequilibrium Contact Unit

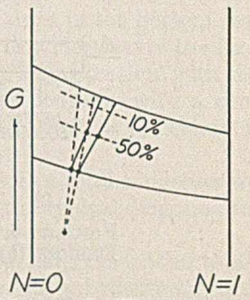


Figure 5. Units with Entrainment

Entrainment

When liquid from the plate is entrained in the vapor, although the vapor has equilibrium composition, the presence of the (equilibrium) liquid causes the B phase point to move down along the equilibrium tie line a distance proportional to the percentage of entrained liquid. Hence any percentage of entrainment may be represented by a curve cutting the equilibrium tie lines in the proper ratio. A curve one-tenth of the distance below the B phase curve represents 10 per cent entrainment (Figure 5), etc. This curve, in conjunction with the original tie lines, is to be substituted for the true equilibrium vapor curve.

The effect may also be represented by a Murphree efficiency factor. From the geometry of Figure 5 it is apparent that the efficiency factor will be less than unity by approximately the fraction of the entrained liquid (*4*).

Reflux Ratio and Total Reflux

The reflux ratio has been defined (*3*) as the ratio of moles of A stream to moles of B stream (i. e., moles of liquid to moles of vapor, O/V) at any particular interunit. From the properties of the diagram (as shown in Figure 5 of the previous paper, *3*) the reflux ratio is simply $\overline{AD}/\overline{BD}$. When the reflux ratio is unity (total reflux), D must move to an infinite distance. This also follows when we observe that in a contactor from which no product is withdrawn and no feed added, the net flow of total material must be zero. When this occurs, the weight of the D point becomes zero and its position indeterminate.

Hence at total reflux the D points are of little value. But there is a definite net flow of component and of heat. The flow of component is:

$$(M_D\mathrm{N}_D) = M_B\mathrm{N}_B - M_A\mathrm{N}_A \tag{1}$$

But the number of moles, M_B, is the same as $M_A = M$:

$$(M_D\mathrm{N}_D) = M(\mathrm{N}_B - \mathrm{N}_A) \tag{2}$$

Similarly the net flow of heat is:

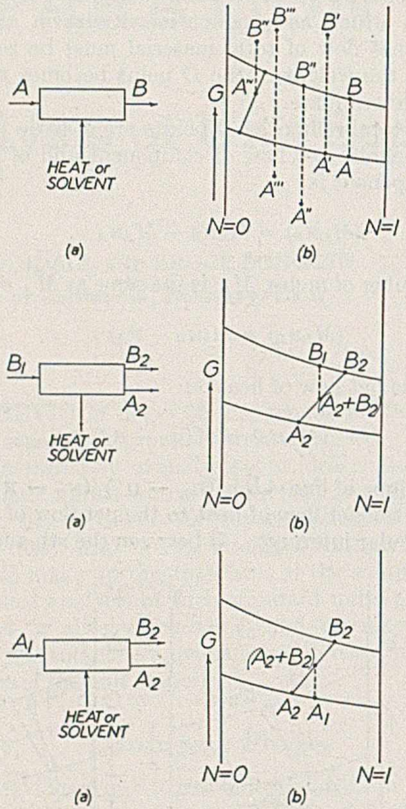
$$(M_D\mathrm{H}_D) = M(\mathrm{H}_B - \mathrm{H}_A) \tag{3}$$

Hence the slope of line $\overline{AB}$ is $(\mathrm{H}_B - \mathrm{H}_A)/(\mathrm{N}_B - \mathrm{N}_A)$, equal to the ratio of the net flow of heat to the net flow of component at the particular interunit. If between the νth and $(\nu + 1)$th interunit no heat or component is added to or withdrawn from the net flow, the two lines $\overline{A_\nu B_\nu}$ and $\overline{A_{\nu+1}B_{\nu+1}}$ are parallel. If heat and component are added, the slope will be different by an amount depending on the change produced in the ratio of net heat flow to net component flow.

Solvent Extraction Processes

The graphical analysis of distillation sections has been discussed as being more familiar than the other types of separation equipment. Before continuing with the description of the auxiliary equipment, let us consider the mechanical significance of solvent extraction processes. These are of two types. In the first a differential distribution of the mixture components between two phases in the same solvent is utilized in effecting the separation. The second makes use of a distribution between two immiscible or only partially miscible solvents.

In either case we plot on the vertical axis of the diagram, in place of molal heat content, the molal solvent content (i. e., number of moles of total combined solvent per mole of solvent-free mixture). Hence quantity of solvent plays to some extent the same role in these processes as is played by heat in the distillations. We may speak of a solvent-rich phase as being "hot," whereas a solvent-poor phase is "cold." When we add solvent to a phase we have "heated" it. In vaporizing a liquid we must add heat to convert one (A) phase into the other (B) phase. Hence we may speak of the solvent-rich phase as the "vaporized" phase. "Vaporization" consists, then, in adding solvent to convert A phase (solvent-poor) into B phase (solvent-rich).



Figures 6, 7, and 8. Flow (*a*) and Design (*b*) Diagrams for Various Units

Figure 6 (*above*). Total vaporizer
Figure 7 (*center*). Partial condenser
Figure 8 (*below*). Partial vaporizer

The foregoing discussion refers only to the case of a single solvent. With two solvents, in order to go from A to B phase it is necessary to replace one solvent by the other. Hence the process analogous to heating must in this case involve in some way the exchange of solvents. It is as if we had two kinds of heat. The greater number of degrees of freedom makes it difficult to pursue the analogy further.

In the case of the single solvent process the above analogies are sufficient to make apparent the operation of processes analogous to familiar distillation processes.

Auxiliary Equipment

In discussing the parts from which a countercurrent process may be built, we have so far considered only the contact section and a feed or withdrawal unit. Certain other pieces of equipment are sufficiently standardized as parts of countercurrent processes to be worthy of discussion. We shall particularly consider distillation apparatus and also indicate analogous solvent extraction equipment.

Total Vaporizer. In the total vaporizer diagrammatically represented in Figure 6*a*, a number of possible conditions are illustrated. Stream A at its boiling point may be completely vaporized to stream B at its boiling point as shown at the right of Figure 6*b*. The difference point represents pure heat and is therefore located at an infinite distance. In a second case represented by $A'B'$ in the diagram, the A stream at its boiling point is vaporized and superheated. In a third case represented by $A''B''$ a liquid stream below its boiling point is vaporized at its boiling point. In a fourth case represented by $A'''B'''$ a liquid stream below its boiling point is vaporized and superheated. In the fifth case represented by $A^{IV}B^{IV}$ the A stream consisting of a mixture of liquid and vapor (which may or may not be in equilibrium), for example, a foam, is vaporized and superheated. In every case the D point is at an infinite distance on the line joining the liquid and vapor stream points.

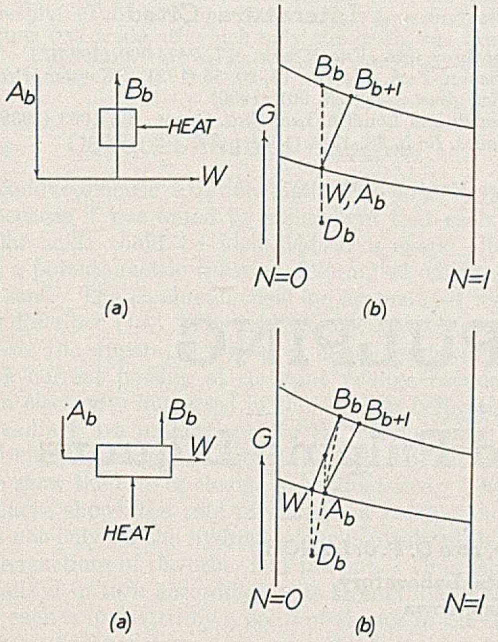
Analogously, solvent is added to A phase to convert it completely to B phase with the same solvent-free composition, but greater solvent content, etc.

Total Condenser. In a total condenser the process is exactly reversed. B phase flows in, heat (or solvent) is removed, and A phase of the same (solvent-free) composition but lower heat content leaves the condenser. Figure 6 serves as well for total condensation when we observe that the direction of flow is reversed. The points BA will represent the diagram for saturated vapor phase being completely condensed to a liquid at its boiling point; $B'A'$ represents superheated vapor being condensed to the liquid at its boiling point; $B''A''$ represents saturated vapor being condensed and cooled below its boiling point; $B'''A'''$ represents superheated vapor being condensed and cooled below its boiling point. Corresponding to $A^{IV}B^{IV}$ we may draw a diagram representing the condensation of a foam to liquid below its boiling point. We must emphasize that heat is easily added or removed in a distillation process and that if we are to select a suitable solvent for an extraction process corresponding to the diagram of Figure 6, we must choose a solvent which may be readily removed from a mixture.

Partial Condenser. A vapor stream (B_1) is partially condensed with the removal of heat. The leaving stream consists in part of liquid, A_2, and in part of vapor, B_2. The sum point, $A_2 + B_2$, differs from the incoming vapor, B_1 only in total heat content. Hence it lies directly below the vapor point B_1 in the diagram. The two leaving phases are determined by a contact condition (e. g., are in equilibrium or at some definite distance from equilibrium) and hence lie at the ends of a contact tie line passing through the sum point (Figure 7). The relative amounts of liquid and vapor stream are represented by the relative distances to the sum point. Modifications to represent superheated vapor or foaming B streams are similar to those used in Figure 6.

Partial Vaporizer. In a partial vaporizer the liquid stream entering is partially vaporized by addition of heat and removed as a liquid and a vapor stream. The treatment is seen from Figure 8 to be similar to that of the partial condenser (but inverted).

BOTTOM EQUIPMENT OF A COLUMN. *Total Vaporization.* The liquid stream, A_b, removed from the bottom of the column is split into two streams, B_b and W. Stream B_b is totally vaporized and returned to the bottom of the column. Hence W stream differs from A_b only in number of moles. Phase points A_b and W hence coincide. Stream B_b differs only in being totally vaporized and hence lies directly above A_b. The difference between A_b and B_b (represented by D_b in Figure 9) is the net flow out of the bottom of the column.



FIGURES 9 AND 10. FLOW (*a*) AND DESIGN (*b*) DIAGRAMS FOR SPLITTER UNIT COMBINATIONS

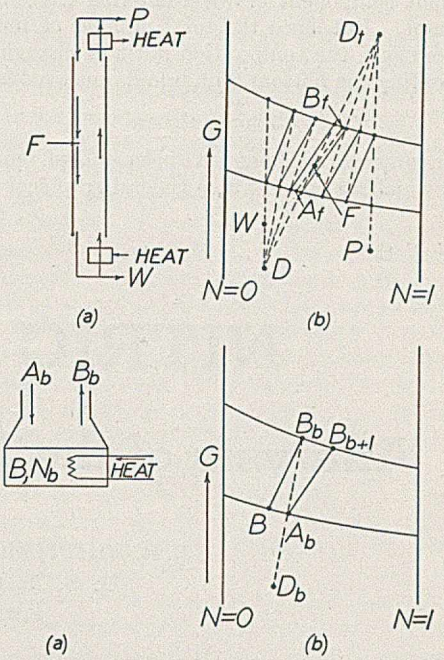
Figure 9 (*above*). Splitter unit with total vaporizer unit
Figure 10 (*below*). Splitter unit with partial vaporizer unit

It must lie on the line joining B_b with A_b and hence vertically below A_b. It differs from W only in the amount of heat added to the vapor phase in the vaporizer. Stream A_b comes from contact with the vapor stream (B_{b+1}) rising from the bottom plate, and hence B_{b+1} is determined by a contact condition. The construction continues into the column section as previously discussed.

Partial Vaporization. The liquid stream from the column is partially vaporized, the vapor is returned to the column, and the liquid is withdrawn as product. Streams A_b, B_b, and W obviously replace streams A_1, B_2, and A_2, respectively, of Figure 8. We need only to add that point A_b (as in the section on "Total Vaporization") fixes B_{b+1} by a contact condition, and that since W can differ from the net flow of material out of the column only by the heat added in the vaporizer, point D_b must lie below point W in the diagram. From Figure 10 the extension of the construction is obvious.

Center Feed Column

The pieces of equipment so far discussed are those from which an ordinary continuous rectification column with center feed may be constructed. Likewise the molal heat content–mole fraction diagram for the center feed column may be constructed from the diagrams representing the individual pieces of equipment (Figure 11).



FIGURES 11 AND 12. FLOW (*a*) AND DESIGN (*b*) DIAGRAMS

Figure 11 (*above*). Center feed column unit
Figure 12 (*below*). Batch tank unit with equilibrium vaporization

If the column is provided with splitter and total vaporizer units as bottom equipment, the graphical construction will start with the diagram of Figure 9. The net flow of material out of the bottom of the column section is represented by point D_b of Figure 9, which represents the difference between the liquid leaving the bottom of the column (which is fed to the vaporizer) and the vapor received by the column from the vaporizer.

From this D point we may start the stepwise construction which represents the section of the column below the feed point. The introduction of feed causes a change in net downflow at the feed level. Graphically the position of the D point representing net flow in the top section is obtained from that representing net flow in the bottom section by the construction given in Figure 8 of the previous paper (*3*). Figure 11 shows a case in which the feed consists of about one-third vapor and two-thirds liquid in mole units.

When we have drawn in sufficient steps in the bottom section to locate the position of the vapor which leaves the feed plate, we then enter into the top or enriching section, with the net flow now D_t rather than D_b. We continue with a construction for a simple column section with D_t as the common D point.

Finally, if the column is equipped with a total condenser we must finish off the construction with the typical diagram of a total condenser.

If the column were supplied with partial, rather than total, vaporization and condensation, we would substitute the diagram of Figures 7 and 10 for those of Figure 9 as end units of the complete rectification diagram. Additional feeds or withdrawals may be represented by incorporating further D points located by the feed or withdrawal construction of the previous paper.

BATCH TANK. *Equilibrium Vaporization.* Liquid is vaporized directly from the contents of a large tank and fed to the bottom of the column section, from which the liquid stream is fed into the tank.

Hence point B_b, representing the vapor, is determined by a contact condition with the tank contents (point B), as shown in Figure 12. The liquid stream is determined by the nature of the column action and the feed conditions. Point A_b is fixed by a contact condition with the vapor rising from the bottom plate (point B_{b+1}); point B_{b+1} is fixed by the remaining graphical construction.

If the total number of moles, B, in the tank remains constant, it is necessary that the column be operating at total reflux. Otherwise the net flow represented by D_b would have to be supplied by a gain or loss of material from the tank. When such a column operates, there is a net loss of light component from the bottom tank equal to the difference in content of light component between entering (A_b) and leaving (B_b) streams. But since the total number of moles in the tank is constant, the composition must be changing. Point B, representing the bottom tank liquid, must move.

Conclusions

The fundamental methods have been studied, more or less in detail, by which we may set up a general graphical analysis of any countercurrent process. This may be done by the use of a molal heat content–mole fraction diagram in the case of distillations; analogous diagrams have been indicated for other processes. Under certain simple conditions the design method reduces to various standard methods. Finally, a set of unit graphical constructions has been developed for use in further work, and the way in which they may be used in design problems has been illustrated.

Acknowledgment

Clerical assistance by the Works Progress Administration is gratefully acknowledged.

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NITRIC ACID PULPING

Analysis of the Used-Acid Pulping Liquors

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THIS paper is the first of a projected series of studies on the use of nitric acid as a pulping agent for the production of alpha-cellulose, particularly from fibrous farm wastes such as bagasse, cornstalks, and straw.

Although the use of nitric acid as a pulping agent is not new, a process having been patented by Barré and Blondel (*2*) in 1861, it is only in recent years that the price of anhydrous ammonia and hence nitric acid has been low enough to make its use commercially possible. In 1932 Lynch and Goss (*17*) found that a nitric acid concentration of only 5 per cent at room temperature produced good cellulose pulp from bagasse. Furthermore, the acid liquors could be re-used many times. Considerable interest has been manifested in this process. Patents were granted to Foster (*9*) and to Hoche (*13, 14*) on the use of nitric acid for pulping bagasse. Hachihama, Onishi, and Takemura (*11, 12*) and Payne (*21*) did further work on the pulping of bagasse with nitric acid. Aronovsky and Lynch (*1*) compared the action of alcoholic and aqueous solutions of nitric acid on bagasse. During 1934 and 1935 the United States Department of Agriculture accepted the offer of private interests in Hawaii to coöperate on an investigation of the merits of the process on a pilot-plant scale. In this work (*16*) it was found that a preliminary wetting, using 0.05 per cent soda followed by a digestion with 2.0 to 2.5 per cent nitric acid at 90° C. (194° F.) and then a 2 per cent soda cook, gave good pulp from bagasse. The recovered pulping acids could be re-used many times and a better quality of pulp obtained, as was noted by other workers (*4, 5, 8*). Re-use of the acid is necessary also for economic reasons.

The object of the present investigation was to develop a rapid analytical procedure to be used to study the change in composition of the re-used liquors from successive cooks to serve as a guide in commercial procedure. It was found that the liquors, although fortified to the original normality (using the conductometric end points) with fresh nitric acid, contained progressively lower percentages of nitric acid, the remainder of the acid content being made up of a mixture of organic acids. Since the chemical analysis of these liquors is both difficult and tedious, the conductometric apparatus developed in this laboratory and recently described as applied to alkaline liquors (*18*) was used to determine quickly and simply the approximate percentages of the principal constituents of the acid solutions. The principal acids present were found to be nitric, oxalic, formic, and acetic.

