



The Editor's Point of View

AID PLUS INVESTMENT. There has been a great deal of effort expended on the part of many individuals and groups with the object of finding employment for technically trained men and women who suffer from a temporary lack of demand for their services. This work has been rewarded with some success, but the number of places found has been out of proportion to the labor expended in either locating or creating them, and despite the best of plans there are well-trained people actually in need.

One of the newest movements involves the co-operation of colleges, universities, and perhaps industries with unused laboratory space with the federal or other government agencies in position to supply funds. This proposal has come out of the many discussions of the Committee on Unemployment and Relief for Chemists and Chemical Engineers, which concentrates its thought upon the problems of the New York Metropolitan Area. There has been some response so far as the laboratories in educational institutions in New York City are concerned, and the plan is recommended to other educational institutions elsewhere. It contemplates that the institutions shall assume the full cost of laboratory materials and the operating expenses for such special research, leaving the funds to be supplied from relief appropriations to be almost wholly devoted to providing a maintenance wage for the research workers. There are other angles to be considered, such as the ownership of any patentable discoveries that may result from such work, but the difficulties are surmountable.

No one seriously contends for the discontinuance of research. Even labor, which in the minds of some has suffered as a result of technical advance, favors the prosecution of research, and we are slowly coming to realize that the fault, if any, is not in the furtherance of science and the application of its results, but rather in how the benefits have been distributed. Too often applied science has meant complete leisure for a few, instead of a little more leisure for all. Even though the application of science is retarded in times of economic stress, research must go forward. We have drawn heavily upon our accumulation of scientific knowledge and have thus far failed to make up for it by the addition of more fundamental information. The

need for the data continues, and there is good reason to believe that, under the direction of those supervising such researches, the money spent from public relief funds in the manner indicated would not only directly aid those requiring assistance, but prove to be a wise investment. This is more than can be said, perhaps, for the majority of the money that may be distributed under the heading of "emergency relief."

The plan is also worthy of support since it involves utilizing the services of these people in the way in which they are best trained to work. Many of them must be helped in any event, and it is far wiser to let that aid take the form of support for the type of work for which they are fitted and in which they would be happiest. Further, the result may be expected to be of value ultimately, if not useful immediately, in that variety of ways which characterizes scientific truth.

There is another group which also deserves any assistance our local sections and individual members can give. We refer to the graduates of 1932. There are hundreds of young men and women who entered college when there was a demand for the type of work they are capable of doing and who in some cases have completed their training at a considerable sacrifice on their part and that of their parents, only to come from our educational halls to find their services in no demand. This is true of bachelors, masters, and even those now equipped with doctors' degrees. Those with special creative ability may be expected to find some new way of earning a livelihood. For such, the present is a real opportunity. Some will be so fortunate as to be able to continue their training in school another year, thereby becoming better fitted for the competition for openings which is certain to exist. Still others should and will be glad to accept any type of employment that offers. This is surely no time to be too particular. Manufacturers and those who direct laboratories should have in mind apprentices of today for the personnel of tomorrow and give these young people an opportunity, provided only their placement is not to the detriment of experienced employees or those with family responsibilities.

The whole matter is, of course, being taken very seriously. There is every disposition to help and reason

to believe that chemists and chemical engineers as a group will come through our present difficult times quite as well as any other professional class. When once the people are able to dispel the unreasoning fear which holds them back, they will rapidly regain the ground that may have been lost.

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CHLORINATED HYDROCARBONS TOXIC. Notwithstanding great improvement in the petroleum derivatives used for dry-cleaning purposes, they are all highly inflammable and their vapors form explosive mixtures under certain conditions. Some of the chlorinated hydrocarbons have long been attractive, therefore, to the dry-cleaning industry because they offered little or no fire or explosion hazard. Carbon tetrachloride was put to some use years ago, but at that time it had not been learned that successful redistillation without decomposition depended on avoiding certain metals in the apparatus, and that moisture should also be absent. This solvent was too expensive to be used and discarded, and being unable to redistil it successfully, the dry cleaners had to forego it.

At present modern closed systems have put carbon tetrachloride actively in the field for dry-cleaning purposes, but unfortunately just what has been meant by closed systems has been misunderstood or misinterpreted in some quarters, with the result that here and there small operators have been induced to install faulty systems. In a few cases a mere enclosure of old apparatus has seemed adequate to the uninformed, and the results have been just what might be expected. Research and demonstration have indicated the type of closed system that is highly effective. With this, satisfactory results have been secured with safety; without it, there is a hazard.

A large part of the difficulty is due to the toxicity of some of the chlorinated hydrocarbons. Those who are interested in the extension of the industrial uses of these compounds should be thoroughly acquainted with all that is involved, and must do their utmost to educate the users. A generation ago the threshold of danger with carbon tetrachloride was placed at 160 parts of the vapor per million parts of air, and more lately with experimental animals it was found that, while a somewhat greater quantity could be withstood, there was every indication that there is a grave risk at concentrations well below 500 parts per million. In these experiments there were cases where oral administration was withstood without difficulty but breathing of the fumes proved fatal. In the case of workmen there is little hazard to be feared from the possible entry of the hydrocarbon orally, but there is danger from inhalation and also through skin absorption. The other chlorinated hydrocarbons now of interest in this industry are trichloroethylene and ethylene dichloride. Far less is known concerning their toxicity than of carbon tetrachloride, for the latter

has been used in various ways in industry for a much longer period, and besides has a medical history.

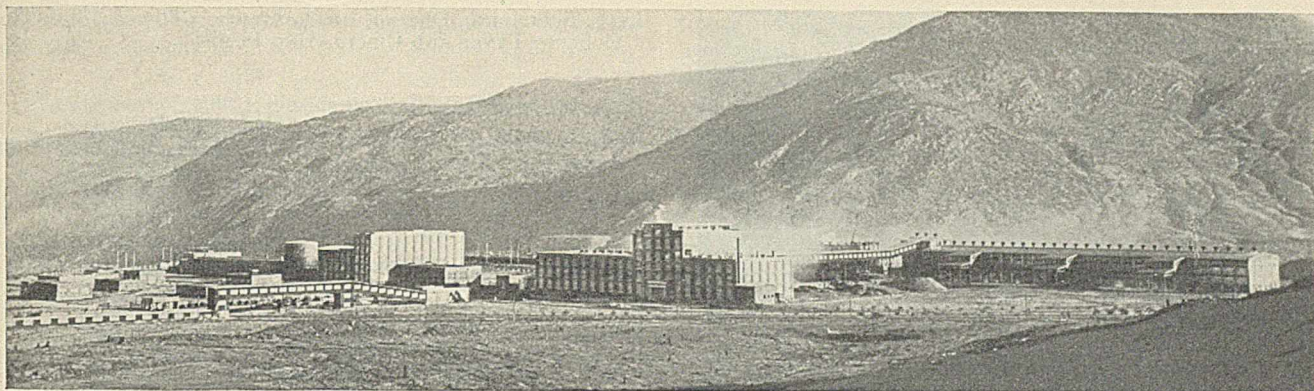
It is difficult for the average chemist to appreciate how careless are workmen and many other people with these and other solvents. There is at least one instance on record where carbon tetrachloride was freely used for shampooing the hair with fatal results, undoubtedly both on account of absorption and inhalation of the fumes. But there is no point in insisting that such reagents be eliminated from industry. It is known that they are perfectly safe to use under proper conditions, and it should not be difficult to ascertain the limits and then to maintain exposures well below them. So far as dry cleaning is concerned, some steps have been taken, notably by the Ohio Industrial Commission, requiring completely closed systems to be used on any large scale. Users have learned that there is great danger from fire where petroleum derivatives are involved. Health hazards exist with certain other solvents, but possible catastrophes may be completely avoided if these hazards are understood, warning heeded, and common sense precautions observed. They should be taught in advance of any possible catastrophes that there is a health hazard in the use of certain other solvents but that it is a simple matter to protect themselves and their workers completely against them by the simple exercise of a little common sense.

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EARMARKED GIFTS. The times have served to stress the importance of bequests left without special designation but for use as changing circumstances may require. Institutions which have suffered a marked decrease in income because of the lowered return from their investments find themselves handicapped in readjusting their resources to meet requirements, since in most cases bequests have been left for particular and definite purposes.

Benjamin Franklin was perhaps one of the wisest of all Americans, and yet he failed in his effort to predict the future. In his will he left bequests to both Boston and Philadelphia, the interest from these sums to be used in aiding artisans and others. They were to repay with certain rates of interest so that a fund might be accumulated for wide usefulness. But other means of financing made their appearance, and those who needed help in Franklin's day were not followed by others who required similar assistance.

There are many examples of money left for special uses where the opportunity to apply the income in the way specified has long since vanished. The changing needs of any institution make it imperative for the trustees to have available unallocated funds which can be directed into the channels most needful at the moment. In no other way can embarrassment be avoided and the greatest good accomplished. Times like these impress upon us the utility of unearmarked money and the futility of endeavoring to provide for a too distant future.



FERTILIZER PLANT

Contact Sulfuric Acid Plant

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THE prospectors who years ago followed the Columbia River on the Canadian side of the international boundary and discovered mineral-laden veins in what is known as the Rossland district, British Columbia, little thought that they were laying the foundation of a great industrial enterprise.

Between then and now the Consolidated Mining & Smelting Company of Canada, Ltd., came into being; copper and lead smelters and a zinc refinery sprang into operation at Trail, just north of the United States boundary line; smoke laden with sulfur dioxide passed over the boundary line into the State of Washington; the International Joint Commission met to consider the effects of smelter smoke on vegetation on the United States side of the boundary; technologists developed and adopted means for recovering sulfur dioxide from smoke; a sulfuric acid plant was established to utilize the sulfur dioxide; phosphoric acid and anhydrous ammonia supplies were made available by appropriate processes; and finally, because there were no industrial centers near enough to utilize these chemicals, they were converted into ammonium sulfate, monoammonium phosphate, and "triple superphosphate," standard fertilizers which are marketed and used in adjoining agricultural areas.

CAUSE OF INTRODUCTION OF SULFURIC ACID PLANT

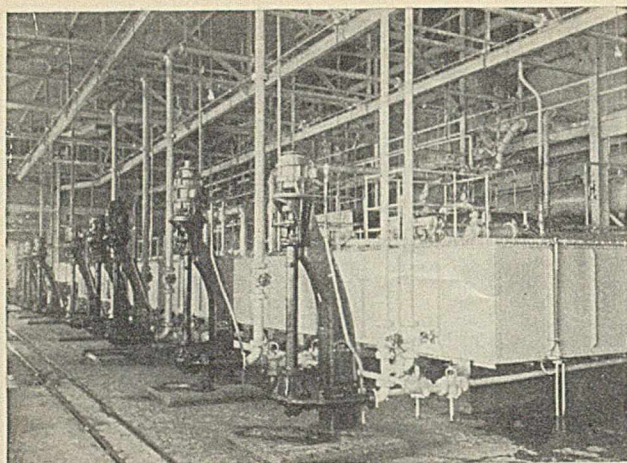
The sulfuric acid plant as a unit of the coordinated operations of the company was introduced in the production program in a logical sequence of events. In the early nineties a copper smelter was constructed at Trail to treat the sulfide ores from the Rossland district only a few miles distant. The usual operations of concentrating, roasting, smelting, converting, and electrolytic refining of the copper constituted the unit processes of the copper smelter. With the roasting, smelting, and converting operations came the initial steps in creating later a smelter smoke problem.

In the subsequent development of the mining regions of British Columbia, silver-bearing lead ores, zinc ores, and complex ores containing both metals, became available at Kimberley, 250 miles from Trail. Differential flotation came into the general plan of metallurgical operations of the company, making available both lead and zinc concentrates. Coincident with the development of concentration by flotation, it was decided to erect at Trail a lead smelter and later an electrolytic zinc plant. Both of these plants produce sulfur

dioxide in calcining operations. In the lead smelter, Dwight-Lloyd sintering machines are used to reduce the sulfur content of the ore containing 14 to 15 per cent sulfur to a sulfur content of 1.4 to 1.5 per cent in the calcine in two sintering operations. Prior to the utilization of sulfur dioxide for the production of sulfuric acid, the zinc-concentrate roasting plant housed twenty-five Wedge mechanical furnaces, each 25 feet in diameter. Each furnace had seven hearths, air-cooled rabble arms, and coal-dust firing equipment. The capacity of each roasting furnace was 36 to 38 dry tons of concentrates per day. The roaster gas passed through a plate-type Cottrell treater to remove dust and arsenic and was delivered to the atmosphere by a 400-foot concrete stack.

The continued operation of the copper, lead, and zinc metallurgical plants finally brought the smelter smoke issue into the foreground. The daily capacity of these units is 425 tons of lead, 400 tons of zinc, and 60 tons of copper. The sulfur, originally in combination with these metals in the form of sulfides, is removed for the most part as sulfur dioxide and delivered to the atmosphere during calcining and other metallurgical operations. The enlargement of these plants from time to time and the construction of larger and higher smoke stacks contributed to a wider distribution of smoke over a larger area and also to a higher concentration of the sulfur dioxide in the atmosphere of the same area.

In the natural course of events there arose the problem of the effects of smelter smoke on vegetation. There were variables in the local situation that created unusual procedures in dealing with the smoke problem. The smelter is located about 12 miles from the international boundary between Canada and the United States. Claims were made that there was injury to vegetation extending for some miles into the State of Washington. The extent and character of the injury were investigated by the scientific staffs of the Canadian and United States Departments of Agriculture, and by the Consolidated Mining & Smelting Company. The results of these investigations were reported to the International Joint Commission in December, 1929. In the summer of 1930 the commission recommended to the Governments of the United States and Canada that the damages for past injury to the private owners of agricultural lands in the State of Washington be paid, and that the Consolidated Mining & Smelting Company continue the efforts already under way to eliminate the possibility of the continued occurrence of damage from smelter smoke in the area investigated.



LEFT: SCRUBBING, DRYING, AND ABSORPTION TOWERS, SHOWING COOLING TANKS AND CIRCULATING PUMPS

CENTER (UPPER): COTTRELL TREATERS FOR REMOVING SULFURIC ACID MIST

CENTER (LOWER): HEAT EXCHANGERS AND CONVERTERS

RIGHT: AMMONIA PLANT; BRYAN DONKIN HYDROGEN AND NITROGEN GAS MIXERS WITH SIX-STAGE COMPRESSORS IN BACKGROUND

Anticipating fully the effects and consequences of delivering large quantities of smelter fumes to the atmosphere, even though not adjacent to an agricultural region, the company over a long period investigated all aspects of the problem. Noted for its progressive policies in maintaining a highly trained technical and research staff, the company developed and officially adopted a costly and extensive remedial program, many months prior to the decision of the International Joint Commission. Adhering to the plans adopted for one unit of the works, a sulfuric acid plant was added as an integral unit of the metallurgical flow sheet of the zinc plant. Purification of the gases from the zinc roasting furnaces and the conversion of the sulfur dioxide into sulfuric acid completely removes the possibility of injury to plant life from that source.

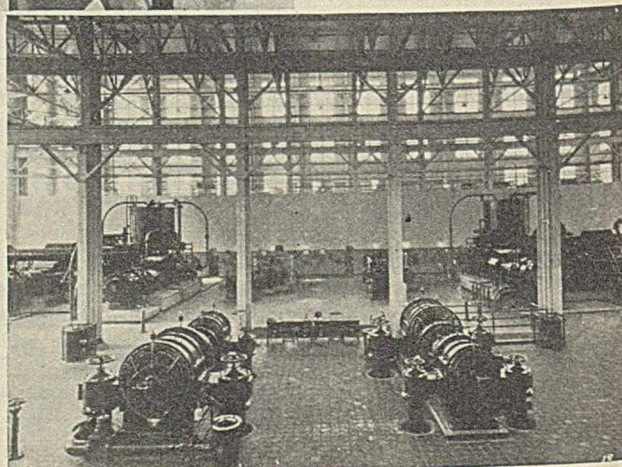
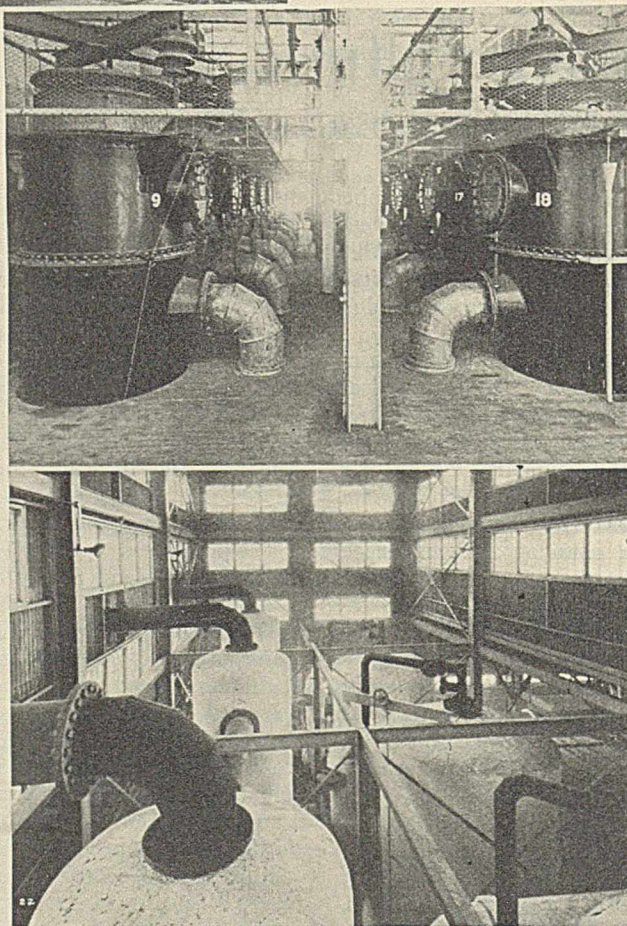
The remedial program made provisions for both the production of sulfuric acid and the utilization of the acid in the manufacture of fertilizers. However, for the industrial chemist and the chemical engineer special interest first centers in the acid plant as the corner stone of the new industrial structure of the company's operations.

PLAN OF CONTACT PROCESS

After due consideration of comparative production costs and of the strength and quality of sulfuric acid desired, it was decided to erect a contact process plant. In fertilizer production, acid of the concentration produced by the chamber process has most frequently been used throughout the country. In this instance, however, it was decided originally to use acid of higher concentration than is usual in the production of

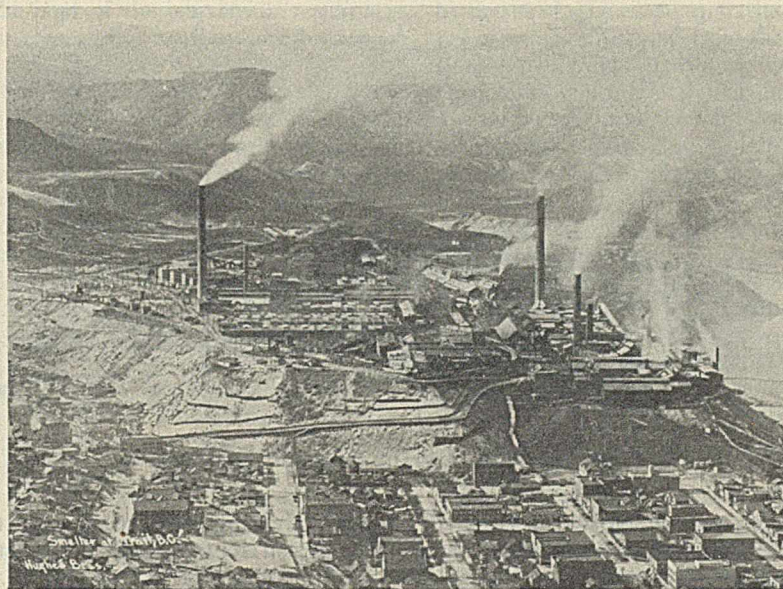
superphosphate. The local market, though small at present, can utilize oleum and 93 per cent acid to the best advantage. Balancing all the variables, both economic and technical, the final results were favorable for the selection of the contact process.

In 1928 a modified Grillo contact acid plant was constructed. This unit has a capacity of 39 tons of acid per day and utilizes a platinum catalyst distributed on magnesium sulfate and asbestos. Later three additional units, each having a capacity of 112 tons of acid per day, were erected. In these units a vanadium catalyst made in England is utilized in the converters in which sulfur dioxide is oxidized to sulfur trioxide. The total capacity of the plant is 375 tons of 100 per cent acid per day.



The flow sheet or ground plan of the plant shows the following unit operations:

- I. Production of sulfur dioxide in calcining department of electrolytic zinc plant.
- II. Purification of roaster gas.
 - A. Before division to the four acid plant units.
 1. Hot plate Cottrell precipitator for dust and arsenic removal.
 2. Weak acid scrubber.
 - B. After division of gas to the separate units.
 1. Water scrubber.
 2. Cottrell precipitator.
 - a. Removal of sulfuric acid mist.
 3. Drying.
 - a. Weak acid, 80 per cent.
 - b. Strong acid, 93 per cent.
 - C. Entrained acid removal by coke filter.
- III. Conversion of sulfur dioxide to sulfur trioxide.
 - A. Heat exchangers.
 - B. Converters.
 - C. Cooling station.
- IV. Absorption of sulfur trioxide in 98.5 per cent sulfuric acid.
- V. Acid cooler.
- VI. Storage of 93 per cent acid.
- VII. Delivery to fertilizer plant by pipe line installation.



COPPER AND LEAD SMELTERS AND ZINC ELECTROLYTIC PLANT

In making arrangements to utilize the sulfur dioxide of the zinc roasting plant, modifications in operating methods and in plant design were necessary in order to increase the sulfur dioxide content of the roaster gases. Calcining in Wedge hearth furnaces was discarded in favor of what is frequently termed "flash roasting," a procedure which is suggested by the fact that the zinc plant handles flotation concentrates in a very fine state of division—200 mesh and finer. The concentrates are brought into the proper physical condition for calcining by a two-stage drying process and by disintegrating lumps in a ball mill. The dry finely divided concentrates are then calcined in a hot chamber in a manner similar to the combustion of powdered coal in metallurgical furnaces. The air blown into the furnace with the concentrates is supplemented by secondary air admitted in proper amounts for the purpose of controlling the combustion reactions. In this method of roasting, the combustion rate is high and therefore no auxiliary heating or firing is necessary as is the case when zinc concentrates are roasted in a hearth furnace.

The flash method of calcining produces a large amount of flue dust of such a degree of fineness that it cannot be successfully recovered in dust chambers of the usual construction. The cyclone collector was therefore substituted for dust chambers. The positive oxidizing conditions and the high temperature of the flash method produce a flue dust that is completely roasted and therefore can be sent directly to the zinc leaching plant; in contrast, the flue dust from a hearth calcining furnace must be returned to the furnace for a second treatment.

The roaster gases from the furnace outlet contain 9 per cent of sulfur dioxide which is satisfactory for sulfuric acid produc-

tion by the contact process. The percentage is reduced by leakages in the purification system. The economic significance of using waste sulfur dioxide for sulfuric acid production becomes apparent when it is noted that the plant under maximum production of 375 tons per day requires 129 tons of elementary sulfur, equivalent to 258 tons of sulfur dioxide on the basis of 95 per cent conversion. The fact that this amount of sulfur dioxide would otherwise be wasted is a very important factor in the consideration of the enterprise from the standpoint of production costs. The treatment of the

roaster gases after leaving the zinc plant is under the control of the acid plant organization.

PURIFICATION PROCESS

There are a number of steps in the purification process in the course of the gas to the converters. Dust and arsenic removal is effected in a hot Cottrell treater which removes 96 per cent of the dust carried by the gas after leaving the cyclone separators. The dust removed at this point goes to the zinc leaching plant. The Cottrell treater is of the plate and

wire type. There is a total of eight sections; each section contains sixteen 10 × 12 foot corrugated iron plates, 8 inches apart, with the high tension wires placed midway between the plates. Unidirectional current at 50,000 volts produced by synchronous motor-driven 25 kv.-amp. rectifiers serves this plant. The entire treater handles 40,000 cubic feet of gas per minute, which enters at a temperature of 720° F. and leaves at 450° F.

The gas from the hot Cottrell treater passes next to the weak acid scrubbers. There are four of these: three are circular, with a diameter of 20 and a height of 28 feet; one is square, 12 × 12 feet in cross section, and 28 feet high. Each scrubber is constructed of lead, lined with acid-proof brick of English manufacture, and filled with brick checkerwork of the general type of construction found in Glover towers used in chamber process plants. The gas passes in counterflow to the acid stream which has a strength of 70 to 80 per cent. The circulation of the acid is accomplished in the following manner: From a large storage tank, supported several feet above the scrubber, the acid flows by gravity to a distribution tank on the top of the tower. The acid is distributed over the brick checkerwork of the tower through thirteen lead pipe nozzles attached to pipe lines leading from the distribution tank. Four feet below the outlet of each nozzle there is a suspended concave disk on which the falling acid strikes. This has the effect of spraying the acid over the checkerwork in a fashion similar to the distribution of sewage on a trickling filter.

From the bottom of the tower the acid passes to three water coolers, each containing four banks of pipes. Sediment is removed by settling, and then the acid is pumped back to the storage tanks above the scrubbing tower by a Lewis hard-lead acid pump. When it is necessary to supply fresh acid to the

circulating system of the scrubber, the old acid is utilized in the zinc leaching plant. Following this preliminary treatment in the hot Cottrell treater and weak acid scrubber, the gas now passes to the main flue. This flue is constructed of lead, and is rectangular in cross section with dimensions 62 × 50 inches. Branches from the main flue carry correctly proportioned amounts of gas to each of the four units of the acid plant. Here the purification of the gas is continued independently in each unit, in the following steps: washing with water, mist removal by a Cottrell treater, two stages of drying, and entrained acid removal by a coke filter.

The water washing station is in all respects similar to the weak acid scrubber previously described. This applies to the dimensions of the scrubber and its design with respect to the circulating system.

Sulfuric acid mist is removed in Cottrell precipitators. Eighteen circular treaters are constructed of steel and lined with lead. In each treater there are twenty-one 6-inch pipes. The lead pipes are grounded, and in the center of each is a suspended steel wire covered with lead, carrying a unidirectional electric current furnished by a mechanical rectifier at 50,000 volts. In the case of a Cottrell treater of this character it is necessary to provide a dry atmosphere in the compartment containing the high tension installation. This is accomplished by piping dry sulfur dioxide gas from the main blower to the top of each treater.

The sulfur dioxide gas used for drying then passes into the circuit with the treated gas. The mist-laden gas enters at the top of each treater. It flows down to the bottom of the treater and then up through the lead pipes in which are suspended the high tension wires. A sealed drip at the bottom of each treater collects the acid removed from the gas stream. The acid recovery for all of the eighteen treaters constituting the mist-removal installation for each unit of the plant is 2 tons of 3 per cent acid per day.

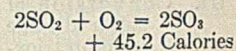
Two stages of drying follow the mist removal in the Cottrell precipitator. In each case the drying towers are circular, with a diameter of 20 and a height of 28 feet. The weak acid (80 per cent sulfuric acid) drying tower is constructed of lead, lined with brick, and filled with brick checkerwork in accordance with the usual construction. On the other hand, the strong acid (93 per cent sulfuric acid) drying tower is constructed of steel, lined with brick, and filled with coke. The gas passes countercurrent to the acid flow in each case. Circulating pumps and tanks are used in operating the washing, drying, and absorption towers. The acid is stored in a tank above the towers from which it passes to the distribution box. Thirteen nozzles equipped with concave spray disks, as previously described, spray the acid over the checkerwork. After passing through the cooling tanks, the acid is returned to the top of the tower by Lewis pumps, and the cycle is repeated. All tanks and coolers have lead-pipe ventilating systems which draw sulfur dioxide gas to the main gas flue at the entrance to the wash water tower.

The last stage in the purification of the gas is the removal of entrained acid. This is accomplished by passing the gases through a box filter filled with coke. This filter, constructed

of lead, is 18 × 18 × 6 feet high; the coke bed is 5 feet 3 inches deep. The bottom of the filter bed is composed of coke pieces, 4 inches in size decreasing to a -4 mesh at the top. The gas is delivered to the bottom of the box and rises through the coke.

The purification process is now completed. Dust, sulfuric acid mist, water vapor, and entrained acid have been removed. Up to this point the gases have been under suction equal to 7 inches of water and are now passed to the preheaters and converters under a pressure of approximately 3 pounds. This suction and pressure is produced by an Elliott turboblower of

350 h. p., operating at 3500 r. p. m., and having a capacity of 17,000 cubic feet per minute. Under the pressure produced by the Elliott blower, the purified gas passes to the heat exchanger and to the converter where conversion takes place according to the reaction:



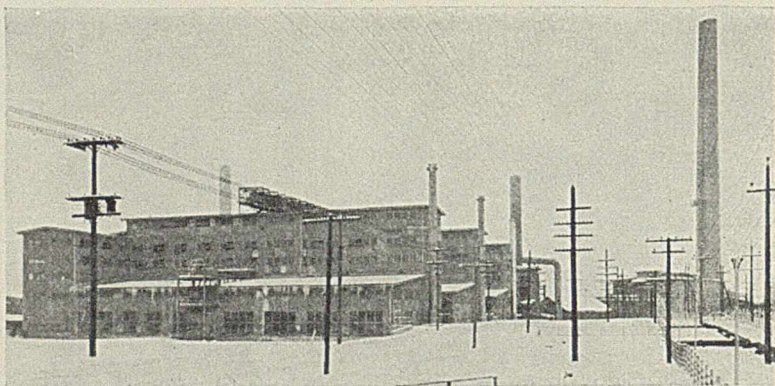
This is a reversible action and therefore has definite kinetic and

thermodynamic requirements. At equilibrium, maximum conversion is obtained at a temperature approximately between 400° and 425° C. (752° and 797° F.). However, within these temperature limits the reaction velocity is too slow for commercial production. It is necessary, therefore, to carry out the reaction at a temperature higher than 400° or 425° C. at some stage of the conversion process. In practice, satisfactory reaction velocity is obtained at temperatures ranging somewhat above 500° C. (932° F.) and in some cases as high as 600° C. (1112° F.) depending upon certain variables. These requirements of the equilibrium reaction and the fact that the same is exothermic indicate that it is advisable in many cases that conversion take place in two stages. In the first stage the higher temperature limits should be used to increase the reaction rate. After intermediate cooling, the gases should then pass to the second conversion stage. In other words, there should be a vertical temperature gradient in the converters which conforms to the theoretical limits stated above, and at the same time it is desirable that there be a uniform temperature distribution in horizontal sections. These theoretical requirements are met in the conversion system described below.

Figure 1 is a diagram showing the flow of gas through the heat exchanger, *A*, and the converter, *B*. The heat exchanger is 4 feet in diameter and 20 feet high. It contains a bank of 1-inch pipes through which the hot sulfur trioxide gas from the converter passes to the air coolers outside the plant. The converter, 18 feet high and 11 feet in diameter, contains 349 vertical tubes, each 5 inches in diameter. These tubes are filled with vanadium catalyst in the case of three of the plant units, and a shelf converter in the fourth unit. Below the tube outlets there is a layer of catalyst 12 to 18 inches in thickness. In each converter using vanadium, there is a total of 11 tons of catalyst.

CONVERSION PROCESS

Considering the operation of the conversion unit, the purified gas containing 5.5 per cent sulfur dioxide enters the



FOUR UNITS OF CONTACT SULFURIC ACID PLANT

top of the heat exchangers at a temperature of 25° C. (77° F.) and under a pressure of 28 ounces. It then flows downward outside the pipes which are heated by the hot sulfur trioxide from the converter. Leaving the heat exchanger at a temperature of 310° C. (590° F.), the sulfur dioxide can be admitted to the converter at two points, *C* and *D*. The main stream of gas enters the converter at *C* above the catalyst layer, and is further preheated by contact with the outside of the hot catalyst tubes as it passes horizontally from one side of the converter to the other, guided by baffles and upward through a perforated baffle to the space above the catalyst tubes. In this manner some of the heat of the conversion reaction is absorbed by the entering gas, prior to the second stage of conversion.

Adjustments in the final temperature of the reacting gas stream can be made by admitting gas at 310° C. direct from the heat exchanger through the by-pass, *E*, to a point, *D*, in the converter. The conversion reaction then takes place as the gas stream passes downward over the catalyst in the tubes. Intermediate cooling occurs through heat absorption by the entering gas and in the space above the 18-inch catalyst layer in the bottom of the converter, where the second stage of conversion takes place.

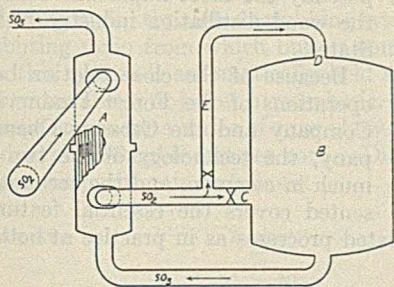


FIGURE 1. FLOW SHEET OF HEAT EXCHANGER AND CONVERSION UNIT

Temperature measurements are taken periodically at points in the converters by the use of Republic electric pyrometers. Four of these measurements are taken within the catalyst mass. Summarizing a set of temperature readings, the gas delivered to the converter has a temperature of 310° C. (590° F.). The gas is preheated so that within the catalyst mass in the pipes the readings are 570°, 603°, 535°, and 552° C. (1058°, 1117°, 995°, and 1026° F.). The average of two readings above the catalyst layer is 440° C. (824° F.) and the sulfur trioxide gas leaves the converter at a temperature of 460° C. (860° F.). Under these operating conditions the average conversion is 94 per cent. In fact, the conversion reaction is carried out under conditions quite within the theoretical limits which govern an equilibrium reaction of this character. In addition to the temperature measurements of the conversion process by electric pyrometers, an Inglehart automatic recorder is used to indicate the sulfur dioxide content of the entering gas. The accuracy of the recorder is periodically checked by chemical analysis. The sulfur trioxide gas passes to the heat exchanger and then to an air cooler en route to the absorption tower.

From the air coolers the sulfur trioxide gas passes to an absorption tower which in its essential parts is similar to the drying and scrubbing towers previously described. This tower, however, is constructed of steel, lined with brick, and filled with quartz. The tower is 15 feet in diameter and 26 feet high. The sulfur trioxide enters the base of the tower and flows countercurrent to the 98 per cent acid used for absorption. Acid of this strength has sufficiently low vapor tension to prevent the formation of sulfuric acid droplets. The absorption acid is pumped into the center compartment of a

cast-iron tray on top of the tower. From the center compartment the acid is distributed over the entire tray, the function of which is to distribute the acid uniformly over the quartz packing. The tray is 3 inches deep and contains a series of holes $\frac{3}{16}$ inch in diameter, centered 5 inches apart. In each hole there is a glass tube which projects $\frac{1}{2}$ inch above the bottom of the tray, through which the acid flows.

Acid of 99.5 per cent strength is drawn off on opposite sides of the bottom of the absorption tower. To the acid from one of these outlets sulfuric acid is added to bring the concentration to 98 per cent. This acid is cooled and pumped by means of a Lewis pump to the absorption tower. The 99.5 per cent acid drawn off from the opposite side of the absorption tower is diluted with water to 93 per cent. This represents the acid production of the plant, which passes through a water cooler and then to storage in one of two 2100-ton steel tanks. Through a 4-inch pipe line the sulfuric acid is pumped to the fertilizer plant storage tanks, a distance of 6000 feet. The difference in level between the two storage systems is 400 feet, and it is interesting to note that each of two four-stage Allis-Chalmers centrifugal pumps deliver the acid at the rate of 1 ton per minute. The contact plant, together with its delivery pipe line, constitutes the connecting link between the metallurgical works (the source of the waste sulfur dioxide) and the new chemical plant designed for fertilizer production.

FERTILIZER PLANT

Erected on an allotted area of 60 acres of ground, for the purpose of utilizing the contact sulfuric acid, the fertilizer plant, representing an expenditure of \$10,000,000, employing three hundred men, utilizing electrical energy at the rate of 34,000 h. p., and producing 300 to 400 tons of fertilizer products per day, is the most impressive part of the new development program of the Consolidated Mining & Smelting Company. An abundance of cheap power, developed by three company-owned electric power plants on the Kootenay River, and sulfuric acid from waste smelter fumes are important considerations in viewing the economic factors of the enterprise. Indicating more directly the role of sulfuric acid, it is utilized in two divisions of the fertilizer plant. In one, ammonium sulfate is produced by the interaction of synthetic ammonia and the contact acid. In the other division, phosphoric acid is manufactured from phosphate rock shipped from Montana and Idaho. The phosphoric acid, in turn, is used to produce monoammonium phosphate and "triple superphosphate."

For the production of synthetic ammonia by Fauser catalyst columns, both hydrogen and nitrogen are required. The hydrogen is produced by electrolysis, using an installation of Knowles, Fauser, and Stuart (bell type cells), and also the Pechkranz filter-press type of cell. Two Claude complete units produce the necessary nitrogen from liquid air.

Located far from industrial and manufacturing centers, the sulfuric acid plant of the Consolidated Mining & Smelting Company has more than usual significance. It has the effect of increasing the interlocking features of the entire production program of the company and sets up a degree of coordination somewhat unusual in metallurgical and chemical operations.

RECEIVED April 18, 1932.

"NONINFLAMMABLE" AIRPLANE FUEL. Development of a "non-inflammable" motor fuel for use in airplanes is being studied by the French Government in conjunction with private French organizations, and recent tests are said to have been highly satisfactory according to *L'Air*. Elimination of the fire risk is said to have been accomplished in the new fuel, which does not leave the residue of carbon accumulation.

Suida Process for Acetic Acid Recovery

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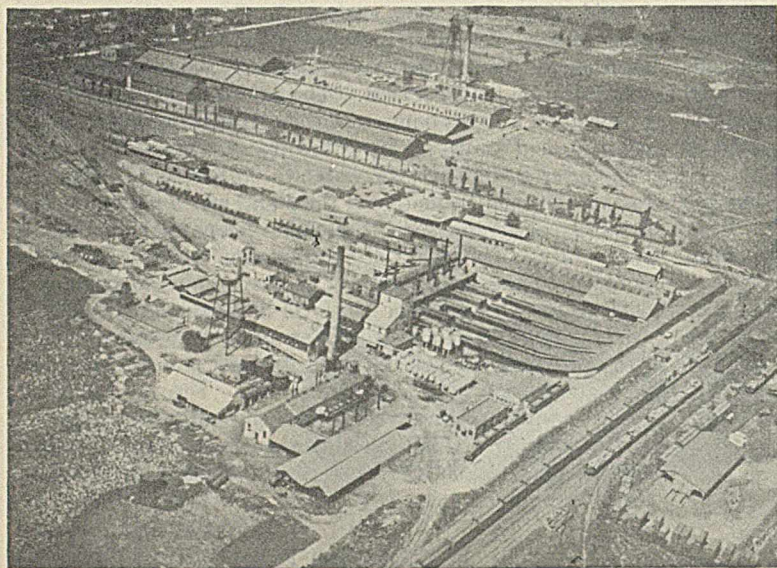


FIGURE 1. AIRPLANE VIEW OF FOREST PRODUCTS CHEMICAL COMPANY

WITH practically the disappearance of the production of charcoal iron and the advent of synthetic acetic acid and methanol, the wood distillation industry suffered a serious decline. No new plants were constructed, and the future of those which continued in operation was far from hopeful. Radical improvements in the industry were in order if it was to survive.

Various efforts to produce acetic acid by direct processes (eliminating the intermediate material, acetate of lime) have been made, and many of them have led to results of commercial promise. With this encouragement, improvements in wood distillation methods have followed those in by-product recovery, and the revival of interest based on these developments will probably bring back to economic importance an industry that was well on the way to obsolescence.

One of the more promising processes for the direct recovery of acetic acid is that devised by Hermann Suida of Vienna, which, following considerable success in Europe, has been introduced into the United States by the Forest Products Chemical Company, of Memphis, Tenn.

The plant at Memphis was originally an acetate of lime operation. About three years ago it was converted to the Suida system without interruption of production. So successful has been the outcome that an associated interest, the Crossett Chemical Company, of Crossett, Ark., has been put into operation based on the experiences at Memphis. Present developments at Crossett and plans for future expansion along additional lines of chemical activity bring this town in the southeastern corner of Arkansas to the front as one of the outstanding points

of interest today along lines of chemical technology.

Crossett is a thriving community of about twenty-five hundred inhabitants, which has developed in connection with the activities of the Crossett Lumber Company. The timber holdings of this company involve 420,000 acres of land which are being scientifically cut and reforested. The village is a typical mill town of the better type with company store, hotel, community center, hospital, school, and playground. The town is served by the Rock Island, the Missouri Pacific, and the Ashley, Drew, and Northern Railroads, the latter the property of the Crossett Lumber Company. In this environment is taking place what is possibly the most important development in the wood distillation industry in the United States.

Because of the close relation between the operations of the Forest Products Chemical Company and the Crossett Chemical Company, the technology of the two plants has much in common, and the account being presented covers the essential features of the

Suida and related processes as in practice at both plants.