Experimental Pulping Procedure

The pulping procedure consists of a mild alkaline steep, a treatment with hot nitric acid, a digestion with caustic soda, and finally a bleach to produce high alpha-cellulose pulp:

Air-dry bagasse which passed through 4-mesh screen and was retained on 12-mesh screen was used. This material (1.5 pounds moisture-free basis) was steeped for 2 hours in 3.5 gallons of 0.05 per cent sodium hydroxide solution at boiling temperature. In each step a 5-gallon 18–8 stainless-steel pot was used, and the mixture was slowly and continuously agitated by a long stainless-steel propeller-type stirrer. The volume was held constant by the addition of water. The pulp was washed thoroughly and pressed to remove excess water. The pulp (yield, 1.46 pounds moisture-free basis, 97.3 per cent on original) was then treated with 3 gallons of 2.1 per cent nitric acid solution, allowance being made for dilution by the water in the pulp. The mixture was held at 90° to 95° C. (194° to 203° F.) for 2 hours. The pulp was filtered and thoroughly washed with gallon portions of hot water. Samples of the drain and of the first three washes were taken. The drain and washes were then combined and evaporated to approximately 2.5 gallons to be fortified with nitric acid and used in the succeeding digestion. The pulp (yield, 1.13 pounds moisture-free basis, 75.3 per cent on original) was boiled with 2.5 gallons of 2 per cent sodium hydroxide for one hour. This alkali-treated pulp (yield, 0.75 pound moisture-free basis, 50.0 per cent on original) was then thoroughly washed and saved for later studies.

A series of seven digestions was made. Samples of the initial acid, drain, mixed drain and washes, and concentrated liquor of each digestion were analyzed conductometrically (Figure 5). Samples of the drained acid from the first and seventh digestions were analyzed chemically and compared with the conductometric results (Table IV and Figure 5). A second series of twelve runs was made, of which only the drain was saved and fortified. Data from this series are also presented (Figures 6 and 7).

Conductometric Analysis

The conductometric titration method of analysis was selected because it was found by experiment that each of the individual acids could be identified in a single titration, whereas a potentiometric titration determined only the total acid present. The conductometric apparatus used was that recently described (*18*). The acids are titrated with standard alkali, and the apparatus measures in milliamperes the alternating current passing at constant voltage between two platinum electrodes immersed in the solution being titrated. These readings are proportional to the conductance of the ions and are plotted against cubic centimeters of the titrating agent to show the rate of change in conductance. The slope of the curve shows the rate of change in conductance and depends not only on the hydrogen ions neutralized, but also upon the reactions of the other ions present. Thus each acid is neutralized in turn according to its strength, and the end point of each is indicated by a point of change in the slope of the curve. An exception, of course, is when side reactions such as precipitation interfere with the usual course of reaction. For example, in the titration of mixed acids such as oxalic and acetic, advantage is taken of the insolubility of calcium oxalate to titrate both the first and second hydrogens simultaneously, the second hydrogen of oxalic acid thus being titrated before the stronger acetic. Each acid alone produces a characteristic curve. In a mixture, secondary effects change the curve, but the result is a composite picture in which the portion corresponding to each acid is readily discernible.

Accordingly a sample approximately equivalent to 1.5 cc. of normal acid contained in 200 cc. of water was titrated, using 0.05 *N* calcium hydroxide. A solution of 1.2 grams of glucose was added, for it was found that such addition gave sharper breaks in the titration curve of the organic acids. Hydrogen-ion concentration changes were observed with a pH meter using a glass electrode.

Chemical Analysis of Liquors

TOTAL ACID was determined by potentiometric titration of the acid liquors.

OXALIC ACID was identified by precipitation as the calcium salt from neutral solution, regeneration, and preparation of the oxalyl toluidide. It was determined by the usual precipitation as the calcium salt, first from a solution slightly acid with acetic acid, then from a slightly ammoniacal solution, and finally from an acetic acid solution. The calcium oxalate was washed with a little hot water after each precipitation. This procedure was necessary in order to rid the precipitate of the yellow color due to the presence of the calcium salt of 3-nitro-4-hydroxybenzoic acid (*10*). The resulting calcium oxalate was then titrated with standard potassium permanganate solution.

NITRIC ACID. The titration of the nitric acid to a definite pH is difficult in the presence of oxalic acid, because of the strength of the first hydrogen of the oxalic acid. The titration (with the addition of the theoretical amount of acid to form potassium and manganese sulfate), after destroying the oxalic acid by potassium permanganate, was not successful because of the strong buffering action of the manganese sulfate.

Precipitation of the nitric acid with nitron was adopted. The method recommended by Cope and Barab (*6*) was used. Since the presence of oxalic acid tends to give high results, the oxalic and 3-nitro-4-hydroxybenzoic acids of a 100-cc. sample were removed by precipitation with barium hydroxide, the excess barium being precipitated with sulfuric acid. The solution was then made alkaline and concentrated to about 40 cc. A brown ligneous precipitate was filtered off, and the resulting liquor was made up to 90 cc. and neutralized with sulfuric acid. An excess of 12 to 15 drops of sulfuric acid (2:3) was added and the solution heated to boiling. Ten cubic centimeters of a 10 per cent solution of nitron in 5 per cent acetic acid was then added. After standing 2 hours in ice water, the precipitate was transferred to a Gooch crucible, washed with 10 cc. of ice water, dried 1.5 hours at 105° C., and weighed. Although the needlelike crystals were darker in color, their structure appeared to be identical with that of the pure nitric acid salt. The results were corrected for the ammonium nitrate present in the liquor. It was found, as shown later, that the amount of picric acid present was too small to cause a serious error.

FORMIC ACID. Donath and Bräunlich (*7*) observed the odor of this acid in a mixture of propionic, butyric, and caproic acids obtained by the action of 7 per cent nitric acid on brown fossil coal. The formic acid was identified by reduction with magnesium ribbon, and the presence of formaldehyde shown by the milk and ferric chloride method (*26*). A sample of the cook liquor showed no formaldehyde in a blank determination. The formic acid was determined quantitatively, by means of the Weihe and Jacobs (*27*) method and apparatus (oxidation to carbon dioxide by mercuric acetate and absorption by repeated passing of the vapors through barium hydroxide solution). The complete distillation of a mixture of pure dilute nitric and formic acids at 60 mm. with absorption of the vapors in barium hydroxide solution resulted in the loss of half of the formic acid, probably by oxidation, indicating that this method is unsuited for the separation of formic acid from the other constituents of the liquor. However, the determination of formic acid in a mixture of nitric, oxalic, acetic, and formic acids by the Weihe and Jacobs method gave results which agreed to two parts in a thousand. It has been shown (*27*) that only 0.08 per cent of the oxalic acid present forms carbon dioxide. Therefore, formic acid determinations were run by this method on 50-cc. portions of the acid liquors.

ACETIC ACID. The acetic (and formic) acid content was obtained by distillation, after removal of the nitric acid by reduction to ammonia, and the total acid corrected for formic to obtain acetic acid content. The nitric acid (and other nitrates) in a 100-cc. sample were quantitatively reduced to ammonia by aluminum and sodium hydroxide according to the method of Bartow and Rogers (*3*). This liquid was transferred quantitatively to a distilling flask, an excess of 15 cc. of phosphoric acid was added, and the solution was distilled. Exactly 500 cc. of distillate were collected in 25-cc. portions, each portion being replaced by the addition of 25 cc. of water. An aliquot of this distillate was titrated for total acid, using phenolphthalein as an indicator, and the formic acid content in another aliquot was determined by the

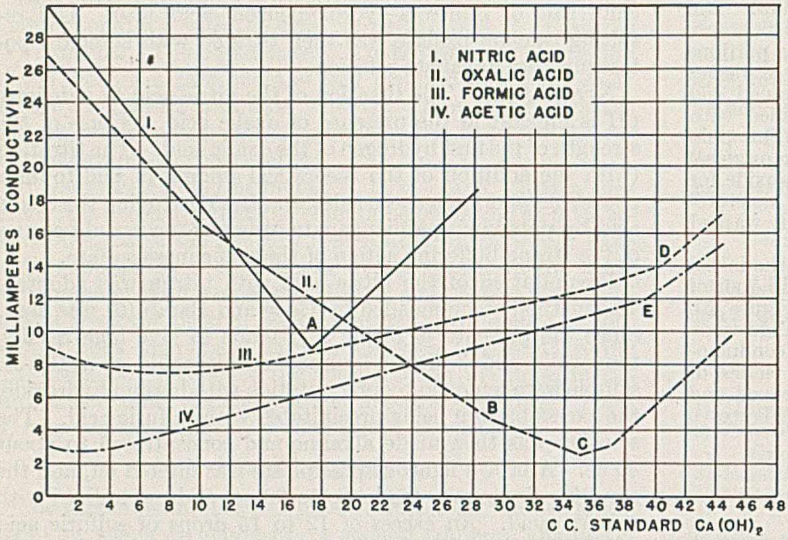

FIGURE 1. CONDUCTOMETRIC TITRATION OF NITRIC, OXALIC, FORMIC, AND ACETIC ACIDS

Readings were taken at 0.25-cc. intervals; samples titrated were not of equivalent normality (Table I).

Weihe and Jacobs method (*27*). The difference between these two determinations gave acetic acid. The formic acid content, as might be expected (*20*), was always lower than that of the original solution. A large amount of furfural due to the pentosan content of the nitric acid liquors came over in the distillate. This has been shown to make little difference in the formic acid determination (*27*).

AMMONIA AND AMINES. During the conductometric titration a flat portion of the curve was noticed just after the neutral point, as indicated by the pH meter, showing the presence of a substance which reacts with calcium hydroxide to produce a compound of very low conductance. After a considerable number of tests it was found that an ammonium salt produced a similar curve in a synthetic mixture (Figure 2). When the nitric acid liquor was made alkaline, a strong ammoniacal fishlike odor was evolved. A sample of the liquor from the twelfth run was made alkaline and distilled into acid solution. The distillate contained 0.6 gram of ammonia and amine, calculated as ammonia, per 100 cc. of solution. The carbylamine test for primary amines gave positive results when applied to the concentrated distillate. Rimini's test (*19, 23*), however, gave only a faint coloration when compared with a solution of equal basicity prepared from pure methylamine. On the basis of these color tests, it appeared that probably not more than one-fifth of the total was methylamine and the remainder ammonia.

No nitrous acid was found by Lynch and Goss (*17*) in the nitric acid liquors. On the basis of the above test for primary amine, it is probable that nitrous acid is diazotized as rapidly as it is formed.

REDUCING SUBSTANCES, aldehydes, and other reducing materials were determined by the Shaffer and Hartmann method (*25*) and calculated as xylose. The following results were obtained on the series of twelve runs in grams per 100 cc.: 0.87, 1.53, 2.10, 2.60, 2.66, 2.83, 3.10, 3.33, 3.53, 3.47, 3.90, 3.93. These results are plotted in Figure 5. Thus, in the twelfth run an amount of reducing material accumulated equivalent to nearly 75 per cent of the weight of the charge being pulped.

TOTAL SOLIDS. No determination of total solids was made because the sugars were oxidized by the nitrates present even when the acids were neutralized and evaporation carried out at 60° C. in a vacuum oven.

MISCELLANEOUS SUBSTANCES. The presence of 3-nitro-4-hydroxybenzoic acid, 3-5-dinitro-4-hydroxybenzaldehyde, and 3-nitro-4-hydroxybenzaldehyde was reported by Hachihama and Onishi (*10*) who obtained them by extracting the used nitric acid liquors with ether. The 3-nitro-4-hydroxybenzaldehyde had been obtained independently in this laboratory by the following procedure: The nitric acid liquors were made alkaline, concentrated, acidified with sulfuric acid, and steam-distilled. The aldehyde in the distillate solidified on cooling. Using the continuous ether extraction method, 0.27 gram of crystalline aldehyde was obtained from one liter of acid: melting point, 137° to 140° C. (reported 139° to 144.5°); oxime melting point, 169° to 170° C. (reported 169°).

Hydrocyanic acid to the extent of 0.23 to 0.27 per cent on the basis of dry bagasse was evolved during the acid treatment according to Hachihama, Onishi, and Takemura (*12*). These figures are in agreement with the results obtained in this laboratory. One titration with cuprammonium solution (*24*) gave approximately 0.3 per cent hydrogen cyanide based on the dry weight of the bagasse. No hydrocyanic acid was found in the cold liquors.

The presence of picric acid was reported by Payne, Fukunaga, and Kojima (*22*). The extract from 100 grams of acid-treated pulp gave a slight color test with potassium cyanide solution (*19A*), and conductometric titration showed a strong acid present to the extent of 0.94 cc. of normal acid (equivalent to 0.23 gram picric acid per 100 grams bagasse). The extract obtained by continuous ether extraction of 100 cc. of the acid liquor gave no color with potassium cyanide, indicating the absence of picric acid in the liquor.

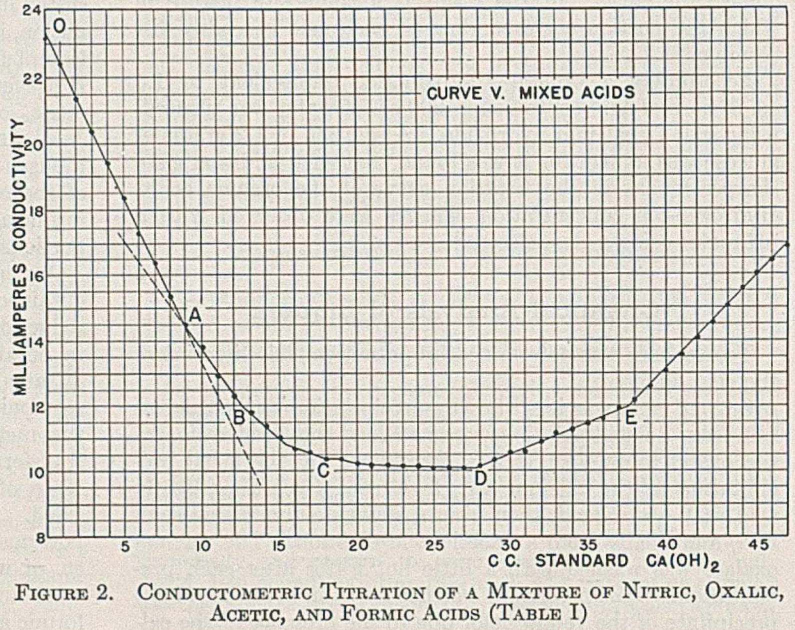

FIGURE 2. CONDUCTOMETRIC TITRATION OF A MIXTURE OF NITRIC, OXALIC, ACETIC, AND FORMIC ACIDS (TABLE I)

Results of Conductometric Analyses

Preliminary conductometric analyses of used acid pulping liquors showed a series of changes in slope when conductance was plotted against cubic centimeters of the titrating agent (0.05 *N* calcium hydroxide solution). In an endeavor to reproduce such curves from the acids known to be present and the position of each acid in that curve, the pure acids were titrated individually and in a combination of known proportions.

Figure 1 shows typical conductometric curves for nitric, oxalic, formic, and acetic acids. The nitric acid shows the characteristic steep straight-line slope of a strong acid. The portion of this curve beyond *A* denotes excess calcium hydroxide. The oxalic acid shows a slope descending through *B* to the end point, *C*. Calcium hydroxide was selected as a titrating agent because it precipitates oxalic acid and thus eliminates the ascending slope characteristic of a weak acid, such as the monobasic salt of oxalic acid. Point *B* is not a dependable mid-point since it varies with the pH change, dilution, and supersaturation. Generally, a slight drop in pH occurs at the calcium oxalate precipitation point which varies between 3.5 and 4.0 pH. The formic acid shows a pronounced curve grading into the straight ascending curve mentioned above, ending at the neutralization point *D*. The acetic acid curve is a short curve grading into a slightly steeper slope to *E*, corresponding to the slightly greater conductance of calcium acetate over that of acetic acid as compared to that of calcium formate over formic acid.

These end points correspond exactly to those obtained by simultaneous determinations of potentiometric and indicator end points.

Figure 2 shows the titration curve of the four combined acids. The ionization constants of these acids indicate that in a mixture they should titrate in the following order:

HNO_3	8.2×10^{-1}
$(COOH)_2{}^{++}$	3.8×10^{-2}
$HCOOH$	2.14×10^{-4}
$H(COO)_2{}^{+}$	4.9×10^{-5}
CH_3COOH	1.86×10^{-5}

According to this, oxalic acid would appear at two places on the titration curve. However, since it is quantitatively precipitated as calcium oxalate at a pH of 4 (*15*) it is completely removed before the succeeding organic acids are titrated and appears at only one place on the curve.

In curve V (Figure 2) a typical titration curve of the four combined acids has been plotted using the experimental data given in Table I. Readings may be taken at smaller intervals, but, in general, at these concentrations enough points to define a line are obtained by reading at 1-cc. intervals. The curve shows a series of slopes to the neutralization point, *E*. The experimental points thus obtained for each acid agree very well with the calculated end points (Table II), the maximum deviation from the theoretical being 0.15 cc. or 1.7 per cent error. This curve is typical of those obtained on mixtures of pure acids.

In Figure 2 the first steep slope of line *O-A* represents nitric acid. The angle at point *A* is not readily discernible on casual observation, but by laying a straight edge on both lines *O-A* and *A-B* and extending them (indicated by dotted lines) the break point is readily apparent. Plotting the points given on a larger scale makes it easily seen. The change in slope, while small, is very definite. Furthermore, an error of location along line *O-A* of any given distance is greatly minimized on the abscissas because of the slope of the line.

Point *B* of curve V corresponds to *B* of curve II (Figure 1), and *C* is the end point between oxalic acid and formic acid. The portion of the curve between *C* and *E* shows the slopes of weak acids, and a break is evident at *D*, indicating the end point between formic and acetic acids.