WOOD DISTILLATION

Each of the two plants is equipped for handling 80 cords of wood per day, though the Crossett plant is designed for expansion to a 200 cord daily capacity. The carbonization cycle is the same in both cases. A charge at Memphis consists of 10 buggies of 8 cords each; at Crossett, 8 buggies of 10 cords each. The wood is first treated in a predrier for 48 hours. Heat for this operation is furnished from flue gases from the retorts. The temperatures realized range from 150°

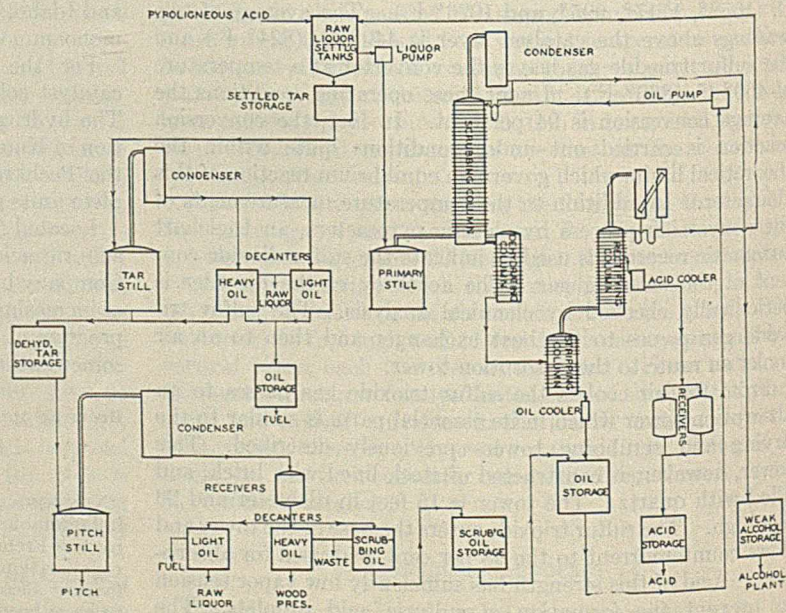


FIGURE 2. FLOW SHEET OF SUIDA PROCESS

to 200° C., driving off about 8 per cent of the moisture originally contained in the wood. The predriers at Crossett are of an improved down-draft design with automatic temperature control realized by admission of cool air as needed to avoid excess heating.

The Memphis retorts are of the conventional end-fired type, using retort gas, tar, and light oil from the plant (supplemented by coal) as fuels. The improved design at the Crossett plant is a radical departure from the usual. The retort gas is supplemented by natural gas. There are four combination burners along each side of the setting. The flame passes across under the retort, up the opposite side, and across the top, and the flue gases are withdrawn through ports in the bottom of the setting. The several units discharge flue gas into a common collecting flue which delivers to the predriers or the atmosphere as desired. The charge remains in the retorts 24 hours, during which time it is heated gradually to a maximum gas temperature of 400° to 425° C. and held at that temperature for the last 3 or 4 hours. The actual temperature of the charge is from 50° to 75° C. above that of the gas.

Gases leaving the retorts pass through water-cooled copper condensers and the condensed pyroligneous acid is led to a collecting tank. Noncondensable gases are conducted to a copper collecting main, through a scrubbing system, and then to a distributing main from which burner connections lead. The gas in this system is automatically held at pressures of 0.2 inch of water above or below atmospheric.

The average figures for a series of runs show a noncondensable gas yield of 6780 cubic feet per cord. During the entire cycle the gas composition is as follows:

CONSTITUENT	RANGE %	AVERAGE %
CO ₂	60 - 40	53
Illuminants	1.7 - 4	2.9
CO	28 - 16	27.2
CH ₄	2 - 36	15.3
H ₂	0 - 2	0.5
B. t. u./cu. ft.	100 - 400	290

After being discharged from the retorts, the buggies of charcoal remain 48 hours in closed coolers and 48 hours in open cooling sheds, following which they pass to a tipple for dumping. The charcoal is carried to the charcoal house for crushing, sorting, and packing.

The gas scrubber is 4 feet in diameter and 25 feet high. The scrubbing operation produces a clean gas which does not

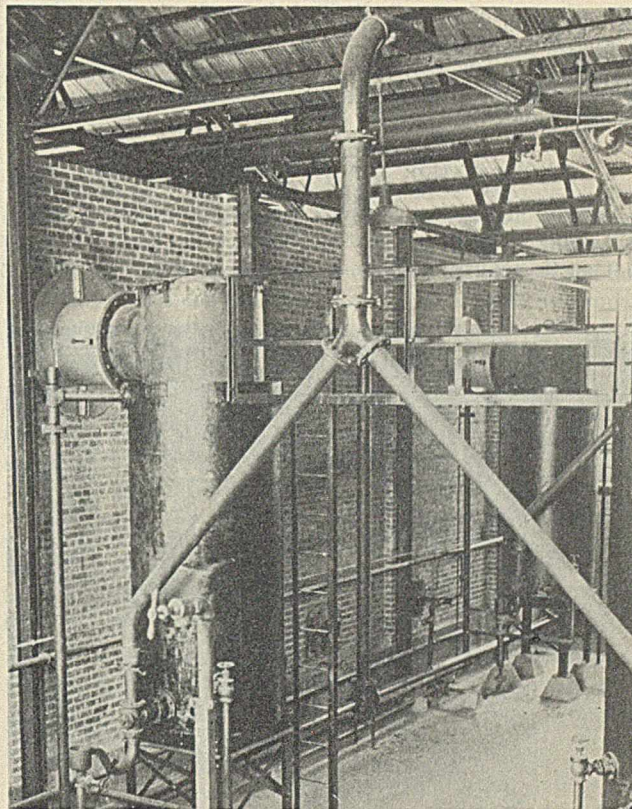


FIGURE 3. RETORT CONDENSERS (CROSSETT CHEMICAL COMPANY)

foul the burners, and the scrubbing liquors which are added to the pyroligneous acid increase the alcohol yield about 1 gallon per cord.

By the application of the down-draft system to the predriers and retorts, only the cooler gases that have given up their heat reach the discharge flue, reducing heat losses to a minimum.

The design of the retort settings makes possible very even and accurate temperature control. An automatic recorder registers the temperature of each retort every 10 minutes. A given typical chart shows four retorts starting at somewhat varying temperatures to have come within a temperature range of 10° C. after 10 hours and to have continued within a range of 20° C. for 7 hours till a maximum of 410° C. was reached.

BY-PRODUCT RECOVERY

The methods of by-product recovery at both plants center around the Suida process for the direct production of acetic acid. The essential feature is the preliminary separation of a scrubber oil in which the acetic acid is later dissolved, followed by its extraction and rectification under vacuum. In European practice the alcohol is removed prior to the scrubbing out of the acetic acid. The modification which has been in successful use at Memphis for three years, and which is in operation at the Crossett plant, removes the acetic acid first, followed by the separation of the methanol by simple rectification methods. The advantages claimed for the Suida process are that it is continuous, yields an acid of high concentration and purity, involves a small number of separate operations, requires a relatively small amount of steam, and uses as the

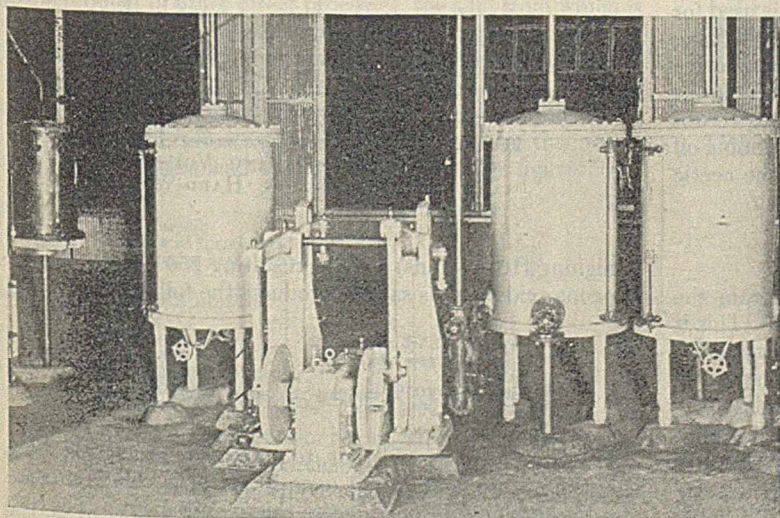


FIGURE 4. METERING FEED PUMPS AND CONSTANT-LEVEL FEED TANKS (CROSSETT CHEMICAL COMPANY)

extraction agent an oil distilled from the hard-wood tar, making the plant independent of the use of materials of outside source. The corrosion of the apparatus in the Suida system is found to be very slight, and maintenance cost as a whole is low.

SEPARATION AND TREATMENT OF TAR

The pyroligneous acid from the wood distillation plant, containing 3.75 to 4 per cent alcohol by weight and 6 to 8 per cent acetic acid by volume, is run into a raw-liquor settling

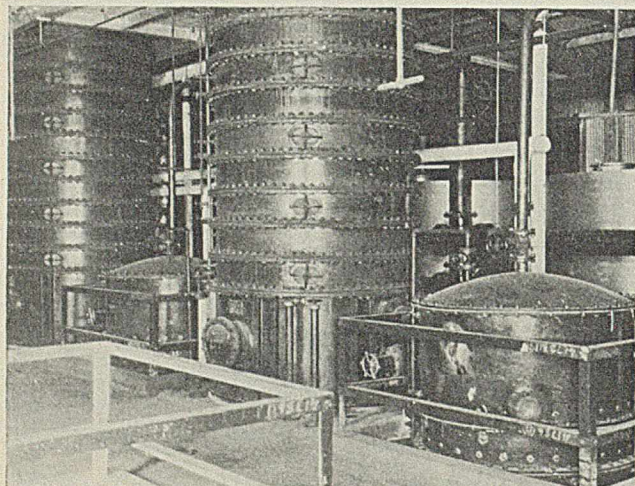


FIGURE 5. LOWER SECTIONS OF SCRUBBING COLUMNS AND UPPER SECTIONS OF DEHYDRATING COLUMNS (CROSSETT CHEMICAL COMPANY)

tank in which the insoluble tar settles out. The amount of settled tar is about 22 gallons per cord. This is drawn off into settled-tar storage tanks and from thence steam-distilled in a copper tar still. The distillate containing certain oils is run into oil decanters, and the lighter separated oils are used for fuel. Heavier oils are used as fuel or added to the tar system as may be desired. The supernatant layers in the decanters are returned to raw-liquor storage, as they contain acid and alcohol values. The residue from the tar stills and portions of the heavier oil from the decanters are run into the dehydrated-tar storage tanks, and this product is distilled under vacuum in the pitch still. The distillate from this operation is cut into light-oil, heavy-oil, and scrubbing-oil fractions. The upper layer in the light-oil fraction is used for fuel, and the lower layer returned to the raw-liquor settling tank. The settled-out heavy oil is sold as wood preservative and similar materials; the upper layer is waste. The lower layer in the scrubbing-oil fraction is drawn off to scrubbing-oil storage; the upper layer is waste. This scrubbing oil is the extraction medium used in the recovery of the acetic acid. The residue in the pitch still is hard-wood pitch.

RECOVERY OF ACETIC ACID

By means of a metering pump the upper layer from the raw-liquor settling tanks is fed into the primary still. This is a copper unit equipped with steam coils and live-steam inlet. By means of the coils the acetic acid and alcohol are vaporized and they pass on to the scrubbing column. The residue from the still is discharged into the fuel system. The unit gradually becomes fouled and is periodically tarred down by live steam.

By means of another metering pump, scrubbing oil is fed into the top of the scrubbing column up through which the vapors from the primary still are passing. The oil with the

acetic acid in solution passes down through a dehydrating column and into a vacuum exhausting column in which the acetic acid vapors are stripped from the oil. The vapors pass into the acetic acid rectifying system while the stripped oil goes through a cooler and returns to the storage tank to repeat the cycle.

The continued use of the scrubbing oil causes it to thicken to an objectionable degree. Periodically a portion of the supply is discarded and fresh oil from the tar system added to maintain the desired consistency.

The vapors from the scrubbing column contain the methanol, and the condensate is conducted to the weak-alcohol storage tanks. The methanol content is about 4 per cent.

The acetic acid vapors which have been flashed off in the exhausting column are rectified in the upper vacuum column. Acetic acid running from 90 to 92 per cent by weight is drawn off at a point part way up the column and is run through a cooler and receiver into aluminum storage tanks. The weaker acid from the top of the column, ranging from 20 to 25 per cent in strength, is run back to the raw-liquor settling tank and passed through the system again.

ALCOHOL RECTIFICATION

The weak alcohol from the scrubbing-column distillate is concentrated in an exhausting and rectifying system producing a product equivalent by gravity to 90 per cent methanol. It contains from 10 to 14 per cent acetone. A second rectification produces fractions designated as weak alcohol, acetone, 99 per cent alcohol, and allyl alcohol. These are further rectified or blended to produce the desired grade of product.

YIELD, QUALITY, AND USE OF PRODUCTS

In addition to the noncondensable gas and other materials consumed in the processing, 1 cord of average hard wood

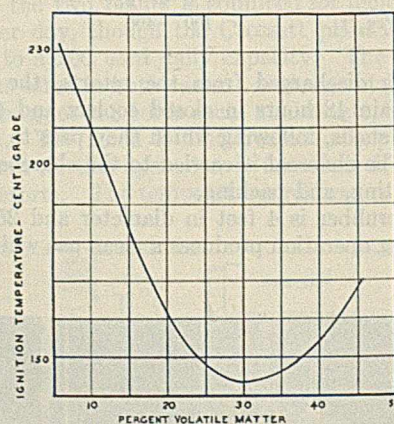


FIGURE 6. RELATION BETWEEN IGNITION TEMPERATURE AND VOLATILE MATTER CONTENT IN HARD-WOOD CHARCOAL

(weighing 4100 pounds) and the resulting 250 gallons of pyroligneous acid yield as salable products the following:

Charcoal (15.5% volatile)	1330 pounds
Oil (wood preserving, etc.)	4-5 gallons
Pitch	40-45 pounds
Acetic acid (100% basis)	120 pounds
Methanol (100% basis)	9 gallons

Practice has indicated that, to avoid spontaneous ignition, charcoal should contain not over 20 per cent volatile matter, and the product obtained meets this requirement. The chief outlet for charcoal is domestic use, and a well-established market is being built up in the southern cities. Considerable

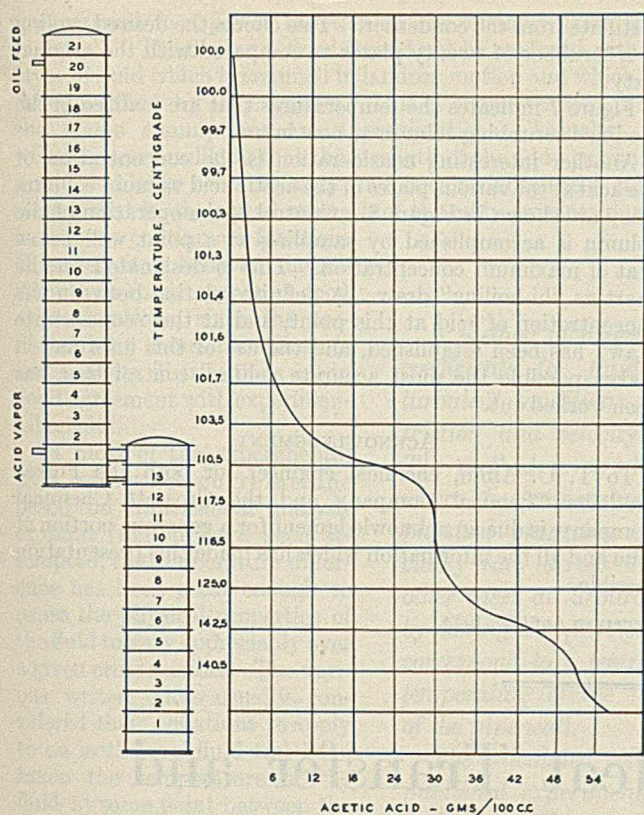


FIGURE 7. RELATION BETWEEN TEMPERATURE AND ACETIC ACID CONCENTRATION IN SCRUBBING COLUMN

quantities are sold for making carbon disulfide and sodium cyanide, and a development which is under consideration is the building of a foundry for making cast iron with charcoal as a fuel.

The oils from the tar-refining operations which are marketable are used in mineral flotation, wood preservation, and as insecticides, with particular reference to termites and poultry lice.

Hard-wood pitch is used as a rubber softener and as electric insulation. It has a very high dielectric strength and is particularly free from damage by petroleum oils.

Although not absolutely water-white, the acetic acid recovered by the Suida method is of sufficient purity to be used commercially without further refining. This is in contrast to the product of other direct processes, the acid from which is usually about 65 per cent in strength and frequently requires further concentration to be of commercial quality. The addition of one more column to the Suida system would produce a water-white product of nearly 100 per cent strength.

Repeated determinations on acid produced by the plants under consideration lead to the following average figures:

	%
Acid as acetic	92.0
Reducers as formic acid	1.0-0.8
Aldehydes as acetaldehyde	0.039-0.034

By sodium salts method:

	%
Acetic acid	99.15
Formic acid	0.85
Acids of higher molecular weights	Trace

The product contains no odor of butyric acid and is miscible with benzene in 1 to 1 proportions.

The chief use to which the acetic acid is put is the manufacture of solvent esters, such as butyl and ethyl acetates, though fair amounts are converted to glacial and other refined forms.

The fractions from the methanol rectification are blended to produce a 94 per cent denaturing grade which makes up about 65 per cent of the output, the balance being marketed as 95 per cent antifreeze and solvent methanol.

RESEARCH AND CONTROL

A system of operations as complicated as wood distillation and by-product recovery calls for constant study and accurate routine checking. A research and control laboratory is maintained at the plant of the Forest Products Chemical Company and a control laboratory at the Crossett Chemical Company. In addition to these, control stations in the still-houses are used for the making of frequent routine tests.

At the Memphis research laboratory a pilot plant was carefully studied before the commercial Suida installation was made. The initial full-sized plant involved several modifications of the European process. Based on more than two years experience with this plant, the one at Crossett was designed to incorporate additional improvements, the merit of which has been demonstrated by about six months operation.

Certain of the many contributions of these developments to the present status of the industry are presented as of particular interest.

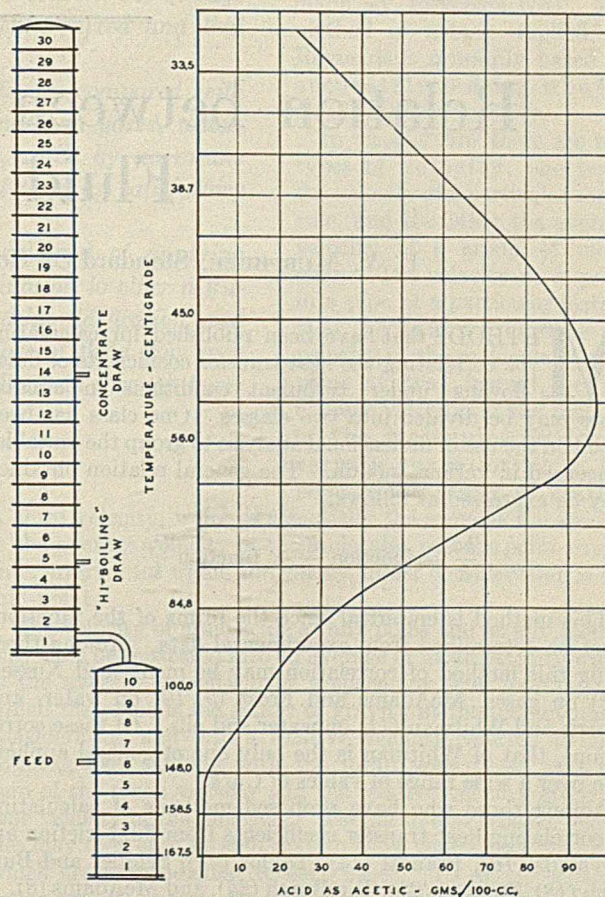


FIGURE 8. RELATION BETWEEN TEMPERATURE AND ACID CONCENTRATION IN VACUUM RECTIFYING SYSTEM

Previous reference was made to the relation between volatile matter in charcoal and the tendency for spontaneous ignition. As the result of a study of this problem the retort treatment has been designed to bring the volatile matter in the charcoal to about 15.5 per cent at 950° C. It was found that the kindling temperature of the charcoal has passed a minimum and is again rising if the volatile matter is reduced to this figure. Insufficient treatment resulting in the lower

kindling temperature has been the cause of spontaneous ignition. The holding of the charge at maximum temperatures for three or four hours at the end of the distillation assures the low volatile content and the resulting higher ignition point.

The relations between temperature of carbonization, percentage volatile matter at 950° C., and ignition temperature of charcoal are indicated in Figure 6.

The change in the order of removal of acetic acid and alcohol has been mentioned in the explanation of the Suida process. In addition to this development, other improvements were worked out at Memphis. The nature of the absorption oil was changed to promote greater efficiency. A more striking improvement has resulted in the use of a smaller scrubbing column.

The original Suida scrubbing unit was made up of sixty plates. Unless there is a means of cooling the upper portion of the column, temperatures at the top run up to 108° C. as compared with 102° C. at the bottom. The original method of reducing the top temperature to the desired 99–100° C. was to accomplish heat loss by radiation in the upper sections. The modification worked out at Memphis involves the return to the upper portion of the column of a small amount of

distillate from the condenser. This effects the desired cooling in a scrubber of twenty plates as compared with the original sixty.

Figure 7 indicates the temperatures that are realized in the modified scrubbing column as now in use.

Another interesting consideration is the concentration of the acid at the various plates of the acetic acid vacuum column. They are shown in Figure 8. Control of the operation of the column is accomplished by sampling at a point well below that of maximum concentration. This is designated on the chart as "hi-boiling" draw. A definite relation between the concentration of acid at this point, and at the "concentrate draw" has been established, and the use of this information makes possible the most accurate column control that has been worked out.

ACKNOWLEDGMENT

To T. C. Albin, chemical engineer for both the Forest Products Chemical Company and the Crossett Chemical Company, is due an acknowledgment for a generous portion of time and all the information which has made this presentation possible.

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Relation between Heat Transfer and Fluid Friction

E. V. MURPHREE, Standard Oil Company of Louisiana, Baton Rouge, La.

METHODS that have been published for calculating or correlating the heat transfer coefficients of fluids flowing under turbulent conditions in circular pipes may be divided into two classes. One class has been based on the use of dimensional analysis to group the variables concerned in various moduli. The general relation obtained may be expressed as follows:

$$\frac{hd}{k} = \text{function} \frac{dG}{\mu} \times \text{function} \frac{C\mu}{k}$$

This method is empirical since the forms of the functions must be determined from experimental data. Among those using this method of correlation may be mentioned Nusselt (12) on gases, McAdams and Frost (9, 10) on water, and Morris and Whitman (11) on water and oils. Of these correlations, that of Whitman is the only one of general application over a wide range of values of $C\mu/k$.

Among those who have proposed methods of calculating or correlating heat transfer coefficients from fluid friction are Reynolds (16), Prandtl (14), Taylor (24), Schiller and Burbach (18), Stanton (23), Ten Bosch (25), and McAdams (8).

Reynolds assumed that a certain relation existed between fluid friction and heat transfer in turbulent flow and suggested that the heat transfer coefficient could be predicted from the equation:

$$h = M + NG$$

where M and N are constants

Prandtl, Taylor, and Ten Bosch have extended Reynolds' analysis to allow for the presence of a film of fluid flowing in laminar motion along the wall. The type of equation proposed is:

$$\frac{hd}{k} = \frac{\int \frac{dG}{\mu} \frac{C\mu}{k}}{1 + m \left(\frac{C\mu}{k} - 1 \right)}$$

The value of m in this equation may either be determined from experimental data on heat transfer coefficients or predicted from theoretical considerations. The value of 0.37 is sometimes used for m . According to Prandtl, m is an inverse function of the one-eighth power of dG/μ .

Prandtl's equation is derived on the assumption that a layer of fluid in laminar flow exists at the pipe wall, and that the temperature gradient for transferring heat in the main body of the fluid is similar to the velocity gradient in the main body.

It should be noted that Prandtl's equation with a constant value for m becomes essentially independent of $C\mu/k$ for values of $C\mu/k = 5$, and higher. That is, in going from $C\mu/k = 5$ to $C\mu/k = \infty$, the heat transfer coefficient for a given value of dG/μ increases only about 10 per cent. This does not agree with data on oils such as those of Morris and Whitman (11) where the effect of $C\mu/k$ is much greater. This is felt to prove fairly conclusively that there is some error in the derivation of the Prandtl equation.

The essential difference between the method of predicting heat transfer coefficients developed in this paper and those previously proposed is that the existence of a viscous film at the pipe wall is not assumed. Instead, it is assumed that the eddy currents, while zero at the pipe wall due to boundary conditions, increase continually from zero at the pipe wall to a value which is constant for the main body of the fluid. It is further assumed that in the region over which the eddy currents vary, herein called the "film," their strength is

proportional to a power function of the distance from the pipe wall. The film as defined should not be confused with a layer of fluid which is assumed in laminar motion and which is called a "film" by some writers. It is of course realized that the above assumptions are approximations. Actually, it would be very unlikely that the strength of the eddy currents would suddenly cease to vary and become absolutely constant; that is, the actual strength of the eddy currents must be a more continuous function. However, it is believed the assumptions made represent good approximations, since the predicted heat transfer coefficients and velocity distributions are in good agreement with experimental results.

In most of the experimental data, with which correlations based on dimensional analysis or fluid friction have been attempted, the temperature difference has been great enough to cause the physical properties of the fluid to vary appreciably over a given cross section. The various writers have usually considered their equations to apply to an isothermal fluid and have taken the temperature of the fluid at some point between the pipe wall and the average fluid temperature. However, Morris and Whitman (11) have taken the properties of the fluid at the average fluid temperature, presenting separate curves for heating and cooling. This method is open to the objection that points for either heating or cooling would fall on a particular curve only for fluids whose physical properties vary similarly with temperature and where the temperature difference is the same. It is obvious that, as the temperature difference decreases, the heating and cooling curves will approach each other and will become identical when the temperature difference is sufficiently small so that the variation of physical properties between the center line of the pipe and the pipe wall is negligible.

The theoretical considerations of this article are limited to those cases in which the physical properties of the fluid have a negligible variation between the temperature of the center line of the pipe and the temperature at the pipe wall. In comparing the calculated results with experimental results where this condition is not fulfilled, an arbitrary correction is made.

DISCUSSION OF FLUID FLOW

It is well established that a fluid may flow in a pipe either in (1) laminar or viscous motion or (2) in turbulent motion, depending mainly on the value of the Reynolds criterion dG/μ . Laminar flow is characterized by the absence of eddy currents; turbulent flow is characterized by the fact that there are eddy currents. The frictional resistance under viscous flow conditions may be calculated from Poiseuille's law, which is based on the assumptions involved in the definition of viscosity and on the assumption that the fluid velocity at the pipe wall is zero. Frictional resistance for turbulent

flow is usually calculated from Fanning's equation, one form of which is:

$$\frac{dp}{dL} = \frac{2f\rho u^2}{a}$$

The friction factor defined above is employed throughout this paper; it is generally used by the English and German writers and is numerically one-half of that employed by Wilson, McAdams, and Selzer (27).

In this formula the friction factor, f , is dimensionless. The formula itself is obtained by dimensional analysis. For relatively smooth pipes, such as brass, copper, or large iron and steel pipes, it has been shown experimentally that f is a function of dG/μ only, and is otherwise practically independent of pipe size.

No complete theoretical treatment of turbulent flow has been developed. The most progress along theoretical lines has been made by Reynolds (16). The method of attack applied by Reynolds is primarily based on accurately defining what is meant by fluid velocity.

In viscous flow there are two types of velocity, one being the velocity of a particular molecule, and the other the average velocity of a group of molecules. The velocity at a point in a pipe at a particular instant may be taken either as the velocity of the molecule at that point at that instant, or the average velocity, at the instant, of the molecules within a certain space for which the point is the center of gravity.

A third velocity, which is essentially the same as the second, is the average velocity of the molecules past the point over a time interval for which the instant under consideration is the mid-point.

The velocity of a molecule at any point and at any instant may then be separated into an average or mean velocity which is the average velocity over a space (or time interval) for which the point is the center of gravity at the instant under consideration and into a relative velocity referred to non-rotating axes moving with the mean velocity so that the sum of the mean velocity and the relative velocity gives the true velocity of the molecule. The mean and relative velocities may then each be split up into three component velocities which are perpendicular to each other. To set up separate equations of motion for the mean velocity, which is the only reason for so splitting up the true velocity, it is necessary that the average energies of mean and relative motion of the space (or time) interval be separable. That is, if v and v' are respectively the components of the mean and relative velocities in the y direction, and m the mass of the molecule, it is necessary that

$$\Sigma^{1/2}m(v + v')^2 = \Sigma^{1/2}m(v^2 + v'^2)$$

where the summation is taken over all the molecules in the space (or time) interval. This necessitates that



A method of directly calculating heat transfer coefficients for fluid flowing in pipes under turbulent conditions from existing data on pipe friction and velocity distribution is presented. The method is strictly applicable only to cases where the temperature gradient is such that the physical properties of the fluid do not appreciably vary across the pipe cross section. For other cases an arbitrary correction may be made by taking the physical properties of the fluid to correspond to a temperature between the average temperature of the fluid when mixed and that of the pipe wall.

The calculated coefficients are compared with published experimental results on gases, water, and oils. The correlation, while by no means perfect, is believed to be at least as satisfactory as any so far presented.

The possibilities are mentioned of applying the author's method of calculation to other diffusional processes such as dehumidification and absorption, and to other types of fluid flow such as flow perpendicular to tubes and through tower packing.



$$\Sigma mv' = v \Sigma mv' = 0$$

Similar considerations apply to the other components. These conditions put certain limits on the minimum size of the space (or time) interval which may be taken. The minimum size of the space (or time) interval will be called the "period of the relative motion." Reynolds has shown that, in order to separate the average energies of the mean and relative motions over a relative motion period, it is necessary that the period of mean motion be infinite as compared with the period of relative motion. It may be shown from energy considerations that the ordinary equations

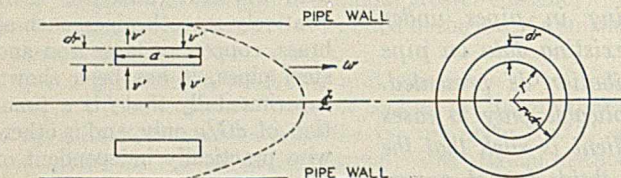


FIGURE 1. TURBULENT FLOW IN CIRCULAR PIPE

of motion for viscous flow refer to mean velocities and not actual molecular velocities. That is, the heat motion of the molecules is not included in the equations of motion. It is reasonably obvious that for this case this separation is legitimate, since the period of the mean motion is very large compared to the period of the heat motion.

The situation is more complicated for turbulent flow than for viscous flow on account of the eddy motion. For turbulent flow it is possible to separate the mean velocity into a mean mean velocity and a relative mean velocity in exactly the same way that the true velocity for viscous flow may be separated into a mean velocity and a relative velocity. The condition for this separation to be of value as previously developed is that the period of the mean mean velocity be infinite as compared with the period of the relative mean velocity. In this separation the relative mean velocity represents the eddy motion and bears the same relation to the mean mean velocity as the relative velocity bears to the mean velocity in viscous flow.

If the turbulent flow is such that the mean mean motion is steady and in one direction, then the period of the mean mean motion is infinite. As periods of relative mean motion are of necessity finite, the period of the mean mean motion is infinite compared to the period of the relative mean motion for this case, and it is possible to separate the average energies of mean mean and relative mean motion over a period of relative mean motion. Separate equations of motion for mean mean and relative mean motion may therefore be set up. The steady flow of fluid in a pipe or conduit meets the above conditions.

By separating the velocities as outlined, Reynolds was able, using exact analytical methods, to obtain certain basic equations for turbulent flow. Recent writers have developed these relations (summaries of which are given in citation 3) more simply using less exact methods similar to the following.

The two-dimensional flow of a fluid under turbulent conditions in the z direction is pictured in Figure 1. The relative radial velocity perpendicular to the mean mean velocity, w , is represented by v' . The length of the cylindrical shell shown in the figure is a and is assumed of such length that the average value of v' over either the inside or outside is zero. On the inside, momentum at the rate of $2 \pi r \rho v' w'$ per unit length is carried into the shell by v' . The average gain of momentum to the shell is $2 \pi r a \rho v' w'$. This gain of momentum acts on the element as a force directed toward the right. The viscous force exerted on the inside of the element by the

mean mean velocity, which also acts as a force directed toward the right, is $-2 \pi \mu a (\delta w / \delta r)$. The total force exerted on the inside of the element by the fluid is then:

$$2 \pi r a \left(-\mu \frac{\delta w}{\delta r} + \rho v' w' \right)$$

In a similar way the total force exerted by the fluid on the outside surface of the shell is:

$$-2 \pi a \left(-r \mu \frac{\delta w}{\delta r} + r \rho v' w' + \frac{\delta}{\delta r} \left[r \left(-\mu \frac{\delta w}{\delta r} + \rho v' w' \right) \right] dr \right)$$

The negative sign is used to designate the fact that this force is directed toward the left. The force exerted by the pressure gradient is $(\delta p / \delta z) 2 \pi r a dr$. Adding these forces, setting the sum equal to zero, and simplifying, one obtains:

$$\frac{\delta}{\delta r} \left[r \left(\mu \frac{\delta w}{\delta r} - \rho v' w' \right) \right] = r \frac{\delta p}{\delta z} = -rS \quad (1)$$

$$\text{where } S = -\frac{\delta p}{\delta z}$$

The term $\rho v' w'$ in Equation 1 represents a rate of transfer of momentum per unit area across a surface. Physically this transfer is due to groups of molecules being thrown by the component of the eddy currents perpendicular to the mean mean velocity from one stream line of mean mean velocity to another. The first stream line may correspond to a higher or lower value of w than the second. If higher, the value of w' is positive, and, if lower, it is negative. From this, w' may be regarded as equal to $(\delta w / \delta r) \tau$ where τ is the distance between the stream lines. The expression $-\rho v' w'$ in Equation 1 may therefore be replaced by $-\rho v' \tau (\delta w / \delta r)$. Let the symbol, E , be defined by the equation:

$$E = -\rho v' \tau \quad (2)$$

Then

$$-\rho v' w' = E \frac{\delta w}{\delta r} \quad (3)$$

and Equation 1 becomes:

$$\frac{\delta}{\delta r} \left[r \left(\mu + E \right) \frac{\delta w}{\delta r} \right] = -rS \quad (4)$$

The symbol, E , will be defined as the eddy viscosity to differentiate it from the true viscosity. The German writers use the term *Austauschgrösse* for E .

If E be taken as constant, and the constant value be denoted by E' , Equation 4 may be integrated as follows:

$$\frac{\delta w}{\delta r} = \frac{-Sr}{2(\mu + E')} + \frac{c_1}{r}$$

Since $(\delta w / \delta r)$ from symmetry is equal to zero for $r = 0$, the value of c_1 must be zero. Integrating again,

$$w = \frac{-r^2 S}{4(\mu + E')} + c_2$$

Let w_0 represent the value of w for $r = 0$. Then $c_2 = w_0$. Let $\frac{S}{4(\mu + E')} = c$. On making these substitutions, one obtains:

$$w = w_0 - cr^2$$

Stanton (20) has shown that for turbulent flow the velocity distribution fits an equation of this form up to within a very short distance of the pipe wall. This fact leads to the interesting conclusion that E must be approximately constant over the main body of the fluid and only varies appreciably near the pipe wall. The experiments of Stanton (22) on velocities

close to the pipe wall show that the velocity approaches zero with approach to the pipe wall, and that the slope of the velocity curve approaches the slope of the velocity curve for viscous flow with the same friction upon approaching the pipe wall. This latter fact has been widely interpreted to indicate the existence of a layer of fluid of finite thickness at the pipe wall which is flowing in viscous flow. The experimental evidence does not warrant this conclusion as it indicates only that the flow approaches more nearly to viscous flow with approach to the pipe wall. The condition of zero velocity at the pipe wall demands that the eddy currents be zero at the pipe wall, and hence at the wall itself the slope of the velocity curve must be the same as for viscous flow. It is reasonable to assume that for a short distance the strength of the eddy currents is a continuous function of the distance from the pipe wall and hence that the eddy currents increase in strength with distance from the pipe wall, and, as a consequence, the deviation of the actual flow from viscous flow steadily increases with distance from the pipe wall. The equations of motion give no indication of the existence of a finite layer of fluid in viscous flow at the pipe wall. From these considerations, the existence of a film of fluid of finite thickness in viscous flow at the pipe wall is regarded, to say the least, as very unlikely.

As the eddy currents must be zero at the pipe wall (assuming no slip), the eddy viscosity must also be zero at the pipe wall. Since Stanton's experiments indicate that the eddy viscosity becomes practically constant at a short distance from the pipe wall, it is reasonable to assume that over this short distance the eddy currents vary as some power of the distance from the pipe wall. It is evident that this assumption can introduce no appreciable error. The short distance over which the eddy viscosity varies will be termed the "film." It should be clearly remembered, however, that it is here assumed that the fluid is not in viscous flow in this film.

Reynolds (16) has shown that $\delta v'/\delta r = 0$ at the pipe wall. Therefore in the film, v' must vary with a higher power of the distance from the pipe wall than the first power. From a consideration of the physical significance of w' , it appears that near the pipe wall it will vary in the same manner as w . From Equation 4 it is evident that near the pipe wall $\delta w/\delta r$ is constant. Near the pipe wall, therefore, w (and hence w') varies as the first power of the distance from the pipe wall. From Equation 3, E is proportional to the product of v' and w' . If we restrict ourselves to integral powers, which is necessary to integrate subsequent equations, then E in the film can vary with no less power than the cube of the distance from the pipe wall. The restriction to integral powers is not necessary from physical considerations, but, as will be shown later, the accuracy of the experimental data on heat transfer does not warrant greater refinement.

It will be shown later that once the power of the distance from the pipe wall with which E varies in the film is fixed, numerical values of hd/k as functions of dG/μ and $c\mu/k$ are completely determined. These values contain no arbitrary constants to be evaluated from heat transfer data. Values of hd/k as functions of dG/μ and $c\mu/k$ were calculated on the assumptions that E varied in the film with both the third and fourth power of the distance from the pipe wall. It was found, particularly for high values of $c\mu/k$, that there was a marked difference in the values of hd/k calculated from the two assumptions. A rough check against the heat transfer data indicated that the third power was preferable. An equation for turbulent flow will, therefore, be derived on the assumption that E varies through the film as the cube of the distance from the pipe wall, and on the assumption that in the main body of the fluid E is constant.

The equations derived will contain as unknowns the eddy

viscosity, E , and the film thickness. These two quantities must be evaluated by two known conditions of fluid flow. The two most accurately known conditions are frictional resistance and ratio of average velocity, divided by center-line velocity. Both of these conditions are known as a function of dG/μ for copper tubes.

The assumptions made in the treatment of turbulent flow are somewhat different from those used by the more recent German writers, in particular Prandtl (15) and Karman (4). The basic assumption made by these writers is that the velocity varies directly as the one-seventh power of the distance from the pipe wall. The fact that this relation is not valid close to the pipe wall, owing to the slope of the curve increasing rapidly to infinity at the pipe wall, was recognized by the above writers. This difficulty is overcome by assuming that a viscous film exists at the pipe wall and that the one-seventh power law holds only from the inside of this film inward. It is also obvious that the relation cannot hold near the center of the pipe because of the fact that the relation does not allow for a maximum velocity at the center of the pipe. The relation can, therefore, be valid only from a point a certain distance from the wall to a point a certain distance from the center of the pipe.

DERIVATION OF EQUATION FOR FLUID FLOW

Let a be the radius of the pipe and b the inside radius of the film so that the film thickness is $(a - b)$. Let E' be the constant value of E over the main body of the fluid. Then over the film in accordance with the assumptions outlined above,

$$E = E' \left(\frac{a - r}{a - b} \right)^3 \quad (5)$$

Integrating Equation 4, one obtains:

$$w = \int \frac{-Srd r}{2\mu \left(1 + \frac{E}{\mu} \right)} + c \quad (6)$$

where c = constant of integration

As E has different forms for film and main body, separate integrations of Equation 6 must be made for the two locations. Over the film—that is, from $r = a$ to $r = b$ —Equation 6 takes the form:

$$w = \int \frac{-Srd r}{2\mu \left[1 + \frac{E'}{\mu} \left(\frac{a - r}{a - b} \right)^3 \right]} + c$$

Let $x = \frac{a - r}{a - b}$, then $dx = \frac{-dr}{a - b}$; and let $\frac{E'}{\mu} = \phi$. Since the variation in r is small compared to variation in denominator, r may be replaced by its average value over the film of $(a + b)/2$ without introducing appreciable error. With these changes, the above equation becomes:

$$w = \frac{S(a^2 - b^2)}{4\mu} \int \frac{dx}{1 + \phi x^3} + c$$

On carrying out the indicated integration and evaluating c so that $w = 0$ when $x = 0$, which is the boundary condition, one obtains:

$$w = \frac{S(a^2 - b^2)}{12\mu\phi^{1/3}} \left[\frac{1}{2} \ln \frac{(1 + \phi^{1/3}x)^2}{1 - \phi^{1/3}x + \phi^{2/3}x^2} + \sqrt{3} \tan^{-1} \frac{2\phi^{1/3}x - 1}{\sqrt{3}} + \frac{\pi\sqrt{3}}{6} \right] \quad (7)$$

The value of w at the inside boundary of the film, where $x = 1$, will be denoted U , which is defined by the equation:

$$U = \frac{S(a^2 - b^2)}{12\mu\phi^{1/3}} \left[\frac{1}{2} \ln \frac{(1 + \phi^{1/3})^2}{1 - \phi^{1/3} + \phi^{2/3}} + \sqrt{3} \tan^{-1} \frac{2\phi^{1/3} - 1}{\sqrt{3}} + \frac{\pi\sqrt{3}}{6} \right] \quad (8)$$

The function in brackets in the above equation will be called $F(\phi)$ so that Equation 8 may be written,

$$U = \frac{S(a^2 - b^2)}{12\mu\phi^{1/3}} F(\phi) \quad (8a)$$

The value of E over the main body of the fluid has the constant value, E' . The value of the velocity is given by the equation:

$$w = \int_0^b -\frac{S}{2\mu} \frac{rdr}{(1 + \phi)} + c \\ = \frac{S}{4\mu} \frac{b^2 - r^2}{1 + \phi} + U \quad (9)$$

where the integration constant, c , has been evaluated so that $w = U$ when $r = b$.