Table I. Typical Conductometric Titration Data as Shown in Figure 2

Cc. of 0.05 *N* $Ca(OH)_2$	Ma.[a] × 10	Cc. of 0.05 *N* $Ca(OH)_2$	Ma.[a] × 10	Cc. of 0.05 *N* $Ca(OH)_2$	Ma.[a] × 10	Cc. of 0.05 *N* $Ca(OH)_2$	Ma.[a] × 10
0	232	13	118+	25	101	37	119
1	224	14	114	26	101	38	122
2	214	15	110	27	101	39	126+
3	204	16	107	28	101+	40	131
4	194	17	105+	29	103+	41	136
5	184	18	104	30	105+	42	141
6	173+	19	104	31	106	43	145+
7	164	20	102+	32	109	44	150+
8	154+	21	102	33	110+	45	155+
9	145	22	102	34	113	46	160
10	138	23	101+	35	114+	47	164+
11	129+	24	101+	36	116	48	169
12	123+						

[a] Ma. × 10 equals milliamperes in units of 0.1 Ma.; + indicates approximately 0.05 Ma.

Table II. Conductometric Analysis of Mixed Pure Acids as Shown in Figure 2

	Cc. of 0.05 *N* $Ca(OH)_2$ Used					
	End Point		Cc. present		Difference	
Acids in Mixture	Calcd.	Obsvd.	Added	Found	Cc.	Per Cent
Nitric (*O-A*)	8.90	8.9	8.9	8.9	0.0	0.0
Oxalic (*A-C*)	17.75	17.9	8.85	9.0	+0.15	+1.7
Formic (*C-D*)	27.70	27.7	9.95	9.8	−0.15	−1.5
Acetic (*D-E*)	37.50	37.6	9.80	9.9	+0.10	+1.0
Total (*O-E*)	37.50	37.6	37.50	37.6	+0.10	+0.27

Experience with the apparatus and repetition of the procedure with identical results increases the operator's accuracy and his confidence in the reproducibility of the curve. On the apparatus used, readings could be made to closer than 0.1 milliampere, and the graphs are readily reproducible with approximately the accuracy shown in Table II. While single readings may be in error, the error is readily noted in the series of points representing a component. As is evident from the above work and Table II, the method is satisfactory when applied to a mixture of these four pure acids.

Curves I, II, and III of Figure 3 give the results by the application of the method to pulping acids which have been used, respectively, one, seven, and twelve times. Curve IV for a synthetic mixture of pure acids corresponds closely to that (III) of the pulping acid re-used twelve times. The flattened portion of the curve of pure mixed acids beyond *E* (the 8.5-pH end point) is produced by the addition of ammonium nitrate, the length of this portion corresponding to its normal equivalence. A similar result is produced by the addition of methylamine to the mixture.

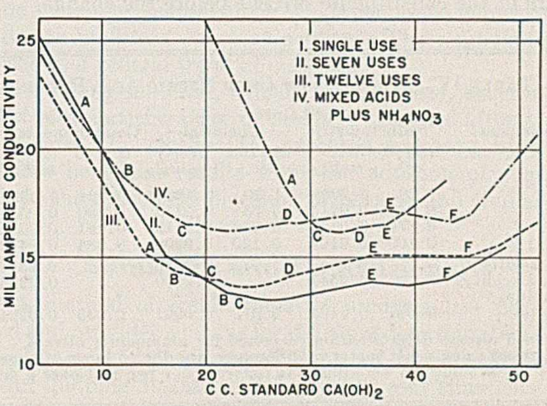

Figure 3. Conductometric Titration of Nitric Pulping Acids Used One, Seven, and Twelve Times, and of Mixed Pure Acids Plus Ammonium Nitrate

Readings were taken at 0.25-cc. intervals (Table III).

Since it has been established that xylose is present in the acid liquors (*10*), its effect on conductometric curves was investigated. Although xylose, glucose, and sucrose exhibited little apparent effect on any one of the individual acids, they intensified the break between oxalic and formic, and that between formic and acetic acids in a mixture of at least three of the acids. Under the conditions used it was found that the addition of 0.6 per cent glucose gave optimum results. There was apparently no titratable reaction between the calcium hydroxide and the sugar.

As an additional confirmation of the conductometric method, each of the four pure acids and ammonium nitrate were added in a known amount to the pulping acid used twelve times. In each case the curve was increased by the amount of calcium hydroxide equivalent to the material added and in the specific portion of the curve that had been assigned to that material. Table III indicates the calculated comparison and shows that both the added material and the same material in the used liquor titrate in chemical equivalents.

TABLE III. EFFECT OF ADDING PURE MATERIALS TO USED PULPING LIQUORS

Material Added	Used-Acid End Point	Equivalent Amount Added	Increased End Point Calcd.	Increased End Point Found	Difference	
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	%
Nitric acid	5.2	13.6	18.8	18.8	0.0	0.0
Oxalic acid	11.5	13.5	25.0	25.0	0.0	0.0
Formic acid	18.0	14.7	32.7	32.4	−0.3	−1.4
Acetic acid	23.3	14.7	38.0	37.4	−0.6	−3.0
Ammonium nitrate	28.3	13.6	41.9	42.6	+0.7	+3.8

The chemical analyses of the first and seventh pulping acids of the series as shown in curves I and II, Figure 3, are compared with conductometric analyses as given in Table IV.

Since each organic acid represents only a small portion of the 5-cc. sample used in the conductometric analysis, the accuracy in the determination of the individual organic acid in this instance is not as high as that of a chemical analysis in which the individual organic acid is determined independently. This discrepancy could be corrected to a considerable extent by modifying the conditions of the conductometric titration to amplify portions of the curve. The rapidity and simplicity of the conductometric titration, together with its approximate agreement with chemical analysis just demonstrated, recommends this method for plant control. Since the pulping solutions change slightly on standing, the rapidity is of a special advantage in obtaining a true picture of the constituents present before the change.

TABLE IV. ANALYSIS OF USED NITRIC ACID PULPING SOLUTIONS

Constituent	Used Once: Conductometric G./100 cc.	Used Once: Conductometric Normality	Used Once: Chemical G./100 cc.	Used Once: Chemical Normality	Used Seven Times: Conductometric G./100 cc.	Used Seven Times: Conductometric Normality	Used Seven Times: Chemical G./100 cc.	Used Seven Times: Chemical Normality
Nitric	1.26	0.200[a]	1.20	0.1903[a]	0.624	0.0991	0.664[a]	0.1053[a]
Oxalic	0.096	0.0215	0.051	0.0113	0.230	0.0511	0.171	0.0380
Formic	0.076	0.0165	0.052	0.0112	0.161	0.0351	0.084	0.0183
Acetic	0.100	0.0167	0.120	0.0200	0.284	0.0473	0.287	0.0479
Calcd. acidity	...	0.2547	...	0.2328	...	0.2326	...	0.2095
Titrated acidity[b]	...	0.2547	...	0.2600	...	0.2326	...	0.2250
Ammonium nitrate	0.081	0.0101	0.073	0.0091	0.235	0.0294	0.226	0.0282

[a] Nitron nitrate determination corrected for ammonium nitrate.

[b] Titrated using a pH meter. Differences are due to lapse of time between determinations. These solutions were found to decrease 6–7 per cent over a period of 3 months.

The chemical analysis shows less total acid, especially in the pulping acid used seven times, owing partially to inherent errors in the methods of analysis and in part to loss in acidity during the period of the investigation. The latter loss was about one-third of the difference. The conductometric analysis, on the other hand, tends to give high results because of the presence of small amounts of organic acids other than the three principal ones. The slight differences in slope between the curves of some of the acids enhance the difficulty of determining the exact intersection. The application of the conductometric method of analysis to this study was considered satisfactory, and an examination was made of the changes in composition of the pulping acid during the two types of digestion previously mentioned.

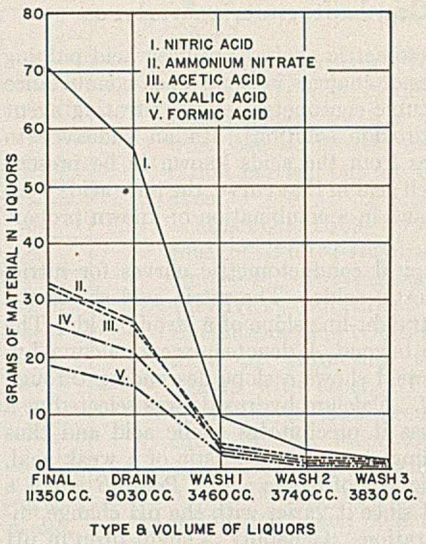

FIGURE 4. DISTRIBUTION OF CONSTITUENTS IN FINAL, DRAIN, AND WASH LIQUORS

A typical wash curve is shown in Figure 4. The relative proportions of the constituents, except for ammonium nitrate, remain approximately the same in each succeeding wash as in the drain. This would be expected from their solubilities and the affinity of acids for cellulose.

The recovery of the pulping acid depends upon the method and efficiency of removal of the drain and washes from the pulp as well as upon the volumes of the washes used. Under the conditions indicated in Figure 4, 79 per cent of the acid content was recovered in the drain, 13 per cent in the first wash, 5 per cent in the second wash, 2 per cent in the third wash, with a final loss of 1 per cent. An examination of Figure 5, however, indicates that the procedure originally adopted of evaporating the combined drain and three washes may be impractical because in nearly every case the loss in nitric acid during concentration exceeds the gain due to wash recovery. An investigation was made to determine the source of loss, and it was found experimentally that acid equivalent to 7.5 per cent of the total acid came over in the distillate from the pulping liquor. Only a small fraction of this is nitric acid, since a loss of only 0.1 per cent was found when pure dilute nitric acid solutions were concentrated. The organic acid content of the concentrates decreases slightly although the loss is less than 7.5 per cent of the total acidity. The nitric acid, therefore, is probably lost in oxidizing the organic matter present in solution, being partially used to produce the volatile acids found in the distillate.

Figure 5 shows that there is a comparatively uniform addition of about 13.5 grams of nitric acid per 100 grams of bagasse treated and a consumption (due to reaction, concentration, and washing loss) of about 15.6 grams of nitric acid. The total acidity of the cooking liquor is held constant and, therefore, the nitric acid content decreases due to the accumulation of organic acids which contribute to the total acidity. This explains why the nitric acid consumption is greater than the acid added. A further source of loss is due to the formation of ammonia, present as ammonium nitrate, which accounts for about 3.5 per cent of the acid consumed. After seven runs the ammonium nitrate represents 33 per

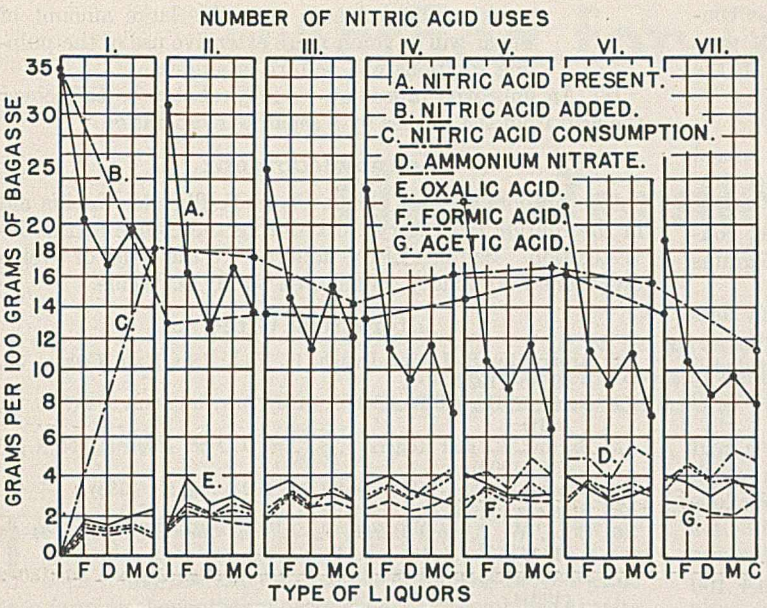

FIGURE 5. DATA ON SEVEN USES OF NITRIC ACID

I = initial pulping liquor
F = final pulping liquor
D = drain liquor
M = mixed drain and first three washes
C = concentrated drain and washes

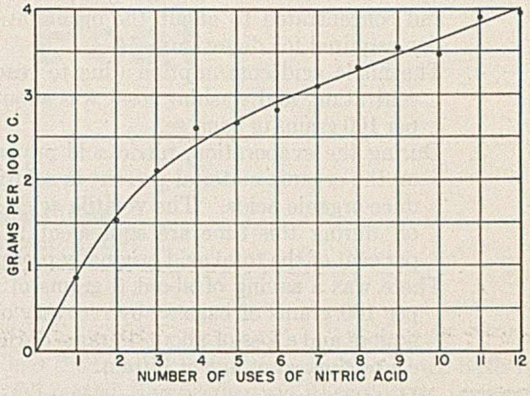

FIGURE 7. REDUCING SUBSTANCES INCREASE, CALCULATED AS XYLOSE, WITH RE-USE OF NITRIC ACID

cent of the total nitrate ion present in the concentrate or 17 per cent of the nitrate ion in the succeeding cook. That this nitrate ion may be available for oxidative purposes is indicated by the fact that after four cooks it consistently decreased during the concentration. Apparently the organic acid content reaches a practical equilibrium after the fourth cook.

Use of Acid Pulping Liquor Twelve Times

After a consideration of the above data, a series of runs was made using the nitric acid twelve times (Figure 6). To simplify the procedure the drain alone was recovered, fortified, and used in each succeeding cook. The objects of this series of cooks were: (*a*) to determine whether less nitric acid would be consumed if the drains and washes were not concentrated, (*b*) to confirm the results of the first series, and (*c*) to determine the equilibrium condition resulting from a larger number of cooks.

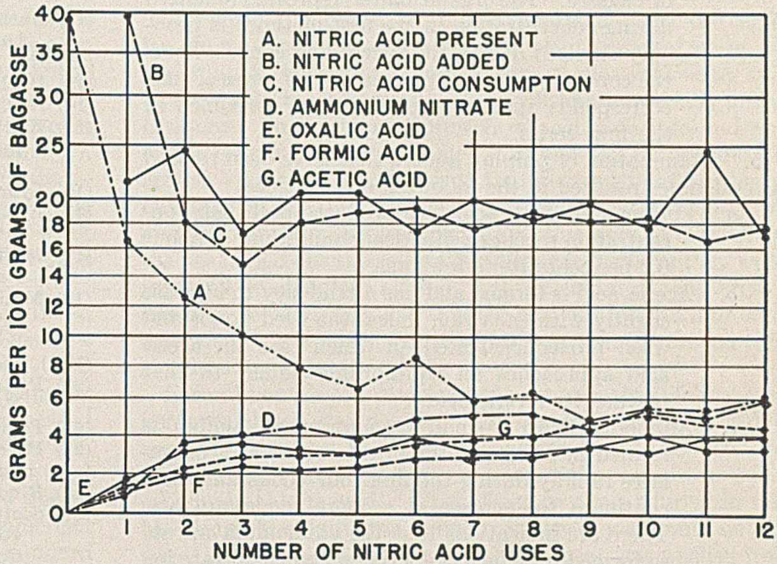

FIGURE 6. DATA ON TWELVE USES OF NITRIC ACID

The average addition of nitric acid was found to be 20 grams per 100 grams of bagasse and the consumption to be 20 grams as compared to 13.5 and 15.6 grams, respectively, when the washes were saved. By calculations based on the volume of drain lost, it was found that about 20 per cent was lost by not saving the washes, which agreed with the loss found in the first series of runs as shown by the wash study in Figure 4. The consumption of nitric acid based on the reacting acid was therefore about 15.5 grams per 100 grams of bagasse or approximately the same as that in the first series of runs. It becomes evident then that the organic matter present in the drains is slowly oxidized whether during the concentration or during the succeeding run. The loss of more than the amount of nitric acid saved in the washes as shown in Figure 5 is, then, unavoidable. A better procedure would probably be to recover the wash acid by a separate evaporation.

In this series of runs the acetic acid continued to increase during the last five runs while the formic and oxalic acids increased more slowly. This increase is due to the fact that there was no evaporation. Since there is an increase in the organic acids, the residual nitric acid is decreased in proportion in order to maintain constant acidity. The ammonium nitrate shows a general trend of increase.

The reducing material, calculated as xylose, accumulates rapidly to a concentration of nearly 4 per cent after twelve runs (Figure 7). Hoche (*14*) patented a process by which he claims beneficial results from the addition of sugar or starch to the nitric acid digestion of bagasse and similar material.

Summary and Conclusions

1. A method of conductometric analysis has been described and provides a means for the rapid determination of the principal acidic and salt constituents of nitric acid liquors used for pulping bagasse. Its rapidity and simplicity recommend it for industrial control work. Its rapidity is especially desirable in the analysis of unstable solutions.
2. Methods of chemical analysis suitable for the determination of the various components of the nitric acid pulping liquor have been selected and described.

3. The conductometric method was checked by the conductometric analysis of pure acids, by the analysis of pure acids added to a pulping acid, and by comparison with the chemical analysis of the pulping acid.

4. Two methods of digestion were studied:

Method I. Drain and wash pulping liquors were mixed and concentrated to about the optimum concentration required for digestion:

- *a.* The nitric acid consumption (due to reaction, concentration, and washing loss) was about 15 grams per 100 grams of bagasse.
- *b.* During the evaporation, nitric acid apparently acts on the organic material present in solution to produce organic acids. The volatile acids that distill off during this time are equivalent to about 7.5 per cent of the total acid originally present.
- *c.* There was a saving of about 3 grams of nitric acid per 100 grams of bagasse by recovery of the wash liquors and a loss of about 4 grams during the concentration, a net loss of 1 gram.

Method II. The drains only were recovered:

- *a.* The nitric acid consumption was 20 grams per 100 grams of bagasse. However, nearly 20 per cent of this is due to washing losses, the consumption due to reaction being about 15.5 grams per 100 grams of bagasse. The organic material present (oxidized during concentration in the first method) is probably oxidized during the succeeding cook. Thus, the consumption of nitric acid in this series of runs corresponds approximately to that consumed in the first series.

5. Examination of pulping liquors that have been re-used several times resulted in the following observations:

- *a.* Formic and oxalic acids are produced and their concentration reaches a practical equilibrium of about 0.2 per cent after a few runs.
- *b.* Acetic acid is formed and has a tendency to increase slightly with each run, unless the used liquor and wash are concentrated, in which case the acetic acid approaches an equilibrium similar to that reached by formic acid.
- *c.* Ammonia (with a small amount of an amine) is formed and fixed as the nitrate salt. It accumulates rapidly during the first four cooks and then continues to increase at a more moderate rate. There are indications that the ammonium nitrate so formed may be a potential source of nitrate ion for oxidation in the presence of increasing quantities of organic acids. Further studies will be made on this phase of the subject.
- *d.* Reducing materials, mainly sugars, increase tremendously, rising to 2.6 per cent after the first three cooks and to nearly 4 per cent in the twelfth cook. The influence that this large amount of sugar will have on more extensive use of the pulping solutions will be further studied.

6. An improved procedure would probably be to recover the acid from the washes by a separate evaporation.

Acknowledgment

The authors wish to thank Clyde Faulkender for his aid in the routine laboratory work during the course of this investigation. Samples of the liquors from the series of twelve digestions were kindly contributed by H. D. Weihe.

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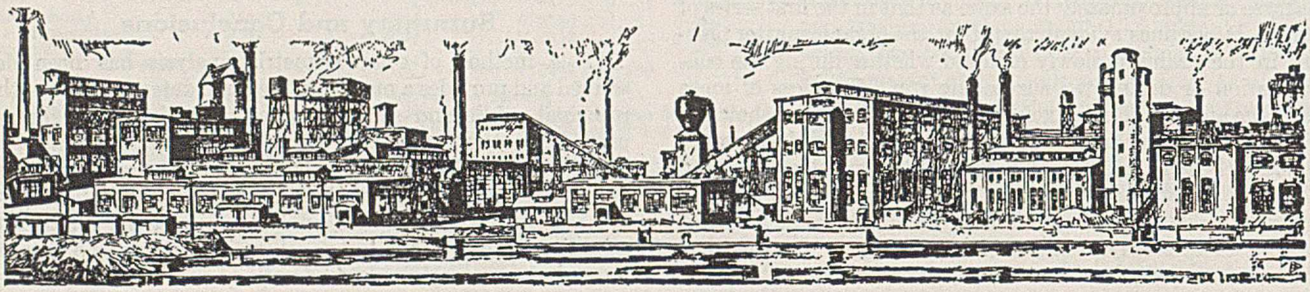

Method for Debasing New Jersey Peat

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IN CONNECTION with the production of the new insecticides nicotine peat and nicotine humate (*2*) it has been found necessary to remove from peat the inorganic base-forming elements that occur chemically combined as salts of the organic acids present. This removal is accomplished by treatment with acids. The base-forming elements (calcium, iron, aluminum, etc.) are largely removed, leaving the uncombined organic acids. Although complete removal is attained only after repeated extractions with acid, it has been established in the preparation of nicotine peat that a single acid treatment does materially increase the nicotine-combining power of those peats high in inorganic base-forming elements and is therefore sufficient for the purpose in hand (*2*).

The process gave no trouble when conducted in the laboratory in numerous trials with various samples of peat. The peat, of about 60-mesh size, was immersed overnight in weak acid, such as 2 per cent hydrochloric acid, and washed on a funnel until free of soluble chlorides.

During the research on these insecticides interest centered chiefly on a commercial New Jersey reed peat. This is a dark, well-decomposed product classified as a muck (*1*). Its pH is 5.1. This specimen, like the various other peats examined, was readily washed free of soluble matter in repeated laboratory tests. The pH of such acid-treated peat is 2.3. A difficulty arose, however, when the process was first tried on a larger scale. For this work a fresh lot of New Jersey peat was purchased. It came from the regular commercial source in 100-pound bags. This product carried a standard moisture content of 65 per cent and felt damp to the touch. A portion of it was immersed overnight in five times its weight of 2 per cent hydrochloric acid. The mixture was strongly acid to litmus. The slurry was transferred to a basket-type centrifuge, which was considered a satisfactory apparatus for industrial washing operations. The expected removal of the liquid and formation of a compact filter cake did not occur. Instead, the basket retained practically all the contents fed to it, both solid and liquid, and because of unequal distribution of the load it soon began to wobble so dangerously that the attempt had to be discontinued.

Two questions immediately arose: Why did this lot of peat behave differently from the earlier material? How could the trouble be remedied?

The questions were answered partly on theoretical grounds and partly from observation of the difference in physical condition of the two lots. The earlier lot came from a supply that had been stored in the open in burlap sacks for a year or more; it was consequently well dried and had, from the feel of it, probably not more than 10 to 15 per cent of moisture, for it was dry enough to crumble in the fingers. The new lot, on the other hand, was decidedly damp to the touch and by actual test had the full 65 per cent moisture on which basis it was sold. Of special significance was the spongy, resilient feel, which indicates a cellular or gelatinous condition. This physical difference, arising from the drying out of the raw peat, pointed at once to the method of achieving the desired filtration characteristics.

Before an experiment was tried, it was conceived that the damp peat, as purchased, retained in large measure the cellular or gel structure of the original plant material or of its degradation products. The cells were swollen with water and packed down to a practically impervious mat, especially under pressure. Furthermore, diffusion of acid both into and out of the cells was necessarily slow. If the cell walls could be broken or the structure altered the process would be one of flushing rather than diffusion and would consequently be more rapid. A possible explanation, therefore, is that when the peat dried out the cell walls collapsed; perhaps they were ruptured or otherwise altered, with an accompanying breakdown of gel structure, and thus the peat was left in a filterable condition. The first lot of peat had apparently reached this condition by natural drying.

Several pounds of the new lot of peat were dried in a chamber over closed steam coils. The material issued very dry and crumbly, and had shrunk considerably. The moisture content was 4 per cent. It was immersed overnight in 2 per cent hydrochloric acid. When the slurry was whirled in the centrifuge, the liquid ran through as speedily as could be desired, and the built-up cake of debased peat was washed free of soluble matter (chloride test) within several minutes. Hence the efficacy of first drying the peat was demonstrated.

A total of 500 pounds of New Jersey peat was subsequently processed in several runs in this way, with the use of commercial equipment such as a vacuum dryer or shelf dryer for drying the peat and a centrifuge for washing out the acid and dissolved bases. No difficulty was encountered.

Just how far the peat must be dried to permit satisfactory filtration is a matter of opinion. A moisture content of 10 per cent was entirely adequate, whereas 21 per cent was found to be too high; that is, filtration was too slow (distinctly slower than with a 10 per cent product).

The information presented here is based upon a study of New Jersey peat. Since different peats vary appreciably in physical properties, it may not be necessary to resort to the drying operation with other types.

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ecular Weights of Celluloses

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reat deal of attention which the subject
here is little agreement among investi-
molecular weights of cellulose and cellu-
he state of dispersion of these materials
ss and his school (*9*, *17*) still maintain
rials dissociate in suitable solvents and
small units, even so far as units of one,
residues. Haworth and his co-workers
group method of determining the molecu-
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Unfortunately a detailed quantitative
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monium hydroxide) for ultracentrifugal
co-workers (*2*, *6*) go so far as to suggest
tically insoluble in cuprammonium, dis-
t only to particles 1–1.5 microns in size,
e particles retain their identity in solu-
ivatives. By means of the ultracentri-
has been reached that the molecular
and certain derivatives may be very
00–3500 glucose residues per molecule.
een obtained supporting qualitatively,
ely, Staudinger's conclusions relating
ics and molecular weights.

ituation, therefore, it is not expected
remove all discrepancies or will be uni-
Neither will it be possible to correlate
n detail with those of other workers.
se of the paper is to outline the experi-
o describe briefly the conclusion to which

vestigating molecular weights, like most
factory theoretical foundation, depends
ions. Therefore, two principal aspects
(*a*) The determination of the sizes of
c units in solutions of celluloses or cellu-
(*b*) the consideration of the question as to whether the particles or kinetic units are single molecules or not.

The first phase can be satisfactorily elucidated with the ultracentrifuge; the second phase requires information of another sort and is admittedly much more difficult to handle in an entirely rigorous manner.

Determination of Kinetic Unit Size in Cellulosic Solutions

For solutions containing large particles, as cellulosic solutions undoubtedly do, the most satisfactory general means for determining particle size experimentally is by the sedimentation-equilibrium method in the ultracentrifuge. This method possesses the following advantages:

1. It has the same thermodynamic foundation as osmotic pressure or vapor pressure methods (*16*).
2. It is accordingly not influenced by particle shape.
3. In general it is not affected by solvation (*13*).
4. Its sensitivity increases with increase in particle size.
5. It can be used with complex solvents like cuprammonium, with which osmotic pressure measurements would be very difficult.
6. It avoids difficulties associated with the use of semipermeable membranes.
7. It permits recognition of the uniformity or nonuniformity of particle size, and it can give a quantitative rating of the degree of nonuniformity (*12*).
8. For solutes containing relatively small molecular weight contaminants, it is much less adversely affected than osmotic pressure and other methods.

The comparison of the intrinsic viscosities and molecular weights of celluloses and cellulose derivatives, determined with the Svedberg ultracentrifuge, demonstrates that a simple relation exists between the two when suitable solvents are used. The different viscosity characteristics of various technical cellulosic products represent different degrees of degradation of the native cellulose chain, the range in chain length being about 1 to 10. Observations of sedimentation velocity in the high-speed ultracentrifuge show that cellulosic materials are not homogeneous in molecular weight and that the heterogeneity is not of the stepwise or discontinuous character as believed by some investigators. Cyclic conversion of cellulose to cellulose acetate and measurement of the molecular weights and intrinsic viscosities of the products provide very definite evidence that the units in solution are truly molecules in the chemist's sense of the term.

and Cellulose Derivatives . . .

With the slow-speed Svedberg ultracentrifuge the particle sizes in solutions of various cellulosic materials have been determined by the sedimentation-equilibrium method; the results obtained are outlined in Table I. As will be shown below, the particle sizes in these particular cases are identical with the molecular weights. In addition to the molecular weights, the tables also present data on the intrinsic viscosities $[\eta]$ of the solutions. The intrinsic viscosity is defined by the equation:

$$[\eta] = \left(\frac{\ln \eta_r}{c}\right)_{c \to 0}$$

where η_r = viscosity of the solution, relative to that of the solvent

c = concentration, grams solute per 100 cc. of solution

η_r is normally measured at a concentration which gives it a value not greater than 1.2–1.3.

TABLE I. MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES

	Mol. Wt.	D. P.[a]	$[\eta]$	$\frac{\text{D. P.}}{[\eta]}$
	Celluloses in Cuprammonium			
Purified cotton linters	300,000[b]	1300	5.05	260
Purified cotton linters	270,000[b]	1200	4.20	285
Purified cotton linters	200,000[b]	890	3.40	260
Regenerated cellulose	110,000[b]	490	1.83	270
Regenerated cellulose	90,000[b]	400	1.20	330
	Cellulose Acetate in Acetone[c]			
Cellulose acetate I	100,000	380	1.64	230
Cellulose acetate I	90,000	340	1.64	210
Cellulose acetate II	90,000	340	1.52	220
Cellulose acetate III	50,000	190	0.74	260
Cellulose acetate IV	68,000	260	1.23	210
Cellulose acetate V	250,000	950	3.78	250
	Nitrocellulose in Acetone[d]			
Nitrocellulose I	102,000	390	1.40	280
Nitrocellulose II	140,000	530	2.00	265
Nitrocellulose III	160,000	600	2.20	270
	Ethylcellulose in Dioxane			
Ethylcellulose I	125,000	540	1.83	300

[a] D. P. signifies degree of polymerization or number of glucose residues per molecule. For the celluloses in cuprammonium they are calculated on the assumption that 1 copper atom is combined per glucose unit.

[b] Molecular weight of the cellulose-copper complex.

[c] About 54 per cent acetic acid.

[d] 12 ± 0.1 per cent nitrogen.

The consistency of the above results, especially of the values for D. P./$[\eta]$, may not appear very good, but they should be considered in the light of the accuracy and consistency attainable by osmotic pressure and other methods. The inconsistencies are partially due to the fact that in most cases the complete calculations of true weight-average or Z-average molecular weights were not carried out, owing to their laborious character. With materials as nonuniform as most cellulose derivatives, the short-cut method of averaging, which was employed, is not entirely free from objection.

The above data support Staudinger's conclusions that an approximately linear relation exists between molecular weight and the intrinsic viscosity $[\eta]$. Using the following values for D. P./$[\eta]$,

Cellulose in cuprammonium	260
sec-Cellulose acetate in acetone	230
Nitrocellulose in acetone	270

the average molecular weights (strictly speaking, the weight-average molecular weights) of numerous cellulosic materials were estimated from intrinsic viscosity measurements. As we have pointed out, these constants are proportional to the reciprocal specific volumes (*11*). The following table gives representative values:

	Mol. Wt.	Degree of Polymerization
Native cellulose	>570,000	>3500
Purified cotton linters	150,000–500,000	1000–3000
Wood pulps	90,000–150,000	600–1000
Commercial regenerated celluloses	30,000–90,000	200–600
Farr and Eckerson hydrocellulose	40,000	250
Beta-celluloses	3,000–15,000	15–90
Gamma-celluloses	<3,000	<15
Dynamite nitrocellulose	750,000–875,000	3000–3500
Plastics nitrocellulose	125,000–150,000	500–600
1/2-sec. nitrocellulose	45,000	175
Commercial cellulose acetates	45,000–100,000	175–360

Molecular State of Dissolved Cellulosic Materials

There is too great a body of data demonstrating beyond any doubt that solutes commonly associate in certain solvents to justify any hope that celluloses and cellulose derivatives always disperse in solvents to the ultimate molecule. Admittedly, each solvent and each solution must be considered separately, and unfortunately molecular weight determinations alone do not, in general, give any evidence on the existence or nonexistence of association in a given solution. It is only by a study of various chemically related solutes in a variety of solvents that a case can be built up on this point. The discussion of the present paper is therefore restricted to the consideration of a limited number of solvents; it is to be definitely noted that no attempt is made to generalize concerning all solutions. Further, these data refer only to very dilute solutions, and no inferences are made concerning the presence or absence of association in more concentrated solutions.

Effect of Solvent on Intrinsic Viscosity

The first item of evidence indicating definitely that certain solvents can disperse cellulose derivatives to the single molecule is provided by the effect of solvent on intrinsic viscosity. The following table reproduces data of Dobry (*4*) for a medium-viscosity nitrocellulose (11.4 per cent nitrogen) in various solvents at a concentration of 0.04 gram per 100 cc.:

Solvent	Intrinsic Viscosity	Solvent	Intrinsic Viscosity
Acetic acid	3.3	Cyclohexanone	3.3
Acetone	2.9	Acetophenone + 3% ethanol	3.2
Acetonitrile	3.1		
Methanol	3.0	Ethyl benzoate + 11% ethanol	3.2
Isobutyl formate	3.0		
Ethyl formate	3.2	Methyl salicylate + 20% methanol	3.3
Nitrobenzene	3.1		

Since viscosity is very sensitive to association and aggregation in dispersions, the constancy of the intrinsic viscosity in the above cases demonstrates that these solvents all disperse the nitrocellulose to substantially the same degree. It seems rather improbable that these solutions contain the same sizes of ramifying aggregates held together by van der Waals's forces and immobilizing so nearly the same volume of solvent. The simpler hypothesis seems preferable that the kinetic unit in all these solvents, which give rise to approximately the same intrinsic viscosity, is the single molecule. We need not consider at this point the mechanism by which a solution of single molecules can have such a high intrinsic viscosity, in contrast to a value of 0.02–0.03 for compact spherical molecules.

Effect of Solvent on Osmotic Pressure

Even more definite evidence that the average particle weight in nitrocellulose solutions is practically constant in the above-mentioned solvents is provided by osmotic pressure measurements, also carried out by Dobry (*5*):

Solvent	(Osmotic Pressure, *cm. H_2O*)/ (Concn., *g./100 cc.*)
Acetone	2.4
Methanol	2.4
Cyclohexanone + 5.8% ethanol	2.2
Ethyl benzoate + 11.3% ethanol	2.4
Methyl salicylate + 20% methanol	2.4
Acetophenone + 3% ethanol	2.4
Acetic acid	2.4
Nitrobenzene	2.35

These ratios of osmotic pressure to concentration, extrapolated to zero concentration, show that the value of the ratio is satisfactorily constant. The necessity for working at very low concentrations is well demonstrated by this work, for already at a concentration of 0.1 per cent the osmotic pressures show a spread of 25 per cent; and at higher concentrations the spread continues to increase. The average molecular weight, calculated from the osmotic pressure data, is 110,000. This, of course, is a number-average value.

Dobry (*3*) published similar data on cellulose acetate solutions:

Solvent	(Osmotic Pressure, *cm. H_2O*)/ (Concn., *g./100 cc.*)
Tetrachloroethane + 13.4% ethanol	3.7
Acetic acid	3.8
Acetonitrile	3.7
Dioxane	3.7
Acetone	3.7
Nitromethane	3.9
Cyclohexanone	3.7
Ethyl formate	3.7

The values again represent an extrapolation to zero concentration, and correspond to a number-average molecular weight of 66,000.