The average velocity, u , over the cross section of the pipe is defined by the equation:

$$\pi a^2 u = 2\pi \int_0^a wrdr$$

or

$$u = \frac{2}{a^2} \int_0^a wrdr$$

The integration must be carried out in two steps, one from 0 to b and the other from b to a . The integral from 0 to b from Equation 9 is:

$$\frac{2}{a^2} \int_0^b wrdr = \frac{Sb^4}{8a^2\mu(1 + \phi)} + U \frac{b^2}{a^2} \quad (10)$$

The integration from b to a , judging from Equation 7, is rather involved and is probably best handled by approximate methods. Let Δ be defined so that ΔU is the average velocity over the film. Then,

$$\pi(a^2 - b^2)\Delta U = 2\pi \int_b^a wrdr \quad (11)$$

Since r varies but little over the film, it will be given the constant value of $(a + b)/2$. On this basis,

$$(a^2 - b^2)\Delta U = (a + b) \int_b^a wrdr$$

Let $x = \frac{a - r}{a - b}$ be substituted for r in the above equation. One obtains

$$\Delta U = \int_0^1 wx dx$$

or

$$\Delta = \int_0^1 \frac{w}{U} dx = \int_0^1 \frac{F(\phi x^3)}{F(\phi)} dx \quad (12)$$

where F is defined by Equations 8 and 8a.

The integral of Equation 12 may be readily evaluated by graphical or approximate means for various values of ϕ . In this way a plot of Δ as a function of ϕ may be prepared.

From Equation 11,

$$\frac{2}{a^2} \int_b^a wrdr = \frac{a^2 - b^2}{a^2} \Delta U \quad (13)$$

Therefore

$$u = \frac{Sb^4}{8a^2\mu(1 + \phi)} + U \frac{b^2}{a^2} + \frac{a^2 - b^2}{a^2} \Delta U$$

or substituting for U from Equation 8a, and letting $y = b/a$,

$$u = \frac{Sa^2}{4\mu} \left[\frac{y^4}{2(1 + \phi)} + \frac{1 - y^2}{3\phi^{1/3}} (\Delta(1 - y^2) + y^2 F(\phi)) \right] \quad (14)$$

Fanning's equation may be written:

$$S = \frac{2f\rho u^2}{a} = \frac{f u}{a^2} (du\rho) \quad (15)$$

where $d = 2a$

Substituting for the first u in the above equation from Equation 14, one obtains after simplification:

$$\frac{f du\rho}{4\mu} \left[\frac{y^4}{2(1 + \phi)} + \frac{1 - y^2}{3\phi^{1/3}} (\Delta(1 - y^2) + y^2 F(\phi)) \right] = 1 \quad (16)$$

The value of the ratio of the center-line velocity, w_0 , divided by the average velocity can be obtained from Equation 9 by setting $r = 0$ and dividing by u . On carrying this out, substituting for U in Equation 9 from Equation 8, substituting for S from Equation 15, and calling $b/a = y$, one obtains after simplification:

$$\frac{w_0}{u} = \frac{f}{4} \left(\frac{du\rho}{\mu} \right) \left(\frac{y^2}{1 + \phi} + \frac{1 - y^2}{3\phi^{1/3}} F(\phi) \right) \\ y^2 = \left[\frac{F(\phi)}{3\phi^{1/3}} - \frac{w_0}{u} \right] \div \left[\frac{F(\phi)}{3\phi^{1/3}} - \frac{1}{1 + \phi} \right] \quad (17)$$

Equations 16 and 17 are basic equations connecting the ratio, y , of the inside diameter of the film divided by the inside diameter of the pipe and the ratio, ϕ , of the constant eddy viscosity over the main body of the fluid divided by the true viscosity of the fluid, with Fanning's formula friction factor, f , and the ratio of the center-line velocity divided by the average velocity. For a given value of $du\rho/\mu$ and with experimental data on f and w_0/u , the equations contain as true unknowns only y and ϕ . As there are two equations and only two unknowns, y and ϕ may be evaluated.

The actual computation of y and ϕ from Equations 16 and 17 is rather laborious. To facilitate calculation, plots of $F(\phi)$ and Δ as functions of ϕ should be prepared. Accurate values of f and w_0/u should be used. The calculation is of a trial and error nature. For a particular value of $du\rho/\mu$, both f and w_0/u are known (at least for copper tubes) from experimental data. Assume a value of ϕ which fixes the value of $F(\phi)$ and Δ . From Equation 17 the value of y for the assumed value of ϕ may be obtained. This value of y is substituted in Equation 16. If, for this value of y , the left-hand side of the equation is equal to the right, the correct value of ϕ has been assumed. If not, other values of ϕ must be assumed until this condition is realized.

For copper tubes the friction factor has been calculated from the following equation derived by Lees (7):

$$f = 0.0765 \frac{(du\rho)^{-0.35}}{\mu} + 0.0009 \quad (18)$$

For small steel tubes of 0.42 inch diameter, the following equation is given by Lander (5):

$$f = 0.141 \frac{(du\rho)^{-0.44}}{\mu} + 0.002 \quad (19)$$

The ratio of w_0/u has been taken from Stanton's work on brass tubes. These values may be assumed to apply to copper

tubes. The calculated values of γ and ϕ for copper tubes and for various values of dup/μ are given in Table I.

Based on $dup/\mu = 40,200$, or Dup/Z of 324, Figure 2 shows the calculated values of w/w_0 for the main body plotted vs. the ratio r/a . An enlarged section for film is also shown, with w/w_0 plotted against x . Stanton's data (19) for the velocity distribution for air flowing isothermally in pipes for

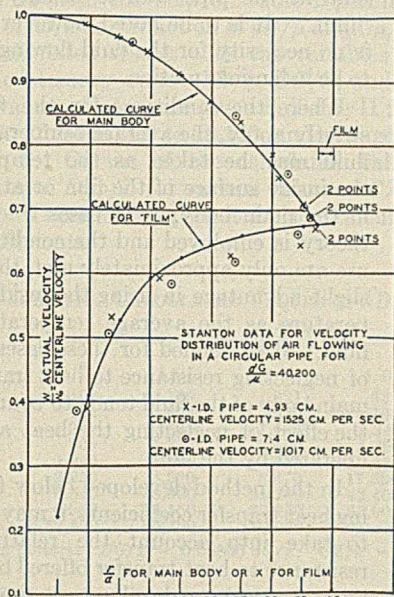


FIGURE 2. CALCULATED VALUES OF w/w_0 VS. RATIO r/a FOR MAIN BODY, AND VS. x FOR FILM

this value of dup/μ are also shown in Figure 2. The agreement between the calculated and observed results for the two sizes of pipe used by Stanton is very close. The excellent agreement in the film would indicate that the assumption made as to the variation of the eddy viscosity in the film is not greatly in error.

TABLE I. CALCULATED VALUES OF γ AND ϕ FOR COPPER TUBES

$\frac{dup}{\mu}$	$\frac{Dup}{z}$	$f \times 10^3$	$\frac{w_0}{u}$	γ	ϕ	$1 - \gamma$
3,000	24.2	5.58	1.380	0.7203	7.2	0.2797
5,000	40.3	4.82	1.317	0.8108	11.7	0.1892
10,000	80.6	3.97	1.275	0.8835	20	0.1165
25,000	202	3.12	1.250	0.9318	42	0.0682
50,000	403	2.64	1.240	0.9541	72	0.0459
100,000	806	2.27	1.235	0.9700	121	0.0300
300,000	2,420	1.83	1.223	0.9837	300	0.0163
500,000	4,030	1.68	1.220	0.9875	470	0.0125
2,500,000	20,150	1.34	1.211	0.9945	1940	0.0051

RELATION BETWEEN FRICTION AND HEAT TRANSFER BY EDDIES

In the above discussion on eddy currents, the relative mean velocity component, w' , in the direction of mean mean flow, was pictured as being due to portions of the fluid being carried from one stream line of mean mean velocity to another by the relative mean velocity component, v' , perpendicular to mean mean fluid flow. The value of w' was considered as being equal to $\tau(\delta w/\delta r)$ where τ represents the distance between the stream line of mean velocity under consideration and the one from which it was thrown. The sign of τ is such that $\tau(\delta w/\delta r)$ has the same sign as v' , and hence for a circular pipe the sign of τ is opposite to that of v' .

To derive an expression for the heat transfer due to eddy currents, consider the heat transferred by the eddy currents across any cylindrical surface in a pipe such as is shown in Figure 3, and assume the fluid being heated by transfer of

heat from the pipe wall. The length of the surface is assumed such that v' for the surface is zero. The eddy currents directed toward the axis of the pipe carry fluid at a higher temperature than that of the cylindrical surface across the surface, and the reverse is true of those directed toward the pipe wall. The former eddy currents can be regarded as carrying positive heat and the latter negative. It is obvious that the temperature of any portion of liquid carried from one stream line of mean mean velocity to another by the component eddy currents perpendicular to the pipe axis is at the temperature of the stream line from which it is thrown. The value of the distance it is thrown is plus or minus, the sign depending on the sign of v' . Therefore, liquid being thrown across the cylindrical surface, whose temperature will be taken as t , toward the axis of the pipe has a temperature of $t + (\delta t/\delta r)\tau$. That thrown across the surface toward the pipe wall has the corresponding temperature of $t + (\delta t/\delta r)\tau$. In general, the heat transferred by the eddy currents over any differential area, dA , is $\rho C v' dA (t + (\delta t/\delta r)\tau - t)$ or $\rho C v' (\delta t/\delta r)\tau dA$. The average rate of heat transfer per unit area due to eddy currents is obtained by integrating this expression over the area, A , of the cylindrical surface and dividing by A . The result is $\rho C \overline{v'\tau} (\delta t/\delta r)$ where $\overline{v'\tau}$ is the average value of the product over the surface. From Equation 2, $\rho \overline{v'\tau} = -E$. On making this substitution, the expression for the rate of heat transfer by the eddy currents becomes $-CE(\delta t/\delta r)$.

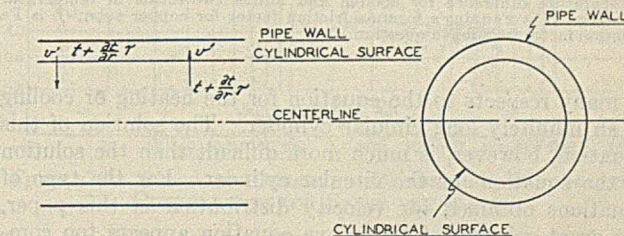


FIGURE 3. HEAT TRANSFER FOR TURBULENT FLOW IN FLUID FLOWING IN CIRCULAR PIPE

(Sign of τ is positive for v' directed toward center line, and negative for v' directed toward pipe wall.)

Besides heat transfer by eddy currents, heat is also transferred by conduction. The total rate of heat transfer per unit area is $-(k + CE) (\delta t/\delta r)$. This type of relation has been derived by other writers (2, 6).

A fluid in turbulent flow, therefore, has an effective thermal conductivity of $(k + CE)$ as compared with the true thermal conductivity of k .

The above derivation is strictly correct only for a fluid of constant density. This error involved due to thermal expansion is negligible, provided specific heats at constant volume and not at constant pressure are used.

The derivation of the effect of eddy currents on heat transfer has been presented for the sake of simplicity in a somewhat approximate form. The same results, however, can be obtained by a more exact analysis.

HEAT TRANSFER COEFFICIENTS

The basic differential equation for the heating or cooling of a fluid flowing in a circular pipe when the temperature of the pipe wall depends on the length only, as derived by Nusselt (13) and others, is:

$$\frac{k}{C_p} \left(\frac{\delta^2 t}{\delta r^2} + \frac{1}{r} \frac{\delta t}{\delta r} \right) = w \frac{\delta t}{\delta L}$$

This equation may be obtained by making a heat balance on a cylindrical element inside the pipe. The equation is similar

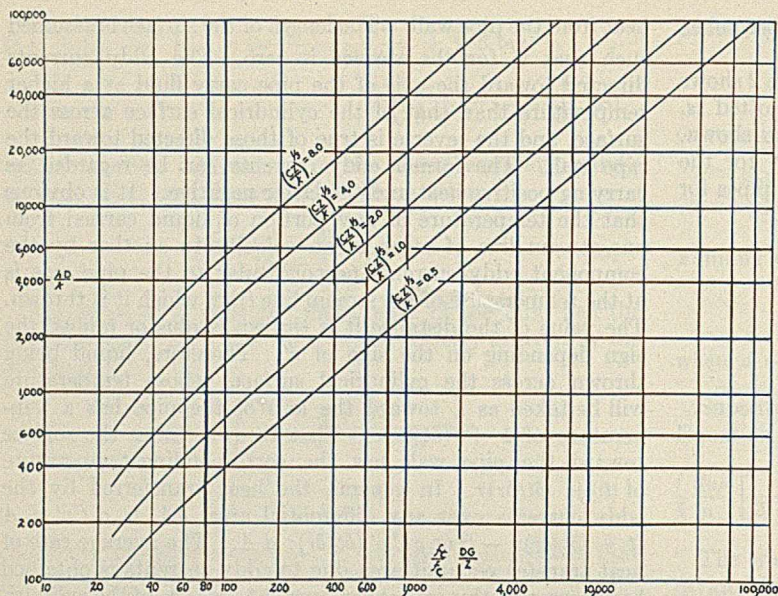


FIGURE 4. HEAT TRANSFER COEFFICIENTS FOR FLUIDS INSIDE OF TUBES. CHART OF hD/k AS FUNCTION OF DG/Z AND CZ/k

h = fluid film coefficient, B. t. u./sq. ft./° F./hour
 D = tube diameter, inches
 k = thermal conductivity of fluid, B. t. u./sq. ft./° F./hour/foot
 G = mass velocity, lb./sec./sq. ft.
 Z = viscosity, centipoises
 C = heat capacity at constant volume, cal./gram/° C.

(Temperature for physical constants taken at wall temperature plus three-fourths of temperature difference for cooling and minus two-thirds of temperature difference for heating; f_c is Fanning's formula friction factor for copper tube; f_t is Fanning's formula friction factor for tube in question.)

in many respects to the equation for the heating or cooling of an infinitely long circular cylinder. The solution of this equation, however, is much more difficult than the solution of the equation for the circular cylinder. For the type of equations obtained for velocity distribution in this paper, the exact solution of the above equation appears too complicated to be feasible.

It is desired to point out one important fact which may be inferred from the differential equation. The values for heat transfer coefficients at any cross section of the pipe obtained by solving the equation will, in general, be a function of the length of pipe traversed in addition to being a function of other variables. This applies even to the simple case where the entire length of pipe wall is at constant temperature. In general, therefore, the heat transfer coefficients for fluid flowing in a pipe do not depend alone on the conditions prevailing at the particular pipe cross section, but also on the length of pipe traversed. This is another way of saying that the heat transfer coefficients depend on the history of the fluid.

For the general case it is believed that the transfer of heat should not be expressed by heat transfer coefficients. The transfer is better expressed by the terms used in the mathematical theory of heating and cooling, such as the ratio of the accomplished temperature change of the fluid to the total possible temperature change.

For the particular case of heat transfer to fluids in turbulent flow where the velocities are in usual commercial ranges, experiments have shown that heat transfer coefficients are affected very slightly by pipe length except for short pipes where the coefficients are increased by entrance turbulence effects. Latzko (6), in a theoretical treatment of entrance effects, reaches the same conclusions shown by experiments.

The practical independence of heat transfer coefficients on pipe length can be explained only on the basis that the temperature gradients in the main body of fluid are almost

negligible, and that the main resistance to heat transfer exists in a relatively thin layer of fluid at the pipe wall. It is also essential that the heat absorbed or given up by the fluid in the thin layer at the pipe wall be negligible in comparison to that absorbed or given up by the main body of fluid. The thin layer of fluid at the pipe wall is usually called the "film." It is to be noted, however, that there is no necessity for the fluid flowing in the film to be in laminar motion.

Where the conditions for the film theory strictly apply, the average temperature of the fluid may be taken as the temperature at the inside surface of the film or at any point in the main body. For cases where the film theory is employed and the conditions for its use are only approximately met, there is some slight advantage in using the inside film temperature as the average temperature of the fluid. If so defined for these cases, the effect of neglecting resistance to heat transfer in the main body of the fluid tends to counterbalance the effect of neglecting the heat absorbed or liberated by the film.

In the method developed below for predicting heat transfer coefficients, it may be possible to take into account the relatively slight resistance to heat transfer offered by the main body by using a development similar to that of Nusselt (13) for laminar flow. It is believed best, however, not to make such a correction unless the heat absorbed or liberated by the film is also taken into consideration.

From the assumptions outlined above which must be made in the use of the film theory, it is clear that the temperature difference used with the coefficient may be the difference between the temperature of the two sides of the thin layer or film in which the main resistance to heat flow is assumed concentrated. Since this film is assumed to have negligible heat capacity, all heat flowing into the film must flow out. Therefore, in the film,

$$2\pi adLh(t_a - t_b) = 2\pi rdL(k + CE) \frac{\delta t}{\delta r}$$

$$\text{or} \quad ah(t_a - t_b) = r(k + CE) \frac{\delta t}{\delta r} \quad (20)$$

where the term $(k + CE)$ is the equivalent thermal conductivity previously derived, and t is restricted to the film—that is, between $r = a$ and $r = b$. Rearranging Equation 20 and integrating, one obtains:

$$\frac{1}{h(t_a - t_b)} \int_{t_b}^{t_a} dt = \frac{1}{h} = a \int_b^a \frac{dr}{r(k + CE)}$$

Since the variation of r is small, it may be replaced by its average value of $(a + b)/2$. Also E may be expressed as a function of r from Equation 5.

The above equation becomes:

$$\frac{1}{h} = \frac{2a}{(a + b)k} \int_b^a \frac{dr}{1 + \left(\frac{C\mu}{k} \phi\right) \left(\frac{a - r}{a - b}\right)^3}$$

or

$$\frac{k}{h} = \frac{2a}{a + b} \int_b^a \frac{dr}{1 + \left(\frac{C\mu}{k} \phi\right) \left(\frac{a - r}{a - b}\right)^3} \quad (21)$$

On carrying out the indicated integrations, one obtains:

$$\frac{k}{hd} = \frac{1-y}{1+y} \frac{1}{3 \left(\frac{C\mu}{k} \phi \right)^{1/3}} F \left(\frac{C\mu}{k} \phi \right) \quad (22)$$

where y has been substituted for b/a , and F is used to symbolize the same function as previously.

Equation 22 with the help of Table I permits the direct calculation of hd/k as a function of dG/μ and $C\mu/k$. Table II gives the calculated results with the variables expressed in their more customary units— hD/k , DG/Z , and CZ/k . The calculated values of hD/k are given in Table II for a range of Dup/Z or dG/Z from 24.2 to 20,150, and a range of $(CZ/k)^{1/3}$ from 0.5 to 8. Curves of the calculated values of hD/k as a function of Dup/Z for various values of CZ/k are given in Figure 4. These curves permit a ready calculation of heat transfer coefficients.

TABLE II. CALCULATED VALUES OF hD/k^2

$\frac{DG}{Z}$	WHEN $\left(\frac{CZ}{k}\right)^{1/3}$ IS:				
	0.5	1.0	2.0	4.0	8.0
24.2	100	169	321	636	1,269
40.3	172	303	585	1,160	2,320
80.6	330	605	1,180	2,340	4,670
202	709	1,337	2,640	5,260	10,490
403	1,246	2,390	4,720	9,430	18,900
806	2,250	4,360	8,670	17,300	34,600
2,420	5,540	10,900	21,740	43,400	86,700
4,030	8,360	16,550	32,950	65,900	132,000
20,150	32,600	65,100	130,000

^a Conversion factors: $DG/Z = 0.00806 dG/\mu$; $CZ/k = 0.413 C\mu/k$.

From Table I it will be noted that the ratio of the film thickness divided by the pipe diameter as expressed by $(1-y)$ is quite large for the lower values of Dup/Z , and it is very doubtful that it is permissible to neglect the heat capacity of the fluid flowing in the film. If this is the case, the use of the film theory is not permissible, as the rate of heat flow for a given temperature difference at any point in the pipe is not determined entirely by the conditions prevailing at the point, but is influenced by the history of the fluid.

APPLICATION TO EXPERIMENTAL DATA

The theoretical equations which have been developed are based on conditions in which the temperature difference is so small that the physical properties of the fluid do not vary appreciably. This condition is necessary as there are little data available on the friction drop of fluids flowing in pipes where this condition is not fulfilled. There are also few data available on the velocity distribution of a fluid flowing in a pipe which is not isothermal. It is obvious that, in applying the equations developed to a fluid which is not isothermal, some correction is necessary. In these cases the true value of the heat transfer coefficient lies somewhere between that corresponding to the coefficient obtained on taking the physical conditions at the pipe wall temperature and that obtained on taking them at the average fluid temperature. The correction factor which should be applied probably depends on the values of DV/Z , CZ/k , the slope of the viscosity temperature curve, and other factors. It is unlikely that any simple correction can adequately cover all conditions. The correction used in this article is to take the physical properties at a temperature equal to the pipe wall temperature minus two-thirds of the temperature difference for heating, and at a temperature equal to the pipe wall temperature, plus three-fourths of the temperature difference for cooling. This method of correction is simply an empirical attempt to make the data fit the isothermal curves and has no theoretical significance other than the fact that the actual heat transfer coefficient must lie somewhere in between those estimated

for the extreme conditions. From this viewpoint there is no need to apply the same correction for heating and cooling.

It is felt that any satisfactory correlation of heat transfer data must be based on a fundamental relation for isothermal conditions and corrections made for the fact that the actual conditions may not be isothermal. For this reason there is definite need of additional experimental data of heat transfer where the temperature differences are sufficiently small so that the physical properties of the fluid do not vary appreciably. With these data it will be possible to accurately establish the isothermal curves.

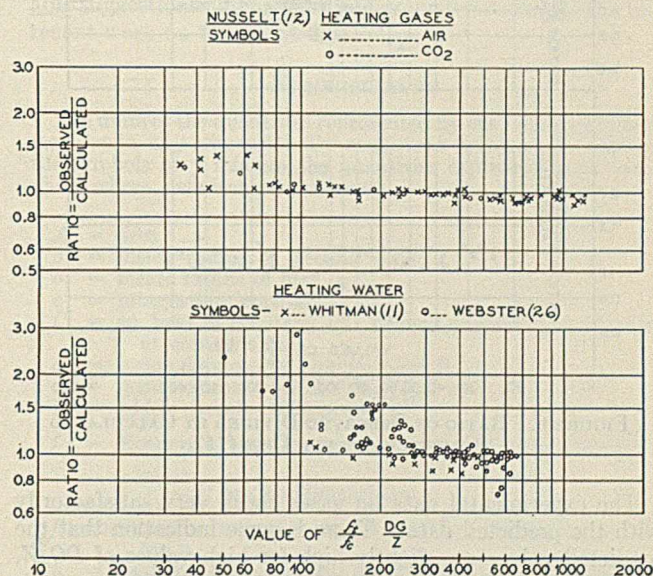


FIGURE 5. RATIO OF OBSERVED DIVIDED BY CALCULATED COEFFICIENTS FOR GASES AND WATER

The equations derived are based on the known friction factors and velocity distribution of fluids flowing isothermally in copper tubes. Where tubes or pipes of other metals are used, a correction is necessary. As the Reynolds number in all the basic equations developed appears as a product with the friction factor, it is felt that a satisfactory correction could be obtained by using $(f_i/f_c)(DG/Z)$ instead of DG/Z . In this expression, f_i is the friction factor for the tube under question, and f_c is a corresponding friction factor for a copper tube.

Under conditions in which the Reynolds number for fluid flowing in a pipe is low and the temperature difference is large, it is known (1¹, 28²) that convection currents are present, owing to the temperature difference, which appreciably affect the rate of heat transfer. No account of such convection currents has been taken in the equations developed. Where the temperature differences are high, therefore, and the value of DG/Z low, it is to be expected that the observed coefficients will be higher than those predicted. This effect will probably be most noticeable with water and gases, as with oils the convection currents will be reduced by the high viscosity.

In comparing the predicted heat transfer coefficients with the experimental coefficients, only data by selected observers have been used. The experimental data used are those of Nusselt (12) on gases, Webster (26) and Morris and Whitman (11) on water, and Morris and Whitman (11) on oils.

The heat transfer coefficient, as predicted from the theory in this article, is a complicated function of both DG/Z and

¹ For vertical pipes.

² For horizontal pipes.

CZ/k . The best method of presenting a comparison between the experimental and predicted coefficients is to plot the ratio of the experimental coefficient divided by the predicted coefficient against DG/Z . Such plots are presented in Figures 5 and 6.

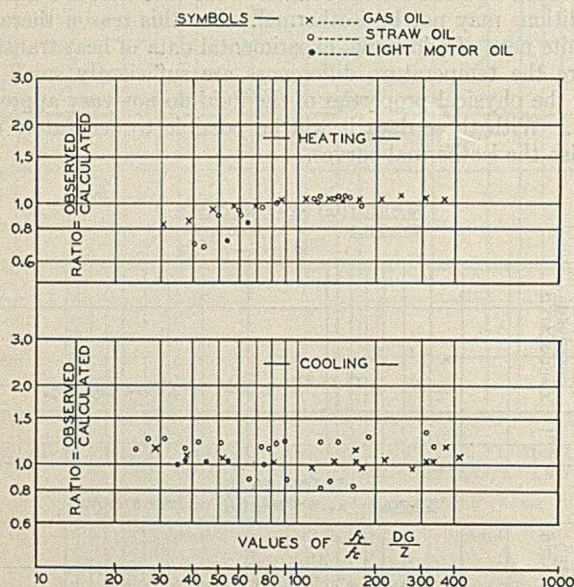


FIGURE 6. RATIO OF OBSERVED DIVIDED BY CALCULATED COEFFICIENTS FOR OILS (11)

The experimental data on gases check very satisfactorily with the predicted data. There is some indication that the predicted values are slightly high for high values of DG/Z . For low values of DG/Z there is some deviation of the experimental from the predicted, the predicted values being too low. This deviation is felt to be due to convection currents, as brought out above.

The agreement of the predicted coefficients with those obtained by Morris and Whitman on water is fairly good. The predicted results tend to be a little high, but there is no indication of trend with DG/Z . The agreement with Webster's data on water is excellent for higher values of DG/Z . For lower values of DG/Z , Webster's data appear exceedingly inconsistent. This inconsistency may be due to convection currents. The deviations of Webster's data for higher values of DG/Z indicate no trend with DG/Z .

The agreement of the predicted results with Whitman's data on heating oil is good, except for low values of DG/Z . Here the predicted results are high, which is the reverse of the results for gas and water. The deviations of data on heating oils indicate no trend with DG/Z .

Whitman's data on cooling oil are in satisfactory agreement with the predicted values except for the data on straw oil. The data on straw oil are rather inconsistent, some being above and some below the predicted values. None of the deviations of the data on cooling oil, however, indicates any trend with DG/Z .

The values of DG/Z and CZ/k covered by the experimental data are over quite a wide range. It is believed that the agreement of the predicted results with the experimental on gas, water, and oil is at least as good as any correlation which has so far been presented when the whole range is considered. It should be borne in mind, however, that the agreement of the predicted results with the experimental depends largely on the correction made for the fact that the experimental conditions are not isothermal. It is believed that the theoretical results are reasonably accurate for isothermal conditions.

COMPARISON WITH PRANDTL'S EQUATION

The equation of Prandtl, mentioned at the beginning of this paper, is essentially a film-theory equation; that is, the heat transfer coefficient predicted by the equation is supposed to depend only on the conditions existing at the cross section of the pipe under consideration and not on the conditions encountered by the fluid before reaching the cross section. Prandtl's equation assumes the existence of a layer of fluid in laminar flow at the pipe wall. Since it is a film-theory equation, it also inherently assumes that that portion of the resistance to heat flow not offered by the layer of fluid in laminar flow at the pipe wall is offered by the main body of fluid. The theory assumes a similarity of velocity and temperature gradients in the main portion of fluid.

The equation developed in this paper has some points of similarity with that of Prandtl. They are both film-theory equations, and in both cases heat transfer coefficients are predicted from pipe friction. Both equations contain one constant which can be, to some extent, predicted on theoretical grounds.

There is no great divergence between the true fluid viscosity and its effective viscosity, as defined in this paper, through the laminar layer assumed by Prandtl. For instance, for $dG/\mu = 50,000$ the effective viscosity as predicted by the method of this paper at the inside of the Prandtl laminar layer is only 1.031 times the true viscosity. Therefore, throughout the Prandtl laminar layer the velocities predicted from both theories will be nearly the same. This is true also for the effective thermal conductivities for low values of $C\mu/k$.

The real difference between Prandtl's theory and that developed in this paper lies in the predicted conditions governing heat transfer after passing through the Prandtl laminar layer. For this region Prandtl assumes a similarity of velocity and temperature gradients. By rearranging and integrating Equation 4, one obtains:

$$\frac{\delta w}{\delta r} = \frac{-Sr}{2\mu \left(1 + \frac{E}{\mu}\right)}$$

By rearranging Equation 20, one obtains:

$$\frac{\delta t}{\delta r} = \frac{ah(t_a - t_b)}{rk \left(1 + \frac{C\mu E}{k\mu}\right)}$$

These equations involve only accepted assumptions. Even for a region where variation in r is small, it is clear from these equations that the velocity and temperature gradients are similar only if $C\mu/k = 1$. This fact was recognized by Prandtl.

The following comparison for $DG/Z = 403$ is typical for results predicted by Prandtl's equation and those by the method of this paper; a value of 0.35 has been used for m in Prandtl's equation:

$\left(\frac{CZ}{k}\right)^{1/3}$	VALUES OF hD/k FOR DIFFERENT VALUES OF CZ/k				
	0.5	1.0	2.0	4.0	8.0
Prandtl's equation	632	2550	4120	4380	4500
Method of this paper	1246	2390	4720	9430	18900
Ratio	0.507	1.07	0.872	0.465	0.238

For values $C\mu/k = 1.0$ or $CZ/k = 2.42$, the agreement between Prandtl's equation and the method of this paper is good. For higher or lower values of CZ/k , the values hD/k predicted by the two methods become increasingly further apart. Both methods should give substantially the same

results for gases. The more correct method should be shown by comparison with the experimental results on oils.

To shorten this comparison, typical points have been chosen from the data of Morris and Whitman on heating and cooling oils. Table III gives a comparison of the results predicted from Prandtl's equation with the experimental and with the results obtained by the method of this article. The points chosen are those with high values of CZ/k and fairly high values of dG/Z . The temperatures mentioned refer to the temperatures at which the physical properties are taken. The temperature used for the method developed in this paper is the wall temperature minus two-thirds the average temperature difference for heating and plus three-fourths the average temperature difference for cooling. The friction factors for Stanton's equation have been calculated from Equation 19.

TABLE III. COMPARISON OF PRANDTL'S EQUATION WITH METHOD OF THIS ARTICLE FOR DATA OF MORRIS AND WHITMAN (11) ON OILS

RUN	REMARKS	$\frac{dG}{Z}$	$\frac{CZ}{k}$	$\frac{hD}{k}$		Ratio obsvd. to calcd.
				Obsvd.	Calcd.	
HEATING OILS						
B-13	Prandtl's equation, main body temp.	242	13.5	4890	3520	1.39
C-21	Prandtl's equation, main body temp.	85.7	39.5	3080	1740	1.77
D-4	Prandtl's equation, main body temp.	34.7	84	1490	807	1.85
B-13	Prandtl's equation, temp. of this paper	298	11.3	4890	4000	1.22
C-21	Prandtl's equation, temp. of this paper	134	26.3	3080	2190	1.41
D-4	Prandtl's equation, temp. of this paper	58	51.5	1490	1170	1.27
B-13	Method of this paper	298	11.3	4890	4700	1.04
C-21	Method of this paper	134	26.3	3080	3060	1.01
D-4	Method of this paper	58	51.5	1490	1770	0.84
COOLING OILS						
E-15	Prandtl's equation, main body temp.	242	12.0	3790	3380	1.12
F-26	Prandtl's equation, main body temp.	102	29.4	2590	1750	1.48
G-20	Prandtl's equation, main body temp.	75.5	40.5	1610	1420	1.13
E-15	Prandtl's equation, temp. of this paper	234	12.8	3790	3300	1.15
F-26	Prandtl's equation, temp. of this paper	80	36.6	2590	1470	1.76
G-20	Prandtl's equation, temp. of this paper	49.5	60.6	1610	1040	1.55
E-15	Method of this paper	234	12.8	3790	3930	0.96
F-26	Method of this paper	80	36.6	2590	2130	1.22
G-20	Method of this paper	49.5	60.6	1610	1570	1.03

It is difficult to compare the two methods of estimating heat transfer coefficients from Morris and Whitman's data, as the results can be quite widely changed depending on the temperatures taken for determining physical properties. It is to be noted, however, that in all cases the results predicted by the Prandtl equation are fairly low. This can be remedied for the heating runs by taking a temperature nearer the pipe wall temperature for determination of physical properties. For cooling of oils, however, even using the main body temperature, Prandtl's equation gives low results. It seems necessary that a lower temperature than that of main body should be used in applying Prandtl's equation to cooling. The results obtained from Prandtl's equation, taking physical properties at temperatures used in this paper, probably give a better comparison. It is felt that the results obtained using the method of this paper are in better agreement with data on oils than those obtained from Prandtl's equation.

It is believed that the method of attack on problems involving transfer of heat or material in fluids under turbulent flow developed is of value for other types of transfer under turbulent flow conditions, such as humidification, absorption, and allied phenomena. As a matter of fact, the calculated results may be directly used for this purpose for fluids flowing in circular pipes with slight obvious modifications. It is

believed that the method used here applies to transfer problems involving fluids in turbulent flow perpendicular to pipes and flowing through tower packing. For these cases, however, an extension of the theory presented in this article will be necessary.

ACKNOWLEDGMENT

The writer wishes to acknowledge valuable aid given by K. T. Nilsson of the Solvay Process Company in calculating a portion of the experimental data presented in this article.

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NOMENCLATURE

The units of the quantities represented by the following symbols may be in any dimensionally consistent system. In addition, the symbols may refer to the quantities expressed in particular units where definitely mentioned.

A	= area
a	= inside radius of circular pipe
b	= inside radius of film
c	= integration constant
C	= sp. heat at constant vol., or heat capacity per unit mass at constant vol.
d	= inside diameter of circular pipe, ft.
D	= inside diameter of circular pipe, in.
E	= eddy viscosity (Equation 2)
f	= Fanning's formula friction factor in equation, $\frac{dp}{dL} = \frac{2f\rho u^2}{a}$ (f has no dimensions)
f (subscript)	= reference to physical properties at av. film temp.
h	= heat transfer coefficient for film, B. t. u./hr./sq. ft./° F.
k	= thermal conductivity of fluid, B. t. u./hr./ft./° F.
L	= length of circular pipe, ft.
p	= pressure of fluid, lb./sq. ft.
q	= area
r	= radius at particular point in pipe cross section
S	= $\frac{-dp}{dL}$ = hydraulic slope, lb./sq. ft./ft.
t	= temp. of fluid
u	= av. fluid velocity across pipe cross section, ft./sec.
v	= component of mean velocity at any point perpendicular to direction of mean mean velocity
v', w'	= components of relative mean velocity at any point perpendicular to direction of mean mean velocity
G	= ρu = av. fluid mass velocity across pipe cross section, lb./sec./sq. ft.
w	= mean mean velocity at any point
U	= defined by Equation 8
x	= coördinate; also $x = \frac{a-r}{a-b}$
y	= coördinate; also $y = \frac{b-a}{a-b}$
z	= coördinate
Z	= viscosity of fluid, centipoises
Δ	= defined by Equation 11
Δt	= temp. difference across film, ° F.
μ	= viscosity of fluid
ρ	= fluid density, lb./cu. ft.
τ	= distance between stream lines of mean velocity
ϕ	= $\frac{E}{\mu}$ = ratio of eddy viscosity to true viscosity

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Heat Transmission to Liquids Flowing in Pipes

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New data are presented on heat transmission to water, acetone, benzene, kerosene, and n-butyl alcohol flowing in both stream-line and turbulent motion through a 0.494 inch i. d. steam-jacketed copper pipe. The data obtained in turbulent flow were found to be well correlated by the Dittus and Boelter equation:

$$\frac{hd}{k} = 0.024 \left(\frac{du\rho}{\mu} \right)^{0.80} \left(\frac{c\mu}{k} \right)^{0.40} = 0.024 \left(\frac{d^2 u^2 \rho^2 c}{\mu k} \right)^{0.4}$$

where h represents the surface coefficient of heat transmission, d the tube diameter, u the mean fluid velocity, and μ , k , c , and ρ represent the fluid viscosity, thermal conductivity, specific heat, and density, respectively, taken at the main-body average

temperature. All variables are expressed in any consistent units.

The equation correlates not only the present data on heating five liquids, but agrees excellently with the data of Nusselt on heating air and with the data of Morris and Whitman on heating hydrocarbon oils at high velocities. It is endorsed as the form of the original Nusselt equation best correlating the data on heat transmission to various fluids flowing in turbulent motion ($du\rho/\mu$ greater than 2320) through clean horizontal tubes. However, it gives high values of h for petroleum oils at one to three times the critical, in which range the exponent on the Reynolds group $du\rho/\mu$ is greater than 0.8.

THE subject of heat transmission to water flowing in pipes has attracted the interest of many workers, primarily because of the importance of the problem in the design of surface condensers, boiler feed-water heaters, and similar equipment. Excellent data are available from which it is possible to predict with reasonable accuracy the film coefficients of heat transmission for water flowing in turbulent flow through clean tubes. However, for the many important cases where it is necessary to design tubular equipment to heat or cool various liquids other than water or oil, no experimental data are available in the literature. With the exception of experiments using different gases, and the work of Morris and Whitman using hydrocarbon oils and water, the authors know of no published data on heat transmission to more than one fluid in the same apparatus. The existing published data are accordingly of little value as an indication of the effect of the physical properties of the fluid on the rate of heat flow.

The majority of the experimenters studying heat flow to fluids flowing in pipes have correlated their results using some form of the Nusselt equation:

$$\frac{hd}{k} = \phi_1 \left(\frac{du\rho}{\mu} \right) \phi_2 \left(\frac{c\mu}{k} \right) \quad (1)$$

where h = film or surface coefficient of heat flow between tube surface and fluid

d = tube diameter
 k = thermal conductivity of fluid
 c = specific heat of fluid
 μ = viscosity of fluid
 ρ = density of fluid
 u = average linear velocity of fluid
 ϕ_1, ϕ_2 = functions to be determined

Nusselt (10) assumed power functions, writing

$$\frac{hd}{k} = a \left(\frac{du\rho}{\mu} \right)^n \left(\frac{c\mu}{k} \right)^m \quad (2)$$

He first assumed n and m equal, since his early data on gases were not sufficient to indicate the true values of these exponents. Nusselt later added the term $(d/L)^p$, where d/L is the ratio of tube diameter to length, and suggested a value of 0.05 for p . Very recently (11) he has analyzed the data on water obtained by Burbach (1) and by Eagle and Ferguson (4). He found values of n , m , and p of 0.764, 0.355, and 0.0552, respectively, from Burbach's data, and values of n and m of 0.819 and 0.365, respectively, from the data of Eagle and Ferguson.

In 1923 McAdams and Frost (8) analyzed the data of several investigators on heating water, wherein L/d varied from 34 to 100. Finding an apparent effect of tube length, they suggested the equation:

$$\frac{hd}{k} = 0.0272 \left(1 + \frac{50d}{L}\right) \left(\frac{du\rho}{\mu_f}\right)^{0.8} \quad (3)$$

Although thus eliminating the $c\mu/k$ group, they employ the viscosity μ , at the mean film temperature.

Recently, Lawrence and Sherwood (7) have reported data on heating water in four lengths of 0.593-inch i. d. copper pipes. The observed effect of the length was negligible, although the tube length was varied from 59 to 224 diameters. It may be noted that Nusselt's exponent of 0.05 on d/L would call for only a 7 per cent variation in h with this range of tube lengths. Lawrence and Sherwood's water data were found to be reasonably well correlated by the equation:

$$\frac{hd}{k} = 0.056 \left(\frac{du\rho}{\mu}\right)^{0.7} \left(\frac{c\mu}{k}\right)^{0.5} \quad (4)$$

Numerous other writers have employed various forms of Equation 1 in correlating data on heat flow to water. In 1928 Morris and Whitman (9) obtained a good correlation of data on heating and cooling various oils, as well as water. They employed a value of 0.37 for m , and indicated the function $\phi_1 (du\rho/\mu)$ graphically by plotting $hd/k/(c\mu/k)^{0.37}$ vs. $du\rho/\mu$. Separate correlations were necessary for heating and for cooling.

The most comprehensive attempts to obtain a general correlation for various fluids are perhaps those of Rice (13) and of Dittus and Boelter (3). Rice analyzed the data of Soenneken, Stanton, and Clement and Garland on heating water, and the data of Pannell, Jordan, and Nusselt on heating and cooling air and other gases. As a result he proposed the equation:

$$\frac{hd}{k_f} = \frac{1}{63} \left(\frac{du\rho_f}{\mu_f}\right)^{5/6} \left(\frac{c_f \mu_f}{k_f}\right)^{1/2} \quad (5)$$

where the physical properties of the fluid are all taken at the arithmetic mean film temperature. Much of the data on which the equation is based deviate from Equation 5 by 30 to 60 per cent, and the basis for the choice of 0.5 for m does not seem to be entirely sound. Rice (14) later changed the equation slightly to

$$\frac{hd}{k_f} = \frac{1}{60} \left(\frac{du\rho_f}{\mu_f}\right)^{0.83} \left(\frac{c_f \mu_f}{k_f}\right)^{0.5} \quad (6)$$

After studying the Rice paper, Cox (2) concluded that m should have been taken as $1/3$, and suggested

$$\frac{hd}{k_f} = \frac{1}{52.1} \left(\frac{du\rho_f}{\mu_f}\right)^{5/6} \left(\frac{c_f \mu_f}{k_f}\right)^{1/3} \quad (7)$$

Numerous investigators, working on heat transmission to single fluids flowing in turbulent motion inside pipes, have shown the exponent on the Reynolds group, $du\rho/\mu$, to be in the vicinity of 0.8. Rice's attempt to determine the effect of the $c\mu/k$ group was inconclusive because of the limited

range of $c\mu/k$ in the data studied, and particularly because of the inconsistencies indicated between the results of any two investigators, even when working with the same fluid.

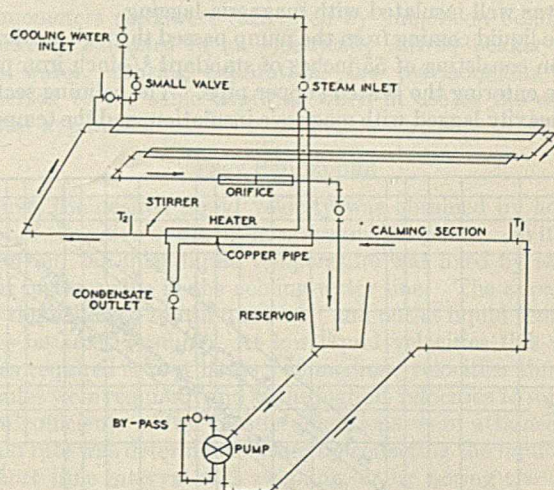


FIGURE 1. GENERAL LAYOUT OF APPARATUS

Dittus and Boelter (3), after studying the data of several investigators on air and water, and the data of Morris and Whitman on heating and cooling oils, proposed the equations:

$$\frac{hd}{k} = 0.024 \left(\frac{du\rho}{\mu}\right)^{0.8} \left(\frac{c\mu}{k}\right)^{0.4} \quad (\text{for heating}) \quad (8)$$

$$\frac{hd}{k} = 0.026 \left(\frac{du\rho}{\mu}\right)^{0.8} \left(\frac{c\mu}{k}\right)^{0.3} \quad (\text{for cooling}) \quad (9)$$

The value of m was given as 0.4 for heating, and as 0.3 for cooling. Two exponents are used in order to correlate Morris and Whitman's data on both cooling and heating several oils. Because of the consideration of these results for oils, the data on which this equation is based covered a much wider range of values of $c\mu/k$ than did the data considered by Rice.

The present paper presents new data on heat transfer to five different liquids, and the results are shown to be in excellent agreement with Equation 8 (of Dittus and Boelter).

DESCRIPTION OF APPARATUS

The apparatus consisted of the double-pipe heat exchanger under test, together with liquid-coolers, orifices, and storage tank. The liquid being tested was recirculated through the system by means of a small rotary pump. The general layout of the apparatus is shown diagrammatically in Figure 1.

The test section is illustrated in Figure 2. It consisted of a 48-inch length of 0.494-inch i. d., 0.675-inch o. d., copper pipe, held in a standard 2-inch steam jacket. The jacket was constructed of two short sections of standard 2-inch pipe,

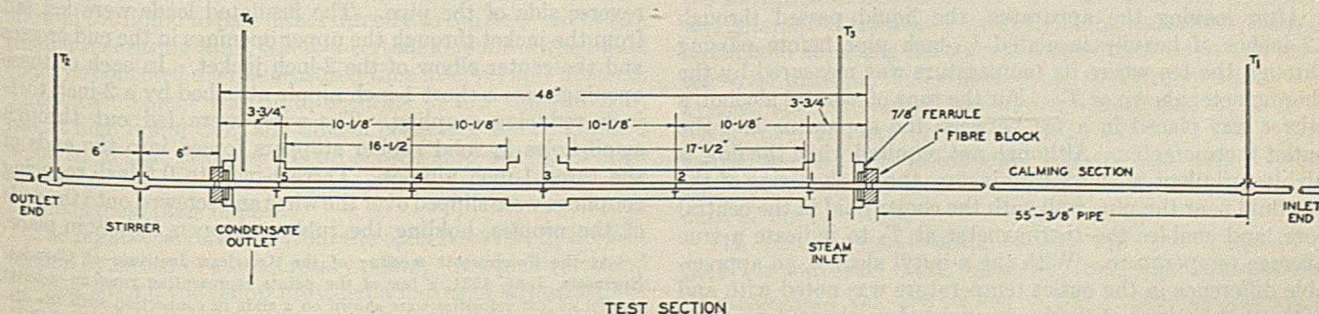


FIGURE 2. DETAILS OF TEST SECTION

joined at the center by a 2-inch tee, with 2-inch crosses at each end. The copper pipe was held in special ferrules threaded into the crosses as shown. The whole section was inclined slightly from the horizontal to cause the condensate to drain, and was well insulated with magnesia lagging.

The liquid coming from the pump passed through a calming section consisting of 55 inches of standard $\frac{3}{8}$ -inch iron pipe, before entering the heated copper pipe. The calming section was heavily lagged with magnesia insulation, and the tempera-

ture of the fluid entering the actual test section was assumed equal to the fluid temperature measured by a thermometer in the elbow at T_1 . Heat conduction along the metal of the approach tube was virtually eliminated by means of a fiber insulating block between the test and calming sections. A fiber block, 1 inch thick, was machined from both faces, making concentric holes 0.675 inch in diameter, 0.25 inch deep from one face, and 0.5 inch deep from the other face. The hole was machined out to exactly 0.494 inch. This block was then fitted over the end of the copper pipe, which was allowed to protrude 0.25 inch through the ferrule in the inlet cross. The end of the standard $\frac{3}{8}$ -inch metal-pipe calming section was threaded, and protruded 0.5 inch through a light iron flange. The protruding end was inserted in the upstream hole in the fiber block, and the flange bolted through the fiber block to tapped holes in the disk holding the ferrule in the end cross. It may be seen that, when thus assembled, the fiber block insulated the two pipes, and yet provided a straight passage of uniform inside diameter through the calming section to the test section. A similar arrangement was used at the downstream end to prevent heat conduction to the outlet pipe.

After leaving the apparatus, the liquid passed through 12 inches of heavily insulated $\frac{3}{8}$ -inch pipe before passing through the tee where its temperature was measured by the thermometer shown at T_2 . For the runs on *n*-butyl alcohol, a stirrer was placed in a tee between the apparatus and the outlet thermometer. Although not required when the flow is highly turbulent, such a stirrer insures thorough mixing of the hot fluid near the pipe wall with the cooler fluid in the central core, and enables the thermometer at T_2 to indicate a true average temperature. With the *n*-butyl alcohol, an appreciable difference in the outlet temperature was noted with and without the stirrer at fluid velocities below about 1 foot per second. With the other fluids used, the stirrer shown was

not in service.¹ In its place a few square inches of wire screen were crumpled up and placed in the outlet pipe approximately in the position shown for the stirrer. This was in place for the runs on water, kerosene, acetone, and benzene. The test section could be disconnected easily from the supply and discharge pipes, facilitating cleaning of the inner surface of the copper pipe. This was done practically every day the apparatus was used, employing a stiff bristle brush. The heating medium was steam for the tests on water and on *n*-butyl alcohol. It was obtained from a high-pressure line, but was sufficiently wet so that, when reduced to atmospheric pressure, it was only slightly superheated. Its temperature was observed by the two thermometers, T_3 and T_4 , indicated on Figure 2. A homemade separator in the high-pressure line served to remove most of the water, and the condition of the steam as it reached the heating jacket was approximately saturated at 1 atmosphere. The steam entered the jacket through a 2-inch pipe leading to the upstream cross, as indicated on Figure 2. The condensate drained to the lower opening of the downstream cross, whence it was removed through a short section of 2-inch pipe. This was reduced after 2 feet to a small pipe and valve, through which the condensate was bled continuously to a receiving bucket. It was collected over measured time intervals and weighed. Hot water was used as a heating medium in the tests on kerosene, benzene, and acetone. This was obtained from a tubular steam-heated water-heater available in the same laboratory, and was supplied and removed through the same connections as was the steam. The temperatures of this water entering and leaving were not measured, but the temperatures in the jacket at T_3 and T_4 were recorded. The temperature of the outer surface of the copper pipe was measured by means of five copper-constantan thermocouples attached at intervals along the pipe length as shown in Figure 2. At each point indicated, the pipe surface was carefully cleaned, and a groove about $\frac{1}{2}$ inch long and $\frac{3}{64}$ inch deep was cut at right angles to the pipe length, using a hack saw and file. Duplicate cuts were made at points 180° around the pipe. The end of the No. 28 gage constantan wire was scraped clean, about $\frac{3}{32}$ inch at the end was bent in a sharp right angle, and this end was soldered into the groove in the pipe. After a few trials, the technic was developed of doing this with a minimum amount of solder, and a smooth solder surface was left, just filling the notch. Extreme care was exercised in removing all traces of solder from the wire protruding from the pipe, as it was found that minute quantities of solder on the wire at the junction with the pipe caused the couple to read practically the temperature of the steam. No. 28 gage copper wire was soldered in the notch on the reverse side of the pipe. The insulated leads were led out from the jacket through the upper openings in the end crosses and the center elbow of the 2-inch jacket. In each of these openings was a short 1-inch nipple attached by a 2-inch to 1-inch reducing coupling. The wires were led out through small holes in solid rubber stoppers forced into the ends of the three 1-inch nipples. Three 1-inch to 0.5-inch reducing couplings were slipped over the wires and screwed onto the ends of the nipples, holding the rubber stoppers tightly in place.

¹ At the Swampscott meeting of the American Institute of Chemical Engineers, June, 1931, a few of the points representing runs on *n*-butyl alcohol at low velocities were shown on a slide in connection with the discussion of a paper by Drew, Hogan, and McAdams. At that time it was erroneously stated that no stirrer was used with the *n*-butyl alcohol tests.

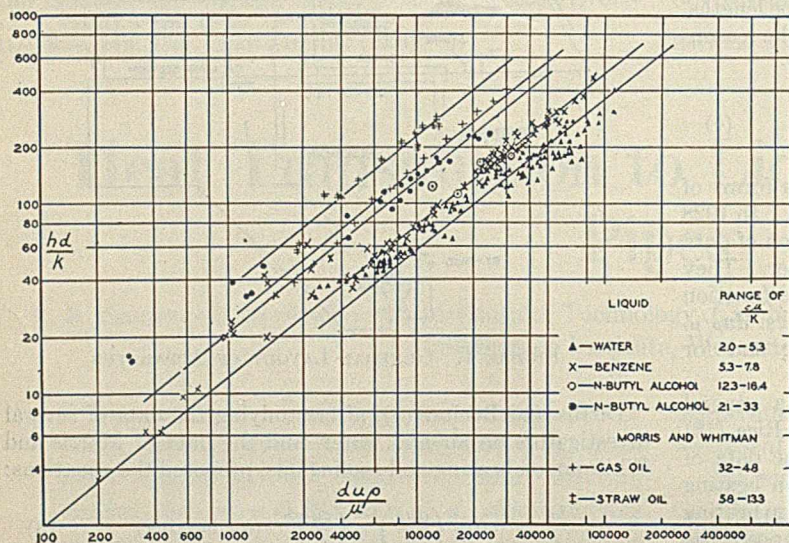


FIGURE 3. CORRELATION OF RESULTS USING VISCOSITY AT MAIN-BODY AVERAGE TEMPERATURE

ture of the fluid entering the actual test section was assumed equal to the fluid temperature measured by a thermometer in the elbow at T_1 . Heat conduction along the metal of the approach tube was virtually eliminated by means of a fiber insulating block between the test and calming sections. A fiber block, 1 inch thick, was machined from both faces, making concentric holes 0.675 inch in diameter, 0.25 inch deep from one face, and 0.5 inch deep from the other face. The hole was machined out to exactly 0.494 inch. This block was then fitted over the end of the copper pipe, which was allowed to protrude 0.25 inch through the ferrule in the inlet cross. The end of the standard $\frac{3}{8}$ -inch metal-pipe calming section was threaded, and protruded 0.5 inch through a light iron flange. The protruding end was inserted in the upstream hole in the fiber block, and the flange bolted through the fiber block to tapped holes in the disk holding the ferrule in the end cross. It may be seen that, when thus assembled, the fiber block insulated the two pipes, and yet provided a straight passage of uniform inside diameter through the calming section to the test section. A similar arrangement was used at the downstream end to prevent heat conduction to the outlet pipe.

After leaving the apparatus, the liquid passed through 12 inches of heavily insulated $\frac{3}{8}$ -inch pipe before passing through the tee where its temperature was measured by the thermometer shown at T_2 . For the runs on *n*-butyl alcohol, a stirrer was placed in a tee between the apparatus and the outlet thermometer. Although not required when the flow is highly turbulent, such a stirrer insures thorough mixing of the hot fluid near the pipe wall with the cooler fluid in the central core, and enables the thermometer at T_2 to indicate a true average temperature. With the *n*-butyl alcohol, an appreciable difference in the outlet temperature was noted with and without the stirrer at fluid velocities below about 1 foot per second. With the other fluids used, the stirrer shown was

The copper leads were joined to a five-point switch, and the constantan wires were led to cold junctions maintained in crushed ice and water in a vacuum flask. Copper leads from the switch to the cold junctions completed the circuits. Copper and constantan leads were then attached to a clean section of the copper pipe 1 inch long, and this couple calibrated by suspending the whole beside a thermometer in a beaker of water. The calibration curve thus obtained was used in interpreting the readings of the couples attached to the test section. A Leeds and Northrup portable potentiometer indicator was used for all thermocouple readings.

After leaving the test section, the liquid passed to two double-pipe coolers, through which it passed in series. The first of these was 10 feet in length, constructed of 1 $\frac{1}{4}$ -inch pipe with a 4-inch jacket. The second was 13 feet of 1 $\frac{1}{4}$ -inch pipe with a 3-inch jacket. The liquid flowed through the 1 $\frac{1}{4}$ -inch pipe, and the cooling water through the jacket in each case. A $\frac{1}{8}$ -inch valve, in a by-pass around the main cooling-water valve, allowed delicate adjustment of the water rate and of the temperature at which the liquid was returned to the heating section. The large ratio of cooling surface to heating surface made possible a variation from roughly 50° to 200° F. in the temperature of the liquid entering the heater.

For the runs heating water, one of two calibrated sharp-edged orifices was used to measure the rise of flow. Each orifice was carefully calibrated by passing water from the city mains through the orifice to weighing tanks.

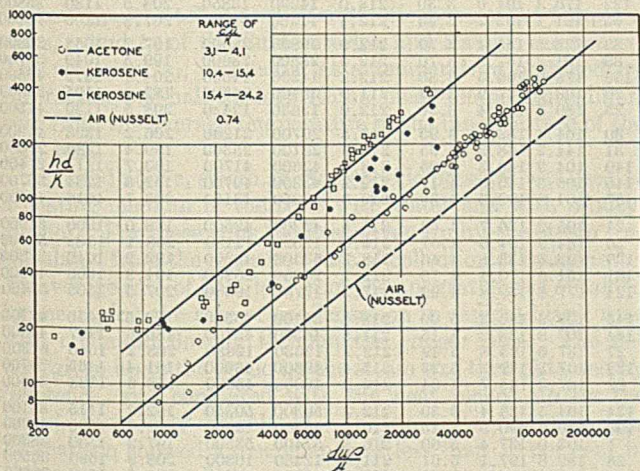


FIGURE 4. CORRELATION OF RESULTS USING VISCOSITY AT MAIN-BODY AVERAGE TEMPERATURE

In the runs using liquids other than water, the rate of flow was obtained by weighing the amount collected in a measured time interval. The liquid leaving the orifice was discharged into an open 10-gallon galvanized-iron reservoir, where any entrained air was released. A loose-fitting cover served to prevent excessive evaporation of the more volatile of the liquids used. At the inlet to the reservoir a swivel connection allowed the liquid to pass either directly to the reservoir or to a smaller measuring tank, where a certain amount of the liquid could be collected over a measured time interval and weighed. This measurement was quite accurate at low rates of flow, but at high liquid rates the time of collecting was as low as 8 seconds, so that even using a 0.1-second stop watch, an error of perhaps 5 per cent was introduced in the rate measurement at the highest rates of flow.

The liquid was returned from the open reservoir to the test section by means of a small rotary pump. A 1-inch valve and by-pass around the pump provided a means of adjustment of the rate of liquid flow through the apparatus. A further variation in the rate of pumping was obtained by the use of

three pulleys of different diameters on the overhead shaft from which the pump was driven by a belt drive.

The thermometers, T_1 and T_2 , at the liquid inlet and outlet were 0–100° C., reading directly to tenths of degrees. All thermometers used were calibrated by immersion beside the laboratory standard in an electrically stirred beaker filled with water. During calibration, the thermometers were immersed to the same depth as when in use in the experimental apparatus.

TEST PROCEDURE

First, the desired liquid velocity was obtained by adjustment of the valve in the by-pass around the pump. With the steam on, the inlet liquid temperature was fixed by adjustment of the valve in the cooling-water line. The apparatus was then allowed to run until inlet and outlet liquid temperatures became constant. At low liquid velocities this sometimes required 3 to 4 hours; at medium velocities about 30 minutes were required; and at the highest velocities 15 minutes were sufficient. After steady conditions were attained, the liquid rate was determined either by collecting the liquid over a short time interval and weighing, or by noting the orifice manometer reading. The thermometers, T_1 , T_2 , T_3 , and T_4 , and the five thermocouples were then read and the readings recorded. From two to six complete sets of readings were obtained in succession after conditions had become essentially constant and the recording of these observations constituted a run. The weight of condensate recorded was collected over the whole period of the run.

PHYSICAL PROPERTIES OF THE LIQUID

Because of the uncertainty as to the true values for certain of the physical properties (particularly the thermal conductivity) of the liquids used, no attempt was made in the calculations to allow for variations of these physical properties with temperature. For the densities, thermal conductivities, and specific heats, constant values were arbitrarily chosen and used in all calculations. For the most part these are based on data from the International Critical Tables (6), although the thermal conductivity of benzene is from the data of Smith (16), and the specific heat of the kerosene was determined directly. A summary of the values used is given in Table I.

TABLE I. VALUES OF SPECIFIC HEATS, DENSITIES, AND THERMAL CONDUCTIVITIES USED IN CALCULATIONS

LIQUID	SPECIFIC HEAT	THERMAL CONDUCTIVITY	
		DENSITY = ρ Lb./cu. ft.	B. t. u./hr./sq. ft./ ° F./ft.
Water	1.0	62.3	0.35
Acetone	0.519	49.4	0.102
Benzene	0.424	54.8	0.0883
Kerosene	0.502	50.1	0.0875
n-Butyl alcohol	0.583	50.5	0.097

The specific heat of the kerosene was determined by direct measurement in a Dewar flask heated by a short nichrome heating element. The liquid was stirred by a small electrically driven stirrer, and its temperature rise compared with the measured electrical input. The net heat-loss correction was determined from tests on water, using the same volume of liquid, and adjusting the current to heat both water and kerosene over the same temperature range in the same time. The average specific heat of the kerosene used was found to be 0.502,² over the temperature range 50–176° F. The experimental method was tested with benzene and with toluene, and results were obtained which compared closely with the data in the literature.

The viscosity-temperature curves, with the exception of that for kerosene, were obtained from the International

² This compares with 0.50 and 0.49 at 113° F. from the equations of Fortsch and Whitman, and of Bur. Standards, *Miscellaneous Pub.* 97, respectively.

Critical Tables. The viscosity of the kerosene used was determined directly, using an Ostwald viscometer, by comparing the time of efflux with that for water at the same temperature. Considerable care was taken in these determinations, and the results given in Table II are believed to be reliable. Similar determinations of the viscosity of benzene checked very closely the values given in the International Critical Tables.

TABLE II. VISCOSITY OF KEROSENE

TEMPERATURE		VISCOSITY	
° F.	° C.	Lb./hr. ft.	Centipoises
50	10	4.75	1.96
68	20	3.82	1.58
86	30	3.17	1.31
104	40	2.67	1.10
122	50	2.30	0.950
140	60	2.00	0.825
158	70	1.73	0.714

The character of the the kerosene is indicated by the Engler distillation data tabulated in Table III. Duplicate tests were made on the fresh kerosene, and on a sample of the kerosene taken from the apparatus after the completion of the tests. A small change due to evaporation from the open

reservoir is indicated by the difference between the two samples.

TABLE III. ENGLER DISTILLATION OF KEROSENE

DISTILLED OVER %	TEMPERATURE	
	Fresh kerosene ° F.	Used kerosene ° F.
0	320	333
10	357	371
20	376	386
30	389	394
50	416	424
70	445	452
90	490	498

The value given in Table I for the density of the kerosene was obtained at room temperature, using a pycnometer.

RESULTS OBTAINED

The average values of the important quantities measured, together with certain calculations based on these values, are tabulated in the order of liquid velocities in Tables IV-VIII, inclusive. The temperatures reported are averages of the several readings of each run, corrected for thermometer errors. The heat picked up by the liquid was calculated from

TABLE IV. DATA ON WATER

RUN	LIQUID TEMP.		AV. LIQUID VE-LOCITY ° F.	HEAT PICKED UP BY WATER ° F.	HEAT GIVEN UP BY STEAM ° F.	MEAN INNER PIPE SURFACE ° F.	h	dup μ	RUN	LIQUID TEMP.		AV. LIQUID VE-LOCITY ° F.	HEAT PICKED UP BY WATER ° F.	HEAT GIVEN UP BY STEAM ° F.	MEAN INNER PIPE SURFACE ° F.	h	dup μ		
	Inlet	Outlet								Inlet	Outlet								
121	76.6	173.0	0.350	211.0	9900	9660	204.1	288	2800	122	176.4	191.0	3.30	218.0	14290	13850	208.5	1180	36800
170	134.8	188.4	0.350	211.7	5600	5640	203.1	311	3390	65	181.1	192.2	3.50	212.1	11580	11800	207.9	1100	40000
169	137.0	186.7	0.400	210.5	5780	6000	202.7	327	3870	32	128.6	155.4	3.70	212.9	29800	28600	197.2	1058	30800
118	84.9	163.4	0.480	213.0	11200	11800	203.0	307	3050	33	131.2	157.2	3.70	212.5	28800	28600	199.5	1049	31700
88	82.2	148.8	0.630	214.4	12420	13310	194.3	334	4270	136	178.0	190.5	3.80	212.2	14220	14500	204.1	1472	42800
175	150.2	184.2	0.675	211.7	6780	6360	203.0	410	6740	20	103.2	137.9	3.82	211.9	39400	36600	187.6	1195	26600
89	83.3	148.0	0.680	214.2	12820	13730	194.3	342	4710	25	180.5	191.4	3.90	212.0	12630	12420	208.5	1130	44500
168	144.0	181.1	0.690	210.5	7450	7450	203.0	394	6700	30	164.4	182.3	3.95	212.5	20700	21200	206.2	1328	41900
91	84.9	148.4	0.740	213.2	13980	13750	193.9	382	5080	31	144.2	168.2	3.95	212.9	28100	25300	199.4	1285	27000
110	139.0	178.2	0.750	214.0	8640	9180	203.1	410	7230	140	104.9	140.3	4.05	218.4	42600	41700	193.7	1214	27400
173	153.5	184.5	0.770	210.5	7020	7080	203.0	448	7870	145	106.3	140.6	4.17	212.2	42300	40700	192.6	1234	35700
103	82.4	143.5	0.820	212.1	14870	14460	198.7	359	5340	157	181.8	192.0	4.33	210.3	13250	13150	203.7	1616	49700
93	85.7	147.5	0.840	213.0	15600	15650	192.3	432	5780	21	105.2	136.7	4.53	211.5	43200	42500	188.0	1300	31900
167	145.2	180.0	0.860	210.5	8900	9180	201.9	476	9510	26	184.9	194.0	4.57	212.0	12520	12180	208.1	1332	53700
94	86.7	148.4	0.900	213.2	16360	16710	193.2	453	6250	139	93.6	138.8	4.66	218.7	63000	43200	192.2	1640	32300
51	86.0	151.6	0.950	211.2	18630	18050	200.2	472	6600	161	151.6	170.4	4.70	212.1	26300	25200	194.3	1600	45300
52	85.3	151.4	0.950	211.5	18630	18050	200.2	473	6600	124	177.8	189.8	4.90	217.2	17700	19380	207.5	1505	55400
104	85.0	142.9	0.950	214.6	16240	16080	198.0	397	6260	143	129.9	156.3	5.00	218.4	39100	36500	193.5	1610	42200
59	89.8	155.0	0.970	212.1	18800	19100	201.2	507	7150	144	107.8	138.2	5.15	211.5	46500	45400	186.6	1427	44600
108	139.5	176.7	0.970	214.0	10550	9660	203.5	494	9320	27	187.6	195.8	5.19	212.2	12630	12880	208.2	1540	61300
58	89.6	152.4	1.00	212.1	18750	19550	201.4	487	7180	138	107.3	139.2	5.23	215.4	49600	46600	191.4	1465	36700
81	87.2	145.0	1.00	214.8	17330	16700	200.5	425	6750	22	107.3	133.7	5.24	212.2	46000	48600	188.6	1383	36600
82	86.9	144.6	1.00	213.2	17330	15650	200.0	425	6720	134	104.5	136.4	5.30	212.2	50300	50350	192.2	1415	36100
34	81.5	149.2	1.02	211.7	20900	21100	203.1	499	6570	153	180.9	190.9	5.45	216.3	16300	15950	202.7	1990	62200
166	141.7	178.2	1.02	211.7	10980	11170	201.6	554	9770	1	103.0	137.4	5.60	216.5	57400	53500	197.2	1500	38300
57	93.8	154.0	1.10	212.8	19800	18050	198.4	554	8100	28	189.8	197.1	5.61	211.9	12280	10800	208.9	1590	66500
105	87.2	143.3	1.10	214.5	18180	18050	196.6	463	8280	23	108.2	137.0	5.63	211.9	48200	46700	186.5	1522	39500
171	155.9	183.8	1.18	211.2	9880	9180	201.6	659	12100	8	132.6	157.7	5.69	222.8	42300	40000	203.1	1458	41000
180	84.2	151.8	1.18	218.2	23400	24000	207.9	583	7900	9	160.5	176.7	5.69	224.6	27200	25300	205.7	1475	57500
80	90.7	143.9	1.28	215.0	20000	18050	196.6	525	8710	2	192.4	199.2	5.70	216.5	11200	12050	211.7	1426	68600
73	168.0	188.1	1.45	212.0	8580	8350	209.5	555	15800	125	180.0	190.4	5.70	215.8	17770	17100	206.6	1680	65000
54	94.3	150.0	1.47	211.6	24100	23100	196.2	665	10200	7	120.6	149.1	5.74	221.2	49200	46600	200.7	1508	45700
50	172.6	191.7	1.53	212.5	9060	8700	206.2	773	17200	4	141.8	164.0	5.80	221.2	38400	35700	202.0	1580	52600
74	134.8	169.4	1.55	212.7	15500	14950	206.8	580	14200	6	112.1	142.5	5.80	218.5	52100	48300	197.6	1435	41700
37	91.2	143.9	1.58	212.9	24900	25300	199.4	623	10800	164	161.3	176.4	5.80	214.8	26300	24600	197.2	1880	59000
75	112.4	156.6	1.59	213.0	20900	20200	202.5	600	12600	3	154.0	172.6	5.84	222.0	32100	29600	204.7	1573	56400
76	94.9	146.0	1.59	212.5	24300	22900	194.4	650	11000	14	103.7	132.7	5.90	214.7	51500	48500	195.3	1333	40000
36	89.6	142.9	1.66	212.9	26800	25300	198.9	645	11100	154	183.4	192.0	6.10	213.2	15490	15050	203.1	1980	72300
79	92.8	143.5	1.66	214.2	24800	22900	194.2	672	11500	29	190.9	197.6	6.15	211.5	12180	11820	208.9	1710	74400
35	87.2	145.0	1.72	202.0	29500	27100	200.5	721	11400	149	110.5	138.1	6.23	216.1	51000	48500	188.9	1588	43800
163	142.1	173.4	1.72	210.5	15670	15150	198.4	805	16000	10	105.6	133.4	6.40	217.8	53300	50400	198.2	1355	43400
38	93.6	143.6	1.77	212.7	26500	25300	198.7	663	12100	11	119.9	145.5	6.40	216.1	48600	46600	201.9	1324	46000
56	103.9	149.6	2.10	212.0	27900	27800	195.0	853	15700	12	192.6	198.2	6.40	213.0	10550	10000	210.2	1442	77600
60	103.7	149.1	2.10	212.5	28500	27700	195.5	830	15600	13	158.1	174.1	6.40	218.0	29900	27500	205.0	1555	63400
147	97.6	145.7	2.10	213.8	29900	30700	195.0	837	14350	24	109.5	138.1	6.50	211.7	54400	53200	185.0	1790	46300
40	101.8	145.4	2.14	212.5	27900	30500	193.9	808	15320	133	106.3	135.9	6.50	211.7	56600	59300	189.8	1665	44700
39	90.7	143.1	2.17	212.5	29700	27500	197.4	765	15100	15	106.7	135.7	6.90	218.7	59700	54500	200.5	1508	48000
61	104.7	148.8	2.18	211.7	29100	30200	195.3	874	16440	126	181.3	190.4	6.90	214.6	19000	17950	204.6	2070	78900
62	106.0	148.2	2.46	212.1	30500	31200	193.0	946	18200	155	184.5	192.3	7.00	212.1	16550	16300	203.1	2280	82000
141	100.6	144.0	2.60	216.5	33700	32200	197.0	890	18100	132	108.6	137.0	7.22	212.0	60800	62700	189.4	1840	50800
69	179.1	192.0	2.70	212.0	10200	10800	208.1	933	31200	150	111.2	136.4	7.25	216.7	54500	51500	183.4	1825	51500
64	109.0	147.3	3.03	213.4	34300	34900	193.2	1075	22300	19	117.7	151.2	7.80	223.6	78500	83600	203.5	2310	61000
63	108.9	147.3	3.05	212.2	34900	34900	192.8	1100	22600	165	165.8	178.2	7.80	212.2	28500	27000	196.6	2340	81500
162	149.3	172.5	3.18	211.2	21600	21400	196.8	1240	30300	151	111.9	135.9	8.10	216.6	57800	54600	182.5	2040	57500
43	109.0	146.6	3.20	212.2	35900	25500	189.0	1157	23800	128	182.5	190.9	8.20	214.0	20700	18950	205.0	2090	

the measured rate of flow, the observed temperature rise, and the specific heat as given in Table I. The temperature drop through the pipe wall was calculated from this rate of heat flow, using a value of 238 B. t. u. per hour per square foot per ° F. as the thermal conductivity of the copper pipe. The calculated temperature drop through the tube wall was seldom greater than 2° F. The average temperature of the inner surface of the tube was obtained by subtracting the calculated temperature drop through the pipe wall from the temperature corresponding to the arithmetic average of the five e. m. f. values for the five couples. The error involved in this method of averaging is believed to be well within the accuracy of the data, particularly since in most of the runs the pipe wall temperature was practically constant from end to end of the tube. The mean temperature difference was taken as the logarithmic mean of the differences between the average temperature of the inner surface of the pipe, and the inlet and outlet liquid temperatures. The film coefficient, h , was calculated by dividing the B. t. u. per hour picked up by the liquid being heated, by the mean temperature difference, and by the area of the inner surface of the pipe. The heating surface used was based on a pipe length of 47 inches, a mean of the actual length of 48 inches and the length of 46 inches exposed to the heating medium. The linear velocity of the liquid through the copper tube was calculated from the measured rate of flow, using the fixed values of the density given in Table I. The Reynolds number, dup/μ , was calculated directly from the weight rate of flow, and accordingly involves no error due to an assumption of a constant density. The viscosity, μ , was taken at the arithmetic mean of the temperatures, t_1 and t_2 , of the fluid entering and leaving the heater. The viscosity, μ_f , was taken at a temperature obtained by subtracting one-half the logarithmic mean temperature difference from the average temperature of the inner surface of the pipe wall.

As noted above, steam at atmospheric pressure was used as a heating medium in the tests with water and with *n*-butyl alcohol. For these runs the heat given up by the steam was calculated from the measured rate of collection of condensate. An average rate of heat loss from the apparatus was obtained by measuring the rate of condensation in several blank runs with no liquid flowing through the copper pipe. The net heat given up to the liquid by the steam was then obtained by difference, and compared with the heat picked up by the liquid, previously calculated. In the tests reported, this comparison showed a discrepancy of less than 10 per cent in these two values. In the tests on benzene, acetone, and kerosene, hot water was used as heating medium, and, since its temperature entering and leaving the jacket was not measured, no such comparison of heat quantities was possible. Accordingly, the runs reported include every test made with these liquids. It may be noted that for several of the acetone runs, the tube wall was above the normal boiling point of acetone.

It is difficult to estimate the probable error in the determination of the coefficient, h , in the tests reported. Extreme accuracy in the various measurements was not attempted, since it was soon found that, in the limited time available for the work (2 years, part time), accuracy must of necessity be sacrificed to a certain degree, in order that series of tests might be completed on several liquids. This policy was believed justifiable in view of the fact that the project was in a certain sense a pioneer investigation, no data existing on heat transmission for several of the liquids used. Because of various offsetting factors, it is possible that the results at medium liquid velocities are the most reliable. With steam as the heating medium, the pipe temperature was practically uniform from end to end, and no appreciable error is introduced by using an average pipe wall temperature in calculating the logarithmic mean temperature difference. When heating

TABLE V. DATA ON ACETONE

RUN	LIQUID TEMP.		AV. LIQUID VELOCITY Ft./sec.	JACKET TEMP.		MEAN TEMP. INNER PIPE SURFACE ° F.	h	$\frac{dup}{\mu}$
	Inlet ° F.	Outlet ° F.		T_1 ° F.	T_2 ° F.			
70	86.2	140.3	0.0797	185.9	179.2	164.2	23.8	944
71	83.8	138.4	0.0812	185.0	179.6	173.7	19.3	950
69	87.8	141.7	0.0983	186.5	180.5	169.6	26.4	1165
67	82.5	139.9	0.118	188.9	181.4	169.6	32.1	1375
68	82.2	138.8	0.118	188.6	181.4	182.3	22.1	1368
19	61.5	136.3	0.139	176.9	172.6	165.8	42.4	1533
34	70.3	136.5	0.165	166.6	162.3	165.2	47.7	1850
72	79.5	136.3	0.226	188.0	179.6	168.8	57.6	2610
66	83.5	127.8	0.327	188.8	178.9	155.0	79.6	3730
65	84.2	124.7	0.373	188.6	178.0	153.2	82.2	4230
64	85.3	121.2	0.466	188.6	178.0	149.8	89.0	5220
63	93.2	123.7	0.503	188.8	178.0	149.3	93.3	5830
18	54.7	110.9	0.505	176.0	169.0	161.8	93.0	5130
73	82.2	136.4	0.667	192.6	181.1	168.8	163	7760
62	98.4	121.2	0.733	189.0	178.0	144.6	119	8530
17	52.9	89.3	0.944	176.0	167.4	134.9	131	9030
61	102.6	120.0	1.025	188.6	177.8	152.0	107	12000
33	65.1	100.8	1.04	166.0	158.0	129.9	194	10500
16	54.2	81.5	1.47	169.0	160.1	122.7	179	13800
60	107.6	119.0	1.75	188.0	176.2	136.4	221	20600
15	55.4	79.7	1.77	166.4	157.5	117.5	211	16600
32	67.8	91.4	1.80	165.2	156.6	121.9	261	18000
59	110.0	119.0	2.26	187.2	175.0	133.4	272	27000
14	58.3	80.3	2.30	167.1	158.0	115.3	266	21700
13	59.0	78.6	2.79	167.0	157.9	112.2	306	26300
58	109.1	117.3	2.87	186.7	174.1	129.1	377	33800
57	116.9	123.8	3.17	189.2	177.8	135.2	370	38600
12	57.4	72.0	3.32	147.0	138.3	97.4	360	30600
56	116.9	124.1	3.51	190.0	178.2	135.2	434	42500
31	72.2	87.8	3.75	170.6	159.8	113.7	433	37400
45	124.7	132.1	3.97	199.4	183.4	144.2	467	50400
2	60.6	76.0	4.00	166.2	155.0	104.5	417	36600
35	122.7	130.5	4.00	195.9	182.7	142.5	496	50400
1	56.3	68.4	4.22	125.4	119.9	91.5	423	38600
46	112.4	121.5	4.24	190.9	117.5	134.5	544	51400
22	73.2	87.8	4.27	168.8	158.0	111.4	497	42600
21	73.6	87.8	4.32	168.8	158.0	109.3	535	43400
10	60.6	76.3	4.34	167.0	152.2	102.4	487	40900
11	56.3	69.1	4.37	151.2	141.8	92.2	460	39800
47	116.2	123.2	4.50	191.4	177.1	134.5	549	54600
23	73.0	86.9	4.56	168.8	158.1	109.5	526	45600
3	60.6	75.0	4.69	165.6	154.4	101.8	484	43800
36	122.2	129.4	4.73	196.8	182.9	141.0	562	58800
48	118.1	125.2	4.75	191.9	178.4	136.7	558	58500
24	73.0	85.7	4.95	169.0	157.2	107.2	554	48800
4	60.4	74.3	5.00	165.4	154.4	99.5	525	46600
37	121.5	127.4	5.05	196.6	181.4	138.4	547	63300
25	72.6	81.7	5.27	170.6	158.1	107.2	403	52000
38	119.3	125.7	5.32	195.8	181.4	135.7	660	65500
49	119.9	124.9	5.45	181.6	170.0	132.7	767	67100
39	120.2	125.7	5.63	197.2	181.4	135.7	627	69300
40	124.1	129.5	5.65	197.6	183.2	138.4	668	71500
50	119.3	123.9	5.72	185.1	172.4	132.7	622	70500
5	60.3	72.5	5.86	165.4	153.8	95.6	605	54000
6	60.3	72.2	6.32	166.0	153.0	98.6	546	58500
26	73.2	84.2	6.42	172.3	159.3	104.1	678	63600
41	124.5	129.2	6.52	197.7	183.0	138.3	748	82000
51	121.5	126.2	6.80	189.8	175.2	134.5	750	84600
55	123.6	127.9	7.10	194.0	178.2	135.2	985	88400
52	121.1	126.1	7.13	194.0	178.2	135.2	749	89500
7	59.9	71.1	7.30	165.6	152.6	91.7	745	67500
27	73.4	83.2	7.48	172.3	158.6	102.8	733	74100
53	122.2	127.2	8.88	196.2	180.1	133.4	1250	112000
54	123.9	128.8	8.88	195.8	180.9	137.4	976	112000
43	123.4	127.3	9.07	197.8	182.0	134.5	943	113000
29	71.8	80.2	9.23	172.4	158.0	97.6	890	90300
28	72.4	80.8	9.30	173.2	158.8	96.3	974	91700
44	123.4	127.6	9.57	197.8	182.3	136.2	1045	119500
8	58.8	67.3	9.93	165.4	151.4	83.7	995	90600
42	120.4	124.7	10.10	197.6	181.4	132.6	1103	103300
9	57.6	66.9	10.20	166.2	152.2	84.8	1040	93000
30	71.6	79.3	10.75	171.9	157.7	94.4	1020	104500

with hot water, however, the flow of the hot and cold streams was parallel, and in a number of runs the pipe temperature at the outlet end was colder than at the inlet end. Under these conditions the true mean temperature difference was less than the logarithmic mean used, and the calculated values of the coefficient, h , are accordingly low. The error, however, is on the safe side, in that use of the reported coefficients in calculating required heating surfaces will result in conservative estimates.