Interrelation of Intrinsic Viscosity and Molecular Weight

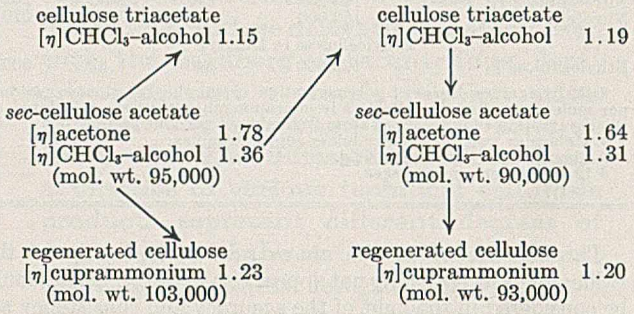
The approximate constancy (Table I) for the ratio D. P./[η] for different cellulosic products constitutes substantial evidence for the conclusion that the particles measured in the ultracentrifuge work are single molecules. Primarily, the constancy of D. P./[η] demonstrates that the solutions in question contain particles of approximately the same size and form, in spite of the marked differences in the chemical character of the solute or the nature of the solvent.[1] In other words, the intrinsic viscosity of solutions of cellulose and cellulose derivatives in suitable solvents depends primarily, but not necessarily entirely, upon the molecular weight of the cellulosic material. It has been suggested that the particle in solution may have a definite size, form, and intrinsic viscosity without being a single molecule, owing to the activity of some skin substance, cementing material, or structure of biological origin, which is capable of holding an assembly of molecules together in the same manner for various derivatives and in various solvents. This is theoretically conceivable, but the simpler hypothesis seems preferable—namely, that the particle in question is in these particular cases the single molecule. At least it is preferable until some one demonstrates in clearer fashion than has yet been done, the existence of such an extraneous structure and shows that its chemical character is such that it can go through etherification, esterification, bleaching, and hydrolyzing reaction either without being affected or, if affected, without more markedly influencing the relations between particle size and intrinsic viscosity.

Additional support for these conclusions is provided by the interrelation of the intrinsic viscosities of celluloses and of cellulose acetates formed from the celluloses without degradation (*10*):

Cellulose in Cuprammonium →		Cellulose Triacetate in $CHCl_3$-Alcohol →	*sec*-Cellulose Acetate in Acetone	
[η]	D. P.(=260[η])	[η]	[η]	D. P.(=230[η])
0.64	170	..	0.75	170
1.20	310	1.30	1.56	360
1.74	450	1.80	2.35	540
2.53	660	2.49	2.85	660
3.31	860	3.40	3.78	870

The equality of the intrinsic viscosities of the celluloses and the corresponding cellulose acetates can most simply be interpreted by assuming that in each case the cellulose or cellulose derivative disperses to single molecules in very low concentration; that true molecular weights, in the chemist's sense of the term, are measured in the ultracentrifuge; that the intrinsic viscosity is primarily determined by the degree of polymerization of the cellulosic material and relatively slightly affected by its chemical character, solvation, or aggregation; and that the form assumed by the dissolved molecules is determined by some property of the long primary-valence chain of glucose residues which make up the cellulose skeleton.

A complete proof of the fact that the chemical conversions mentioned above can be carried out without appreciable degradation may be obtained by closing the cycle and determining the molecular weight of the cellulose regenerated from the *sec*-cellulose acetate. Data on this point are as follows:



The molecular sizes of the two members in each pair of similar derivatives are substantially alike. It is quite unlikely that any assembly of cellulosic molecules held together by van der Waals's forces or by cementing substances could be broken down by agencies reducing the intrinsic viscosities of cellulose or cellulose derivatives and yet not be broken down by reactions used in the interconversions of cellulose and cellulose derivatives; it is also unlikely that, when broken down, the disintegration could occur without influencing the relations of form, degree of swelling, and intrinsic viscosity to particle size. The conclusion therefore seems inevitable that cellulose and cellulose derivatives form dilute solutions in suitable solvents, in which the molecular kinetic unit is the single molecule, and that, accordingly, in these cases the particle size values obtained with the ultracentrifuge are, strictly speaking, molecular weights.

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[1] The results also indicate that the cellulose-copper complex is almost completely dissociated, so that the centrifugible component is simply the cellulose-copper complex anion.

By means of the ultracentrifuge the above type of analysis could be carried out in much greater detail. Particularly important would be information on the nonuniformity, with respect to molecular weight of cellulosic materials, on molecular weights of a given material in a variety of solvents, and on sedimentation-velocity relations. However, the data along these lines are not yet sufficient for public presentation. However, the present status of the subject seems to justify the use of intrinsic viscosity measurements for characterizing the degree of degradation of cellulosic materials and estimating the average (weight-average) degree of polymerization by means of the constants relating it to intrinsic viscosity, which have been determined with the ultracentrifuge.

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RECEIVED March 12, 1938. Presented before the Division of Cellulose Chemistry at the 93rd Meeting of the American Chemical Society, April 12 to 15, 1937. Contribution 179 from the Experimental Station of E. I. du Pont de Nemours & Company, Inc.

CORRESPONDENCE

Distillery By-Products

SIR: The June, 1938, issue of INDUSTRIAL AND ENGINEERING CHEMISTRY contains a description of "Distillery By-Products" by Lloyd Cooley (*3*) and gives a flow sheet of the Hiram Walker & Sons plant at Peoria, Ill. None of this equipment was in the distillery on the day before its opening, July 4, 1934, except the conveyor mixer and the rotary steam dryers, nor was it then contemplated. Stricter laws compelled the adoption of the process of saving the soluble solids. Cooley's historical review (*3*) omits some of the earlier work because this author has been engaged in the work only since the repeal of prohibition.

There is an idea among the newer generation that little chemical work had been done before prohibition in the arts of distilling and utilizing the by-products (*1*). Feeding slop to cattle had been practiced for many generations and was stopped only after legislation against it was passed in many states, for the waste from the cattle barns was more polluting than the hot slop. It became illegal to feed milch cows with slop because of the resulting unsanitary condition of the barns. No objection to using dried solids as a feed stuff was ever made.

Screening and pressing the grains for slop were developed at the end of the last century. Patents issued to Hinken (*4*) for a filter press specially adapted for slop filtration and to Turney (*5*) for a rotary dryer heated by inside steam tubes gave practical means for saving the insoluble solids in the slop.

Saving the soluble solids began in 1905, following the work of the great pioneer, Otto Behr, who experimented with cornstarch and glucose and made "gluten meal," etc. This was done mostly to prevent pollution of the Mississippi tributaries, as a result of laws on the subject. During prohibition the industry died and was revived with repeal. As Cooley states, the prewar slop saving was "in principle much like the methods used today" except that the later units "have greater capacity."

That "they use less steam, and/or fuel, labor, and water" is open to question. Figure 1 is a diagram of an apparatus from a patent issued to me in 1910 (*2*). This illustration gives a better understanding of the processes than those published by Cooley. The beer still, 1, is omitted in Cooley's paper; the still shown here has a superheater, 36, that receives part of the slop and evaporates it by steam coils, 39. The tubes boil the slop, and the water condensed in the process returns to the steam boilers as pure distilled water. Practice shows that about 20 pounds of steam condense to water in distilling a hundred pounds of "beer." Keeping this out of the slop by use of the superheater means a 20 per cent saving in evaporation and in fuel by this system. The screens illustrated by Cooley and by 23 of my drawing have been improved by arranging them double and in tandem. The coarse grain falls on the lower screen, and the filtrate from the upper screen passes again through the grains on the lower screen, thus producing a thin slop nearly equal to that from the centrifugals. As described, this centrifugal process is not attractive on account of the expense of installation, the driving power required, and the labor, although it yields a product with only 20 per cent solids and 80 per cent water. Perhaps these centrifugals might be of the milk type and produce a sludge cream that would contain about the same percentage of solids. The presses mentioned are quite old and have been successful in breweries for squeezing the brewers' grains fairly dry. The roller press, 24, is the most popular at present. Cooley mentions returning the "screen effluent." This is the old process of "slopping back." It has the advantage of furnishing the yeast with nitrogen, organic acids, and potash. Since yeast is a vegetable, it needs fertilizers (as Pasteur found out); Cooley showed that it is also advantageous when the slop is slopped back, since that means a saving in evaporation. This is most important when all solids

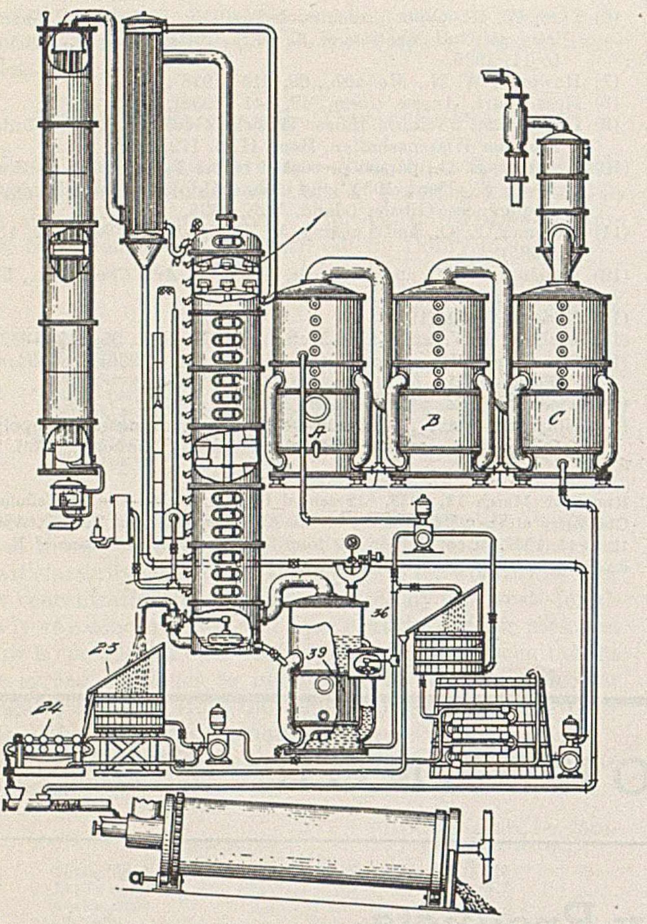

FIGURE 1

are to be saved. The multiple-effect evaporators sketched in Cooley's paper compare with the *A*, *B*, *C* effects here illustrated, but it is probably preferable to have 2 third effects with valves so that either one may be taken off alternately and used as the "cast-iron finishing pan," while the other evaporates the slop to a point where it is ready for the finishing under higher steam pressure. It is stated that if the (screened) liquid could be dumped into the sewer, it would hold half the solids and save most evaporation costs. In prewar days the grains gave 9 pounds of cattle feed, and the complete saving was 18 pounds from Bourbon mashes. Cooley claims only 15 pounds.

The "ten panels with buttons" reveal the modern tendency to operate plants with buttons; in prewar days they were operated with brains.

It is hoped that this more detailed description of what is possible with this process of by-product recovery and elimination of nuisances will be profitable to manufacturers in other lines who have problems that can be solved in the same way.

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50 EAST 41ST STREET
NEW YORK, N. Y.
June 6, 1938

H. O. CHUTE

....

SIR: H. O. Chute has furnished a welcome and informative elaboration of my recent article on "Distillery By-Products." However, his second sentence, "except the conveyor mixer and the rotary steam dryers," should have had added to it, "and screens and rotary presses."

Installation of evaporators had been seriously contemplated prior to the building of the distillery, but the cost of installing and operating them had appeared to outweigh probable profits. Permission was requested of the authorities to delay the installation of the evaporators until at least a year's investigation could be made of better methods. This permission was denied.

Because the recovery units are larger than former units, the labor cost is lower. The over-all cost for steam per ton of product is lower than formerly, because of the fact that sirup is sent to the dryers at double the customary concentration.

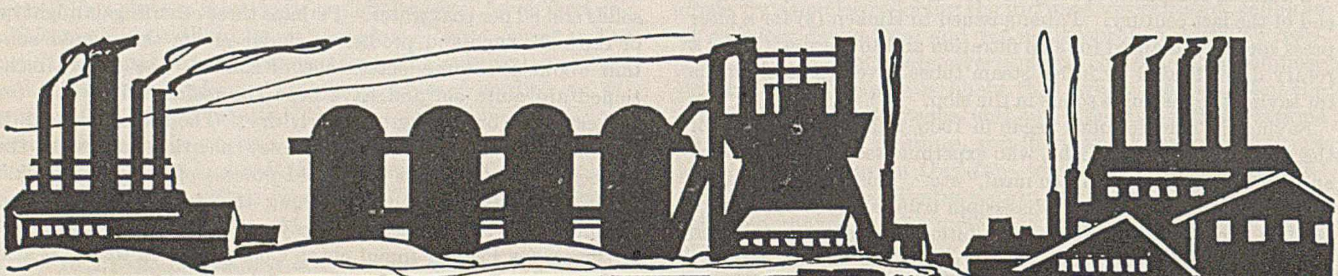
Fair comparisons of yield are difficult to make because of variations in the fermentable contents of the grain. A yield of 15 pounds of dried feed per bushel of grain mashed would be very satisfactory if the yield of alcohol were also good. A yield of 19 pounds per bushel might imply a low starch content or a poor yield of alcohol, leaving more solid matter to be recovered in the feed.

A closed heater for the beer still would save steam in the evaporating process. The subject was considered seriously by the engineers at the time the distillery was built, but in view of the projected supply of low-cost exhaust steam, the large heaters needed for the size of the beer stills, and the probable operating troubles, it was deemed wise to omit closed beer heaters or vaporizers at that time.

In regard to Chute's remarks about operating plants "with buttons. . .brains," it is of interest to note that only graduate chemical engineers were employed to operate the cookers, stills, and evaporators. The brains had to see beyond the buttons.

15 ENOS PLACE
JERSEY CITY, N. J.
July 27, 1938

LLOYD C. COOLEY



CHEMICAL MARKET PRICES

SEPTEMBER 12, 1938

Compiled from weekly current price listings in the *Oil, Paint and Drug Reporter,* with permission of the publisher under its copyright. These prices, unless otherwise specified, are those prevailing in the New York market for technical grades in usual large commercial quantities.