The plots of the data, discussed below, serve as a rough indication of the over-all error in the determinations. The points indicate a considerable uncertainty in the determinations for the runs in viscous flow, and particularly in the region around the critical velocity. The uncertainty of

the data in the latter region may be due to the possibility of having stream-line (viscous) flow over part of the tube length, and turbulent flow over the remainder of the length. The data obtained in viscous flow are not claimed to be wholly reliable, but serve to indicate the general trend. In the turbulent region the points fall in narrow bands when plotted in the usual ways, and it is estimated that the probable

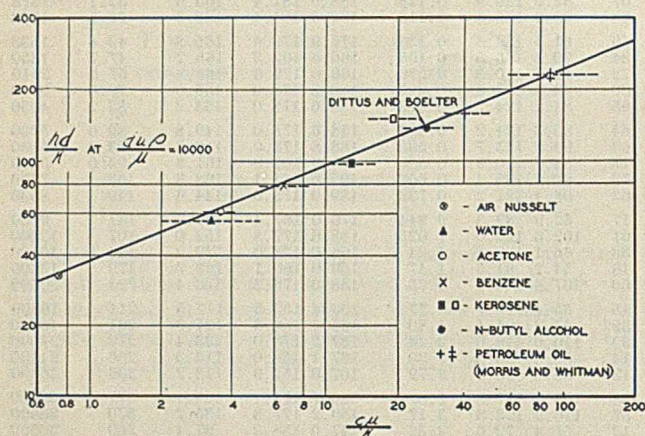


FIGURE 5. COMPARISON OF PRESENT DATA WITH DATA OF NUSSLETT ON AIR, AND MORRIS AND WHITMAN ON HEATING OILS, USING VISCOSITY AT MAIN-BODY AVERAGE TEMPERATURE

error in determinations of h in this region is less than 10 per cent. However, it is noted that errors in measuring the rate of flow of liquid appear to the same extent in both h and in the group dup/μ , and so become much less noticeable on logarithmic plots where one quantity appears in the ordinate, and the other in the abscissa.

CORRELATION OF RESULTS

The data are first shown plotted as $\frac{hd}{k}$ vs. $\frac{dup}{\mu}$ in Figures 3 and 4. The points representing the data on the five liquids fall in bands, and the points representing the runs at higher liquid temperatures fall in the lower edges of their respective bands. The slopes of the lines are in the neighborhood of 0.8, except for kerosene, for which line the slope is definitely greater. The steep slope of the kerosene line at velocities from one to ten times the critical may be compared with the data of Morris and Whitman (9), and of Sherwood, Kiley, and Mangsen (15), who obtained similar results with other petroleum oils. It is quite possible that at velocities above the range of the present data, the slope of the curve decreases, as in the case of the curve representing the data of Morris and Whitman.

Since it is possible that the proper introduction of the cmu/k group might offset this widening of the bands of points, the elevations of the lines have been compared with the range of the values of cmu/k for each liquid. For this purpose, values of hd/k , at $dup/\mu = 10,000$, were read from the lines of Figures 3 and 4, and these intercepts plotted against cmu/k as shown in Figure 5. The line from which the intercept was obtained was deliberately drawn with a slope of 0.8 through the main mass of points in each case. The lengths of the horizontal dotted lines drawn through the points of Figure 5 indicate the range of values of cmu/k covered by the data for each liquid.

In order to extend the range of the group, cmu/k , the data of Morris and Whitman on heating gas oil and on heating straw oil are included on Figure 3, and, in addition, a line representing the data of Nusselt on heating air is shown. The points representing these lines are also included on Figure 5. The

TABLE VI. DATA ON BENZENE

RUN	LIQUID TEMP.		AV. LIQUID VELOCITY FT./SEC.	JACKET TEMP.		MEAN TEMP. INNER PIPE SURFACE ° F.	h	$\frac{dup}{\mu}$
	Inlet ° F.	Outlet ° F.		T ₃ ° F.	T ₄ ° F.			
78	61.9	144.2	0.0305	203.0	198.7	185.0	7.4	206
60	64.4	125.4	0.0565	186.8	179.2	156.1	13.2	362
17	87.2	132.6	0.077	179.6	175.1	167.8	13.3	549
59	62.4	133.8	0.088	186.8	181.4	173.7	19.8	569
77	61.2	140.4	0.103	202.7	197.0	187.8	22.3	690
75	62.4	152.9	0.133	197.6	192.2	181.6	41.9	940
74	62.1	153.2	0.136	197.8	192.2	182.3	42.7	960
73	61.5	152.9	0.140	197.4	191.7	180.5	47.6	1045
71	59.9	153.4	0.151	194.0	188.0	179.6	50.5	1055
72	60.1	152.7	0.151	194.9	188.6	178.8	50.6	1055
79	63.6	151.4	0.154	203.0	197.4	185.0	44.0	1085
18	85.0	133.2	0.223	178.9	174.3	167.4	41.2	1600
70	59.6	142.2	0.238	191.1	185.0	159.8	91.4	1580
69	58.8	139.8	0.247	190.7	184.0	163.4	81.0	1610
80	65.6	146.6	0.262	205.1	196.0	180.3	71.3	1810
76	62.6	146.4	0.397	200.2	195.8	188.6	95.8	2720
81	57.2	134.6	0.412	200.2	190.7	158.3	12.9	2640
19	85.0	118.7	0.419	177.5	171.2	149.0	68.8	2810
82	54.5	110.5	0.596	199.4	188.6	151.6	110	3500
57	60.6	91.9	0.780	181.3	172.4	138.1	86.3	4340
83	53.6	103.0	0.808	201.2	189.4	189.2	77.2	4570
61	60.6	92.2	0.863	187.4	177.1	146.2	84.3	4790
68	57.8	90.2	0.98	182.9	175.0	139.2	103.3	5380
67	58.8	90.5	1.01	182.5	174.3	139.9	104	5580
20	85.5	107.3	1.07	176.4	169.6	141.8	119	6920
16	90.0	107.5	1.12	179.6	171.6	136.3	126	7390
62	57.2	83.2	1.13	186.8	176.0	125.6	113	6000
63	57.4	81.4	1.33	187.8	175.9	121.3	129	7060
23	92.3	107.3	1.35	176.2	168.0	131.4	141	8950
66	59.4	86.4	1.39	178.4	170.6	132.7	132	7530
84	54.3	76.8	1.54	203.5	190.0	132.7	113	8180
15	90.7	105.4	1.61	178.9	170.2	130.5	160	10450
21	88.2	102.2	1.75	176.0	167.0	125.5	176	11200
56	61.7	81.5	1.81	169.0	160.9	118.3	164	9750
14	91.4	105.7	1.88	178.8	170.0	129.1	190	12400
55	62.1	77.0	2.35	188.2	173.7	106.7	197	12400
54	62.1	76.0	2.46	186.8	172.6	103.7	209	12900
53	61.0	72.5	3.47	187.8	172.8	98.4	268	17700
24	93.4	101.3	3.80	177.8	167.0	115.7	357	24600
22	91.9	100.3	3.87	176.0	166.0	116.5	343	24800
1	98.8	107.3	3.97	180.0	170.2	124.1	348	27100
65	59.6	69.1	4.13	187.4	170.0	90.4	319	20800
2	101.0	109.0	4.20	178.8	168.8	124.7	383	29100
3	101.5	109.1	4.23	180.7	170.2	124.1	372	29000
25	94.7	101.8	4.24	178.4	167.6	115.5	376	27400
51	59.9	70.0	4.26	185.0	169.6	99.4	275	22000
52	60.8	70.5	4.26	187.0	171.9	91.7	335	22000
13	93.6	101.2	4.43	179.6	169.2	117.3	387	28600
26	95.4	102.2	4.43	179.1	168.4	115.7	390	28600
37	59.7	68.2	4.67	188.2	170.9	89.5	319	23600
35	65.5	70.0	4.68	163.4	155.2	79.5	349	24400
36	61.2	66.2	4.68	167.0	152.6	77.2	361	23600
27	96.3	102.8	4.94	179.8	168.8	115.5	425	32600
38	59.7	67.8	4.96	187.8	170.2	86.7	356	25000
5	101.0	106.7	5.10	180.5	172.3	118.3	412	34900
4	102.8	108.6	5.11	181.8	171.2	121.9	416	35600
50	59.7	68.4	5.13	184.5	168.8	87.6	393	25800
28	97.0	102.8	5.24	180.5	168.8	113.0	486	34700
39	59.2	66.4	5.30	187.8	169.9	83.5	387	26500
6	103.5	109.8	5.36	176.9	167.1	123.9	435	37800
64	58.4	68.9	5.40	188.1	172.4	92.2	414	27300
49	59.2	67.4	5.45	183.2	167.4	85.9	413	27500
40	59.0	65.8	5.90	188.6	170.6	82.2	427	29300
12	106.7	111.9	6.10	184.7	173.2	122.4	528	43300
41	58.6	65.1	6.13	188.9	170.6	79.5	470	30400
34	100.1	104.9	6.67	180.1	168.8	115.0	575	48000
48	59.4	66.4	6.76	183.2	167.8	82.2	512	33800
7	104.3	109.8	6.87	180.5	170.6	122.0	557	48300
42	58.1	63.0	6.88	188.0	169.2	75.9	423	34000
9	105.6	110.9	7.02	184.9	170.9	121.9	620	50000
10	106.3	111.4	7.19	184.0	172.4	121.0	667	51000
33	99.9	104.0	7.57	180.5	168.8	113.4	584	51100
47	59.9	66.8	8.07	183.2	167.4	83.2	578	41000
29	98.6	101.8	8.32	180.5	168.8	110.5	585	55500
43	56.1	60.4	8.36	190.4	170.9	74.2	472	40000
44	56.1	60.3	8.38	191.9	172.1	73.2	478	40300
32	99.5	103.2	8.56	180.5	168.8	112.1	510	57600
11	106.7	110.9	8.67	183.2	171.0	120.8	665	61500
46	55.6	59.9	8.83	195.0	174.2	73.4	503	42200
31	98.8	101.8	10.5	180.7	168.4	109.5	750	70000
8	105.7	109.1	11.1	180.9	169.4	118.0	793	78000
45	59.9	59.2	11.6	193.7	171.9	69.6	657	55500
30	99.0	101.8	13.0	180.5	168.4	108.7	1005	86700

data of Morris and Whitman on oil and of Nusselt on air were chosen for comparison since they not only extended greatly the range of values of cmu/k covered, but represent, in the authors' opinion, the best comparable published data on heat transfer in turbulent flow for these fluids. The line shown on Figure 5 represents Equation 8 of Dittus and Boelter which, it is clear, is excellently supported by the present data.

TABLE VII. DATA ON KEROSENE

RUN	LIQUID TEMP.		AV. LIQUID VELOCITY FL./SEC.	JACKET TEMP.		MEAN TEMP. INNER PIPE SURFACE ° F.	h	dup / μ
	Inlet ° F.	Outlet ° F.		T ₃ ° F.	T ₄ ° F.			
75	82.4	183.4	0.0905	210.4	209.0	210.4	33.7	319
76	83.2	184.9	0.103	210.8	209.2	209.2	40.0	363
42	67.3	109.3	0.105	185.6	179.2	167.8	13.5	271
43	68.9	145.2	0.106	185.0	179.2	167.0	37.5	256
30	67.1	126.7	0.138	188.4	181.1	163.4	30.3	356
77	82.1	169.8	0.151	210.2	208.4	208.4	43.2	504
41	64.4	128.6	0.179	185.3	178.0	159.8	47.5	502
40	63.0	125.6	0.187	185.1	177.8	159.0	46.6	470
31	70.7	129.0	0.201	188.1	180.7	163.4	47.5	530
29	62.8	120.0	0.204	188.6	180.7	161.6	42.0	502
44	70.0	127.3	0.212	185.0	177.8	159.8	51.4	476
45	65.8	106.0	0.225	185.0	176.7	152.6	52.4	530
78	81.0	151.6	0.242	210.2	208.4	209.5	45.8	747
64	85.7	123.9	0.260	187.2	179.6	163.8	40.3	724
79	82.9	146.6	0.281	209.0	208.4	209.5	46.6	850
74	86.9	143.1	0.327	210.4	209.2	209.5	46.4	1000
73	86.7	142.1	0.329	210.3	208.7	209.2	45.8	1000
80	84.0	137.2	0.373	209.9	208.1	209.2	41.9	1090
81	87.2	124.1	0.550	209.9	204.6	208.5	46.6	1680
32	72.4	99.2	0.690	188.1	179.6	156.2	62.2	1620
63	90.4	106.0	0.776	186.1	178.0	158.7	47.6	2020
38	54.5	75.7	0.885	185.0	175.0	145.4	55.6	1660
46	53.8	75.7	0.910	185.0	174.2	145.2	59.2	1710
62	96.5	109.7	1.03	185.0	176.9	158.8	58.1	2830
37	56.5	74.3	1.23	185.0	175.0	142.0	68.2	2330
72	100.4	122.7	1.34	211.0	208.2	207.7	74.2	3970
47	53.4	69.8	1.37	185.5	173.4	134.5	73.2	2480
33	63.0	80.3	1.43	188.1	179.6	139.9	85.8	2910
28	59.4	75.8	1.76	188.4	176.9	139.9	96.0	3430
27	59.7	74.5	1.92	188.4	176.0	122.2	123	3730
61	101.3	111.2	2.03	185.0	174.8	142.5	132	5750
36	62.2	78.3	2.09	187.6	176.1	135.9	122	4220
60	104.9	113.0	2.77	184.0	173.4	137.0	190	8050
71	137.4	154.2	2.81	214.8	212.9	209.2	177	10900
26	61.4	73.2	2.82	188.6	174.2	113.7	173	5450
48	55.1	66.0	3.22	185.3	170.2	103.9	193	5730
35	65.1	78.6	3.30	183.6	172.1	122.9	194	6720
25	62.1	72.4	3.43	189.0	174.5	106.9	214	6620
70	142.5	157.9	3.68	212.5	211.2	207.0	236	14900
53	104.7	112.0	4.04	180.7	170.4	134.5	274	11700
65	129.6	145.8	4.10	210.5	219.0	203.0	243	15000
34	65.6	76.8	4.23	183.0	170.6	116.6	243	8580
24	61.6	70.3	4.27	189.6	174.2	102.4	259	8130
13	63.4	74.2	4.28	186.1	172.3	107.3	284	8330
66	132.8	143.3	4.50	217.0	203.7	185.1	239	16500
14	63.5	74.2	4.53	186.8	172.4	106.3	302	8930
15	63.7	73.2	4.73	188.0	172.6	104.1	302	9260
54	106.3	111.9	4.74	180.3	169.6	130.9	312	13750
69	145.2	158.6	4.75	211.7	210.2	204.6	390	19500
16	63.5	72.8	4.85	188.6	173.4	102.3	310	9530
55	107.3	113.1	4.96	182.0	170.8	130.9	358	14400
17	63.0	72.2	5.07	188.9	173.2	97.6	332	9910
49	57.6	65.3	5.30	184.7	168.8	93.0	308	9570
18	62.8	71.4	5.33	189.4	173.2	99.5	338	10200
12	61.7	72.6	5.61	181.4	166.0	104.1	395	10950
19	62.1	70.3	5.67	189.8	173.4	97.4	356	10900
56	108.0	113.1	5.75	182.5	171.0	129.9	314	16830
50	58.1	65.6	6.00	185.0	167.8	90.4	375	10800
1	67.1	77.2	6.03	178.6	166.6	108.0	413	12500
20	61.4	68.9	6.33	190.0	173.2	95.7	387	11950
11	60.4	71.4	6.51	181.4	166.0	101.8	473	12400
2	66.2	75.6	6.71	177.8	165.6	106.5	416	13450
21	60.8	67.6	7.13	190.0	172.6	90.4	445	13250
57	109.3	113.5	7.37	183.0	170.8	127.3	483	21800
3	65.1	73.9	7.60	179.6	166.8	102.8	481	15100
68	146.4	158.0	7.75	212.0	210.2	204.6	404	31800
51	58.4	64.4	7.80	185.0	167.0	85.0	466	14100
22	60.3	66.0	8.41	190.0	172.4	87.2	486	15400
4	64.4	72.2	8.65	179.4	165.8	99.4	516	17000
6	62.4	70.3	8.93	181.4	167.0	97.4	545	17100
5	63.2	70.9	9.23	179.2	165.2	97.4	560	17900
10	59.9	67.6	9.36	181.8	166.0	93.8	566	17300
58	109.8	113.1	9.90	183.3	170.6	122.5	664	29200
59	110.3	113.3	10.00	183.2	170.6	122.7	694	29800
52	57.9	62.6	10.15	185.0	165.8	81.2	580	18000
7	61.9	68.9	10.70	180.5	165.4	94.1	633	20000
23	59.6	65.6	10.75	190.0	172.1	80.6	581	19400
8	61.2	66.6	14.80	178.9	164.8	86.4	845	27300
9	60.3	64.0	15.50	180.3	164.4	79.5	804	28200

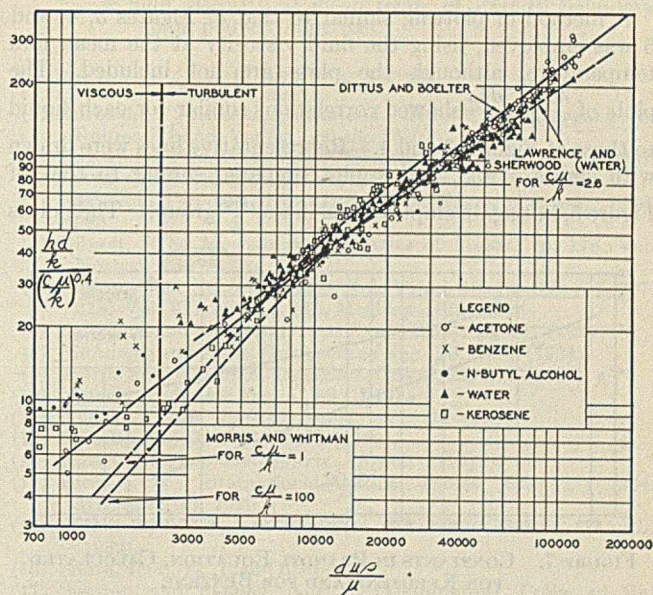


FIGURE 6. COMPARISON OF DATA WITH EMPIRICAL EQUATION OF DITTS AND BOELTER

the Reynolds group, $\frac{dup}{\mu}$. The solid line represents Equation 8, and the dashed lines represent the Morris and Whitman curve for heating oils, the two curves representing different values of $\frac{C\mu}{k}$. Equation 8 is seen to fit the data well, although the kerosene data fall below the empirical line at velocities just above the critical, and in viscous flow break off to a line having a flat slope. Close inspection of the points will reveal that the kerosene data follow closely the Morris and Whitman curves. The dotted line represents the Lawrence and Sherwood equation for water, which may be seen to agree well with the present water data. Equation 8 is clearly unreliable at very low Reynolds numbers and should not be applied in a viscous flow, or in the vicinity of the critical point. It applies, of course, only to clean tubes.

TABLE VIII. DATA ON n-BUTYL ALCOHOL

RUN	LIQUID TEMP.		AV. LIQUID VELOCITY FT./SEC.	AV. STEAM TEMP. ° F.	HEAT PICKED UP BY LIQUID B.t.u./hr.	HEAT GIVEN UP BY STEAM	MEAN TEMP. INNER PIPE SURFACE ° F.	h	dup / μ
	Inlet ° F.	Outlet ° F.							
46	70.7	150.5	0.158	210.5	1763	1920	210.3	37.0	297
24	60.8	133.0	0.198	209.9	2010	1837	210.7	34.7	310
20	78.2	133.7	0.593	211.2	4660	4680	208.9	89.8	1060
39	78.2	117.3	0.792	211.2	4330	4560	209.5	76.6	1270
38	79.3	116.8	0.834	210.8	4380	4630	209.5	78.0	1340
19	83.2	129.4	0.873	211.2	5670	5220	208.1	111	1550
36	96.5	120.3	2.40	211.2	7980	7920	208.9	157	4410
17	86.6	111.3	2.64	213.4	9130	8350	207.5	168	4280
58	150.5	165.0	3.72	211.2	7500	6770	208.7	290	12400
14	91.3	115.0	3.76	211.5	12400	11560	205.3	240	6450
35	104.2	123.7	3.82	211.9	10300	9800	206.6	220	7520
34	105.8	125.8	4.00	210.4	11150	10360	205.5	246	8120
2	89.5	114.5	4.05	212.2	14100	13000	203.3	275	6880
28	105.2	124.2	4.66	211.7	12600	11870	206.2	272	9300
52	152.5	162.6	4.94	212.0	6610	6780	208.1	261	16500
51	153.5	163.1	5.03	211.8	6660	6780	208.1	266	16900
29	105.9	124.0	5.37	210.4	13720	14280	204.1	304	10730
5	92.6	113.5	5.47	210.8	16100	14620	201.6	322	9420
6	94.2	114.5	5.96	212.2	16720	15420	201.4	341	10300
57	159.2	168.7	6.20	211.9	8470	8160	206.9	389	22000
12	95.1	114.6	6.40	218.0	17430	16420	202.7	353	11250
8	96.3	114.7	7.42	214.8	19120	18180	200.0	400	13100
55	158.2	166.8	7.45	212.0	9070	9250	207.9	396	26200
7	95.5	114.0	7.56	215.3	19680	18200	201.0	404	13200
30	107.6	123.8	7.60	210.4	17400	18000	202.7	397	15300
53	160.0	167.2	9.15	212.5	9480	10200	206.9	423	32500
31	109.0	123.7	10.6	214.8	21800	20300	199.5	520	21600
10	96.7	113.3	10.95	218.8	25600	26000	198.0	546	19200
9	95.9	112.2	11.75	214.8	26300	26100	196.8	562	20300
32	111.4	125.5	11.8	210.4	23000	23000	199.4	562	24000

Its excellent correlation of the data on air and oils, as well as the present data on five intermediate liquids, suggests its general applicability to widely different types of fluids. Although it is probable that data on any one liquid can be better correlated than by the Equation 8, this equation would appear to be of value for fluids where data are meager, or entirely lacking.

Equation 8 is compared directly with the present data in Figure 6, where the ordinate is $\frac{hd}{k} / \left(\frac{C\mu}{k}\right)^{0.4}$ and the abscissa is

A method of plotting similar to that of Figures 3, 4, and 5 was employed, using the fluid viscosity at the mean film temperature, although the plots are not included. The plots of $\frac{hd}{k}$ vs. $\frac{d\mu_p}{\mu_f}$ showed correlations similar for each liquid to those of Figures 3 and 4. Representative lines were drawn with slopes of 0.8, and a plot prepared similar to that of Figure 5, but again employing μ_f in the $\frac{c\mu_f}{k}$ group. The points

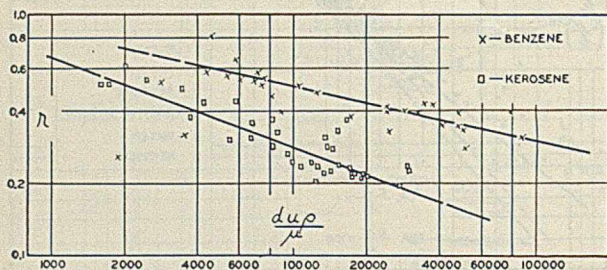


FIGURE 7. CONSTANTS IN PRANDTL EQUATION, CALCULATED FOR KEROSENE AND FOR BENZENE

were definitely scattered, and no general correlation was indicated. By comparison with Equation 6 (Rice) and Equation 7 (Cox), it was found that both equations were high, but that the Cox equation fitted the data better than did that of Rice.

The use of viscosity at a mean film temperature doubtless has a better theoretical basis than the use of viscosity at the main-body average temperature as in Equation 8. However, correlations involving film viscosities introduce trial and error methods in many design calculations, and are unsatisfactory from a practical viewpoint unless definitely called for by the data. The great majority of the available data on heat transmission to fluids have been obtained with low-pressure steam as the heating medium, and consequently with little variation in tube-wall temperature. In such experiments main-body average temperature and film temperature are not independent variables, and the true effect of each cannot be determined. Until experiments are carried out varying liquid and tube temperatures independently, it seems advisable to employ the viscosity of the fluid at the average temperature of the main body, which, in the case of the present data, gives the better correlation.

Because of the wide general interest in the Prandtl (12) modification of the Reynolds analogy between heat flow and fluid friction, the data have been compared with the Prandtl equation:

$$h = \frac{fc\rho u/2}{1-r+\tau(c\mu_p/k_p)} \quad (10)$$

Prandtl pictures a thin liquid film flowing in stream-line motion next to the tube wall. At any cross section the velocity increases from zero at the tube surface to a maximum at the center line of the tube. The ratio of the velocity at the core boundary of the laminar film to the average velocity of the fluid through the pipe is represented by r . The ratio of the thermal resistance of the laminar film to that of the turbulent core is given by the Gibson (5) relation:

$$\frac{r \left(\frac{c\mu_p}{k_p} \right)}{1-r} = \frac{\text{temp. drop through laminar film}}{\text{temp. drop from film boundary to main body of fluid}} \quad (11)$$

The velocity ratio, r , is stated by Prandtl to be a function of the friction factor, f , and, in turn, of the Reynolds number. The physical properties, μ_p , and k_p are taken at the mean temperature of the laminar film.

In calculating values of r from the present data, c and k_p were assumed constant as in Table I. The viscosity, μ_p , was taken at the mean of the temperature of the wall and the temperature at the outer boundary of the film, as calculated from Equation 11. Since this relation involves the unknown, μ_p , a trial and error calculation is involved for each point. Because of this, values of r were calculated only for about half of the runs reported. Figure 7 shows the calculated r 's plotted against $d\mu_p/\mu_f$ for benzene and for kerosene. The points are seen to deviate considerably from smooth curves, but to indicate a definite trend of decreasing r 's with increasing values of $d\mu_p/\mu_f$. For the other three liquids the points are scattered so widely as to indicate no definite curves, and the plots are omitted. It may be pointed out, however, that the calculation of r is very sensitive to uncertainties in the $c\mu_p/k_p$ group, especially where the difference $(c\mu_p/k_p - 1)$ is small. The friction factors used in the calculation were not measured, but were obtained from the Stanton and Pannell (17) curve for smooth copper pipe, employing the viscosity, μ_f , at the mean film temperature, in the Reynolds group.

TABLE IX. VALUES OF PRANDTL CONSTANT, r

LIQUID	RANGE OF r	AVERAGE r
Water	0.22-0.90	0.595
Acetone	0.25-0.71	0.48
Benzene	0.12-0.80	0.43
Kerosene	0.10-0.62	0.31
<i>n</i> -Butyl alcohol	0.32-0.62	0.38

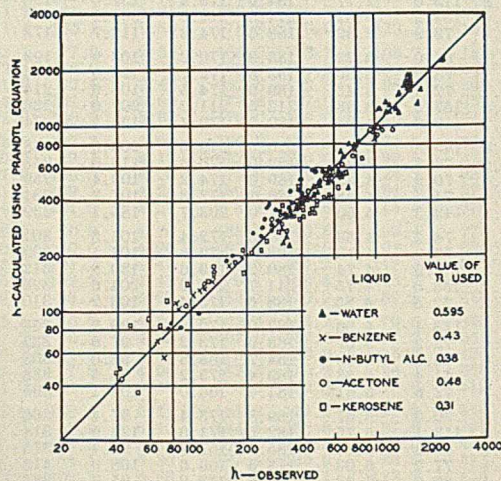


FIGURE 8. COMPARISON OF DATA WITH VALUES CALCULATED FROM PRANDTL EQUATION, USING VALUES OF r GIVEN IN TABLE IX

Arithmetic averages of the values of r calculated for each fluid are tabulated in Table IX. Using these average values of r , the film coefficients were calculated by the Prandtl Equation 10, estimating the friction factors from the Stanton and Pannell curves, as outlined above. The values of h calculated in this way are plotted on Figure 8 vs. the observed values of h . A fairly good agreement of calculated and observed values is indicated, in spite of the wide variation of the individual r 's from the average values used for any one fluid.

The scattering of the calculated r 's indicate that r is a function of variables other than the Reynolds group. Unless the correlation of the ratio, r , can be accomplished more simply than the correlation of the film coefficient itself, the Prandtl equation becomes less interesting from a practical viewpoint.

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TABLE OF NOMENCLATURE

- c* = heat capacity at constant pressure, B. t. u./pound/° F.
d = inside diameter of tube, feet
f = friction factor in Fanning equation: $\Delta H = \frac{4f Lu^2}{2gd}$,
 where *g* = acceleration due to gravity, 4.18×10^8 feet/hour²
 ΔH = drop in fluid head due to friction, feet
h = av. surface coefficient of heat transfer between tube surface and fluid, B. t. u./hour/square feet/° F.
k = thermal conductivity, B. t. u./foot/hour/° F.
L = heated length of tube, feet
r = factor in Equation 10 (Prandtl)
*t*₁ = temp. of fluid entering heated section, ° F.
*t*₂ = outlet temp. of fluid when mixed, ° F.
u_p = mass velocity of fluid through tube, pounds/hour/square foot of cross section
 μ = fluid viscosity at main-body av. temp. (i. e., at $\frac{t_1 + t_2}{2}$), pounds/hour feet
 μ_f = fluid viscosity at mean film temp., pounds/hour feet. The film temperature is taken as the mean temperature of the inner surface of the tube, less half the logarithmic mean temperature difference between tube surface and average fluid temperature

μ_p = fluid viscosity at mean temp. of Prandtl boundary film, pounds/hour feet

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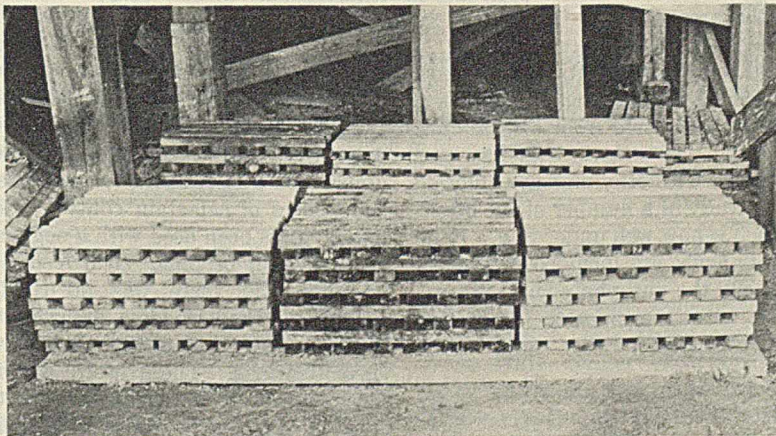
Ethylmercury Compounds as Agricultural Disinfectants

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CERTAIN inorganic salts of mercury have long been recognized as valuable fungicides and bactericides and have been applied in the fields of medicine and agriculture. The organic mercurials are of comparatively recent development for agricultural purposes. A study of some of the phenol derivatives of mercury was initiated in Germany about twenty years ago. Following the World War, more extensive investigations were undertaken in Germany and America to further explore the field of organic mercurials, especially for agricultural disinfectants. Many publications are now available recording the effectiveness of numerous organic mercurials. Among the organic mercury compounds to find practical application are the chlorophenol, nitrophenol, cresol, cyanocresol, furfuralamide, phenyl, and ethyl derivatives and mercury aminochloride. The organics having established usage as seed, plant, and soil disinfectants have desirable qualities not

possessed by bichloride of mercury which has commonly been used in agriculture. Although some of them are not superior to bichloride as disinfectants, they are much less likely to injure plants and are not corrosive to metal parts of tools and machinery. For these reasons they have a wider range of application.

Investigations during the past five years by the du Pont and Bayer-Semesan Companies and by many state and federal agricultural agencies have led to the adoption of certain ethylmercury compounds as disinfectants for specific purposes. Ethylmercury chloride was the first of this series of compounds to be studied. After preliminary investigation there was some question as to whether it could be used successfully as a disinfectant because of its toxic nature. It was found to be much more toxic to fungi and bacteria than the inorganic mercurials or any of the organics previously used for the purpose.



TYPICAL SMALL-SCALE TEST PILES OF SAP GUM

Front right pile treated with ethylmercury chloride
 Front left pile treated with ethylmercury phosphate
 Front center and rear left piles untreated
 Rear center and rear right piles treated

Little was known, however, of its toxicity to animal life. After thorough chemical and biological analysis from the standpoint of both plant and animal life, it was found that the product could be used with a marked degree of success, with safety to plants and animals, if properly diluted with the inert materials best suited to application. Like all mercurials, the ethylmercury compounds are toxic, and caution is necessary in handling them.

SEED DISINFECTION

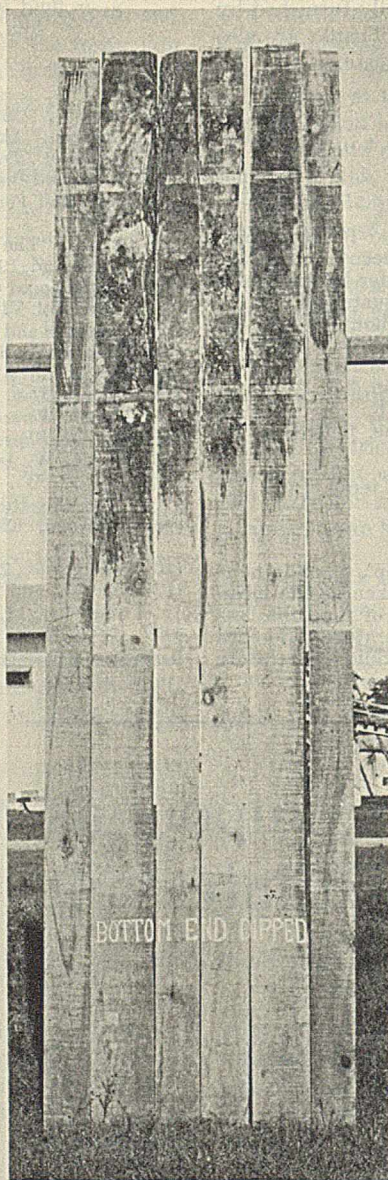
A brief summary of the effectiveness of ethylmercury chloride as a seed grain disinfectant was published in 1929 (7). Powders containing 1 to 2 per cent of this compound dusted on wheat and sorghum with a rotary dusting machine at the rate of 2 ounces per bushel and on oats and barley at the rate of 3 ounces per bushel controlled such seed-borne diseases as stinking smut of wheat, loose and covered smuts of oats, kernel smut of sorghum, and covered smut and stripe disease of barley. This discovery made it possible to use a dust treatment for all small grains including oats and barley which had required a liquid treatment up to this time. The ethylmercury compound is sufficiently volatile to penetrate beneath the hulls of these grains and kill fungus spores adhering to the inner seed coat. Ethylmercury chloride is now being used successfully as a dust seed treatment for the control of certain seed-borne diseases of cereals, cotton, flax, and other crops.

In many cases the yield of crops from treated seed shows greater increase than is accounted for by control of the diseases known to be present. This may possibly be explained by protection by the treatment of the germinating seed from organisms, generally assumed to be saprophytic, which feed on them and lower the vitality of the seedlings. There is a possibility of some stimulative effect aside from disease control.

The promising results obtained with ethylmercury chloride resulted in the beginning of a study of a number of the ethylmercury salts, a program which is now well under way. Salts of both organic and inorganic acids are included. Some of the compounds tested, especially the phosphate and arsenate, are showing greater promise than the chloride for specific purposes, and may consequently find a wider range of application.

SOIL DISINFECTION

Soil disinfection is of necessity being given more consideration with the increasing intensification in agricultural practices. Some of the ethylmercury salts, owing to their high degree of effectiveness, are showing promise for the control of certain soil-borne parasitic fungi. Ethylmercury chloride



LOWER ENDS OF SAP GUM BOARDS
DIPPED IN ETHYL MERCURY CHLORIDE
BEFORE STACKING

Upper ends were left undipped.

(K-1-P), powdered around the base of pepper plants in very small quantities, controlled southern blight, *Sclerotium rolfsii* (6). Ethylmercury chloride (K-1-X), when mixed in small quantities in the surface layers of the soil, greatly reduced southern blight in cotton (2). Bottom rot of lettuce (*Rhizoctonia solani*) is controlled satisfactorily in the muck soils of New York by dusting a 2.4 per cent ethylmercury phosphate powder on the soil underneath the plants at the rate of 25 pounds per acre (8). This treatment has resulted in an average increase in yield of one hundred sixty crates of lettuce per acre.

PLANT SPRAYS

Experiments well under way indicate that certain of the ethylmercury salts may prove effective and practical as sprays for the control of fungus and bacterial diseases of growing plants. One part of the mercury compound in 20,000 parts of water has proved effective in these experiments. In addition to controlling the diseases, they often produce a greener color in the sprayed foliage.

PREVENTION OF SAP STAIN OF LUMBER

Fungous stains of lumber, commonly called "blue stain" or "sap stain," occurring in the sapwood of freshly sawed lumber curing in the yards, are effectively controlled by dipping the lumber in solutions of ethylmercury chloride or ethylmercury phosphate. In 1928 preparations of ethylmercury chloride were contributed by the du Pont Company to the United States Forestry Service to be tested for the control of sap stain in its California Experimental Station. Freshly sawed pine lumber dipped in a solution containing 1 part of ethylmercury chloride in 10,000 parts of water remained exceptionally free from sap stain through the period of curing in the yard (1).

In 1929 the Bureau of Plant Industry of the Department of Agriculture, in cooperation with the Southern Forest Experiment Station and the American Pitch Pine Export Company, undertook a more extensive and intensive study of the chemical phases of sap-stain control. Sodium carbonate had for many years been used with a degree of success for the control of sap stain of pine. The results were not entirely satisfactory, and there was no treatment available for sap gums and hard woods. A number of mercury compounds, including ethyl and phenyl derivatives, were included in these investigations. These were compared with many other chemicals. In the preliminary tests only a few compounds proved sufficiently effective to merit further consideration. Of the promising materials, ethylmercury chloride and ethylmercury phosphate were found to be satisfactory on both pine and sap gum, the two kinds of lumber used in the tests. Experiments also have shown ethylmercury phosphate to be an effective preventive of sap stain in stored logs (3).

Large-scale tests were conducted in 1930 at a number of southern mills to compare the effectiveness of the more promising compounds and to perfect practical methods of application. Additional small-scale tests were conducted to make a further study of these promising compounds in different modifications and to compare them with new chemicals which had not previously been tested. The results of some of these studies are now published (4, 5). The records of these experiments agreed with the previous preliminary tests in proving the ethylmercury compounds to be the most generally effective chemicals used. A solution containing 1 part of either of the ethylmercury salts in 10,000 parts of water proved to be an effective dip for the control of sap stain of both pine and gum. A few other compounds, when used in greater concentration than this, were found to be effective on certain kinds of lumber, but none of them appears to be satisfactory on both pine and gum. Borax and sodium tetrachlorophenolate were effective on sap gum but not satisfactory on pine, while sodium *o*-phenylphenate was effective on pine but not sufficiently effective on gum.

The extensive large-scale tests in 1930 indicated that the ethylmercury compounds could be used successfully for dipping lumber on a commercial scale for the control of sap stain. Ethylmercury chloride was then offered the lumber industry, diluted sufficiently with water-soluble inerts to make it safe to handle by exercising the precautionary measures recom-

mended for handling poisonous disinfectants. The concentration is adjusted so that 1 pound in 50 gallons of water gives the required strength for application. This solution is prepared in a vat so constructed that the lumber passing on the green chain from the saws to the sorting and grading floor is drawn through the solution. A thorough wetting of all surfaces of the lumber is all the treatment necessary.

Although not entirely beyond the developmental stages, ethylmercury chloride is producing good results in the control of sap stain of lumber, and is filling a real need in the lumber industry.

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Hydrogenation of American Coals

Preliminary Investigation

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THE increased demand for liquid fuels during the past decade has stimulated research having as its object the conversion of coal into the more desirable liquid products. The most promising method developed is that of high-pressure hydrogenation.

The first attempt to hydrogenate coal was made by Berthelot (4) some sixty years ago. He treated finely powdered coal with a saturated hydriodic acid solution at 270° C. for several hours. This method was later modified by Tropsch (9), who added red phosphorus to the reaction mixture and found in general that the younger coals were quite susceptible to hydrogenation. For most of the pioneering work and the successful commercial application, however, credit is given to Bergius, who succeeded in producing virtually complete liquefaction of coal. The process, as described in his patent (2), involves treatment of coal with hydrogen at high pressure and at temperatures between 300° and 500° C. The patent specifies dispersion of coal in liquid hydrocarbons; although it mentions no catalyst, ferric oxide is used in the process, presumably for the purpose of fixing the sulfur present. More recent investigation by Skinner (20), however, shows

For the conditions investigated, coal ash does not appear to act as a catalyst for the hydrogenation of phenol at 400° C. The "B" product has been found in the two coals before and after hydrogenation. Qualitative and quantitative data have been presented for hydrogen absorption by two American coals of the bituminous class. Temperatures between 300° and 350° C. have been found to give optimum conversion of the coals into phenol-soluble constituents. The conversions of these coals at optimum conditions compare favorably with those reported for European coals.

that with most coals, ferric oxide reacts as a catalyst.

Since the pioneering work of Bergius, much research has been carried on in Great Britain by the Fuel Research Board and by the Mines Research Laboratory (Birmingham). In a series of experiments at the Mines Research Laboratory (10), a study was made of coal hydrogenation, both with and without catalysts. Bergius' process was used without ferric oxide or other catalysts, and with a change of dispersion medium. From runs covering twenty-nine different

coals, data were obtained that showed some conversions in excess of 80 per cent. With nickel oxide or ammonium molybdate catalysts, some of the same coals showed conversions greater than 90 per cent.

In Italy similar experiments have been conducted by Levi, Padovani, and Amati (13), in Japan by Oshima and Tashiro (16), and in France by Arend (1). For the investigation of Canadian coals, a laboratory has been installed at the University of Alberta (17). Except for some work on Canadian coals reported by Graham (11), results of hydrogenation studies on American coals do not appear in the literature.

TABLE I. RESULTS OF PHENOL HYDROGENATION AND EXTRACTION AND OF CONSTANT-VOLUME EXPERIMENTS

EXPERIMENT	TEMP. ° C.	PRESSURE		RUN	PRODUCTS						CARBON		HYDROGEN		RATIO C/H	
		Lb./sq. in.	Kg./sq. cm.		A %	B %	C %	D %	E %	F %	A %	B %	A %	B %	A %	B %
Phenol hydrogenation	400	3200	225	1	0	0	0	0.9	0.2	0
Coal extraction:																
Eastern	50	14.7	1.03	2	86.1	10.2	3.7	0	0	0	81.8	80.3	4.7	4.6	17.4	17.5
Western	50	14.7	1.03	3	85.1	7.6	5.4	0	0	0	79.0	78.1	5.2	4.9	15.2	16.6
Constant-vol. nitrogen: ^a																
Eastern	350	1700	120	4	83.8	3.4	8.2	0.3	0.8	3.6	86.4	81.7	3.6	4.2	23.8	19.6
Western	350	1750	123	5	77.5	4.3	10.2	0.3	0.7	5.4	84.0	83.0	4.0	4.5	21.0	18.6
Constant-vol. hydrogen: ^a																
Eastern	350	1700	120	6	40.8	42.2	15.4	9.4	85.2	83.6	3.7	4.1	23.0	20.4
Western	350	1750	123	7	40.6	23.7	14.7	3.4	3.6	26.5	83.1	83.5	3.8	4.2	21.8	19.6

^a Pressures for constant-volume experiments reported as initial pressure at room temperature.

PRESENT INVESTIGATION

Studies of American coals were begun in the fall of 1930 at the chemical engineering laboratories of the University of Washington. The first work was confined to representative bituminous coals from both the eastern and western sections of the United States, and the final selection of samples was dependent upon these and other available analytical data of the respective coals.

The experimental system adopted differed from that of other investigators in one respect: the reaction bomb was of the stationary type and employed no stirring device. Graham, heating externally by means of a gas flame, used a rotating bomb; Bergius, in his American patent, specifies a revolving stirrer in the reaction mixture.

The selection of a dispersion medium was conditioned largely by available methods of analyzing the products. Bergius used a saturated oil and separated the products by a combined process of extraction with raw petroleum and destructive distillation. Fischer (7, 8) used no dispersion medium and analyzed the products by both ether extraction and destructive distillation. Shatwell and Nash (19) used saturated oils, but were unable to effect a satisfactory separation of the products from the oil used. Shatwell and Graham (18) used phenol and worked out a separation of products depending upon phenol and chloroform extractions. In general, the yields obtained by workers using no dispersion

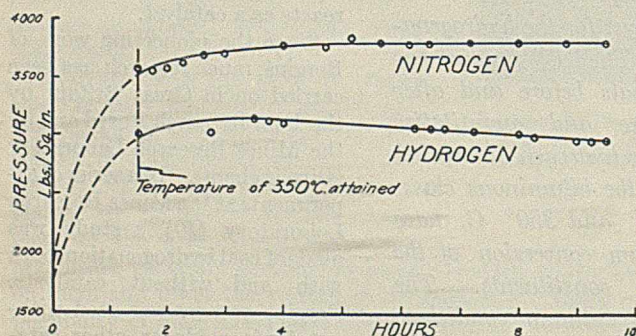


FIGURE 1. CHANGE OF PRESSURE OF NITROGEN AND OF HYDROGEN WITH TIME (EASTERN COAL)

medium were unsatisfactory. The method of separation effected by Bergius, although more applicable industrially, does not yield as complete information of the coals as does the method of Graham. Phenol was therefore adopted as the dispersion medium.

Initial experiments were made upon the hydrogenation of phenol in the presence of a small amount of coal ash. This work was followed by phenol extractions of the raw coal.

Both coals were then subjected to a constant-volume nitrogen distillation at 350° C. and 211 kg. per square centimeter (3000 pounds per square inch) pressure, with phenol as the dispersion medium. Similar runs were made with hydro-

gen gas instead of nitrogen. After these initial runs, the coals were hydrogenated at constant pressure between the limits of 250° and 450° C., and 120 and 296 kg. per square centimeter (1700 and 4200 pounds per square inch) pressure, with phenol as the dispersion medium.

The samples of coal selected were received from the United States Bureau of Mines. The eastern coal, furnished through the courtesy of A. C. Fieldner, was a *p*-bituminous sample (Seyler's classification) from the Ocean No. 2 mine, Pittsburgh bed, Allegheny County, Pa. This coal analyzed as follows (6):

ULTIMATE ANALYSIS ^a (%)				
C	H	O	S	N
85.4	5.9	5.9	1.1	1.7
PROXIMATE ANALYSIS (%)				
VOLATILE MATTER		FIXED CARBON		
37.6		62.4		
LOW-TEMPERATURE CARBONIZATION, 500° C. (%)				
COKE	GAS	TAR OIL	LIQUOR	
77.6	7.1	8.5	6.3	
Softening temperature of coal			320° C.	
Initial temperature of active decomposition			390° C.	

^a All results reported in this paper are expressed on the ash-free and moisture-free basis.

The western coal, furnished through the courtesy of H. F. Yancey of the United States Bureau of Mines, University of Washington station, was a *per-m*-lignituous sample from No. 3 mine, Roslyn bed, Roslyn, Wash., and analyzed as follows (21):

ULTIMATE ANALYSIS (%)				
C	H	O	S	N
82.6	6.3	8.5	0.5	2.1
PROXIMATE ANALYSIS (%)				
VOLATILE MATTER		FIXED CARBON		
43.7		56.3		
LOW-TEMPERATURE CARBONIZATION, 550° C. (%)				
COKE	GAS	TAR	LIQUOR	
70.1	6.42	17.9	5.05	

LABORATORY INSTALLATION. Briefly, the system employed a stationary reaction chamber involving no stirring. It was heated electrically by means of an external coil. A thermocouple well passed through the head and was immersed in the reaction mixture. Controls from the hydrogen storage cylinders to the reaction chamber were so situated that runs could be made at either constant pressure or constant volume. Pressures up to 350 kg. per square centimeter (5000 pounds per square inch) were obtained by means of a three-stage compressor which received the gas from a gas holder at atmospheric pressure. From the compressor the gas passed through a felt-packed oil trap to the storage cylinders.

EXPERIMENTAL METHOD. The reaction cylinder was charged with an intimate mixture of 50 grams each of coal and phenol. The cylinder was placed in the reaction bomb, which in turn was connected to the high-pressure system. A buffer cylinder was brought to the pressure of the desired run and opened to the control manifold, which in turn opened to the reaction chamber. The apparatus was then ready for a constant-pressure run.

The desired temperature of the reaction chamber was attained and maintained for a period of 8 hours. At the end of a run,

the heat was shut off; the system was closed to the pressure line and then allowed to cool to room temperature. The gas was then passed through sampling bottles and measured by a wet meter. The charge was removed and analyzed.

In order to make comparisons between European and American coals, Graham's method was followed, and a separation was made into the following fractions:

- A. Residue insoluble in phenol
- B. Fraction soluble in phenol, insoluble in chloroform
- C. Fraction soluble in phenol and chloroform
- D. Light oil boiling under 150° C.
- E. Water
- F. Gas

DETAILS OF SEPARATION. The liquid portion was distilled up to 150° C. and the distillate was washed successively with dilute sodium hydroxide, dilute sulfuric acid, and water. The solid portion, together with the stripped liquid portion, was treated with an excess of sodium hydroxide solution to remove the phenol. The solid was filtered, ground in a mortar, washed with sodium hydroxide and finally with water, then dried *in vacuo* at 105° C., and weighed. This procedure gives the total weight of the products A, B, and C.

The mixture was then placed in a Soxhlet extractor and extracted with phenol. The phenol-insoluble residue from the thimble was leached with a 20 per cent solution of sodium hydroxide, washed with water, and dried *in vacuo*, giving product A.

The phenol solution was treated with a slight excess of sodium hydroxide solution which caused the precipitation of a black tarry mass. This precipitate was filtered, washed, and dried, then placed in a Soxhlet extractor, and extracted with chloroform. The portion remaining in the thimble after extraction was product B. The chloroform was removed from the extract by evaporation on a steam bath, leaving product C.

Combustion analyses were made for carbon and hydrogen on all the A and B products and on a few of the C products. Analysis of the gaseous products was made in some cases.

DISCUSSION OF RESULTS

In Table I are summarized the results of phenol hydrogenation, of phenol extraction of eastern and western coals, and of the constant-volume nitrogen and hydrogen experiments.

According to Lush (15), phenol is not an appropriate dispersion medium for coal hydrogenation because, under the conditions prevailing, it is readily converted into cyclohexane. Kling and Florentin (12), however, claim that phenol is not hydrogenated without the use of catalysts. In a test reported by Shatwell and Graham (18) in which phenol was treated for 4 hours under a hydrogen pressure of 134 kg. per square centimeter (1900 pounds per square inch) and at a temperature between 400° and 406° C., no conversion of the phenol was observed. The catalytic effect of coal ash upon the hydrogenation of phenol, however, does not appear to have been reported in these or other investigations. Run 1 of the present investigation (Table I), in which phenol was treated with hydrogen in the presence of a small quantity of coal ash, shows very little hydrogenation at 400° C. In this experiment, phenol was hydrogenated in the presence of one per cent of A product from the Roslyn coal. This product contained 42 per cent ash of the following composition (5): silica, 41.6 per cent; alumina, 39.3 per cent; ferric oxide, 10.3 per cent; calcium oxide, 7.9 per cent; magnesia, 1.3 per cent; and phosphorus, 0.62 per cent.

In correlating the results from phenol extractions of the coals with those from nitrogen and hydrogen experiments at constant volume, several interesting observations regarding hydrogenation were noted. The B product yields of 10.3 and 7.6 per cent from phenol extractions of eastern and western coal, respectively, show that this fraction, although one of the principal ones resulting from hydrogenation, is not solely due to the action of hydrogen, but is present in the original coal. These results do not substantiate those of Graham (10), who states that the B fraction is a definite product of hydrogenation. The effect of temperature alone is clearly shown in a comparison of the phenol extractions with the nitrogen experiments. Both coals under the action of increased

temperature showed a small decrease in A, a large decrease in B, and a greatly increased yield of C. These results indicate that temperature increase has only a slight effect upon the A product but exerts a marked cracking action on the B portion, tending to break it into lighter components.

Figures 1 and 2 illustrate the change of pressure with time when the coals were heated in atmospheres of nitrogen and of hydrogen. These curves were obtained under constant-volume conditions and indicate qualitatively the effect of temperature rise and of hydrogenation. A quantitative measure of the hydrogen absorbed is shown in Table II and amounts to 1.6 per cent for the eastern and 2.8 per cent for the western coal. Because the cracking of the coal liberates

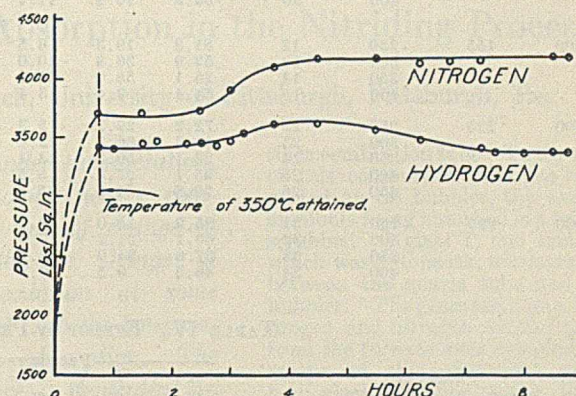


FIGURE 2. CHANGE OF PRESSURE OF NITROGEN AND OF HYDROGEN WITH TIME (WESTERN COAL)

gases, progressive increases in pressure for experiments with nitrogen are to be observed. Hydrogenation experiments under identical initial conditions, however, show a marked decrease in pressure which clearly indicates hydrogen absorption. Both hydrogen curves, moreover, show definitely that the absorption is more rapid in the early stages of the experiment and becomes almost negligible toward the end of the runs. Furthermore, the product percentages reported in Table I for these experiments show that the hydrogen reacts not only with gaseous and phenol-soluble products, but also with the solid coal.

TABLE II. HYDROGEN ABSORPTION FOR CONSTANT-VOLUME EXPERIMENTS

	(Volume in liters at normal temperature and pressure)							
	EASTERN COAL				WESTERN COAL			
	NITROGEN EXPT.		HYDROGEN EXPT.		NITROGEN EXPT.		HYDROGEN EXPT.	
	Total gas	Total N	Total gas	Total H	Total gas	Total N	Total gas	Total H
Initial	26.1	26.1	26.1	26.1	28.8	28.8	28.8	28.8
Final	29.8	26.3	23.9	17.9	34.0	29.0	24.8	15.8
Absorption ^a	1.6	2.8

^a Grams hydrogen per 100 grams coal.

Bergius (3) observed that hydrogenation began at a temperature relatively low, and that treatment at temperatures between 300° and 350° C. for several hours resulted in a fairly large absorption of hydrogen, although the product was a solid pitchlike mass. Continued treatment at 450° C. converts this product to a liquid. Levi, Padovani, and Mariotte (14) state that hydrogenation takes place in three stages:

(1) Up to 300° C., transformations occur without the formation of gas or vapor, and with very little hydrogen absorption.

(2) Between 350° and 400° C., hydrogenation is principally of the liquid phase and corresponds essentially to destructive distillation.

(3) From 400° to 500° C., cracking of more resistant molecules takes place with hydrogenation essentially in the vapor phase.

TABLE III. EFFECT OF TEMPERATURE ON HYDROGENATION OF COAL

PRESSURE Lb./sq. in. Kg./sq. cm.	TEMP. ° C.	RUN	PRODUCTS					CARBON		HYDROGEN		RATIO C/H		
			A %	B %	C %	D %	E %	A %	B %	A %	B %	A %	B %	
EASTERN COAL														
2200	155	250	8	83.8	16.7	5.3	81.7	82.4	4.3	4.5	19.0	18.2
		300	9	39.5	49.9	10.5	83.0	82.0	4.4	4.5	18.8	18.3
		350	10	33.8	51.5	14.0	3.1	3.7	82.5	83.0	4.0	4.3	20.6	19.3
		400	11	50.7	20.6	14.8	1.6	4.0	88.7	85.0	3.6	3.7	24.7	22.6
3200	225	250	16	75.0	8.2	14.8	0.4	0.3	82.2	85.9	4.4	4.3	18.7	20.0
		300	17	21.1	67.9	12.2	0.0	1.8	81.1	81.8	4.0	4.5	20.2	18.2
		350	18	34.5	31.4	34.9	0.7	4.3	84.9	81.1	3.7	3.5	23.0	23.2
		400	19	69.7	10.3	12.9	2.3	3.6	86.1	81.7	3.6	4.2	23.9	19.5
		450	20	78.5	3.3	10.1	4.2	4.3	87.8	82.5	3.5	3.9	25.0	21.1
		500	21	92.3	0.0	7.1	13.1	3.8	90.7	..	3.2	..	28.1	..
4200	295	250	27	87.1	13.7	8.3	81.3	82.5	4.6	4.7	17.7	17.4
		300	28	42.3	47.5	10.2	0.8	1.9	83.2	80.0	4.7	4.4	17.5	18.2
		350	29	27.6	40.2	14.1	2.7	3.6	88.0	83.5	3.9	4.0	22.6	20.8
		400	30	53.3	10.4	11.1	6.4	4.3	90.0	85.0	3.5	3.8	25.7	22.4
WESTERN COAL														
2200	155	250	12	81.8	19.3	6.5	79.6	81.2	5.3	4.9	15.2	16.7
		300	13	52.9	36.8	10.0	81.2	81.0	4.8	4.6	17.0	17.6
		350	14	26.1	58.0	21.1	82.1	83.8	4.2	4.6	19.6	18.2
		400	15	54.4	9.4	13.4	3.0	3.4	86.4	85.1	3.6	4.0	24.0	21.2
3200	225	250	22	72.2	29.7	5.3	78.3	79.8	5.0	5.0	15.7	16.1
		300	23	19.3	66.8	22.4	0.0	1.3	75.7	81.4	4.6	4.5	16.6	18.3
		350	24	23.1	59.7	14.4	2.6	4.2	79.4	80.4	4.6	4.3	17.3	18.7
		400	25	55.1	27.6	5.5	2.7	3.9	86.3	82.1	3.8	4.9	22.6	16.8
		450	26	70.8	1.6	5.4	12.2	4.3	89.3	..	3.5	..	25.7	..
		4200	295	250	31	85.9	13.0	6.7	79.0	79.9	5.1	4.8
300	32	66.1		21.2	7.9	0.2	1.0	79.6	79.3	4.6	4.6	17.2	17.1	
350	33	37.6		34.0	13.1	3.7	2.9	84.5	84.2	3.6	4.3	23.4	19.6	
400	34	46.5		9.5	9.8	3.5	3.1	87.3	83.6	3.6	4.0	24.2	20.9	

TABLE IV. EFFECT OF PRESSURE ON HYDROGENATION OF COAL

TEMP. ° C.	PRESSURE		RUN	PRODUCTS					CARBON		HYDROGEN		RATIO C/H	
	Lb./sq. in.	Kg./sq. cm.		A %	B %	C %	D %	E %	A %	B %	A %	B %	A %	B %
EASTERN COAL														
350	1700	120	35	34.4	62.7	15.1	80.9	80.2	4.1	4.2	19.7	19.1
	2200	155	10	33.8	51.5	14.0	3.1	3.7	82.5	83.0	4.0	4.3	20.6	19.3
	2700	190	36	35.7	53.3	11.5	82.7	81.9	4.0	4.0	20.6	20.4
	3200	225	18	34.5	31.4	34.9	0.7	4.3	84.9	81.1	3.9	3.5	23.0	23.2
	3700	260	37	30.0	50.0	16.1	83.6	82.8	4.1	4.2	20.4	19.7
	4200	295	29	27.6	40.2	14.1	2.7	3.6	88.0	83.5	3.9	4.0	22.6	20.8
	WESTERN COAL													
350	1700	120	38	37.5	41.4	15.7	79.5	83.5	3.9	4.4	20.1	19.0
	2200	155	14	26.1	58.0	21.1	82.1	83.8	4.2	4.6	19.6	18.2
	2700	190	39	17.9	63.6	16.5	78.7	83.0	4.5	4.5	17.5	18.4
	3200	225	24	23.1	59.7	14.4	2.6	4.2	79.4	80.4	4.6	4.3	17.3	18.7
	3700	260	40	49.4	17.3	17.5	4.7	2.4	84.6	83.6	3.8	4.2	22.4	19.9
	4200	295	33	37.6	34.0	13.1	3.7	2.9	84.5	84.2	3.6	4.3	23.4	19.6

Data presented in Table III show very little absorption of hydrogen and virtually no conversion of the coal at a temperature of 250° C., irrespective of the pressures investigated. Between 300° and 350° C., maximum absorption of hydrogen together with maximum conversion of the coal was obtained. Experiments at 400° and 450° C. showed diminishing yields. It is the belief of the authors that this last result is due to the fact that active decomposition of the coal has already commenced at these higher temperatures; consequently, any hydrogenation taking place affects merely the low-temperature distillation products and not the coal itself. These results appear to be entirely in accord with those of the investigators cited. Because of the rapid rise in temperature, the desired point being attained from 30 to 40 minutes after heat was applied, the time of hydrogenation between the limits of 300° and 350° C. was no more than 10 minutes for all experiments where the maximum temperature was above 350° C. Hence it is believed unlikely that any appreciable hydrogenation occurred below the temperatures reported for any experiment.

Table IV shows that pressure has little effect upon the yields throughout the range investigated for eastern coal, although the higher pressures appear to give yields slightly higher. For western coal, however, a marked optimum is shown in the vicinity of 211 kg. per square centimeter (3000 pounds per square inch).

According to a prediction made by Graham (10), based on his studies of European coal, the *p*-bituminous class (Seyler's system) which corresponds to Parr's "eastern bituminous

type" should be more readily acted upon by hydrogen than should those of the *m*-lignitous or "western bituminous type." For the two coals investigated, it will be observed that the western coal shows a slightly better conversion. The six best results reported by Graham from a series of twenty-nine samples show between 16.3 and 22.5 per cent residue (*A* product). Yields obtained at optimum conditions for eastern and western American coals, respectively, were 21.1 and 19.3 per cent residue. From these data it appears that the American coals investigated compare favorably with those of Europe with respect to the degree of hydrogenation.

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The Nitridding of Iron and Its Alloys

I. Ammonia Dissociation and Nitrogen Absorption in the Nitridding Process

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DURING the past five years considerable interest has been aroused in the nitridding process as applied in producing very hard and somewhat corrosion-resistant surfaces on steel. Therefore, at the inception of the studies reported in this series of papers, it appeared worth while to consider quantitatively what takes place in the gaseous ammonia phase surrounding steel during the process of nitrification and to obtain a quantitative indication of the amount of nitrogen absorbed over a range of temperatures. The present paper describes the research carried out with these objectives.

The decomposition of ammonia accompanied by nitridding action, when reaction takes place between ammonia and steel, is considerably more rapid than a decomposition of ammonia by heat alone or by heat plus a surface such as quartz, glass, glazed porcelain, etc. In this connection it is important to indicate at the start that true equilibrium is probably never reached in commercial nitridding. The original determination of the ammonia equilibrium was reported by Haber and Van Ordt (2) and was followed later by the additional contributions by Haber and his co-workers. Perman and Atkinson (4) showed that at 1100° C. in a porcelain bulb a given volume of ammonia gas, under static conditions, was completely decomposed in 20 minutes. This fact in itself is evidence that, in nitridding, decomposition is not due to heat effects alone, but also to surface and catalytic effects. Ramsay and Young (5) and also White (7) have shown that ammonia decomposition under conditions of flow through tubes depends to a large extent on the chemical composition of the surfaces with which the ammonia comes in contact, the physical structure of the surface, and its total area. They have shown in addition that decomposition starts at a little below 500° C. and is practically complete when iron is present at or near 800° C.

EXPERIMENTAL PROCEDURE

In determining the percentage decomposition taking place when gaseous ammonia is passed over a sample of steel, the apparatus shown in Figure 1 was employed.

The ammonia supply was connected through a reduction valve to a constant-pressure leak (not shown in the diagram) and finally to the designated train of apparatus. This train consisted of a calcium oxide drying tower, connected to a flowmeter, and an electric furnace of the Hoskins type, fitted with a fused

In contact with the steels under consideration, ammonia decomposition becomes nearly complete at 800° C., while the rate of change of ammonia concentration with the change of temperature becomes a maximum at some definite temperature coincident with the temperature of maximum nitrogen absorption. The temperature of this coincidence is dependent on the steel.

silica combustion tube. To the end of this combustion tube was connected an oil bubbler, the excess ammonia being absorbed in a water scrubber. A glass T, one arm of which was a stopcock, was inserted between the quartz tube and oil bubbler. The gases ammonia, hydrogen, and nitrogen which issued from the furnace were sampled by means of this stopcock, using two glass sampling bulbs filled with heavy liquid petrolatum saturated with ammonia. The temperature was read by a

thermocouple located in a quartz protection tube inside the combustion tube, as shown at 2. The small steel samples ($1 \times \frac{7}{16} \times \frac{1}{4}$ inch, finished to a smooth commercial grind) were inserted in the fused silica combustion tube so as to be just at the end of the thermocouple, thus insuring a coincidence between the temperature of the sample and the indicated temperature.

The procedure included regulation of the temperature of the furnace as desired; sweeping the train out with ammonia; regulating the flow until constant at 0.06 cubic foot per hour; and then, after allowing these conditions to prevail for 30 minutes, inserting the weighed samples in the combustion tube and taking gas samples at intervals through the stopcock. The resultant gas samples were analyzed for ammonia and hydrogen in an Orsat apparatus, removing the ammonia with

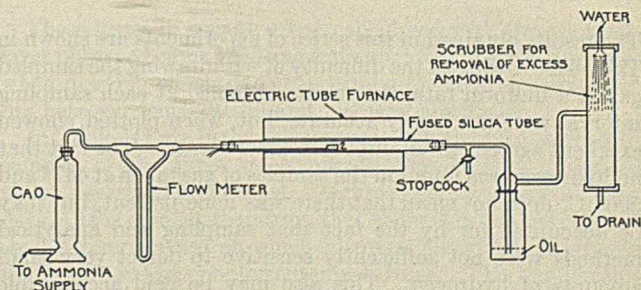


FIGURE 1. DIAGRAM OF APPARATUS

sulfuric acid, and burning the hydrogen by passing through a copper oxide furnace, the balance being considered as nitrogen. In this manner errors introduced should be found in the balance.

AMMONIA DECOMPOSITION

As previously stated, ammonia decomposition in contact with fused silica should be considerably different (as regards rate) from decomposition in contact with a catalytically active substance such as steel. Consequently, a series of

determinations at five different temperatures were made with no steel specimen in the furnace. The results are shown in Figure 2. The amount of ammonia present starts decreasing at 500° to 550° C., but at 775° C. there still remains 83 per cent ammonia in the effluent gases. This, as we shall see later, is not the case when ammonia passes over hot samples of steel instead of hot fused silica walls.

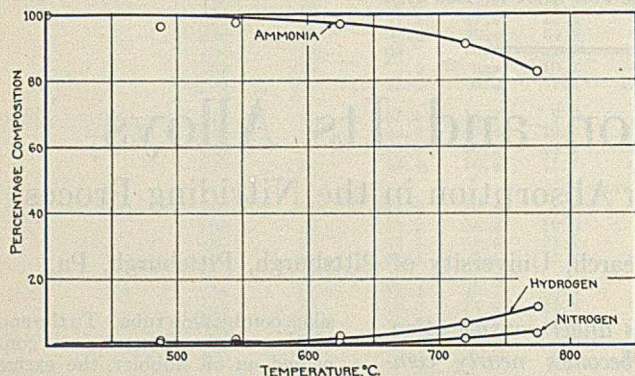


FIGURE 2. DECOMPOSITION OF AMMONIA IN CONTACT WITH FUSED SILICA TUBE

It is interesting to point out in passing that this difference in ability to decompose ammonia has been utilized recently in a practical manner by Sergeson and Deal (6). In order to effect an economy in the amount of ammonia used in nitriding, these investigators have resorted to enamel-lined nitriding boxes, thus insuring contact of ammonia with a ceramic material that decomposes ammonia to only a limited extent under the conditions found in commercial nitriding.

Using the above described method, steel samples were inserted in the tube furnace and the effluent gases analyzed at stated intervals of time. Such determinations were carried out over a period of seven hours at eight different temperatures for steel samples of the compositions shown in Table I.

TABLE I. COMPOSITION OF STEEL SAMPLES

ANALYSIS	STEEL 1	STEEL 2	STEEL 3
	%	%	%
Carbon	0.19	0.45	0.24
Manganese	0.64	0.51	0.87
Aluminum	2.50	0.93	0.81
Molybdenum	0.85	None	0.80
Phosphorus	0.010	0.010	0.016
Sulfur	0.023	0.038	0.018
Silicon	0.29	0.26	0.47
Chromium	None	1.71	None

The results obtained in this series of experiments are shown in Table II. Owing to the difficulty of withdrawing the sampled gas at a uniform rate, the results obtained at each sampling interval were not highly accurate, but, when plotted, showed excellent agreement on duplicate experiments. The fact that no hydrogen was found in the samples of gas taken at 447° and 500° C. does not mean that there was none present, but may be accounted for by the fact that sampling and analytical methods were not sufficiently sensitive to detect very small amounts of hydrogen. This also may be held accountable for the fact that the relatively small amounts of nitrogen absorbed by the steel did not show up in the hydrogen-nitrogen analysis.

The data given in Table II permit several observations to be drawn. At temperatures between 450° and 500° C. the amount of ammonia decomposition is not very different from that found in the case of a fused silica tube (Figure 2). As the temperature is increased, the percentage of ammonia in the effluent gas decreases slowly at first, but more and more rapidly later until at 800° C. the decomposition becomes nearly complete. The percentage of ammonia present at any temperature decreases during the first period of the experi-

ments until a nearly constant value is reached, at which point any decrease becomes much slower. This finding probably means that the original fresh metal surface has a tendency to act as a catalyst, and for a short time forms, as well as decomposes, some ammonia. As time progresses, however, the original surface changes from one of a more or less clean steel to one contaminated with nitrides, and in this manner the decomposition of ammonia is increased. That this drop in concentration is not due to the temperature lag present in bringing the specimen up to temperature was demonstrated by the observation that at the lower temperatures as many as 3 or 4 hours were necessary to reach the stage indicating a greatly decreased rate of ammonia decomposition, and a specimen weighing only 13 grams would reach the furnace temperature in a very few minutes. The nature of the sample surface continues to change upon longer periods of nitriding, as shown by the fact that at the end of 24 hours the quantity of ammonia present had dropped to 82.5 per cent at 500° C., 58.7 per cent at 600° C., and 9.1 per cent at 700° C. This shows that no true equilibrium is reached throughout the nitriding process, but that a marked decrease in the rate of change at any temperature does take place.

TABLE II. DISSOCIATION OF AMMONIA IN CONTACT WITH STEEL 1 AT VARIOUS TEMPERATURES

TEMP. ° C.	TIME OF SAMPLING Minutes	(Area and gas flow constant)			BALANCE %
		NH ₃ %	H ₂ %		
447	60	99.0	0	0.9	
447	120	98.7	0	1.3	
447	225	98.3	0	1.7	
447	270	98.6	0	1.4	
447	330	98.3	0	1.7	
500	30	97.7	0.5	1.9	
500	60	96.9	1.4	1.7	
500	125	96.7	1.7	1.5	
500	210	96.5	2.2	1.2	
500	270	94.2	2.1	1.8	
500	330	94.6	3.1	2.4	
500	430	94.2	4.3	1.6	
555	30	96.4	1.8	1.8	
555	70	97.0	1.5	1.5	
555	100	93.6	4.1	2.2	
555	195	89.5	7.5	3.2	
555	255	88.0	7.9	4.1	
555	315	84.9	10.5	4.7	
555	375	86.1	9.8	4.2	
600	30	75.6	17.8	6.6	
600	67	75.6	17.6	6.7	
600	120	72.0	20.8	7.1	
600	210	67.7	24.6	7.6	
600	270	68.9	22.3	8.7	
600	330	67.4	24.9	7.7	
600	390	69.0	23.2	7.8	
650	35	59.8	29.2	10.9	
650	95	57.8	33.2	9.3	
650	220	48.5	39.1	12.4	
650	280	47.5	39.6	12.8	
650	340	47.5	39.7	12.8	
650	400	47.5	41.1	13.2	
700	30	26.7	59.5	13.8	
700	60	22.4	60.1	17.5	
700	115	18.0	59.8	22.2	
700	235	15.6	63.3	21.1	
700	385	10.1	68.2	21.7	
750	30	12.7	65.5	21.7	
750	60	11.1	67.5	21.4	
750	130	8.6	69.4	22.0	
750	250	8.3	69.5	22.2	
750	400	5.0	71.5	23.5	
800	30	4.5	70.8	24.7	
800	100	4.2	70.2	25.6	
800	195	3.6	70.5	25.9	
800	320	1.9	74.0	24.1	
800	395	2.4	73.7	23.9	

In Figure 3 the compositions of the effluent gases at the end of 7 hours of treatment are plotted against the temperatures of nitriding. From this set of curves it may readily be seen that the amounts of hydrogen and nitrogen present in the reaction gases increase with the temperature, while the ammonia concentration falls off.

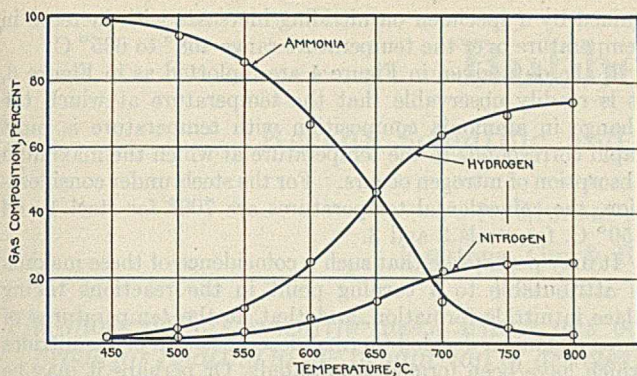


FIGURE 3. DECOMPOSITION OF AMMONIA IN CONTACT WITH STEEL 1 AFTER NITRIDING FOR 7 HOURS

Similar data have been obtained on two other nitridding steels at 500°, 600°, 700°, and 800° C. These data are presented in Figure 4, where the ammonia concentration has been plotted against temperatures, omitting the nitrogen and hydrogen curves. A replot of the data given on steel 1 is also included here for comparison. These two steels had the chemical composition shown in Table I.

The same conclusions may be drawn from these results as were drawn from the data obtained on steel 1. It is also apparent that the steels may be arranged in a definite order, this order depending upon the amount of ammonia decomposition apparent at the end of 7 hours. This is more readily seen by examining Figure 4. Here the curves for these steels are ranged one above the other in the order 1, 2, 3. This is in the order of decreasing aluminum content of the steels and indicates the well-known fact that aluminum is very active in decomposing ammonia. In addition, it is to be noted that in passing from one temperature to another (from 500° to 800° C., for example) the rate of change of the rate of ammonia decomposition, as indicated by the points of inflection of these curves, moves toward a lower temperature in the same order.

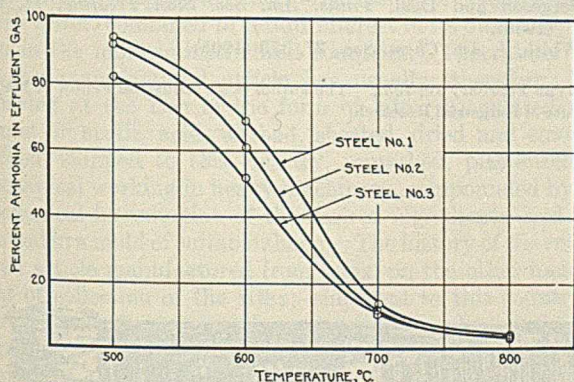


FIGURE 4. DECOMPOSITION OF AMMONIA IN CONTACT WITH STEELS 1, 2, AND 3 AFTER NITRIDING FOR 7 HOURS

Harder, Gow, and Willey (3) recently published results on a steel of nearly the same composition as steel 2. Unfortunately the exact rate of ammonia flow was not recorded in their paper, so it is rather difficult to compare the two sets of data. Harder and his co-workers found in general, however, that ammonia decomposition increases with rise in temperature and that, dependent on the gas flow maintained, the percentage of ammonia decomposition occurring at 635° C. varied from 74 to 84 per cent. Similar results are reported for two other steels, although little difference is shown from steel to steel. Grossman (1) gives the ammonia dissociation occurring during the nitridding of Nitralloy (0.31 per cent carbon)

as varying from 25 per cent at 510° C. to 90 per cent at 650° C.

It is well to bear in mind when considering the discrepancies which may seem to be present in the work of various investigators on the subject of ammonia dissociation at various temperatures during nitridding that varying the area of the surface as well as the gas flow has a large effect on the amount of decomposition. Sets of data have been included to emphasize these points. Working with steel 1, the area was varied and the gas flow held constant at 0.06 cubic foot per hour at 500°, 600°, and 700° C. The results are tabulated as follows, all decomposition values being taken at the end of 7 hours:

AREA	NITRIDING	NH ₃	AREA	NITRIDING	NH ₃
Sq. cm.	TEMP.	DECOMPOSED	Sq. cm.	TEMP.	DECOMPOSED
	° C.	%		° C.	%
11.11	500	5	10.30	700	85
41.61	500	9	41.87	700	96
81.45	500	10	80.64	700	98
9.94	600	31			
39.50	600	55			
79.56	600	63			

Holding the temperature and area constant but varying the gas flow also shows quite marked differences in ammonia decomposition at the end of 7 hours as follows:

GAS	NITRIDING	NH ₃	GAS	NITRIDING	NH ₃
FLOW	TEMP.	DECOMPOSED	FLOW	TEMP.	DECOMPOSED
Cu. ft./hr.	° C.	%	Cu. ft./hr.	° C.	%
0.06	600	30.0	0.06	700	85.0
1.00	600	9.0	1.00	700	27.0
2.75	600	4.0	2.75	700	8.0

NITROGEN ABSORPTION

The nitrogen absorption occurring during the nitridding cycles described above was determined by weighing each sample before and after nitridding. The gain in weight was considered as the nitrogen absorbed. At high nitridding temperatures this measure of nitrogen absorbed is not strictly correct, as some decarburization occurs owing to hydrogen reduction. As an indication of the amount of decarburization to be expected over the temperature range 500° to 800° C., standard samples of steel 1 showed the following losses in weight due to the removal of carbon after heating for 24 hours at the indicated temperatures in a stream of hydrogen:

TEMP.	LOSS IN WEIGHT	TEMP.	LOSS IN WEIGHT
° C.	Gram	° C.	Gram
500	0.0004	700	0.0042
600	0.0006	800	0.0118

These losses in weight, when considered with the relatively large observed gains resulting from nitridding, may be neglected when drawing conclusions concerning the relationships existing between temperature and nitrogen absorption.

In Table III are listed the amounts of nitrogen absorbed by samples of the three steels nitridded for 7 hours under the above described conditions. Figure 5 shows a plot of these data. It is evident therefrom that there is in the case of each steel a temperature at which nitrogen absorption is greater than at either higher or lower temperatures. This temperature of maximum nitrogen absorption is not the same for all steels but is variable, and in these particular cases falls in the neighborhood of 700° C. for steel 1, and 650° C. for steels 2 and 3.

TABLE III. NITROGEN ABSORBED BY STEEL SAMPLES IN 7 HOURS

STEEL	NITRIDING	NITROGEN	STEEL	NITRIDING	NITROGEN
	TEMP.	ABSORBED		TEMP.	ABSORBED
	° C.	Gram		° C.	Gram
1	447	0.0077	2	500	0.0228
1	500	0.0219	2	600	0.0500
1	600	0.0458	2	700	0.0481
1	650	0.0650	2	800	0.0263
1	700	0.0715	3	500	0.0169
1	750	0.0641	3	600	0.0460
1	800	0.0460	3	700	0.0455
			3	800	0.0267

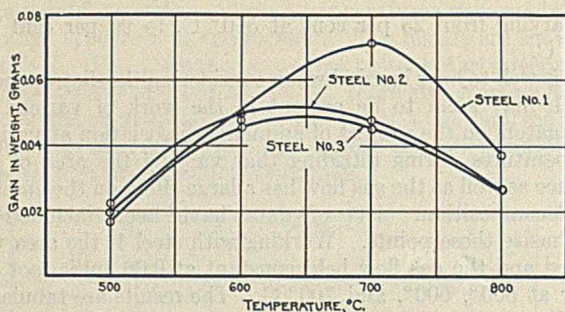


FIGURE 5. GAIN IN WEIGHT OF STEELS 1, 2, AND 3 AFTER NITRIDING FOR 7 HOURS AT VARIOUS TEMPERATURES

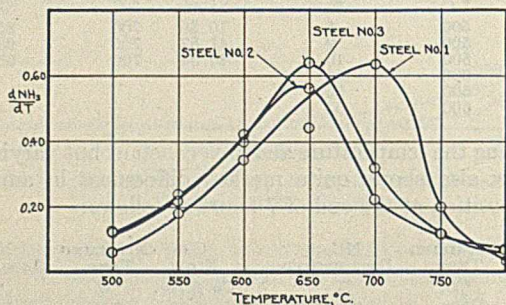


FIGURE 6. RATE OF CHANGE OF AMMONIA CONCENTRATION WITH TEMPERATURE

These gain-in-weight curves, indicating the relative nitrogen absorbing ability of the steel, demonstrate that aluminum plays a large part in nitrogen absorption during the nitriding process. In addition, these data point to a pronounced decomposition of nitrides with increased temperature above the temperatures of maximum absorption. Such a condition predicts the possibility of arriving at a temperature where the nitrides will be decomposed as rapidly as formed. It seems entirely probable that the chemical nature of these steels differs from one to another in such a way as to influence the receptiveness of the metals toward nitrogen as well as the ability of the steel to decompose ammonia.

Harder, Gow, and Willey have shown in this connection that with a given set of conditions the amount of weight

gained by a specimen on nitriding increases with increase in temperature over the temperature range 468° to 635° C.

If the data given in Figure 4 are replotted as in Figure 6, it is readily observable that the temperature at which the change in ammonia composition with temperature is most rapid corresponds to the temperature at which the maximum absorption of nitrogen occurs. For the steels under consideration, the coincidental temperatures are 700° for steel 1 and 650° C. for steels 2 and 3.

It may perhaps be that such a coincidence of these maxima is attributable to a turning point in the reactions taking place in nitride formation, and that at the temperatures of these maxima a decided thermal decomposition of the nitrides which have been formed is initiated. Or perhaps it may be that at these temperatures the metal atoms have a thermal vibration which is peculiarly well suited to ammonia decomposition and nitrogen absorption.