Acetaldehyde, drums, c/l., wks.	lb.	.14
Acetamide, tech., kegs, 1000-lb. lots, dlvd.	lb.	.39
Acetanilide, tech., 95%, bbls.	lb.	.29*
Acetic anhydride, drums, c/l., frt. allowed	lb.	.10½
Acetone, C. P., drums, c/l., dlvd.	lb.	.05¾
Acetophenone, drums, 100 lbs.	lb.	1.05
Acetphenetidin, bbls., 1000 lbs.	lb.	1.00
Acid, abietic, drums, c/l.	lb.	.08¾
Acetic, 28%, bbls., c/l.	100 lbs.	2.23
56%, bbls., c/l.	100 lbs.	4.15
Glacial, synth., drums, c/l.	100 lbs.	8.43
Glacial, U. S. P., drums, c/l.	100 lbs.	10.25
Acetylsalicylic, U. S. P., bbls.	lb.	.60
Anthranilic, tech., bbls.	lb.	.75
Battery, cbys., c/l., E. wks.	100 lbs.	1.60
Benzoic, tech., bbls.	lb.	.43
Boric, tech., gran., bbls.	ton	106.00
Butyric (99%), drums, c/l., wks.	lb.	.22
Chloroacetic, mono-, tech., bbls., wks.	lb.	.15
Chlorosulfonic, drums, c/l., wks.	lb.	.03½
Chromic, 99%, drums	lb.	.15¼
Cinnamic, bottles	lb.	2.85
Citric, U. S. P., cryst., bbls.	lb.	.22
Cresylic, H. B., drums, c/l., wks., frt. equal	gal.	.73
Formic, 90%, cbys., f. o. b. stock points, c/l.	lb.	.10½
Gallic, tech., bbls.	lb.	.70
Hydriodic, 57%, 5-lb. bot.	lb.	2.75
Hydrobromic, 10%, U. S. P., cbys., wks.	lb.	.20
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.15
Hydrofluoric, 30%, bbls., wks.	lb.	.07
60%, lead cbys.	lb.	.15
Hydrofluosilicic, 35%, bbls., wks.	lb.	.09
Hypophosphorus, U. S. P., 30%, 5-gal. demis	lb.	.75
Lactic, dark, 22%, bbls.	100 lbs.	2.50
Light, 44%, bbls., wks.	100 lbs.	6.50
Maleic, powd., drums	lb.	.30
Mixed, tanks, wks.	N unit. lb.	.05
	S unit. lb.	.0085
Naphthenic, S. V. 120–200, drums	lb.	.07
Nitric, C. P., cbys.	lb.	.13
36°, cbys., c/l., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.10¾
Phosphoric, U. S. P., 50%	lb.	.12
Picramic, kegs	lb.	.65
Picric, bbls.	lb.	.35
Pyrogallic, tech., bbls.	lb.	1.05
Salicylic, tech., bbls.	lb.	.33
Sebacic, tech., drums, wks.	lb.	.37
Stearic, d. p., bags, dlvd.	lb.	.10½
Sulfanilic, tech., 250-lb. bbls.	lb.	.17
Sulfuric, 66°, cbys., c/l., E. wks.	100 lbs.	1.50
66°, tanks, E. wks.	ton	16.50
60°, tanks, E. wks.	ton	13.00
Oleum, 20%, tanks, E. wks.	ton	18.50
Tannic, tech., bbls.	lb.	.40
Tartaric, U. S. P., cryst., bbls.	lb.	.27¼
Tungstic, tech., kegs	lb.	1.65
Alcohol, ethyl, 190 proof, from molasses, bbls., c/l.	gal.	4.56½
Amyl, from pentane, tanks	lb.	.106
Butyl, drums, c/l., wks., frt. allowed	lb.	.09½
Cinnamic, bottles	lb.	2.00
Denatured, C. D. 14, drums, c/l., wks.	gal.	.33
Diacetone, tech., drums, c/l.	lb.	.11½
Alcohol, furfuryl, tech., drums, c/l., works	lb.	.20
Isoamyl, drums	lb.	.27
Isobutyl, ref., drums, c/l.	lb.	.08½
Isopropyl, ref., 91%, drums, c/l., f. o. b. dest.	gal.	.33½
Wood, *see* Methanol		
Aldol, 95%, drums, c/l., dlvd.	lb.	.20
Alpha-naphthol, bbls.	lb.	.52
Alpha-naphthylamine, bbls.	lb.	.32
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.40
Potash-chrome, bbls.	100 lbs.	6.25
Potash, lump, bbls., wks.	100 lbs.	3.65
Soda, bbls., wks.	100 lbs.	3.25
Aluminum, metal, 98–99%, drums, c/l.	lb.	.20
Chloride, anhyd., commercial, drums extra, c/l., wks.	lb.	.06
Stearate, 100-lb. bbls., c/l.	lb.	.19
Sulfate, comm'l, bags, c. l., wks., frt. equal	100 lbs.	1.15
Iron-free, bags, wks.	100 lbs.	1.30
Ammonia, anhydrous, fertilizer, tanks (50,000 lbs.), wks.	lb.	.04½
Pure, cyls.	lb.	.16
Ammonia, aqua, 26°, tanks (on NH_3 content), dlvd. E.	lb.	.05
Ammonium acetate, kegs	lb.	.27
Bifluoride, bbls.	lb.	.14½
Bromide, bbls.	lb.	.35
Carbonate, tech., bbls.	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.50
U. S. P., gran., bbls.	lb.	.12
Iodide, 25-lb. jars	lb.	3.45
Linoleate, bbls.	lb.	.12
Nitrate, tech., bags, c/l., wks.	100 lbs.	3.60
Oleate, bbls.	lb.	.14
Oxalate, kegs	lb.	.19
Persulfate, cases	lb.	.21
Phosphate, dibasic, tech., bbls.	lb.	.07½
Sulfate, bulk, c/l., f. o. b. ports or ovens	ton	27.00
Sulfide, liq. 35–40%, basis 100%, tanks, delvd.	lb.	.11
Amyl acetate, from pentane, tanks, works	lb.	.10
Chloride, normal, drums, wks.	lb.	.56
Chlorides, mixed, tanks, wks.	lb.	.06
Mercaptan, drums, l. c. l., wks.	lb.	1.10
Oleate, drums, l. c. l., wks.	lb.	.25
Stearate, drums, l. c. l., wks.	lb.	.26
Amylene, tanks, wks.	lb.	.09
Anilin oil, drums	lb.	.15
Anthraquinone, subl., bbls.	lb.	.65
Antimony, chloride, soln., cbys.	lb.	.17
Metal, N. Y.	lb.	.11¼
Oxide, bbls., c/l.	lb.	.11½
Salts, 65%, kegs	lb.	.26
Argols, test 75–80%, basis 100%	100 kilos	32.00
Arsenic, metal kegs	lb.	.40
Red, kegs, cases	lb.	.15¾
White, c/l., kegs	lb.	.03
Barium carbonate, natural, 90% bags, c/l., wks.	ton	41.00
Chloride, tech., cryst., bgs., c/l.	ton	77.00
Dioxide, drums, wks.	lb.	.11
Hydroxide, bbls.	lb.	.04¾
Nitrate, casks	lb.	.06¾
Barytes, floated, 350-lb. bbls., wks.	ton	23.65
Benzaldehyde, tech., drums	lb.	.60
Benzidine base, bbls.	lb.	.70
Benzol, tanks, frt. allowed e. of Omaha	gal.	.16
Benzoyl chloride, drums	lb.	.23
Benzyl acetate, F. F. C., drums	lb.	.44
Chloride, tech., drums	lb.	.25
Beta-naphthol, tech., bbls.	lb.	.23
Beta-naphthylamine, tech., kegs	lb.	.51
Bismuth, metal, ton lots	lb.	1.05
Nitrate, cans	lb.	1.20
Oxychloride, kegs	lb.	2.95
Subnitrate, powd., fib. drums	lb.	1.18
Blanc fixe, dry, bags, c/l.	ton	55.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone black, 4, bbls., c/l., frt. allowed E.	lb.	.08½
Borax, tech., gran., sks.	ton	43.00
Bordeaux mixture, drums	lb.	.11
Bromine, cases	lb.	.30
Bromoform, jars	lb.	1.40
Butyl acetate, drums, c/l., frt. allowed	lb.	.09½
Aldehyde, drums, l. c. l.	lb.	.16½
Carbinol, norm., drums, wks.	lb.	.60
Carbinol, sec., wks.	lb.	.60
Lactate, drums	lb.	.22½
Stearate, drums	lb.	.26
Cadmium, metal, cases	lb.	1.05
Bromide, 100 lbs., wks., frt. equal.	lb.	1.66
Sulfide, boxes	lb.	1.50
Caffeine, 100-lb. drums, 10,000 lbs. or more	lb.	2.20
Calcium acetate, bags	100 lbs.	1.65
Arsenate, bbls.	lb.	.06¾
Carbonate, precip., bags, 50 lbs., c/l., wks.	lb.	.02¾
Chloride, bags, flake, c/l., deliv.	ton	22.00
Gluconate, U. S. P., bbls., 125 lbs.	lb.	.50
Phosphate, dibasic, 38–42% P_2O_5, bags, Atlan. pts.	unit-ton	.80
Tribas., bbls.	lb.	.06½
Calomel, bbls., kegs, 50 lbs. or more	lb.	1.28
Camphor, synthetic, gran., powd., drums, ton lots	lb.	.47
Carbazole, 95% drums, ton lots, wks.	lb.	.70
Carbon, bisulfide, drums, c/l.	lb.	.05
Black, standard, bags, c/l., dlvd. N. Y.	lb.	.0375
Dioxide, liq., cyl.	lb.	.06
Tetrachloride, drums	lb.	.05
Casein, dom., 20–30 mesh, bags., c/l.	lb.	.09½
Cellulose acetate, flakes, cs., wks.	lb.	.40
Cerium oxalate, bbls., wks.	lb.	.35
Charcoal, willow, powd., bbls.	lb.	.06
China clay, bulk, c/l., wks.	ton	7.00
Chloral hydrate, drums	lb.	.80
Chlorine, liq., c/l., cyl., dlvd.	lb.	.05½
Tanks, frt. equal., wks.	100 lbs.	2.15
Chlorobenzene, mono-, drums	lb.	.06
Chloroform, tech., drums	lb.	.20
Chromium acetate, 8% soln., bbls.	lb.	.05
Coal tar, bbls., c/l., wks.	bbl.	7.50
Cobalt oxide, black, kgs.	lb.	1.67
Copper carbonate, 52/54%, bbls.	lb.	.14
Chloride, bbls.	lb.	.12½
Cyanide, drums	lb.	.34
Metal, elec.	lb.	.10⅛
Oxide, black, bbls., tons, wks.	lb.	.14¾
Sulfate, bbls., c/l., wks.	100 lbs.	4.25
Copperas, cryst., bulk, c/l.	ton	13.00
Cream of tartar, bbls.	lb.	.22¾
Cresol, U. S. P., drums, c/l., wks.	lb.	.10½
Crotonaldehyde, 97%, drums, dlvd.	lb.	.22
Cyanamide, bulk, Atlantic ports	Ammonia unit	1.15
Diamylamine, drums, c/l., wks.	lb.	.47
Diamylene, tanks, wks.	lb.	.08½
Diamyl ether, tanks, wks.	lb.	.07½
Diamyl oxalate, drums, l. c. l., wks.	lb.	.30
Diamyl phthalate, tanks	lb.	.18
Diamyl sulfide, drums, wks.	lb.	1.10

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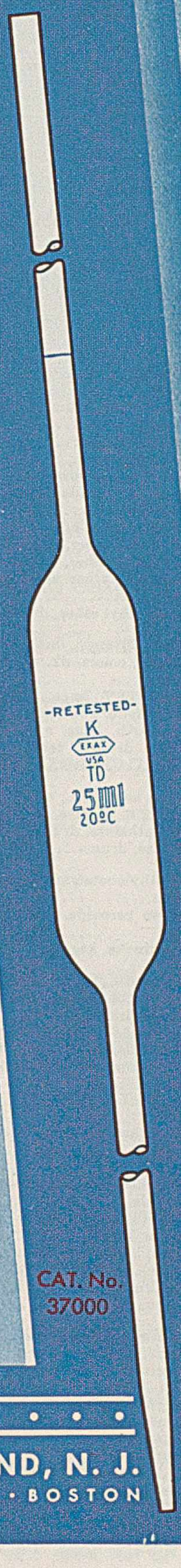
* Nominal.

(Continued on page 40)

KIMBLE VOLUMETRIC PIPETTES

NORMAX *and* EXAX

CAT. No.
37010



CAT. No.
37000

Kimble Normax and Blue Line Exax Volumetric Pipettes are made from carefully selected, automatic-machine-made, extra heavy tubing of very uniform bore.

OUTSTANDING ADVANTAGES

1. Designed to deliver contents accurately and at a proper speed.
2. Delivery ends are tapered gradually; tips are ground and slightly bevelled.
3. The tops are smoothly finished.
4. Volumetric pipettes have joints that are carefully made without constrictions.
5. Expertly calibrated at 20°C to deliver capacity by free outflow through tip. No drainage period allowed.
6. All calibration lines are deeply acid-etched and filled with a durable blue fused-in glass.
7. Retested and retempered (strain-free).

NORMAX TOLERANCES

Capacity	*Tolerance*	*Capacity*	*Tolerance*
1 ml	±0.006 ml	25 ml	±0.03 ml
2	.006	50	.05
5	.01	100	.08
10	.02	200	.10
20	.03		

EXAX TOLERANCES

Capacity	*Tolerance*	*Capacity*	*Tolerance*
1 ml	±0.012 ml	15 ml	±0.06 ml
2	.012	20	.06
3	.02	25	.06
4	.02	50	.10
5	.02	100	.16
10	.04	200	.20

Fully detailed Kimble Normax and Exax Catalogs are forwarded promptly upon request.

●

Stocked by leading laboratory supply houses throughout the United States and Canada.

• • • *The Visible Guarantee of Invisible Quality* • • •

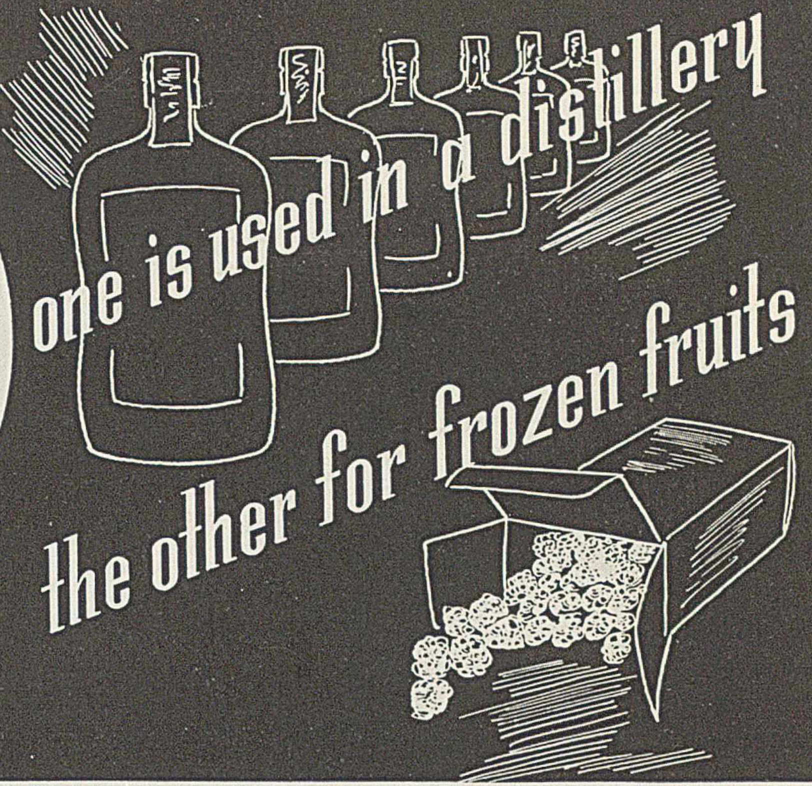
KIMBLE GLASS COMPANY . . . . VINELAND, N. J.

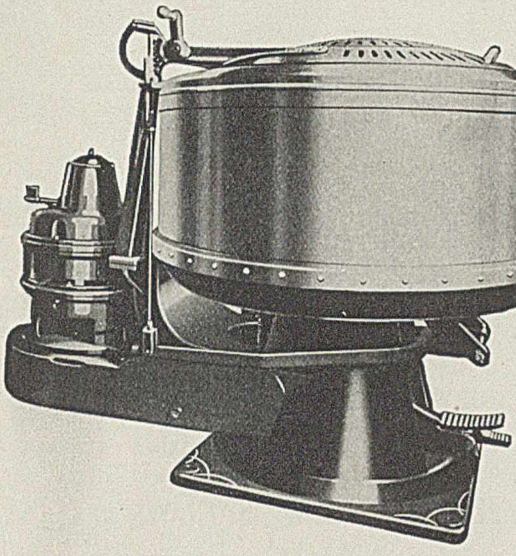
NEW YORK • • CHICAGO • • PHILADELPHIA • • DETROIT • • BOSTON

MARKET REPORT (continued from page 38)