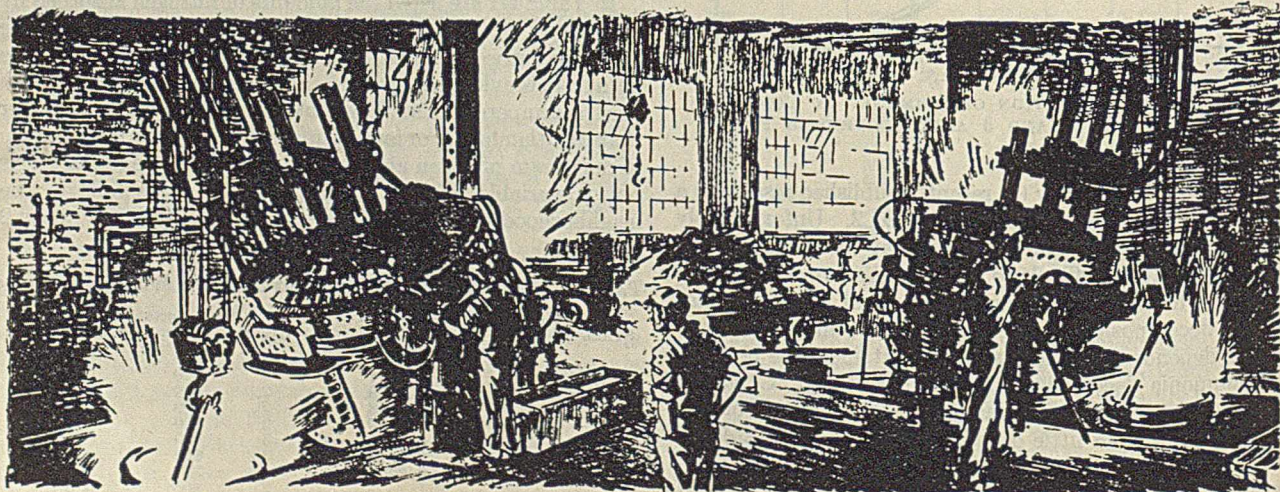
ACKNOWLEDGMENT

This series of two papers presents the results of an investigation of the nitriding of steel conducted at Mellon Institute of Industrial Research during the period 1927-28. The fellowship work, which was sustained by the H. H. Robertson Company, Pittsburgh, Pa., was carried on coöperatively by that company and the Molybdenum Corporation of America. Acknowledgment is here made of the assistance rendered by the Molybdenum Corporation in making all analyses of steels and alloys and in the machining of all samples. The author wishes to take this opportunity to express his appreciation of the helpful advice and criticism of J. H. Young, under whose direct supervision the research was performed.

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Rubber Latex

Recent Scientific and Technical Developments

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The more or less scientific work which has been carried out on the rubber plantations, and the problems relating to the production of articles from latex in the factories of America and Europe are discussed. A review is given of the actual and proposed uses for latex and products made from latex.

TEN years ago, latex, the white liquid obtained from the rubber tree, was as much a stranger to manufacturers in Europe and America as it is to the public today. At the Fifth International Rubber Exhibition in London, in 1921, latex is said to have been gazed upon as a curiosity even by scientists connected with rubber-manufacturing concerns. In the past decade, however, the direct utilization of this liquid in rubber and other industries has had such a rapid advance that 9,190,362 pounds of rubber, in the form of latex, were imported into the United States in the first ten months of 1931. It is significant to note that the importation of latex was 19.3 per cent greater in 1930 than in 1929, despite the fact that the consumption of crude rubber decreased 20 per cent (16).

The opportunity for revolutionizing a major industry does not often occur. Given the proper economic conditions, it is not outside the realm of possibility that the direct use of latex could accomplish such a revolution in the rubber industry. The earliest manufacturers of rubber articles (the natives of the Amazon district) used latex as their raw material. The difficulty formerly encountered in the transportation of latex without coagulation and the necessity for transporting so much water, combined to retard interest in its direct application in the more industrialized countries. The rubber in a modern manufactured article has usually, therefore, been collected at the tree in the form of latex, coagulated with formic or acetic acid, washed, sheeted, dried and smoked, packed, shipped to this country, unpacked, plasticized by mechanical working in heavy machinery, compounded by the mechanical introduction of the desired ingredients, and vulcanized in a mold of suitable shape. The history of the rubber in an article manufactured from latex, on the other hand, is that of collection of the latex; shipment to this country in the presence of a preservative; compounding by stirring the ingredients into the liquid latex in the presence of suitable protective agents; forming by dipping, deposition, or other methods; and finally drying and vulcanizing. The simplicity of the latter procedure as compared with the former is obvious.

Simplicity in manufacture is by no means the only advantage claimed for products made from latex. Investigators in the field are generally agreed that latex products, if properly made, are superior in physical properties, since no mechanical deterioration of the rubber occurs as a consequence of milling. Further advantages claimed for latex products include great saving in power consumption in the mixing procedure, greater uniformity in product, better dispersion of compounding ingredients, better aging, lower accelerator costs, and elimination of fire and health hazards in processes formerly requiring rubber cements (made with toxic and inflammable solvents).

It is true that all of the advantages claimed have not been accepted without dispute. The writers have found, for instance, that, despite the supposed presence of naturally occurring antioxidants, products made from preserved latex do not always withstand aging well (particularly if the latex remains in the unvulcanized state). Furthermore, in order to obtain the high resistance-to-tear desired of certain latex products it usually seems necessary to maintain a somewhat "undercured" state, which results in high permeability and high permanent set. The present extraordinarily low price of crude rubber also places latex (with its high cost of transportation) at a disadvantage.

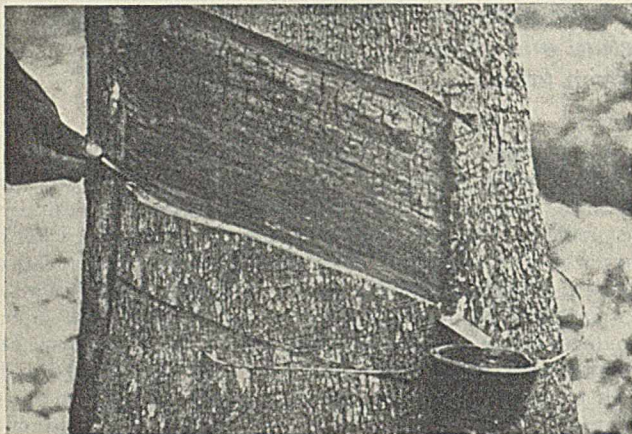
Great as has been the commercial adoption of latex in recent years, the increase in the literature pertaining to latex seems to have been even greater. The direct utilization of this material so appeals to the imagination that it has stimulated both inventive and literary effort. The literature has been increasing at such a rate, in fact, that even in 1924 van Rossem (126) considered it inadvisable to attempt to review it all in one paper. Early in 1927 Hauser published his book on the subject of Latex (71). In view of the adequate manner in which this book covers developments prior to that time, the present article has been confined very largely to the scientific and technical developments of the past five years. Since the writers have listed hundreds of references to patents and journal articles pertaining to latex which have appeared in this period (about two hundred in 1930 alone), no attempt has been made to cover every reference in this review. Only those which seem to be of most interest have been discussed. Although some investigations of a strictly scientific nature have been reviewed, emphasis has been placed on the developments having possible practical application.

SCIENTIFIC INVESTIGATIONS OF LATEX SYSTEMS

INFLUENCE OF ANATOMY OF TREES ON YIELD OF LATEX. A means of predicting the future yield of young Hevea trees has been the object of many researches. Such a method would avoid the planting of poor yielding trees, or would enable them to be detected and replaced before the tapping age was reached. For this reason the method suggested by Ashplant (17) has created widespread interest. It depends upon the determination of the bore of the latex tubes and the number of latex rings. Trees with latex tube bores below a certain average are said to be poor yielders, and good yielding trees are said to possess latex tubes above average bore. Whether or not a tree with large tube bore is a good yielder depends on the number of latex rings. Some workers have failed to confirm Ashplant's results. With respect to the data of Frey-Wyssling (63), Ashplant has claimed that they support (as far as they go) his results, but that too few trees and

trees of too restricted tube bore were studied. Ashplant makes the statement that this method has been of value in rejecting poor trees and was preferable at the time of its introduction to the indiscriminate planting then taking place.

Eaton and Fullerton (57) have reported that a greater dry rubber content is obtained by shallow tapping than by deep tapping, while Sanderson and Sutcliffe (125) have established correlations between the girth of the tree, number of latex rows at 20 inches above the ground, cortex thickness, and the yield of latex. They were also able to correlate the yield of one year with that of another.



Courtesy of Reverte Corp. of America

FIGURE 1. TAPPING A HEVEA TREE WITH A QUARTER CUT

Another method of predicting the yield, which is advocated by Hauser (70), and applies to grafted trees, consists of determining the shape of the particles in the latex. If the shapes of the particles in the latex from grafted stock are the same as those of the particles in the latex from the mother tree, the graft is usually successful from the standpoint of latex yield.

STRUCTURE OF LATEX PARTICLE. The structure of the latex particle is still the subject of considerable dispute. Hauser's theory of the two-phase structure of latex has been subjected to criticism, especially by von Weimarn (163a). The latter considers latex a polydisperse system of isoaggregated particles (isospherulites), the general consistency of which is fluid-gelatinous. He also believes that the serum constituents are present not only in the surface film but also on the inside of the latex particle, and play an important role in the changes the isoaggregates undergo during the drying and other coagulating processes.

Von Weimarn disagrees with Hauser in finding many spherical or near-spherical particles, and has reported that in certain cases some of the particles flow together. This was especially true when the temperature was raised to 100° C. or when the protein film was removed with a "dispersator" such as lithium iodide.

Hauser (73) repeated his previous experiments on the dissection of the latex particle, using an improved apparatus (Leitz dark ground illuminator), and confirmed the previously described structure. He reported that the interior of the particle is fluid but gels when the particle is coagulated or dried or when it is punctured. The consistency of the fluid interior varies with the age of the tree, being even gelatinous in the case of very old trees. (See Figure 2.)

METHODS OF MEASURING pH IN LATEX. The measurement of the hydrogen-ion concentration of latex has been an important problem and one which has proved difficult to solve. The Wulff colorimetric foil method, recommended by

Hauser, has been stated by MacKay (102) to be unreliable in certain ranges. The diffusion of indicator outward from the gelatin foil is another objectionable feature. The use of the glass electrode in latex has been described by McGavack and Rumbold (110) who found it to be sufficiently accurate over the range investigated (pH 8 to pH 12). Van Harpen (69) has used the quinhydrone method in a thorough study of the hydrogen-ion concentration of fresh latex and the adsorption of hydrogen ions by the latex particles.

SURFACE TENSION OF LATEX. Hauser and Scholz (76) have determined the surface tension of different lattices and have found values of 40.5 dynes per centimeter for fresh, and of 35.5 for ammonia-preserved latex. They also found that the surface tension passed through a minimum upon dilution with water, as do surface tensions of potassium soap solutions. Scholz (132) later found the surface tension of fresh latex to vary inversely with the percentage of nonrubber constituents in the serum. He also observed that the surface-active substances remained in the serum upon coagulation.

NONRUBBER CONSTITUENTS IN LATEX. Though the non-rubber constituents in latex have received considerable attention in the past few years, not until very recently had any extensive series of determinations of these constituents been reported in the literature. From the results of several hundred determinations, Scholz and Klotz (134) conclude that in fresh normal lattices of varying rubber content (from 35.2 to 49.4 per cent) the variation in nonrubber constituents is only from 3.0 to 2.6 per cent; and for that important class of lattices of rubber content between 37 and 43 per cent, the non-rubber content is 2.9 per cent.

Although the value of these materials was formerly much disputed, the rather extensive investigations of Martin (105) appear to have proved definitely that some material in the serum remaining after coagulation is capable of improving the aging properties of rubber to a marked extent. This investigator reported, for instance, that a crepe rubber-sulfur mix, to which had been added 3 per cent of dried serum, suffered no loss in tensile strength after 6 days in the Geer oven at 70° C., whereas a similar mix containing no serum had its tensile strength reduced from 1950 to 750 pounds per square inch.

Interest in the antioxidizing power of dried latex serum has not been confined to the Far East. Patents for the use of this material as a compounding ingredient in rubber have been issued both to Italian and to English interests (140). In regard to investigations along this line in America, Hopkinson (82) states that the substance which improves the aging property of sprayed rubber has been isolated in the laboratory. He reports that it is an antioxidant, "one form of which we are now preparing and using to improve the aging of products not containing sprayed rubber."

The nonrubber constituents of latex possess accelerating as well as antioxidizing power. Thus Hopkinson states that an accelerator of excellent properties is naturally present in the latex. Rubberstocks containing this accelerator are said to have a very flat curing curve and not to be prone to overvulcanizing or to burning on the mill. The more rapid curing characteristics of sprayed latex rubber are attributed to this natural accelerator. Some work carried out in Malaya on the isolation and study of various ingredients in the serum is of interest in this connection. Eaton, Rhodes, and Bishop (58) extracted a lipin from latex and found it to have noticeable accelerating power.

Another ingredient of the serum to be given recent attention is quebrachitol, the monomethyl ether of hexahydroxycyclohexane. McGavack and Binmore (109) and Levi (99) have proposed methods of recovering this material. In discussing the possible uses of this compound, McGavack and Binmore state that it may serve as a substitute for saccharin

or as a raw material for the manufacture of quinones, photographic developers, or therapeutic chemicals.

The studies made on the resins, yellow pigment, etc., in latex are also worthy of mention. Frey-Wyssling (62) has reported some interesting microscopic investigations. Among other things, he found that the resins occur in the form of globules which are perfect spheres and which are generally larger than the caoutchouc particles. These resins account for the yellow or red color of latex from new tappings. Having a higher specific gravity than the rubber hydrocarbons, they concentrate in the serum during centrifuging.

DETERMINATION OF RUBBER CONTENT OF LATEX. The usual methods of determining rubber or total solids of latex, although sufficiently accurate, are time-consuming. For this reason the method of Ward and Gehman (162) has proved interesting. The method, which consists of determining the obscuring power of the lattices in a microturbidimeter, calibrated with lattices of known rubber content, is said to have an accuracy of 1 per cent in 35 per cent rubber latex, when dilutions of 15 per cent or less are used. The turbidity of latex is dependent upon the refractive index of the serum and the number and size of the latex particles. Fortunately the refractive indices of water and of the serums of various fresh and preserved lattices are similar, and, by the use of color filters, small variations are nullified. It remains to be seen whether the variations in particle size encountered in lattices from young and old trees affect the accuracy of the method.

Scholz and Klotz (133) have recently proposed modification of the usual method for the determination of total solids. By carefully drying the latex in a nickel dish over an open flame, they were able to obtain accurate values for dry total solids in 8 to 10 minutes.

COAGULATION OF LATEX. Among the more extensive investigations of the coagulation of latex have been those relating to the effects of hydrogen-ion concentration (176). Although latex is ordinarily coagulated by acids and stabilized with alkaline substances, there is (for lattices of suitable concentration) a second zone of complete dispersion in the acid range. According to Fullerton's recent experiments, samples of latex, diluted to a rubber content of 4 per cent, were completely coagulated at pH 0.8; partially coagulated from pH 0.8 to 1.0; completely dispersed from 1.0 to 3.5; partially coagulated from 3.5 to 3.8; completely coagulated from 3.8 to 4.83; partially coagulated again from 4.83 to 4.91; decreasingly flocculated from 4.91 to 5.30; and completely dissociated at higher pH values.

It has been so common in discussions of the production of rubber to refer to acetic acid as the coagulant that it is doubtful whether even the rubber technologists of this country and Europe realize to what extent this material has been replaced by formic acid. According to van der Burg (31), 80 per cent of the estates in the Dutch East Indies were using formic acid as early as 1927. He contends that the economy said to result from the substitution of this material for acetic acid is merely an illusion, since formic acid corrodes the mill rolls, coagulating vessels, and other utensils so much more rapidly than acetic acid. O'Brien (116) has countered with the statement that his experiments indicate that it would require fifteen years for formic acid of twice the strength used for coagulation to corrode through a good grade of aluminum coagulating pan.

Another substitute for acetic acid which has been investigated considerably and used to some extent is sodium silicofluoride (Na_2SiF_6). Aluminum pans cannot be used with this coagulant, owing to corrosion. O'Brien (116), van Harpen (176), and others have successfully used a mixture of sodium silicofluoride with a small proportion of formic acid as coagulating agent.

Other coagulants, to which some attention has been given

during the past four years, include alcohol, alum, sodium biformate, guanidines, and amines. The volume of alcohol required is too great to permit its being considered commercially. The use of guanidines, such as diphenylguanidine, as coagulating agents was suggested in connection with "heat-sensitized" latex, which will be discussed later (120). Gracia (66) has proposed the use of amines (for example, allyl or benzyl) as coagulants in cases where compounding ingredients capable of reacting with acids have already been added to the latex.

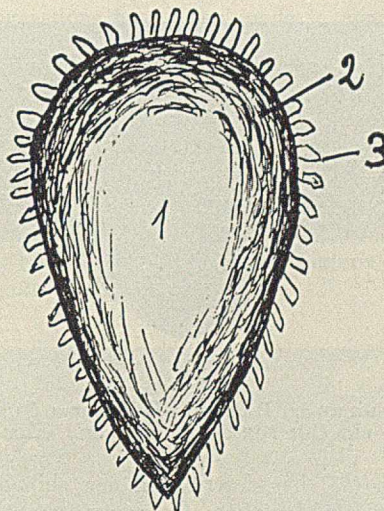


FIGURE 2. STRUCTURE OF LATEX PARTICLE (ACCORDING TO E. A. HAUSER)

1. Viscous rubber interior
2. Nearly solid elastic rubber shell
3. Adsorption layer of albumins and resins

There have been a number of investigations of coagulation which are of scientific interest but no great practical significance. These can be given but very brief mention in an article of this nature. They have involved, among other things, the effects of enzymes, of bacteria, and of freezing in promoting coagulation, and the role of proteins in retarding coagulation (41, 176).

PRESERVATION AND SHIPPING

PRESERVATION. Although ammonia is still the most widely used preservative for latex (9), a large number of other materials have been suggested (182). Sulfonic acid salts, which prevent coagulation by their protective and not germicidal action, are of especial use in latex to be applied to fabric. McGavack and Sheve have used sulfonic alkyl-aryl reaction products, with or without formaldehyde or other preservatives, while the former has found alkali salts of selenious or tellurous acids and also certain alcohols and ketones to be efficient preservatives.

Nekitin has found that certain aliphatic hydrocarbon mixtures, such as gasoline or kerosene, assist phenols in preservation. Mixtures of formaldehyde and trisodium phosphate; neutral or alkaline salts of ester acids, such as methyl sulfuric acid; and mixtures of borax and boric acid have also been suggested. It is interesting to note that alkylamines have been patented as preservatives for fresh latex by the I. G. Farbenindustrie Akt.-Ges., and as coagulants for compounded latex by Gracia.

SHIPPING. The shipping of latex has changed remarkably in the last few years. Instead of drums or even small tinned cans, ballast tanks in steamers, or even tank ships are being used for the purpose (12).

It has been reported by the Department of Commerce that

a new type of vessel has been designed. The ship is fitted with special tanks which are electrically heated so as to carry latex or coconut oil in bulk to any climate in exactly the same condition as when loaded.

Latex, concentrated by centrifuging, is being shipped to the Dunlop Company in England in the new Kenward barrels (163). These consist of two shells, fastening in the center, and are capable of being nested like beakers for the purpose of reducing the freight charges when returning them empty to the plantation.

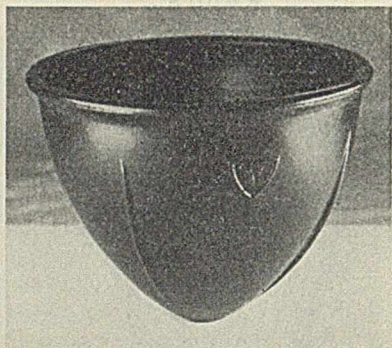


FIGURE 3. RECENTLY DEVELOPED RUBBER CUP FOR COLLECTION OF LATEX

Hopkinson (81) has described a new shipping container made from sheets of rubber. After emptying the latex, the container may then be used as ordinary rubber.

CONCENTRATION OF LATEX

Since latex contains considerable water (60 per cent or more) and must ordinarily be transported thousands of miles before it is used industrially, it is apparent that any method which allows removal of much of the water on the plantations should serve as a boon to the direct use of this material in manufacturing. The several methods for concentrating latex, which have been developed or at least investigated in recent years, are discussed under the headings of Evaporation, Centrifuging, Creaming, and Filtration.

EVAPORATION. As mentioned by Hauser (71) in his discussion of the methods of concentrating latex by evaporation, it is customary to increase the stability of latex by adding alkaline preservatives or protective colloids before or during evaporation. In a method patented by Gibbons and Shepard (65), ammonia is continually added to latex in a flat pan. A heated gas is passed over the surface, which is kept at a constant level, and a stirring device is used to prevent the formation of a surface film. In the manufacture of Revertex, a concentrated latex which has been marketed for several years, stability has been insured by introducing both potassium hydroxide and a potassium soap into the latex prior to evaporation. Several patents relating to the Revertex process (Figure 4) or the preservatives to be used therewith have appeared in the past four years (122). According to the latest patent, the potassium salts of hydrotropic substances are recommended as preservatives, a hydrotropic substance being defined as one containing both a hydrophilic group and a hydrophobic group having an affinity for organic solvents.

According to a recent statement by Twiss (155), the Dunlop Rubber Company makes considerable use of latex concentrated after compounding. He states that "concentrated compounded" latex has a uniform composition, is free from undesirable tendencies to gravitational separation, and is capable of producing goods of considerable thickness by a dipping or spreading process with a small number of coats.

In the preparation of this material, Twiss states that the initially fluid compounded latex is maintained throughout the evaporation process in swirling movement to keep the compounding ingredients in uniform dispersion. According to Warren (163), the Twiss concentrator, which has been called "the latex prototype of the ordinary mixing mill" (155), consists of a jacketed stainless-steel bowl with water circulating in the jacket. Hot air is blown into a hollow lid from which it is distributed through perforations to the surface of the latex. Concentrated compounded latex, having a total solid content of 70 to 80 per cent, can be made by this process (156).

Worthy of mention also is the recent proposal of Twiss and Murphy (157) for concentrating latex to a water content of 3 per cent or less. In this process the water is largely replaced, during evaporation, by polyhydroxy compounds such as glycerol or diethylene glycol. These liquids serve as media in which the added protective colloid (e. g., soap) continues to function after the water content has become quite low. The reversible concentrate so produced may be rendered irreversible by molding or kneading.

The possibility of making, by a spraying process, the ideal concentrated latex—a dry powder which can be dispersed in water—has not been overlooked. Carrington (34) discusses the spray-drying of Revertex, whereby there is produced a reversible powder which can be peptized by dilute ammonia. Nyrop (115) has protected a process for obtaining a reversible concentrate by spraying latex simultaneously with a suspension of protective agents and fillers. A latex-hemoglobin mixture may also be spray-dried to give a reversible powder according to Wescott (167). The unfortunate disadvantage of spray-dried powders of this nature is their pronounced instability towards pressure.

CENTRIFUGING. Among centrifuging processes, that of Utermark (159) seems to have been given the greatest commercial exploitation, the product obtained by this method having been on the market for some time. In discussing the process used, Carrington (34) states that latex treated with about 0.3 per cent ammonia is centrifuged at about 8000 to 9000 r. p. m. The product, which has a total solid content of about 60 per cent, has been freed of much of its protective matter, and must therefore be handled with care.

Wescott (164) has proposed the addition of such a material as hemoglobin or Irish moss to protect the latex and at the same time to aid separation in the centrifuge. Another patent by this investigator combines centrifuging and spray-drying. In this process the latex, treated with hemoglobin, is concentrated and then sprayed into an atmosphere of low humidity. The resulting product may have a cheeselike appearance or be in the form of a dry noncoherent powder which may be redispersed, preferably by dilute ammonia.

De Vries and co-workers (160) report that rubber made from centrifuged latex has a slow rate of drying, is generally light in color, has low tensile strength and slow rate of cure, ages rather poorly, and (contrary to previous claims) is not especially uniform. Of practical interest is the fact that this rubber is decidedly plastic. In this connection, de Vries and Beumée-Nieuwland (160) state that centrifuging is the only method to date for producing a plastic rubber that has no tendency to deteriorate on storage.

CREAMING. The creaming of latex is analogous to the creaming of cow's milk, although separation takes place more readily in the latter case. Although latex, preserved with ammonia, creams only on long standing, that preserved with sodium hydroxide does so very readily. Since most of the protective serum constituents remain in the lower layer, the cream is quite unstable. Carrington (34) states that rubber from creamed latex has chemical properties resembling those of

smoked sheets or pale crepe, whereas its physical properties in the vulcanized state approach those of sprayed latex both before and after aging.

Although evaporation and centrifuging processes have so far been given greater commercial development, the number of recent patents on creaming processes indicate an increasing interest in this latter method of concentrating latex. The usual procedure is to add a creaming agent to hasten the separation. According to the patent literature (139, 174), substances which facilitate separation of the rubber globules in latex include glue, gelatin, carrageen moss, Iceland moss, Irish moss, pectin, gum arabic, Karaya gum, alginic acid, various alginates, and buffer solutions, such as a mixture of primary and secondary sodium phosphates. McGavack (108) has recently protected by patent the idea of repeatedly using the serums from creaming operations in new creamings, thus reducing the requirement of creaming agent. It is claimed by Hauser that separation is more satisfactory when the creaming is carried out above 90° C. Hill and co-workers (60) report that, although vulcanized latex creams unsatisfactorily, the addition of creaming agents with the vulcanizing agents will effect good creaming during vulcanization and subsequent standing. The addition of about 25 per cent of natural latex is also said to facilitate the creaming of vulcanized latex. A somewhat radical proposal—that of the I. G. Farbenindustrie Akt.-Ges. (88)—is to cream by rapidly adding acids until a pH value less than 2 is attained. The viscous paste, which can be separated from the serum by filtration after standing 24 hours, is said to be redispersible in dilute ammonia.

FILTRATION. Filtration as a method of concentrating latex does not appear to have been used commercially. A recent patent to Pestalozza (121) covers a process in which latex is passed back and forth between two containers and is exposed to ceramic filters during passage. Loss of serum through the filters results in a gradual increase in the rubber content of the material remaining.

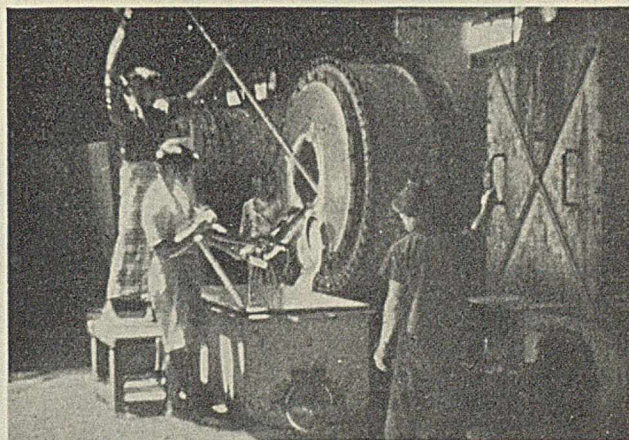
INCORPORATION OF COMPOUNDING INGREDIENTS INTO LATEX

Since nearly all of the rubber put to practical use is compounded rubber, the methods of incorporating compounding ingredients into latex are of prime importance. The introduction of these ingredients or pigments (to use the rubber compounders' term) is, in the case of latex, a fundamentally different process from that with crude rubber. A pigment which can be milled into crude rubber with comparative ease may be difficult to distribute uniformly in an aqueous dispersion such as latex. The principal difficulties with compounding ingredients for latex have been attributed by various investigators to electrical charge (e. g., magnesium oxide will discharge and coagulate the negative latex particles); dehydrating power (e. g., carbon black); tendency to settle out; and failure to be wetted by latex. A procedure which lessens one of these difficulties may often aggravate another. In this connection, the writers have observed that passage of the pigment suspension or of the compounded latex through a colloid mill or through a paint mill, will usually improve dispersion and retard settling, but may greatly increase the tendency toward coagulation.

INCORPORATION OF FINE POWDERS. Stevens (143) states that most fine powders, when stirred into latex, coagulate it, the coagulation manifesting itself either as a sudden or a gradual stiffening of the paste. The presence of anticoagulants, such as caustic soda, sodium carbonate, or ammonia, retard this coagulation. According to Stevens, the best method of introducing pigments is to put them into the form of a paste with water or an alkaline solution, before stirring into the latex. Even then the incorporation of certain pigments, such as carbon black and zinc oxide, is very difficult, and resort

to the use of protective colloids is necessary. Stevens mentions soap, glue, hemoglobin, and gelatin solutions in this connection. Casein, fatty oils, fatty acids, glue, gelatin, and resinic acids are included in the list of protective colloids given by Wiegand (169). Among the agents which the writers have used successfully may be mentioned gum tragacanth, gum ghatti, potassium soap, and saponin. A certain specificity has been observed in the protective influence which the various colloids exert on the different pigments, an effective agent for one pigment not necessarily being of much service for another.

Several suggestions have been made in connection with carbon black, which is probably the fine powder most difficult to incorporate. According to Wiegand (169), the use of saponin in a carbon black-water paste facilitates wetting and aids in the subsequent mixing of the paste with latex. A neutral or slightly alkaline solution of cellulose xanthate is also said (47) to be a good medium for dispersing carbon black prior to introducing it into latex. Park's recent suggestion (117) for increasing the dispersibility of carbon black in latex is to treat the black with the vapors of a material such as pine oil or petroleum distillate.



Courtesy of Revertex Corp. of America

FIGURE 4. EMPTYING A CHARGE OF FINISHED REVERTEX

SPECIFIC METHODS FOR INCORPORATING VULCANIZING INGREDIENTS, SOFTENERS, AND OTHER MATERIALS. To facilitate the introduction of sulfur, the large particle size of which is ordinarily objectionable, it has been proposed (49) either to retard settling by introducing bentonite clay into the latex system, to fuse the pigment first with kieselguhr and introduce the ground product thereafter, or to add the sulfur to a vulcanizable oil and then introduce the mixture. The use of sulfur of particle size much smaller than normal has also been suggested (30). For certain purposes, sulfur may be advantageously introduced into latex in the form of the hydride (28) or of a polysulfide, such as ammonium or calcium polysulfide (143).

The same general considerations apply in the case of accelerators as with inorganic compounding ingredients. Since water-soluble accelerators can be mixed with latex very readily (provided they are not of such a nature as to coagulate the latter), it is often desirable to use this type. In the case of latex articles which are formed to shape and which therefore do not require any further processing, such as milling or calendering, the field of applicability of ultra-accelerators is much greater than with articles made from crude rubber. The specific suggestions of Murphy and Twiss, of Grove-Palmer, and of others (172) for accelerators suitable for latex include the diethyl-ammonium salt of diethylthiocarbamic acid, dithiofuroic acid and dithiofuroates, mercaptobenzo-

thiazole, and certain ultra-accelerators which are zinc salts and which therefore require no zinc oxide for activation. Aumarechal and Robrieux (18) propose forming accelerators in preserved latex by causing carbon disulfide or certain aldehydes to react with the ammonia or aromatic amine preservative present.

For the coloring of articles made from latex, it is said (173) that almost any dyestuff carrying a negative charge may be used, provided the latex is vulcanized at or near ordinary temperature by use of super-accelerators. Insoluble dyes may first be run through a colloid mill with a protective colloid, or dissolved in a suitable organic solvent and the solution then emulsified. Lakes may be used if in a fine state of subdivision. To employ vat dyes, it is necessary to agitate the mixture of latex and the leuco compound while exposed to the air.

Although the patent literature covers references to the incorporation of various other ingredients, such as selenium, oils, factice, reclaim, wood tars, resins, antioxidants, and stearic acid (19), many of these are not of sufficient interest to warrant discussion in this paper. In general, the waxes, oils, resins, and bituminous materials are neither soluble in water nor can they be introduced in the form of a suspension of fine powders. Emulsification is the usual expedient employed, the nonrubber constituents of the latex sometimes serving as the emulsifying agent. Karaya gum and saponin are additional emulsifying agents which have been used by a number of investigators. Worthy of mention is Gibbon's suggestion for adding stearic acid to latex by first forming ammonium stearate and stirring in the latter. Szegvari's method for introducing resinous antioxidants, such as that formed by condensing aldol with a naphthylamine, is to dissolve them in "rubber oil" (an oily product obtained by the dry distillation of rubber), and emulsify the solution before mixing into latex.

SPECIAL METHODS OF INTRODUCING PIGMENTS. Although the normal procedure in compounding latex is to mix the ingredients into the latex directly with a stirrer of some type, other methods for compounding have been investigated. Chapman and Patterson (39) have made a novel suggestion for the introduction of pigments usually difficult to incorporate. The pigments are first milled into reclaimed rubber or other plastic material, a water dispersion of the compounded stock is formed, and the latter is mixed with latex. Another proposal is to add the pigments on a

mill having a fluted roller, which manipulates the latex and continuously exposes new surfaces (91).

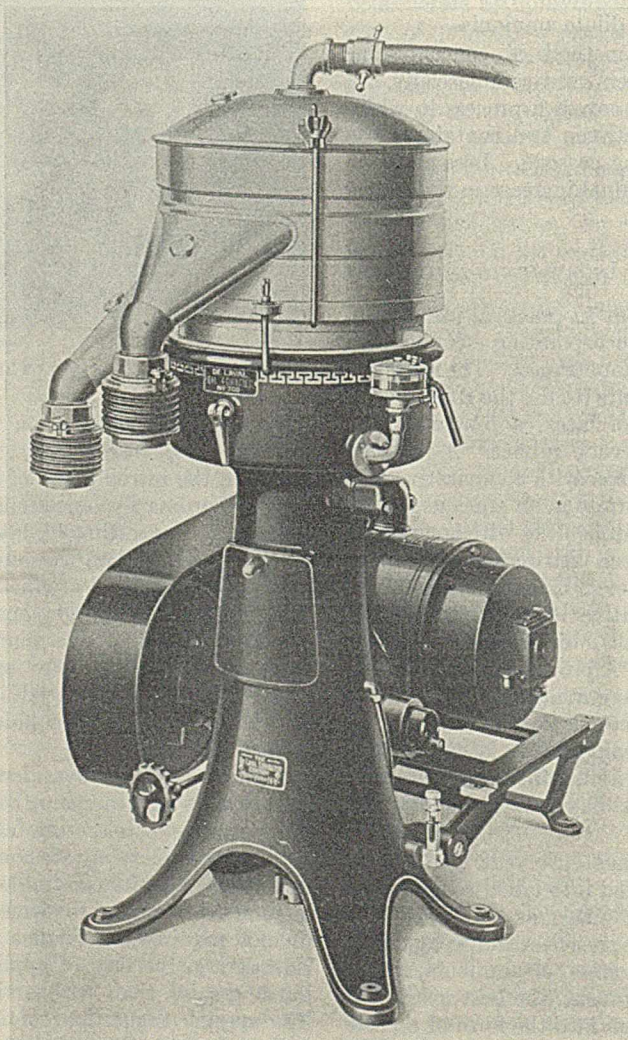
One method of introducing compounding ingredients, which is feasible for latex but not for crude-rubber compounding, is to form the ingredient in the latex (or in water immediately before addition to latex) by a double decomposition or similar reaction between two soluble substances. Especially attractive in this connection are reactions, such as that between barium sulfide and zinc sulfate, in which both products formed are insoluble and of interest as rubber pigments. Patents issued to English and American interests (90) cover the production of such ingredients as barium sulfate, cadmium and other sulfides, lithopone, silicic acid, various silicates, calcium oxalate, and calcium and other carbonates by this method. It is claimed that white or colored stocks with mechanical properties equal to those of stocks containing carbon black may be thus produced.

METHODS FOR PREVENTING SETTLING OF PIGMENTS. After the compounding ingredients have been dispersed satisfactorily in latex, the problem of keeping them in suspension still remains. The use of latex thickened by concentration (Revertex, for instance) reduces the tendency towards the sedimentation of compounding ingredients. When starting with Revertex, which is a comparatively viscous paste, the pigments may be incorporated either as dry powders or as pastes in a mixer of the Werner-Pfleiderer

type (72). For introducing the dry pigments, a brush-sieve arrangement, operating simultaneously with the blades of the mixer, is recommended. If the percentage of compounding ingredients is high, extra water or a solution of casein or of alkali should be added continually during mixing to prevent coagulation.

Various methods for thickening normal latex (without concentrating) and thus retarding the settling of fillers have been proposed. Included among these suggestions (183) are those of Sutton for thickening with finely divided zinc oxide (in the presence of ammonia), of Teague for using ammonium soaps of higher fatty acids, of Wescott for the use of a zinc oxide-hemoglobin gel, and of Hauser for employing the thixotropic properties of bentonite clay or other substances.

The handling of ordinary latex, after compounding ingredients have been incorporated, requires considerable care. Aside from their previously mentioned function, protective colloids may help to retard the settling of pigments from a



Courtesy of DeLaval Separator Co.

FIGURE 5. CENTRIFUGAL SEPARATOR OF TYPE USED FOR CONCENTRATING LATEX

latex suspension. Methods for pumping and thus keeping the suspension in circulation to avoid settling have been developed by the Dunlop Company and others (53). No general remedy can be given for the ever-present danger of partial coagulation of the sensitive pigment-latex system during handling. To avoid the necessity of entirely discarding partially agglomerated latex, Szegvari (147) has patented a process whereby it is circulated through tanks provided with filters which continuously remove the agglomerates.

MANUFACTURE OF RUBBER GOODS BY DIPPING

Probably the simplest method of manufacture of articles from latex consists of alternate dipping of a nonporous mold in latex and drying of the deposited layer. Products made in this manner have found increasing use and are, at present, competing quite successfully with goods made by dipping in rubber cements. Among the articles made by this method may be mentioned surgeons gloves, electricians gloves, finger cots, coated screens, and balloons. As is the case when dipping in rubber cements, the chief disadvantages are that the latex flows after the mold is removed from the bath, causing unevenness in thickness, and that the thickness of the layer obtained by a single dip is very slight. Robertson (125) has succeeded in avoiding the former disadvantage by regulating the speed of withdrawal of the mold from the bath so that the latex film sets by the time the mold is completely withdrawn. Increasing the thickness of the film obtained by a single dip or decreasing the time necessary between the dips have been the subject of much investigation during the past few years. The methods discussed below have been suggested for these purposes.

CONCENTRATION AND THICKENING OF LATEX FOR DIPPING. Hadfield (68) has increased the efficiency of the dipping process by using a heated mold in a concentrated vulcanizing latex with alternate dipping and drying of the surface of the deposit. Twiss (154) also used concentrated latex but, instead of alternate dipping in latex and drying, used alternate dipping in latex and in a coagulant. As previously discussed, he is of the opinion that concentration after compounding gives a better product for the purpose than compounding after concentration.

Use of thickening agents, such as polysaccharides, albuminoids, or plant extracts, to facilitate dipping has been made (4). Hauser has used bentonite for this purpose (77).

DIPPING WITH ACCOMPANYING OR SUBSEQUENT COAGULATION. Mention has already been made of the method of alternate dipping in concentrated latex and in coagulant used by Twiss (154). The same worker has used molds covered with either a coagulant-containing jelly (154) or a solution of a coagulant, and, in conjunction with Murphy and Thorpe (158) has advanced the idea of an alternate dipping and coagulating with a volatile coagulant. Methods similar to the latter have been advocated by MacKay and Thorpe (103) and by Teague (149).

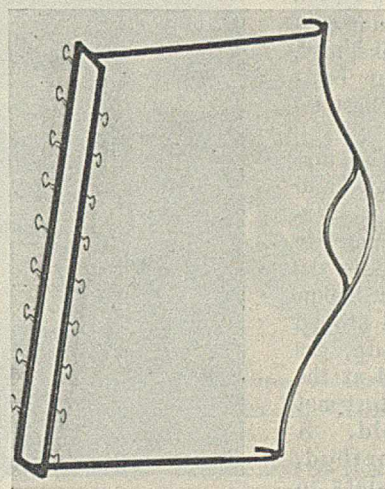
In all the above methods, care must be taken in washing in order to assure complete removal of the coagulant prior to cure, as otherwise the rate of cure and aging of the resulting product are adversely affected.

DIPPING IN CONJUNCTION WITH HEAT. One of the most interesting methods of facilitating the production of rubber articles by dipping has been proposed by Pestalozza (119). Heat-sensitive latex is prepared by adding solutions or suspensions of salts of bi- or trivalent metals. Upon the introduction of a heated form, the adjacent latex is heated and coagulated. The thickness of the coagulated layer may be controlled by varying the time of dipping or the temperature of the former. A similar method has also been suggested by

Chapman, Murphy, Pounder, and Parkes (38) who propose the use of ammonium persulfate, with or without trioxymethylene or sodium silicofluoride as sensitizing agents. Trowbridge (153) has found that the use of a heated form in untreated latex is advantageous. Campbell (33) has been able to obtain deposits of appreciable thickness by applying heat and pressure to latex in a mold. Specific mention is made of the applicability of this process to the manufacture of tubes.

MANUFACTURE OF RUBBER GOODS BY DEPOSITION FROM AGGREGATED LATEX

A very interesting modification of the dipping process has recently been developed in this country. Usually the deposition of latex on porous molds is an exceedingly slow process, since the latex particles are of such size that ultra-filters must



Courtesy of Miller Rubber Co.

FIGURE 6. ELECTROPLATING RACK COVERED WITH RUBBER BY ANODE PROCESS

be used. Even with ultra-filters the process is difficult, as the resistance to flow of serum through the deposited layers becomes very high as the layer increases, and the deposition becomes progressively slower. Owing to the deformability of the latex particle, the deposit becomes compact if high pressure is used.