Diatomaceous earth, dom., bags, c/l., Pacific Cst.	ton	22.00
Dibutylamine, drums, l. c. l., wks.	lb.	.55
Dibutyl phthalate, drums, wks., frt. allowed	lb.	.19
Dibutyl tartrate, drums	lb.	.45
Dichlorethyl ether, drums, c/l., wks.	lb.	.15
Diethanolamine, drums, c/l., wks.	lb.	.24
Diethylaniline, drums	lb.	.40
Diethylene glycol, drums, c/l., wks.	lb.	.16
Monobutyl ether, drums, wks.	lb.	.23
Monoethyl ether, drums, c/l., wks.	lb.	.15
Diethyl carbinol, drums, wks.	lb.	.60
Diethyl phthalate, drums, c/l.	lb.	.19
Diethyl sulfate, tech., drums, wks.	lb.	.13
Diglycol oleate, light, bbls.	lb.	.20
Dimethylaniline, drums	lb.	.26
Dimethyl ethyl carbinol, drums, wks.	lb.	.60
Dimethyl phthalate, drums, c. l., dlvd.	lb.	.18½
Dinitrobenzene, tech., drums	lb.	.18
Dinitrochlorobenzene, bbls.	lb.	.14
Dinitronaphthalene, bbls.	lb.	.35
Dinitrophenol, bbls.	lb.	.22
Diphenyl, bbls., c/l., wks.	lb.	.15
Diphenylamine, bbls.	lb.	.31*
Diphenylguanidine, bbls.	lb.	.35
Epsom salt, tech., bags	100 lbs.	1.80
Ether, conc., drums	lb.	.09
Nitrous, bots., 100 lbs.	lb.	.08
Ethyl acetate, 85–88%, tanks, frt. allowed	lb.	.05½
Acetoacetate, drums, c/l., wks.	lb.	.27½
Bromide, drums	lb.	.50
Chloride, drums	lb.	.18
Formate, drums	lb.	.23
Methyl ketone, drums	lb.	.06½
Ethylene dichloride, drums, wks., frt. allowed	lb.	.0545
Glycol, drums, c/l.	lb.	.16
Monobutyl ether, drums, wks.	lb.	.18
Monoethyl ether, drums, wks.	lb.	.15
Monoethyl ether acetate, drums, wks.	lb.	.13
Monomethyl ether, drums, wks.	lb.	.17
Feldspar, 20 mesh, bulk, wks.	ton	9.75
Film scrap, colors, dk. cs., 1000 lbs., E. wks.	lb.	.12½
Fluorspar, 98%, bags	ton	31.50
Formaldehyde, bbls., c/l.	lb.	.05¾
Fuller's earth, bags, c/l., mines	ton	10.00
Furfural, drums, tech., contract, works	lb.	.10
Glauber's salt, bbls., c/l.	100 lbs.	.95
Glycerine, C. P., dms., c/l.	lb.	.14¼
Glycol phthalate, drums	lb.	.38
Stearate, drums	lb.	.25
Hexamethylenetetramine, tech., drums	lb.	.35
Hydrogen peroxide, 100 vol., cbys., c/l.	lb.	.20
Hydroquinone, kegs	lb.	.90
Indigo, synth., liq., bbls.	lb.	.16½
Iodine, resubl., jars	lb.	1.75
Iodoform, drums, 100 lbs.	lb.	3.95
Iron acetate, N. F. IV, cbys.	lb.	.15
Iron chloride, tech., cryst., bbls.	lb.	.05
Isobutyl carbinol (128–132° C.), tanks	lb.	.32
Isopropylacetate, tanks	lb.	.05½
Lead acetate, white, broken	lb.	.10
Arsenate, bags	lb.	.12½
Metal, N. Y.	100 lbs.	4.90
Oxide, litharge, bbls., 20-ton lots	lb.	.0640
Peroxide, cans, wks.	lb.	.46
Red, bbls., 20-ton lots	lb.	.0740
Sulfate, bbls.	lb.	.06
White, basic carb., bbls.	lb.	.06¾
Lime, live, chemical, bulk, wks.	ton	7.00
Lime-sulfur, dry, bags, c/l.	lb.	.07½
Lithopone, bbls.	lb.	.04⅜
Magnesite, calcined, 500-lb. bbls., wks.	ton	56.00
Magnesium carbonate, tech., bags, c/l.	lb.	.06¼
Chloride, drums	ton	39.00
Fluosilicate, cryst., bbls.	lb.	.09½
Oxide, light, bbls.	lb.	.26
Manganese chloride, bbls.	lb.	.07½
Dioxide, 85–90%, bbls., c. l., wks.	ton	59.00
Sulfate, casks	lb.	.07
Mannitol, comm., cryst., ton lots, bbls.	lb.	.55
Menthol, syn., tech., cs.	lb.	2.25
Mercury bichloride, cryst., drums, 50 lbs. or more	lb.	1.13
Mercury, flasks, 76 lbs.	flask	80 00
Meta-nitroaniline, bbls.	lb.	.67*
Meta-phenylenediamine, kegs	lb.	.65
Meta-tolylenediamine, bbls.	lb.	.65
Methanol, pure, synthetic, drums, wks., frt. allowed, c/l.	gal.	.38
Tanks, wks., frt. allowed	gal.	.33
Methyl acetone, nat., tanks	gal.	.25
Chloride, cylinders	lb.	.32
Formate, l. c. l., drums	lb.	.35
Hexyl ketone, drums, tech., wks.	lb.	.60
Propyl carbinol, drums, wks.	lb.	.60
Salicylate, drums	lb.	.40
Monoamylamine, drums, c. l., wks.	lb.	.52
Monobutylamine, drums, l. c. l., wks.	lb.	65
Monoethanolamine, drums, wks.	lb.	.24
Naphthalene, crude, imp., bags, Atlantic ports	100 lbs.	1.40
Nickel salt, single, bbls.	lb.	.13
Niter cake, bulk	ton	16.00
Nitrobenzene, drums	lb.	.08
Nitrocellulose, alcohol-sol., bbls., wks.	lb.	.28
Nitrogen solution unit	unit	1.02
Octyl acetate, tanks, wks.	lb.	.15
Oil, castor, No. 3, tanks	lb.	.08½
China wood, dms.	lb.	.13¼
Coconut, crude, tanks, Pac. Cst.	lb.	.02⅞
Cod, N. F., bbls.	gal.	.38*
Corn, crude, tanks, mills	lb.	.07¼
Cottonseed, refined, bbls.	lb.	.09¼
Linseed, boiled, tanks	lb.	.0790
Menhaden, crude, tanks, f. o. b. Baltimore	gal.	.30
Neat's-foot, pure, bbls.	lb.	.11¾
Oiticica, bbls.	lb.	.10¾
Oleo, No. 1, bbls.	lb.	.09¼
Olive oil, denat., bbls.	gal.	.94
Foots, bbls.	lb.	.07½
Palm, Niger, bbls.	lb.	.03⅝
Sumatra, bulk	lb.	.02¾
Peanut, crude, tanks	lb.	.07¼*
Perilla, drums	lb.	.10¼
Rapeseed, denat., bbls.	gal.	.75
Red, bbls.	lb.	.08⅜*
Soy bean, crude, tanks	lb.	.05⅞
Sperm, 38°, bbls.	lb.	.10
Whale, bbls., natural, refined	lb.	.0770
Ortho-dichlorobenzene, drums	lb.	.06
Ortho-nitrochlorobenzene, kegs	lb.	.15
Ortho-nitrotoluene, drums	lb.	.08
Ortho-toluidine, bbls.	lb.	.16
Para-dichlorobenzene, drums, c/l.	lb.	.11
Para-formaldehyde, drums	lb.	.34
Paraldehyde, tech., drums	lb.	.16
Para-nitraniline, drums	lb.	.47
Para-nitrochlorobenzene, drums	lb.	.15
Para-nitrophenol, bbls.	lb.	.35
Para-nitrotoluene, bbls.	lb.	.35
Para-phenylenediamine, bbls.	lb.	1.25
Para-toluidine, bbls.	lb.	.56
Paris Green, 250-lb. kegs	lb.	.23
Phenol, drums, c/l., wks.	lb.	.14½
Phenolphthalein, yellow, drums, ton lots	lb.	.80
Phenylethyl alcohol, bottles	lb.	2.70
Phloroglucinol, tech., tins, wks.	lb.	15.00
C. P., tins, wks.	lb.	20.00
Phosphorus, red, cases	lb.	.40
Oxychloride, 175-lb. cylinders	lb.	.15
Trichloride, cyl.	lb.	.15
Phthalic anhydride, bbls.	lb.	.14½
Potash, caustic, solid, drums	lb.	.06¼
Potassium acetate, tech., bbls.	lb.	.26
Bicarbonate, gran., bbls.	lb.	.15
Bichromate, casks, c/l., wks.	lb.	.08⅞
Binoxalate, bbls.	lb.	.23
Bromide, U. S. P., gran., bbls.	lb.	.31
Carbonate, 80–85%, calc., casks	lb.	.05½
Chlorate, cryst., kegs	lb.	.09¼
Chloride, tech., cryst., bgs.	lb.	.04
Cyanide, drums	lb.	.50
Meta-bisulfite, bbls.	lb.	.12
Muriate, fert., bulk, per K_2O unit		.53½
Permanganate, tech., drums	lb.	.18½
Prussiate, red, casks	lb.	.30½
Yellow, casks	lb.	.15
Pyridine, denat., drums	gal.	1.53
Pyrocatechin, C. P., drums	lb.	2.15
Quinine, 100-oz. cans	oz.	.76
Resorcinol, tech., kegs	lb.	.75
Rochelle salt, powd., bbls.	lb.	.16¾
Saccharin, drums	lb.	1.70
Salt cake, bulk, wks.	ton	15.00
Saltpeter, gran., bbls.	100 lbs.	6.50
Silica, 99%, 325 mesh, bags, c/l., wks.	ton	22.00
Silver nitrate, vials	oz.	.31½
Soda, ash, 58%, light, paper bags, contract, wks.	100 lbs.	1.05
Caustic, 76%, solid, drums, contract, wks.	100 lbs.	2.30
Sodium abietate, drums	lb.	.10
Acetate, flake, bbls.	lb.	.04
Alginate, drums	lb.	.69
Antimoniate, bbls.	lb.	.12
Benzoate, U. S. P., bbls.	lb.	.46
Bicarbonate, powd., bbls., c/l., wks.	100 lbs.	1.85
Bichromate, c/l., wks.	lb.	.06⅞
Bisulfite, bbls.	100 lbs.	3.30
Bromide, U. S. P., bbls.	lb.	.31
Chlorate, cryst., bags	lb.	.06¼
Chloride, bags	ton	13.20
Cyanide, 96–98%, dom., drums	lb.	.14
Fluoride, white, 90%, bbls., c/l., f. o. b. Phila.	lb.	.07¼
Metallic, untrimmed bricks, drums, f. o. b. Niagara Falls	lb.	.15½
Metasilicate, gran., bbls.	100 lbs.	2.20
Naphthionate, bbls.	lb.	.50
Nitrate, crude, bulk	ton	27.00
Nitrite, bbls.	lb.	.06¾
Perborate, bbls.	lb.	.14¾
Phosphate, disodium, bags, c/l., wks.	100 lbs.	1.85
Phosphate, trisodium, bags, c/l., wks.	100 lbs.	2.00
Picramate, kegs	lb.	.65
Prussiate, yellow, bbls.	lb.	.09½
Silicate, drums, tanks, 40°	100 lbs.	.80
Silicofluoride, bbls.	lb.	.05¼
Stannate, drums	lb.	.29
Sulfate, anhyd., bags	100 lbs.	1.45
Sulfide, cryst., bbls.	lb.	.02¼
Solid, 60%	lb.	.03
Sulfocyanide, bbls.	lb.	.28
Thiosulfate, reg., cryst., bgs.	100 lbs.	2.25
Tungstate, tech., kegs	lb.	1.05
Strontium carbonate, pure, bbls.	lb.	.30
Nitrate, bbls.	lb.	.07¾
Sulfur, bulk, mines	ton	18.00
Chloride, drums	lb.	.03
Dioxide, commercial, cyl., wks.	lb.	.07
Tetrachlorethane, 50-gal. drums	lb.	.08
Thiocarbanilid, bbls.	lb.	.24
Tin, Straits	lb.	.4290
Crystals, bbls.	lb.	.34½
Oxide, bbls.	lb.	.48
Tetrachloride, anhydrous, drums, bbls.	lb.	.21¾
Titanium dioxide, bags, wks.	lb.	.15
Toluene, tanks	gal.	.22
Triamylamine, drums, c/l., wks.	lb.	.77
Triamyl borate, drums., l. c. l., wks.	lb.	.27
Tributylamine, drums, l. c. l., wks.	lb.	.70
Trichloroethylene, drums, wks., frt. allowed	lb.	.09
Tricresyl phosphate, tech. 2, drums	lb.	.23½
Triethanolamine, drums, c/l., wks.	lb.	.21
Triphenyl phosphate, drums	lb.	.38
Tungsten, tech., powder	lb.	2.80
Urea, dom., 46 + % N., bags, f. o. b. wks. or seaboard	ton	95.00
Vanillin, 25-lb. tins	lb.	2.10
Whiting comm. dry-grd., bags, c/l., wks.	ton	12.00
Xylene, 10°, tanks	gal.	.29
Xylidine, drums	lb.	.35
Zinc ammonium chloride, bbls.	lb.	.0515
Chloride, granulated, drums	lb.	.05
Dust, bbls., c/l.	lb.	.06¾
Metal, slabs, at N. Y.	lb.	.0515
Oxide, Amer., bbls.	lb.	.0625
Stearate, bbls.	lb.	.20
Sulfate, cryst., bgs., c/l., wks.	100 lbs.	2.75

TWO R-E CENTRIFUGALS

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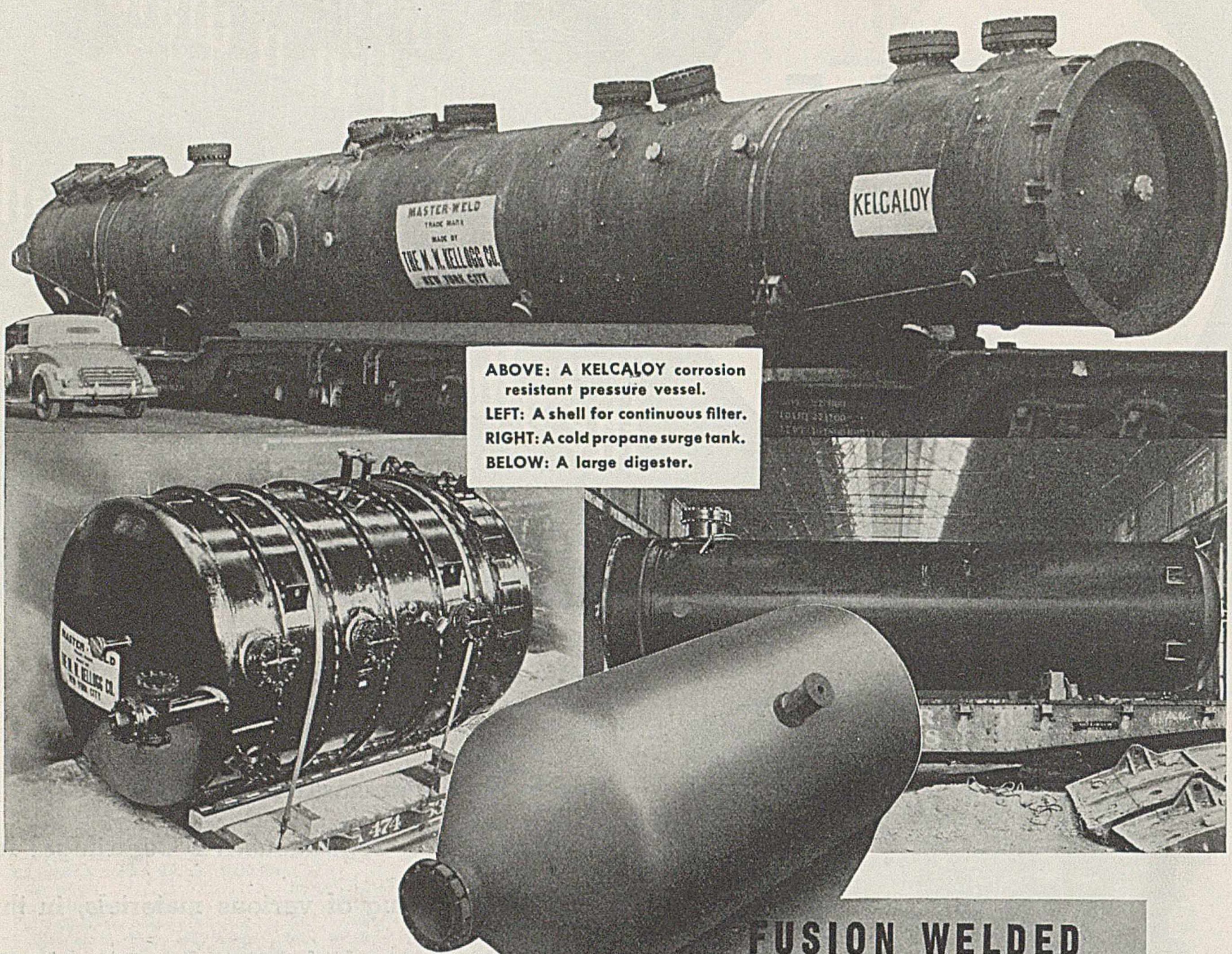
2

1 A 30″ Underdriven R-E Centrifugal with Safety Interlocks as used in a distillery for the removal of whiskey from filter mass and aging chips.

2 Automatic, Semi-Continuous R-E Centrifugal for automatic handling of various materials, in this case for the removal of excess freezing solution from quick-frozen fruits and vegetables, frozen by Immersion or Spray processes.

If centrifugal force is applicable, regardless of its complexity or the materials of construction, an R-E Centrifugal can be designed and built that will do the job. Why not let an R-E Engineer make a "no obligation" survey of your processing methods? His recommendation may be the answer to a vital processing or cost problem. Rochester Engineering and Centrifugal Corp., 108 Buffalo Road, Rochester, N. Y.

ROCHESTER ENGINEERING & CENTRIFUGAL CORP.



ABOVE: A KELCALOY corrosion resistant pressure vessel.
LEFT: A shell for continuous filter.
RIGHT: A cold propane surge tank.
BELOW: A large digester.

KELLOGG-BUILT PRESSURE VESSELS

for the process industries

FUSION WELDED

PRESSURE VESSELS

Integrally Lined Corrosion Resistant Pressure Vessels

HEAT EXCHANGERS AUTOCLAVES

DIGESTERS

PIPING - PLAIN AND CORRUGATED

CHEMICAL PROCESSES generally impose unusually exacting requirements upon pressure vessels. Kellogg customers in the process industries have found that the knowledge, resourcefulness and ability of Kellogg engineers is of the greatest economic and technical value to them in designing and fabricating processing equipment to meet the most severe operating conditions confronting them.

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"Masterweld" pressure vessels for the Power, Refinery and Chemical Industries. Power Plant and Industrial piping. Heat Exchangers, Radial Brick Chimneys, Plastic Refractories. Cross, Holmes-Manley, de Florez and Tube and Tank cracking units. Gas Polymerization Units. Deasphalting, Dewaxing, Solvent Extraction, Acid Treating Plants, Absorption Plants and Pipe Stills.

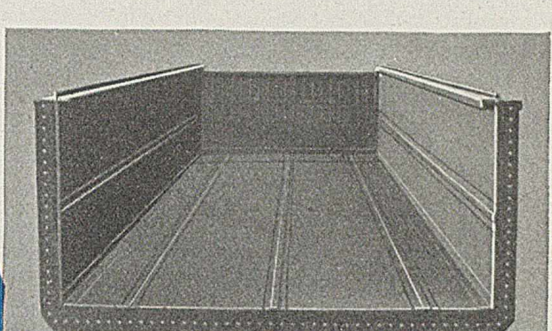
PLIOWELD

for every corrosion-proofing job

THERE is no job too large and none too small for Goodyear Plioweld Rubber Lining. It bonds permanently to any metal surface from small pipes, pumps and valves to largest processing and pickling tanks. It does not loosen, split or crack with vibration — is not affected by alternate wetting or drying or temperature changes and withstands severe impacts without rupturing.

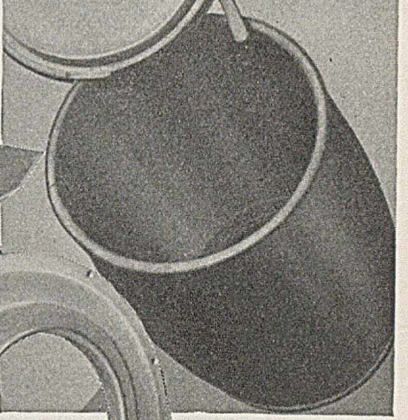
Because of these advantages Plioweld practically eliminates maintenance expense and permanently safeguards chemicals from discoloration, toxic changes and "iron pick-up." Every installation is specially formulated to meet your individual chemical problem. The G. T. M. — Goodyear Technical Man — will be glad to give you full information, backed by performance records, on this money-saving lining. To consult him, write Goodyear, Akron, Ohio, or Los Angeles, California.

THE GREATEST NAME IN RUBBER
GOODYEAR



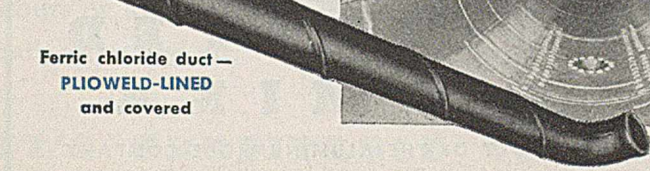
Section of 60′ continuous pickling tank — PLIOWELD-LINED

Sewer pipe elbow — PLIOWELD-LINED



Acid drum — PLIOWELD-LINED

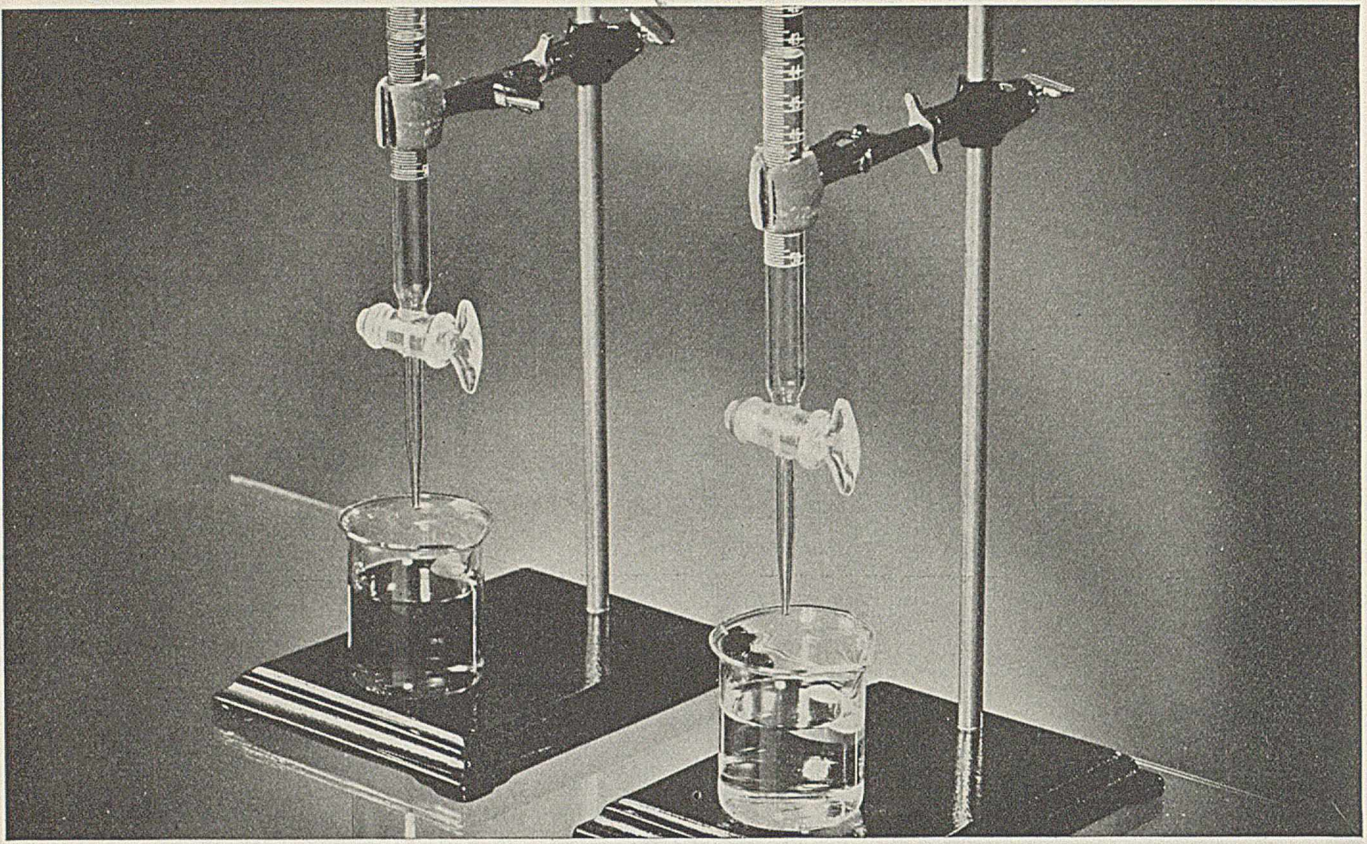
Tank car — PLIOWELD-LINED



Ferric chloride duct — PLIOWELD-LINED and covered

Fan wheel and side plate — PLIOWELD-LINED

BELTS
MOLDED GOODS
HOSE
PACKING
Made by the makers of Goodyear Tires



ANOTHER PROBLEM SOLVED BY ADSORPTION!

ACTIVATED ALUMINA EFFICIENTLY REMOVES MOISTURE FROM LIQUID MIXTURES

Ingenious applications of this adsorption phenomenon of Activated Alumina are meeting a constantly widening circle of process problems. It's a versatile function. Name your need! For you, it will efficiently remove moisture from air and other gases, or effectively dehydrate liquids. With such characteristics, Activated Alumina can serve hundreds of diversified uses — recovering valuable vapors and gases, reconditioning oils, etc. It is also employed as a catalyst and as a catalyst carrier. Would it expedite your process? Get all the facts about it, send for the free booklet, "*Activated Alumina, It's Properties and Uses.*" ALUMINUM ORE COMPANY. Sales Agent, ALUMINUM COMPANY OF AMERICA, 1911 Gulf Building, Pittsburgh, Penna.

Activated Alumina is easy to use

ADSORPTION: Activated Alumina removes moisture from gases and vapor at substantially 100% efficiency.

REACTIVATION: Controlled heat, applied by any convenient means (electric resistors, hot gas, or coils for circulating steam or hot oil) reactivates Activated Alumina. Thus it is adapted to simple cycles of use and reactivation.

INERT: Activated Alumina is chemically inert and nontoxic, insoluble in most commercial fluids.

STRONG: It resists abrasion, and has mechanical strength which prevents packing.

MANY SIZES: All variations of pressure, flow-rate, and viscosity can be met by mesh sizes of Activated Alumina ranging from powder to 1½ inch lumps.

ALORCO

ACTIVATED ALUMINA

A PRODUCT OF THE ALUMINUM ORE COMPANY

"Have you heard of the wonderful one-hoss shay,
That was built in such a logical way
It ran a hundred years to a day?"

INDUSTRY IN MASSACHUSETTS

TODAY AS ALWAYS

STILL BENEFITS FROM CONSCIENTIOUS CRAFTSMANSHIP

Just as in the days when Oliver Wendell Holmes' worthy deacon built himself the perfect chaise, labor in Massachusetts continues to be proud of its skill. Thousands of intelligent workers with that splendid heritage of pride in a job well done still contribute a priceless asset to industry in this State.

But, the opportunity of employing the best and most level-headed labor in the world is but one of the advantages Massachusetts bestows on industry. Within the compass of 500 miles from the heart of Massachusetts are most of the major markets of the North American continent — reached in 24 hours or less, linked by improved highways, rail, water and air.

In every way, industrial-minded Massachusetts encourages industry. Manufacturing corporations here enjoy the lowest taxes of any industrial state, and Massachusetts banks, long familiar with industrial needs, stand ready to support any industry new or old which justifies their aid. Special steps have been taken to provide ready financing for industries to settle here.

Massachusetts invites new industries and offers unparalleled inducements. Write for "Industrial Advantages of Massachusetts", a brief, readable book of accredited facts.

THE MASSACHUSETTS DEVELOPMENT AND INDUSTRIAL
COMMISSION · STATE HOUSE, BOSTON, MASSACHUSETTS

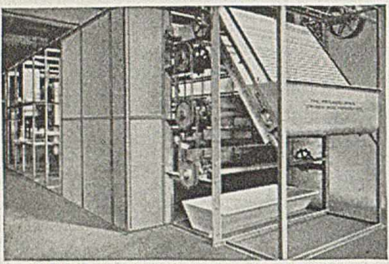
IT'S PROFITABLE TO PRODUCE IN MASSACHUSETTS

LOWER DRYING COSTS ✓
GREATER CAPACITIES ✓✓
HIGH SPEED DRYING

WITH MODERN "HURRICANE" DRYERS

Depending on the materials to be dried, "Hurricane" High-Speed Dryers frequently save as much as 50% in operating costs and labor. In many cases *one "Hurricane" has replaced 3 or 4 old* machines. In all cases, labor and steam costs are greatly reduced. Faster drying, increased capacity, and higher quality products are assured.

Truck-Tray Dryer



Multi-Pass Continuous Conveyor Dryer

"Hurricane" Dryers embody many exclusive engineering features: Aero-Therm Units, which circulate larger volumes of heated air—higher drying speeds—stream-lined construction—maximum output in minimum space.

Let us conduct TESTS in your plant, without cost, to prove just WHAT YOU CAN SAVE.

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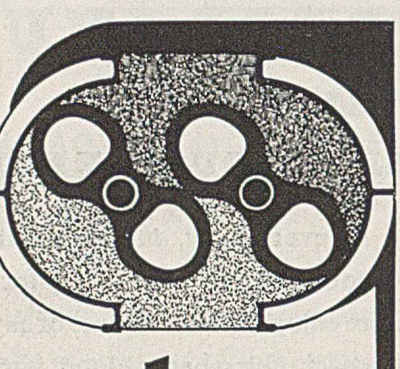

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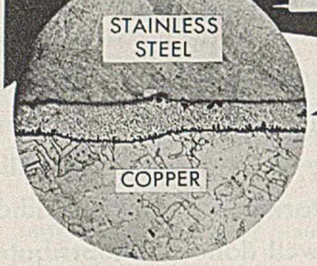

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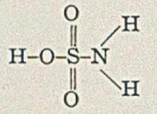

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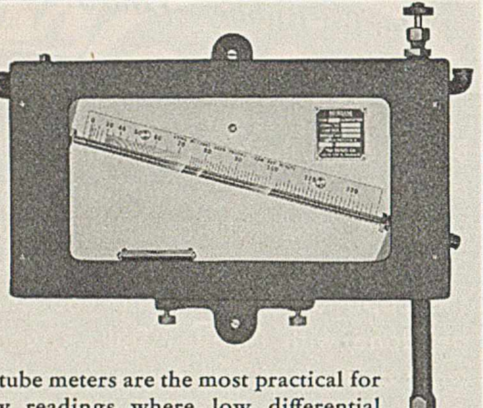

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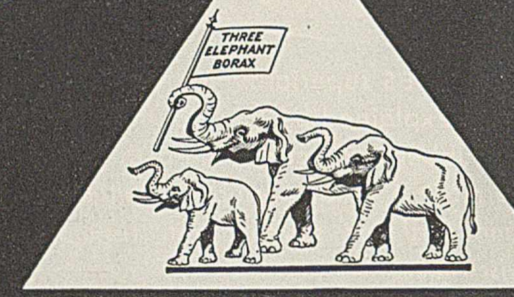

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THE FACTS: Louisville Dryer engineers were called in to correct existing dryer which was turning out only $39,900 of dried product, at the extremely high cost of $35,700.

RESULTS: New Louisville Dryer was designed and installed. Profits upped from $4,200 to $30,450 per year!

★ ★ ★ ★

The manufacturer featured above is now making $26,250 *extra profit* every year by his use of a Louisville Dryer.

This is *not* an unusual performance. It is probably fairly close to the *average* improvement achieved by the *average* Louisville Dryer over "competitive" equipment. It is probably close to the figure *you* could save by "changing to Louisville."

FORMER DRYER
(Steam-jacketed batch type)

Annual output, tons	2,100
Value, at $19 per ton	$39,900
All drying costs	$35,700
Net annual return	$4,200

LOUISVILLE DRYER
(Rotary, Continuous type)

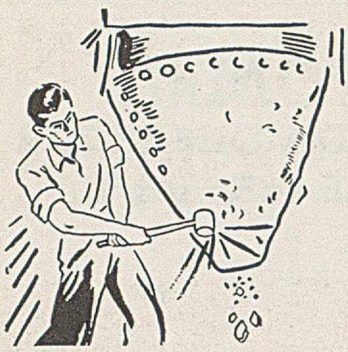
Annual output, tons	2,100
Value at $19 per ton	$39,900
All drying costs	$ 9,450
Net annual return	$30,450

SUMMARY

Net annual return, Louisville Dryer	$30,450
Net annual return, "Competitive" dryer	$ 4,200
Annual net increase in profit	$26,250
Installed cost, Louisville Dryer	$25,000
Annual return on investment	105%

All over the country, hundreds of obsolete dryers are wasting from $10,000 to $40,000 per year for their owners—figuratively *burning up a fifty dollar bill, or a hundred-dollar bill, every day they operate.*

If you would like to know the relative efficiency of your *drying* operations, Louisville will gladly study your plant, and tell you exactly what would happen if you should install a Louisville system. After that, it's up to you . . . *Address:* Louisville Drying Machinery Company, *Incorporated*, 433 Baxter Avenue, Louisville, Kentucky.



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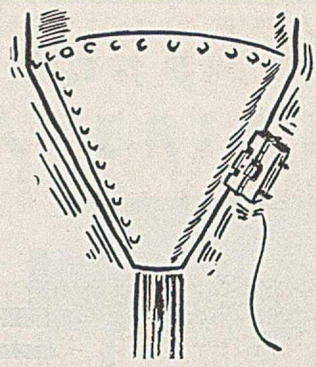

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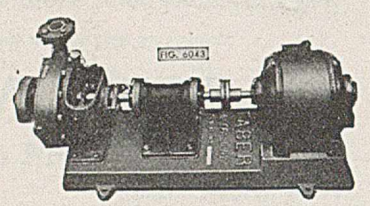
ADAPTED TO YOUR NEEDS



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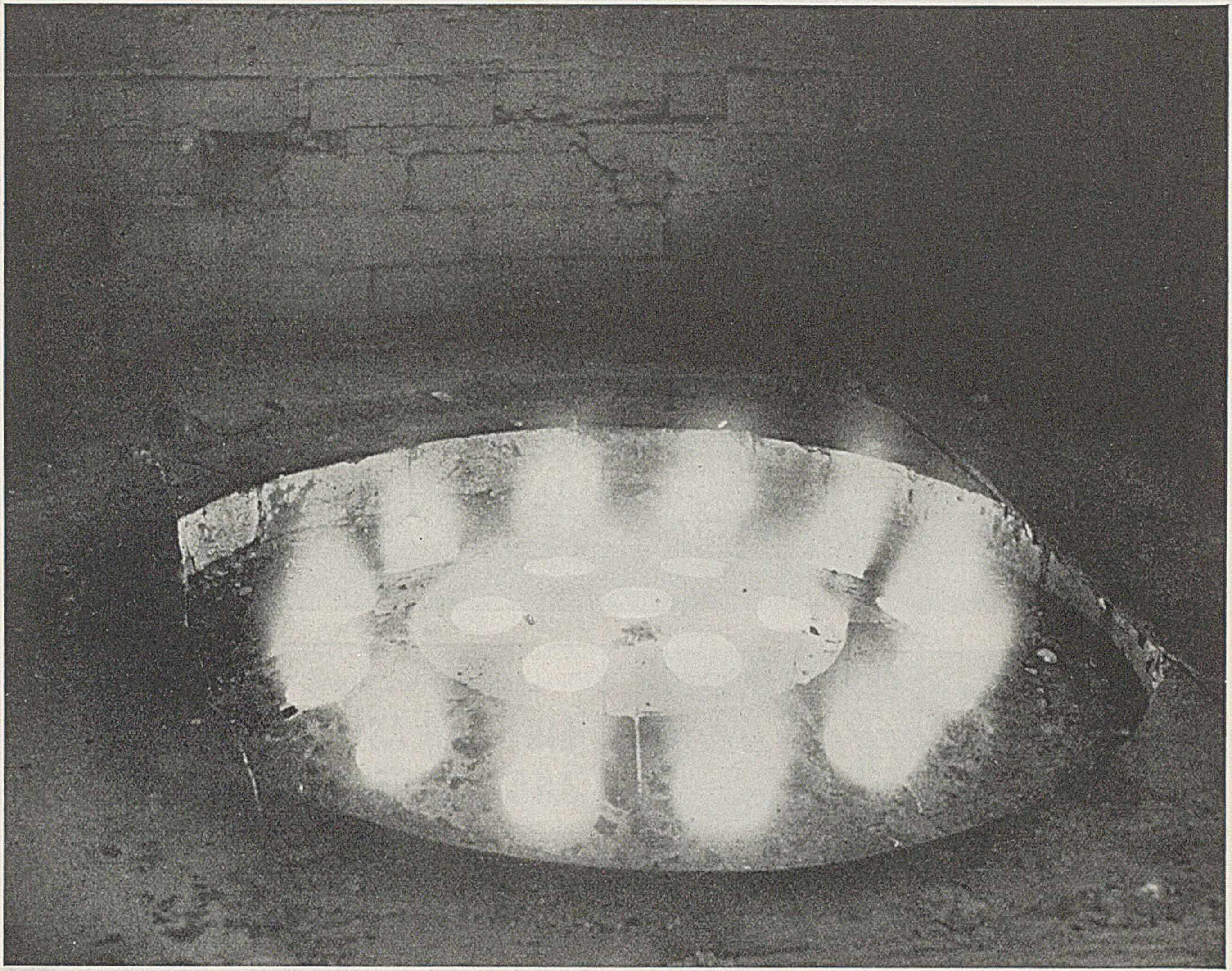

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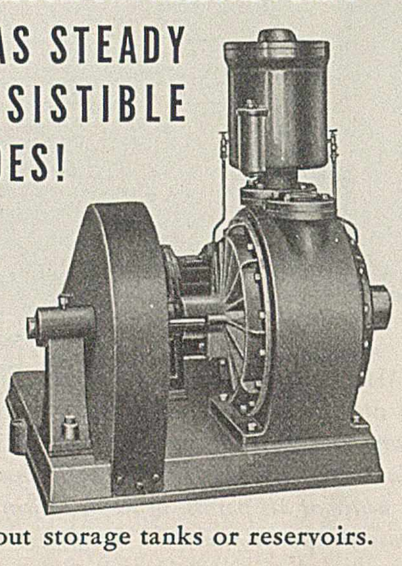

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