These difficulties are avoided, and deposition is made comparatively simple by increasing the effective size of the particles. This is accomplished by aggregation of the latex particles into relatively large groups (55). A number of means have been described for obtaining aggregation; probably the first of these is the one described by Hopkinson and Gibbons (83). Organic colloids, such as Irish moss, were found to promote aggregation, especially if considerable quantities of pigments, such as whiting, were present. The same workers (84) have also found that by freeing latex of ammonia and adding small amounts of phenol and trisodium phosphate, aggregation and increased filterability are obtained after one month. Smith (139) found that buffer solutions of primary and secondary sodium phosphates were effective when a sufficient quantity was added to decrease the pH of the latex to approximately 6. Further decrease in pH resulted in increased filterability and decreased stability down to the point where coagulation occurred. Cadwell and Hazell (32) have used aldehydes, such as cinnamic, butyr- and furfuraldehydes to obtain aggregation. Greenup (67) has mentioned the use of boric acid for the same purpose. According to Hazell

(78), greatly increased filterability is obtained by treating latex with zinc oxide or zinc salts, and alkali sulfides or polysulfides followed by stirring and heating. The manufacture of inner tubes by a process similar to the above has been described by Hopkinson and Gibbons (84).

ELECTRODEPOSITION

PROCESS IMPROVEMENTS. The electrolytic deposition of rubber upon the anode is well known and is the subject of numerous patents. Many of these are concerned with overcoming difficulties encountered in the practical application of the process. Gas formation is one of these, as it causes porosity in the final product. It is also necessary, according to Klein (95), to obtain constant conductivity, alkalinity, and rubber content, for the best results.

One of the first remedies (2) used to prevent gas formation and porosity was to deposit the rubber on a hollow porous mold around the electrode, gas being formed at the electrode but not on the mold. A second method, which consists in using current potentials below the decomposition potential of

water, has been suggested by the Anode Rubber Company (3) and by Williams (171), but this means increased time for deposition. Beal and Sheppard (20) have protected the use of artificial cooling to permit the use of higher potentials. Klein and Szegvari (97) add materials, such as sodium thiosulfate, which react with the oxygen liberated. Cowper-Coles (44, 45) has used intermittent deposition with removal of the anodes between successive depositions to permit the removal of gases. This yields a compact layer. According to the same worker, the conductivity of the deposition bath is improved, and a softer deposit is obtained when ammonium acetate is added. Softer and less compact deposits are also obtained by the addition of soft soap, according to Klein and Healy (96). Shellac is said by Jenny (87) to increase the adhesion of the deposit to metals, while, according to Davies (46), co-deposition of synthetic resins and rubber yields products of characteristics quite different from those of the usual deposits. The thickness of deposited layer in a given time is increased by the addition of starches, glue, and dextrin according to the Toto Company (150).

MODIFICATIONS OF ELECTRODEPOSITION PROCESS. Several modifications of the electrodeposition process have recently been suggested. These consist of cathodic deposition, alternating current deposition, and internal current deposition.

Cathodic deposition is, as its name implies, deposition of the rubber particles upon the cathode. This is accomplished by deposition from latex in which the electrical charge on the particles has been reversed (54). James and Twiss (86) have used such materials as acetic acid and formaldehyde in con-

junction with protective colloids for this purpose, while the Siemens-Elektro-Osmose Gesellschaft (137) has used thorium nitrate.

The use of alternating current for deposition is made possible by using two different materials, such as aluminum and carbon, for electrodes. According to Madge, Round, and Twiss (104), a partial rectification of the current takes place. Deposition with alternating current has also been proposed by the Siemens-Elektro-Osmose Gesellschaft (137).

Still another modification of the anode process is that of Williams (170) in which the deposition bath is itself the source of current. Ammonium chloride is added to the latex in such

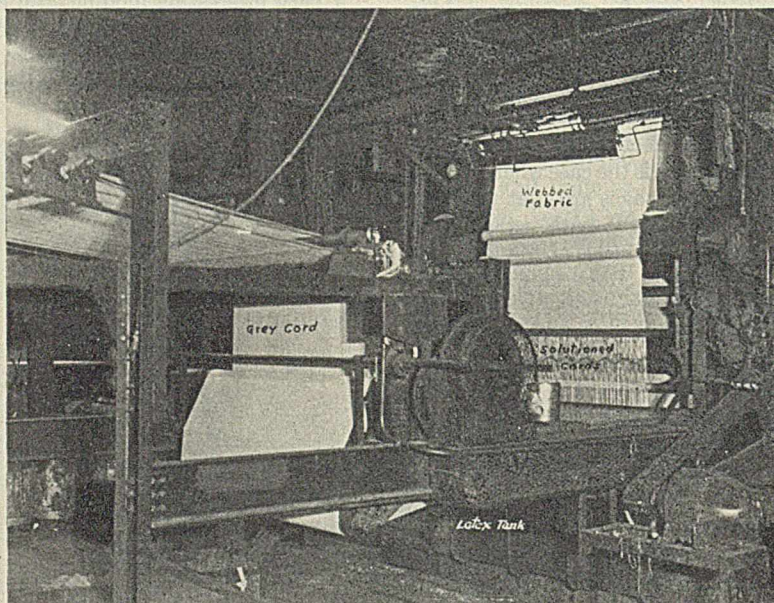
quantity that coagulation does not occur. Carbon and zinc are used as the electrodes. When the circuit is completed, a current flows through the cell, and rubber is deposited.

OTHER METHODS OF MANUFACTURE

GELLING. Although the gelling of latex or compounded latex cannot alone be classed as a method of manufacture, it has been investigated as a preliminary step in the production of porous and other types of articles by molding, spreading, dipping, spraying, etc. By the gelling process, the consistency of

the latex is so changed that manufacture of the final article is often facilitated. A sharp distinction cannot always be drawn between a gelling process and the thickening processes discussed in the section on Incorporation of Compounding Ingredients in Latex, although the function of the thickening is primarily to retard the settling of pigments, rather than to facilitate any specific manufacturing operation. According to patents granted to Davies; Teague; Wescott; Gabor; Beckmann; McGavack; Hayes, Madge, and Jennings; and others (47, 177, 183), there are quite a number of substances which have a gelling effect on latex. Among these may be mentioned formaldehyde (alone or mixed with such substances as phenol and tannic acid), silicic acid, sodium silicofluoride, alum, calcium chloride, magnesium sulfate, saponin, gelatin, agar-agar, carrageen moss, hemoglobin-zinc oxide mixture, hemoglobin alone, other proteins and albumens, and cellulose xanthate. The time required for the gelling to take place varies with the agent used. Some of the materials, such as hemoglobin, also require a moderate heating.

In fact, the addition of agents having little or no effect at room temperature, but a gelling or coagulating action at a somewhat higher temperature, has been the subject of a number of patents granted to Pestalozza (119) and to certain English investigators (56). Although a considerable quantity of a salt of a bi- or trivalent metal will coagulate latex in the cold, a smaller portion will merely have a slight thickening effect. Further thickening and, finally, coagulation are said to take place as the temperature is raised toward the boiling point. The nature of the agents used for this purpose has been dis-



Courtesy of United States Rubber Co.

FIGURE 7. LATEX-DIPPING OF CORD FABRIC TO BE USED IN MANUFACTURE OF TIRES

cussed under the subheading, Dipping in Conjunction with Heat. It is claimed that latex so treated can be used satisfactorily in the direct production of rubber goods not only by dipping but also by extrusion and by introduction into heated molds.

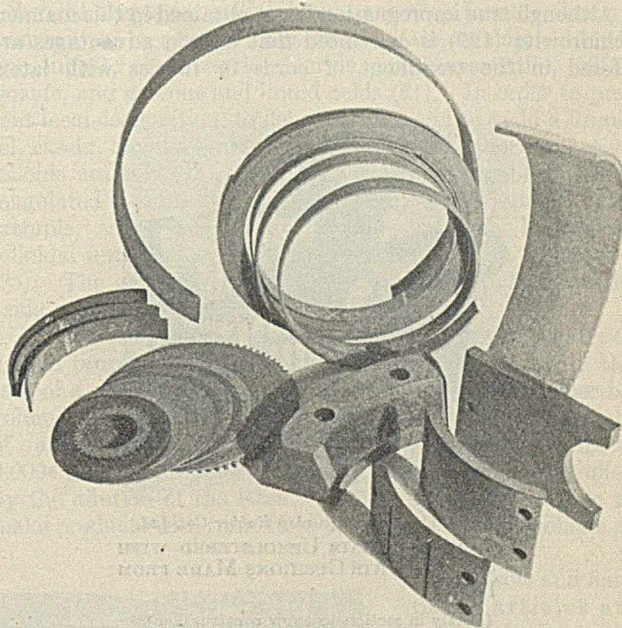
MOLDING. The manufacture of molded articles from compounded latex is often difficult, since the consistency of the mixture is frequently too thin. The water content, moreover, is usually too high, unless a porous product is desired. It is necessary, therefore, either to gel the mixture to obtain the proper consistency or to coagulate it partially and remove the excess water. Patents, respectively illustrative of these two methods of surmounting the difficulties mentioned, have been issued to McGavack (107) and to Loomis and Stump (101). According to a process protected by the Dominion Rubber Company (51), molded articles may be made by coagulating the latex in molds and drying at a moderate temperature. By using concentrated compounded latex, Carrington (34) states that mats, sheets, etc., can be molded by direct drying, an empirical allowance for shrinkage being made. Careful control of the water content of the mixture is, of course, necessary.

EXTRUDING. The manufacture of articles such as threads and tubes by extruding the properly compounded latex into a coagulating or dehydrating bath offers possibilities which appear to have received no great amount of attention in recent years. Patents issued to Murphy and Twiss (112) cover a process which consists in allowing concentrated compounded latex to flow by gravity through an orifice under the surface of a setting or dehydrating bath. The specific gravity of the bath, which in a typical case may contain sodium chloride and ammonium acetate, is so adjusted that the coagulated rubber rises to the surface. By using a die with an annular orifice, it is said to be possible to extrude a tube.

SPRAYING. Rubber manufacturers have become more or less familiar with crude rubber prepared by spray-drying, the process for which has recently been described in some detail by de Leeuw (98). Of more interest in connection with the present discussion is the suggestion of Stevens (144) that the rubber "snow" (the initial fluffy product settling to the bottom of the spray chambers) may serve as a molding powder from which certain rubber articles may be manufactured by a direct process. When it is considered that compounded latex can also be sprayed, the possibilities of a spray process for the manufacture of articles from latex become broader. Theoretically, the number of articles which might be manufactured by spraying compounded latex into molds or upon formers of suitable shape is very large. The possibility of using a spray process in the manufacture of inner tubes, solid tires, hose, and rubber-coated articles has been discussed by Hauser (71). The spray process appears to be particularly adaptable for the production of rubber coatings on objects which are of such intricate shapes or are in such inaccessible positions that other methods of coating cannot be used.

The difficulties attending the spray method are sufficient, however, to have limited its use thus far to a relatively narrow field. Notable among these difficulties are clogging of the spraying devices, lack of smoothness in the dried film, and a tendency toward a lack of uniformity in the product. It is the writers' experience that sheets formed by the spray-drying of latex containing compounding ingredients are often striated. Stocks containing a high proportion of pigments often exhibit a low tensile strength after being spray-dried and vulcanized. A brief period of milling of the dried stock before vulcanization has been observed to increase the tensile strength considerably. Rupture of the individual rubber globules and the consequent improvement in the dispersion of the solid ingredients probably account for the increase.

Means of overcoming at least a part of these difficulties have been worked out. Carrington (34) states that the tendency toward premature coagulation in the spraying jets may sometimes be avoided by simultaneously spraying two different suspensions, each of which contains only a part of the final composition. One of the recent patents issued to Maynard (106) describes a spraying device so constructed that a continuous stream of latex is blown off the bottom of a rounded



Courtesy of Dewey and Almy Chemical Co.

FIGURE 8. LATEX-BONDED BRAKE AND CLUTCH LININGS

tip. Clogging is claimed to be avoided by this device. The production of inner tubes by a spraying process is covered by another patent granted to this same investigator.

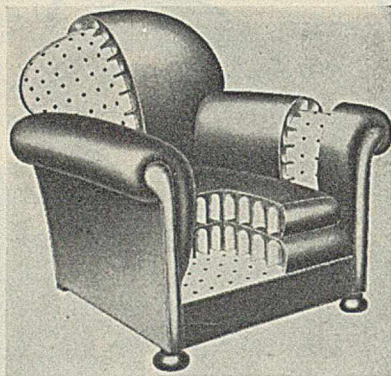
MILLING AFTER COMPOUNDING AND COAGULATING. Despite the fact that one of the main objects of investigations involving latex has been to obviate the use of mixing mills in the rubber industry, the possible combination of latex compounding and subsequent milling of the dried latex stocks has not been overlooked. As pointed out by Twiss (155), the latex particles retain enough of their individuality after drying the compounded latex so that the foreign particles tend to remain outside the globules rather than to penetrate them uniformly. By using suitably protected latex, it is possible, according to Twiss, to introduce very large quantities of carbon black (100 per cent or more on the basis of the rubber present). The crumblike coagulum (113), which forms, resembles the spray-dried stocks discussed above in that it does not exhibit the properties of reinforced rubber upon being dried and vulcanized. According to Twiss, milling of such a stock for 2 or 3 minutes suffices to distribute the carbon black within the rubber globules so that reinforcement is at once manifest. Hauser (72, 74), who has also proposed a brief period of milling for stocks made from compounded concentrated latex, has pointed out that good tear resistance is not to be expected from a dried latex stock which is so heavily compounded that the latex particles are entirely covered by pigments.

IMPREGNATION OF FABRIC

The impregnation of fabric with rubber by means of latex dipping was naturally one of the first uses suggested for latex. After a few trials it became evident that, instead of true impregnation of the individual fibers, only a superficial

coating was obtained. Dieterich (50) was able to show by means of photomicrographs that this was the case, while Hauser and Hünemörder (75) came to the conclusion, after studying microscopically the rubber left upon removal of the cotton with sulfuric acid, that even less impregnation was obtained with latex dipping than with frictioning. The poor impregnation has been attributed to the different electrical charges on the fabric and latex particles, and consequent coagulation on the surface of the fabric.

Although true impregnation is not obtained in this manner, Schidrowitz (129) is convinced that certain advantages are offered in the treatment of cords or fabrics with latex.



Courtesy of Dunlop Rubber Co., Ltd.
FIGURE 9. CHAIR UPHOLSTERED WITH CELLULAR AIR CUSHIONS MADE FROM LATEX
 (Partly in section to show construction.)

Gibbons (64), using the United States Rubber Company's flexing machine, has shown that from the standpoint of flexing life, latex-treated web fabric is far superior to cord fabric of the same construction.

Numerous means have been tried for obtaining true impregnation. Biddle (26) has found that the use of pressure is advantageous, while Trowbridge (152) has passed dipped fabric over a porous plate with simultaneous application of vacuum to force the latex into the cords. An attractive method of obtaining a coating of the individual fibers is that of Bongrand and Lejeune (27) which consists of applying the latex on the spinning frame while the fibers are in the roving stage. The twist for converting the rovings into thread is given after the impregnation. Although the process appears very promising from the theoretical standpoint, a considerable number of mechanical difficulties would have to be overcome before its practical application could be assured.

Another method of obtaining impregnation, which has received considerable attention during the past three years, is that of impregnating with latex to which a wetting agent has been added. These wetting agents, which are polar compounds, are adsorbed on the latex particles and prevent the latter from being adsorbed on the surface of the fabric. It is evident that they influence markedly the interfacial tension between fabric and latex. Among those materials which have been used are sulfonated oils, sodium sulfanilate, thiourea, orthotoluidine, ammonium linolenate, saponin, and soluble salts of sulfonic acids, such as sodium isopropyl naphthalene-sulfonate, and sodium butyl naphthalenesulfonate with liquid alcohols (148). Some of those suggested, although strong protectives against coagulation with pigments or dilute electrolytes, are valueless for obtaining true impregnation.

USES FOR AND PRODUCTS FROM LATEX

The actual and potential uses for and the products from latex, which have been described in the literature of the past

five years, are so numerous that many of them can receive no mention whatever in this article. Such uses as have been previously discussed are given little, if any, further attention in this section. The attempt has been made to confine the discussion largely to those uses which have either received extensive development, offer the greatest promise, or possess novelty.

LATEX IN TIRE AND TUBE MANUFACTURE. The latex used in impregnating cord fabric (Figure 7) constitutes a considerable proportion of the total amount of latex imported into America (13). The possibility of manufacturing other parts of a tire (such as the tread) from latex seems to have received more discussion than actual development (34, 112, 118).

The manufacture of inner tubes appears to be a more feasible proposition. The fact that latex inner tubes were marketed in small quantities by one of the large American rubber companies as early as 1928 gives indication of the commercial possibilities of such a process. The possible manufacture of tubes by electrodeposition has been extensively investigated by another company. The literature indicates, furthermore, that two of the other large rubber companies in this country have been interested in the possibilities inherent in latex inner tubes (67, 127). It seems, therefore, that the use of latex in the manufacture of inner tubes might be considerable, were it not for the fact that latex (with its high cost of transportation) is placed at a decided disadvantage by the low cost of rubber.

OTHER LATEX PRODUCTS FOR AUTOMOBILE INDUSTRY. Other latex products which are of particular interest to the automobile industry, and which have been developed beyond the experimental stage, include latex-bonded brake and clutch linings (14). According to Wescott's patent (166), they are manufactured from latex and asbestos fiber. (See Figure 8.)

Recent reports indicate that latex has invaded the field of automobile manufacture even further. It is now being utilized in the production of the sponge-rubber seats used in certain English cars (8). The rubber base for the mohair upholstery used in some automobiles is now also made from latex.

CEMENTS, ADHESIVES, AND SEALING COMPOUNDS. One of the largest uses for latex at the present time is in the manufacture of adhesives and sealing compounds. Practically all the sealing compounds are used in the sealing of cans. The merits of such compounds have been fully discussed by Hauser (71). According to Cord (42), sealing compounds may be made by adding fillers such as kaolin, talc, asbestos, or barium sulfate to the latex. The American Can Company (1) has used a thickener such as sodium alginate in conjunction with fillers such as aluminum oxide. Dewey (48) has vulcanized latex, added bentonite clay, and used the products as a sealing compound. Egan and McGowan (59) have found that mixtures of latex and solid peptized fillers are satisfactory. Aluminum oxide, when mixed with sodium silicate, is said by them to be a suitable filler.

The use of latex in the shoe industry has grown so rapidly in the past five years that at the present time latex cements are available for every cementing operation. It is said (10) that over twenty different types of cements are used for such operations as fitting and stitching, lasting, making, packing, wood-heel building, wetting, heel building, and applying sole leather. Sutton (145) has stated that the best method of attaching shoe soles is by using latex in conjunction with a self-vulcanizing rubber cement. The leather is given a coat of latex and, when dry, a coat of rubber cement. After the joint has been made, the vulcanizing agents migrate from the cement and vulcanize the latex. It is claimed that a permanent joint, unaffected by the weather, is obtained. Still another method is advocated by Cavanaugh (37) who applies

latex to the surfaces and unites them with pressure after drying. This method is said to be especially applicable for attaching shoe heels. Many of the shoe cements in use today contain thickeners, such as bentonite clay, and tack producers such as resins and pitches.

One of the processes, recently developed for attaching rubber to metal, calls for the use of a latex-protein cement. Wescott (165) found that a mixture containing 50 parts of rubber in the form of latex, 40 parts of hemoglobin or certain other proteins, and 10 parts of vulcanizing agents would cause satisfactory adhesion. Levin (100) used formaldehyde to harden a cement of latex and albumen, and applied heat to effect coagulation of the albumen and make the bond. Carson (36) has also made cements of latex, hemoglobin, tanning material, and vulcanizing agents. The usual procedure for applying is to coat the metal with a layer of cement, dry, bake at a temperature considerably above 100° C., and apply a coat of rubber cement and then the rubber stock. The bond is completed during the cure. Cements of this sort have been used for attaching rubber wringer rolls to the metal shafts and in rubber-metal automotive parts.

Revertex particularly has found considerable use as a waterproofing cement in the textile industry (111). Two layers of cloth are bound and waterproofed by an intervening layer of Revertex applied by spreading. In some cases penetration catalysts such as have been mentioned in the discussion of the impregnation of fabric are used. The rubber layer is cured by passing the plied material through strongly heated calenders. Similar cements are being used in applying a backing to artificial leather or rayon.

Cements made from latex have found numerous other applications. A mixture of latex and bentonite clay has been on the market for some time as an adhesive for attaching paper labels to tinned containers; while Dry Seal, a latex adhesive for envelopes, is claimed to be economical and to retain its adhesiveness for five years if kept free from dust (6). Mathey and also Johnson and Johnson (89) have proposed to make an adhesive from latex by successive creaming with gum tragacanth and addition of formaldehyde and sodium silicate. Biddle (25) has proposed to make adhesives from latex, casein, and sodium silicate; from latex, tapioca meal, and lime; and from latex, casein or albumen, and an "insolubilizing" agent, such as an alkaline earth hydroxide. Reitz (123) prepared an adhesive from latex by treating it with the vapors of an aldehyde, while Whittelsey (168) has added rubber solvents to latex in the presence of an emulsifying agent. Similarly, Traube (151) used a rubber solvent in the presence of gall or gall-containing materials.

POROUS- AND SPONGE-RUBBER PRODUCTS. As early as 1914, Schidrowitz and Goldsbrough (130) found that, by vulcaniz-

ing coagulated latex in steam, a porous product was obtained. They also formed a product which contained both macroscopic and microscopic pores, by adding carbonates to the latex prior to coagulating with acetic acid.

A more recent but somewhat similar process is the one developed by Beckmann. It consists of coagulating or gelling latex and curing in steam or moist vapor so that syneresis does not take place. In this way the network structure of the gel is retained.

Several agents for gelling latex have been found. Among them may be mentioned magnesium sulfate, calcium chloride, zinc sulfate, alum, ferric chloride, manganese salts, sulfur dioxide, and gaseous and liquid acids (21). In order to prevent local coagulation, to delay setting, and to yield a firmer gel, casein, blood albumin, hemoglobin, and other protective colloids are used (23). Materials which are capable of being coagulated to form hydrophilic gels may also be added. For example, silicic acid, tannic acid, aluminum hydroxide, colloidal ferric oxide, and hemoglobin have been mentioned (93). The gels may be toughened by exposure to sulfur dioxide or volatile acids.

The porous material obtained by this process possesses unique properties (24). It has been estimated that, in the case of a porous rubber containing 40 per cent of rubber by volume, some 500,000 pores occur in each square centimeter of surface, and that the average diameter of the pores is 0.0004 mm. The porosity of the cured rubber is controlled by the dilution of the latex. It has been found possible to make products with from 15 to 85 per cent of their volume as voids.

Both soft and hard rubber articles are made. As far as the writers can ascertain, the largest use is for storage battery separators, where the chemical resistance of the hard rubber and the low electrical resistance of the highly porous material are of advantage. Battery separators are now made from latex in Germany and in England. It is understood that they are being experimented with by several of the leading battery manufacturers in this country.

Among the other products made of this material may be mentioned filters, bath mats, and oil-

bearing wicks.

A recent development in the field of sponge rubber products made from latex is that of the Dunlop Rubber Company (56a). In this process a frothing agent such as soap and a gelling agent such as sodium silicofluoride are added to concentrated or thickened latex. The mixture is beaten into a froth with a mechanical beater and poured into a mold of the desired shape. It is then allowed to gel at room temperature prior to drying or is simultaneously gelled and dried by heating in the open air at 95° C. If desired the product obtained may be given a further vulcanizing by



Courtesy of Dunlop Rubber Co., Ltd.

FIGURE 10. POURING COMPOUNDED LATEX FROTH INTO MOLDS DURING MANUFACTURE OF CELLULAR AIR CUSHIONS

heating in steam. The material obtained differs from that made by the Beckmann method in having its structure composed of closed cells instead of having a network structure.

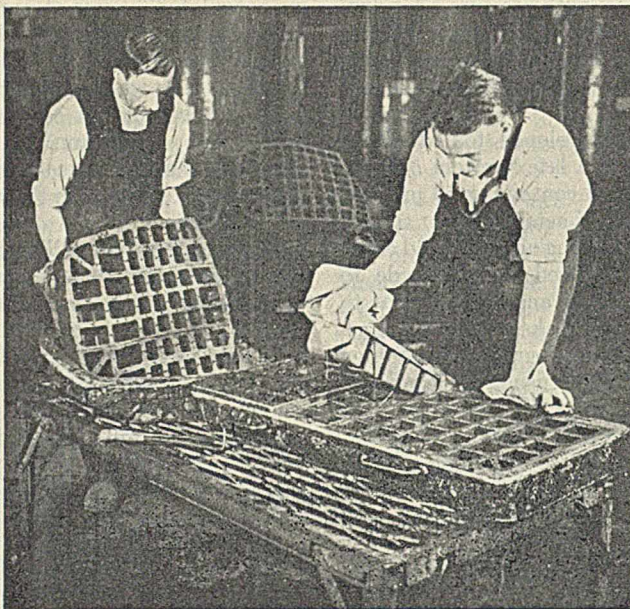
Several practical applications have been found for the material made by this process. As illustrated by Figures 9 to 12, it is used for automobile cushions and furniture upholstery.

LATEX IN THE INSULATION INDUSTRY. Although the use of whole latex in the manufacture of electrical insulating material has been patented, the most significant development involves the use of deproteinized latex. Nuttall (114) states that in the case of hard rubber the breakdown voltage can be increased 300 to 400 per cent by an initial treatment of the latex with caustic soda to destroy the proteins present. His assumption is that the proteins, when present, tend to prevent that maximum polymerization during vulcanization which is desirable for a good dielectric material. According to Kemp (94) Paragutta, the remarkable new insulating material for submarine cables, etc., contains a certain portion of deproteinized rubber. The best deproteinized rubber can be made from latex, the nitrogen content of the rubber produced being less than 0.1 per cent. The method of K. D. P., Ltd., (92) for improving the insulating properties is to remove the serum constituents from the latex by dialysis, while that of Sheppard and Beal (136) is to wash thoroughly rubber deposited from latex.

LATEX IN THE SHOE AND LEATHER INDUSTRIES. Although the most thoroughly developed application of latex in the shoe industry is undoubtedly as latex cement, the possibilities of additional uses are numerous. Composition soles may be made (181) by using latex either with felt, with long cotton fiber, with tire scrap, or with silicon carbide or other abrasive substances. Darex soles, which are made of felt and compounded latex, are said not to mark floor surfaces, to be waterproof, and to be free from a tendency to spread. According to the process described by van der Schuyt (135), sole crepe may be made by spraying latex from a series of small jets upon a conveyor. To the uniform layer obtained, cork, leather, felt, or other nonskid material may be added mechanically. A material which consists of cotton fiber treated with latex is specially prepared for insoles, middle soles, etc. This material, which is marketed under the name of "Laflex," is also manufactured in the form of cutting blocks to replace the wooden cutting blocks of the shoe and other industries. According to other suggestions having to do with the shoe industry, latex may be used in the manufacture of heels and linings, and even in the production of shoe laces (118, 131, 131).

In connection with the leather industry in general, it has been stated (29) that a two-color effect may be produced on leather by applying compounded latex to the depressions in the leather after embossing. A proposed compound for finishing leather also contains latex (138).

The use of latex in the manufacture of artificial leather or



Courtesy of Dunlop Rubber Co., Ltd.

FIGURE 11. REMOVING CELLULAR SPONGE RUBBER FROM MOLDS AFTER GELATION AND VULCANIZATION OF LATEX COMPOSITION

substitutes for leather has been given considerable attention. When Schidrowitz visited this country in 1928, he exhibited many articles made from artificial leather of this type. In compositions of this kind, the latex is usually either mixed with stiffening agents, such as casein or cellulose xanthate, or used as a binder for such materials as leather scraps or pulped rabbit skins (178). Imitation leather may also be made from cloth or paper and latex.

LATEX IN PAINT MANUFACTURE. A latex-bitumen composition, which can be diluted and used as a paint, was shown at the Public Works Exhibition in London in November, 1931 (151). Furthermore, it is understood that experiments with

paint containing latex have been in progress in the Middle East for some time.

Recent patents covering latex as an ingredient of paint have been issued to Ayres (19), Hopkinson and Teague (85), Traube (151), and others. Latex has been suggested as the base for certain paints, whereas with others it is merely one of the ingredients added to some other base material. The paint vehicle of Traube is a gel obtained from latex, a gall solution, and an organic solvent, such as turpentine.

LATEX IN PAPER AND RAYON INDUSTRIES. The paper industry was one of the first to be invaded by latex. The Kaye process for the manufacture of paper was discussed in the literature as early as 1922. In this process the latex used as a binder imparts to the paper exceptional resistance to breaking, tearing, and folding. According to Hauser (71), this process has not fulfilled its early promise, since the product soon loses its superiority on aging. He states that paper made with vulcanized latex should have a greater capacity for withstanding aging. According to recent patents issued to Kaye, Ross-Wright, Ruderman, and others (179), latex is of value not only as an ingredient to be mixed with the paper pulp in manufacture, but also as a constituent of compositions for the sizing, waterproofing, and greaseproofing of the paper sheets. It is understood that considerable latex is being used by one of the largest paper companies in America.

The possibility of incorporating latex with viscose or similar materials in the manufacture of artificial silks has been discussed by Dreaper and by Iwasaki and Masuda (52). Experiments carried out in Japan indicate that a small amount of latex in viscose will increase the strength of the spun thread, whereas a larger quantity will result in decreased strength and a milky-white color.

LATEX IN MANUFACTURE OF CARPETS, RUGS, AND RUBBER FLOORING. Another development of considerable interest involves the use of latex in the manufacture of rugs and carpets. According to a recent discussion of this process (11), the object of the treatment of the back of cut-pile carpeting with latex is to penetrate the structure of the back of the goods and embed the loop of the pile yarn securely in a rubber bond. The latex treatment also coats the back of the carpeting with a layer of rubber which prevents slipping. It is said

that this type of carpeting possesses another unusual advantage, in that rugs of any size and shape can be built up from a dealer's stock of one width, since the cut edge will not ravel. Furthermore, the properties are such that damaged portions of a rug can be cut out and replaced readily without marring the general appearance. In a similar connection, Fisher (61) reports that latex-impregnated animal hair is being used for stair treads. Even in cases where latex has played no role in the original manufacture, compositions containing this material may still be of service in producing a nonslipping rug. Application to the back of the rug may be by brush or spray-gun (141).

The use of latex in the manufacture of rubber flooring has been the object of some investigation. Although the production of latex mixtures which can be applied in a paste form in manufacturing the completed floor has been discussed, the actual developments in the use of latex appear to have been more closely along the lines of the usual rubber flooring. According to the suggestions (180) in the literature, latex may be used either with sand or sawdust to make flooring blocks; with asbestos, clay, or wood in a flooring composition; or as the top layer of a flooring having a fibrous base. It is further reported that a recent development has made possible the manufacture of rubber flooring and mats from Revertex and ground scrap rubber (124).

Latex appears also to have distinct possibilities as a binding material for the more conventional forms of rubber flooring—i. e., those made from compounded crude rubber. According to a recent statement (7), a satisfactory method of attaching rubber flooring to a base, such as wood or concrete, is to coat the base with properly stabilized latex, allow the latter to dry, and then treat with naphtha before applying the flooring. Beckmann (22) has gone one step further by proposing to coat the underside of the rubber flooring first with a layer of sponge rubber (made from latex), the function of the spongy layer being to aid in the attachment of the flooring to the base when using glue or other binding agents.

PRODUCTS OF ELECTRODEPOSITION PROCESS. The number of articles manufactured entirely or in part by the electro-deposition process is rather large (80, 163). Among these may be mentioned various types of tubing; electricians' gloves; surgeons' gloves; gloves for use with corrosive liquids; and many rubber-coated articles such as door handles, telephone receivers, inspection-lamp cases, pliers, filter-press plates, fan blades, conoidal fans for handling corrosive fumes, spinneret tubes for the rayon industry, screens for corrosive liquids, racks for electroplating, dipping baskets, and intricately shaped articles. It will be apparent from the previous discussion of electro-deposition that this process is peculiarly suitable for the manufacture of many of these articles. (See Figure 6.)

VULCANIZED LATEX AND ITS USES. The vulcanization of latex by the so-called Vultex process was developed by Schidrowitz a number of years ago. By this process there is obtained a vulcanization of the dispersed rubber globules of the latex without appreciable alteration in the colloidal condition of the system. The possible methods of application of Vultex are consequently about as extensive as those of ordinary latex. Manufacture is usually simpler when Vultex is used, however, since drying (without vulcanization) suffices to complete an article, once it has been formed to shape. A further advantage in the use of vulcanized latex is that it can be employed with fine fabrics and with many dyes and pigments which would be destroyed by the heat employed during vulcanization.

The more recent developments in connection with the process of vulcanizing latex have had to do largely with modifications in the accelerator and in the form of sulfur used, and with applications of the process to concentrated latex (28, 184). Ultra-accelerators which have been recommended for vulcanizing latex include tetramethylthiuram disulfide, piperidinium pentamethylenedithiocarbamate, and salts of thiol acids. Sulfur may be added not only in the sublimed, precipitated, or colloidal form, but also as polysulfides, or even as the hydride. Twiss (155) states that, despite repeated expressions to the contrary, it is impossible to vulcanize latex by the action of sulfur dioxide and hydrogen sulfide by a method similar to that of the Peachey process. His explanation is that the nascent sulfur is formed in the water phase and leaves the rubber globules unaffected.

According to the recent literature (40, 141, 161), Vultex is of use in the manufacture of nonslipping rugs, hospital sheeting, imitation leather, impregnated fabrics (which are waterproofed, improved in resistance to wear, and prevented from raveling), rubber soles, golf balls, electrical insulation, dental rubber, latex cements, meteorological balloons, and various forms of dipped goods (such as surgeons' gloves, fountain-pen ink sacs, toy balloons, and druggists' sundries). A development still in the experimental stage is that of the manufacture of inner tubes from vulcanized latex.

MISCELLANEOUS PRODUCTS FROM LATEX. In addition to the previously described use of latex in can-sealing, this material may be of service in the manufacture of other products used in sealing containers. Thus latex has been suggested

for use in connection with the production of rubber stoppers, milk bottle stoppers, rubber-lined bottle caps, and artificial corks. An even more radical suggestion which has been made is the sealing of tropical fruits in a film of dried latex before transporting them. Spoon (142) states that this process has not proved very successful, the latex coating sometimes having a tendency to affect the flavor adversely and to promote rather than retard the growth of molds.

For use in manu-



Courtesy of Dunlop Rubber Co., Ltd.

FIGURE 12. TRIMMING VULCANIZED AND DRIED CELLULAR CUSHIONS (MADE FROM LATEX)

facturing operations in general, there are a number of products in the making of which latex may be used. Abrasive wheels and other abrasive articles, driving belts, packings, gaskets, and rubber-impregnated ropes are examples (79). The use of the serum from latex as a binder for finely divided molding material, such as sand, is said to be advantageous.

Chewing-gum base is a material which is now being made from latex, hydrogenated oils, and certain other ingredients (146). In this process the latex and other ingredients are continuously agitated while being heated to expel the water. This latex base has been found to be of particular value in the production of the so-called bubble gum, which has gained considerable popularity with children.

The prevailing low price of rubber has further stimulated interest in rubber roadways. A paving of rubber which could be applied in the same manner as is asphalt would appear to be a very interesting type. According to the recent literature, such pavings are being investigated in America, and have been tried on an experimental scale in Singapore (15). Somewhat similar to the use of latex in paving is its suggested use in compositions for covering athletic grounds and for filling expansion joints (48).

Patents covering the manufacture of transparent rubber articles indicate that latex constitutes a desirable raw material for the purpose (5). The use of ultra-accelerators permits of vulcanization at a low temperature. Furthermore, ultra-accelerators, which are of the zinc salt type and which therefore obviate the necessity for adding zinc oxide, can be used. (Excess zinc oxide is deleterious to transparency.) An added advantage of latex is that, if desired, it can be dialyzed before use to remove part of the colored serum substances.

Further indication of the broad possibilities of latex as a raw material is contained in the references to its use or suggested use in diverse fields (175). Thus, Liesegang has

employed latex in the production of certain emulsions in the photographic industry. Latex makes its contribution to music in the form of rubber-impregnated wood for violin manufacture, and to medicine as an anatomical injection fluid and as a raw material for the manufacture of radium applicators. Book binding with latex is feasible, according to Grammer. That latex may even be of service as a lubricant, when mixed with petrolatum, is indicated by preliminary experiments conducted by the Rubber Growers' Association.

In conclusion, attention should be called to the manner in which latex has been invading some of the newer industries (175). In connection with the aviation industry, for instance, porous ebonite (made from latex) may be used in the manufacture of light rubber board for airplanes. The Trans-Lux Daylight Picture Screen Corporation has been granted a patent for the production of a projection screen by spraying a latex composition upon a suitable fabric base. The ideal gas mask of the future will, according to Barker, have its rubber parts manufactured from latex. The radio industry also now has an opportunity to take advantage of this useful material, since a process for the manufacture of latex-impregnated diaphragms for loud speakers has been patented by Fagan. Perhaps the most interesting feature of all is the fact that America's newest large-scale industry—the manufacture of dirigibles—has placed reliance on latex (35). The precious helium of the U. S. S. Akron is retained by fabrics of very low permeability, in the preparation of part of which latex was one of the materials used. Although latex was off to a late start industrially, it is certainly now keeping up with the times.

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Isolation of Symmetrical Xylenol from Crude-Tar Acids

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SYMMETRICAL xylenol is a compound not at present marketed in this country although it occurs in considerable quantities in both low- and high-temperature coal tars. It is easily isolated and purified and hence might become readily available if it were found to have industrial usefulness. It should be of particular interest to the synthetic-resin industry because of the two meta-alkyl substitutions. The compound is a white crystalline substance melting at 63–64° C. and boiling at 220.2° C. under a pressure of 760 mm. When pure it will remain perfectly white for long periods. It enters readily into most of the reactions characteristic of phenols.

To separate it from the tar acids, three methods are available that may be used singly or in combinations of the first with the second or third.

SEPARATION OF XYLENOL FROM TAR ACIDS

The first and simplest method consists in merely fractionating the acids carefully under a column and crystallizing the 217–222° C. cut from petroleum ether. A temperature several degrees below 0° C. is necessary for the best yields. This method, however, can be used only on tar acids that are relatively rich in the compound, as the solubility of the symmetrical xylenol in petroleum hydrocarbons, even at low temperatures, is greatly increased by the presence of other phenols.

If the acid fraction is not rich in the compound, as evidenced by its refusing to crystallize when chilled either by itself or in petroleum ether solution, or if it is desired to recover additional quantities after recrystallization of the fraction from petroleum ether, use may be made of the insolubility of its sodium salt. The crude fraction is shaken with an equivalent of 25 per cent caustic soda. On cooling (which should be gradual for the formation of filterable crystals), a heavy crop of the sodium salt of symmetrical xylenol precipitates, which is further increased to almost quantitative proportions by

chilling the mass in an ice-salt mixture. The solid material is filtered and washed with 25 per cent caustic, which renders it almost pure white. The sodium salt is not oxidized easily by the air, is nonhygroscopic and nondeliquescent. If desired, it may be purified by recrystallization from water to which a small amount of caustic has been added, or from acetone. The crude material, however, will yield symmetrical xylenol in a fair degree of purity by merely dissolving it in water, and "springing" with mineral acid. A single recrystallization then from petroleum ether completely purifies it.

Still another means by which symmetrical xylenol can be recovered from mixtures of the proper boiling point involves a modification of the method of Brückner (3) which makes use of the resistance of this compound to sulfonation and the relative ease of cleavage of its sulfonic acid.

The fraction is heated 2 to 3 hours at 103–105° C. with an equal weight of concentrated sulfuric acid. This treatment sulfonates the interfering phenols but affects only a portion of the symmetrical xylenol which is restored in the next operation. The charge is diluted with four volumes of water, refluxed one hour, and extracted repeatedly with ether. The ether solution is washed once or twice with water and distilled to dryness, the xylenol cut being taken when the thermometer starts to rise rapidly.

As an alternative to the ether extraction, the diluted sulfonation mixture may be steam-distilled to remove the symmetrical xylenol. Care must be taken in this case that the dilute sulfuric solution does not concentrate, as it is easily possible to reach a cleavage point of some of the sulfonic acids of other phenols in solution. The resulting material by either method is reasonably pure symmetrical xylenol that will crystallize when chilled. It may be purified to a melting point of 63.2° C. by recrystallizing out of petroleum ether. This is the highest melting point obtained by this laboratory, although 64°, 64.5°, and 68° C. have been reported.

The sulfonation method, like the soda method, may be used subsequently to the straight-crystallization method to aug-

ment the initial yield if the petroleum ether is first distilled off. Of the two, the soda method is productive of somewhat better yields.

The following are the more important literature references dealing with symmetrical xylenol and its derivatives.

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Toxic Action of Coal-Tar Creosote

With Special Reference to the Existence of a Barren Nontoxic Oil

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SEVERAL years ago Bateman (1, 2) proposed a theory of the mechanism of the toxic action of coal-tar creosote. According to this theory, coal-tar creosote consists of two groups of compounds: one is sufficiently soluble in water to render the water toxic; the other is comparatively insoluble and hence nontoxic. The toxic compounds, however, are far more soluble in the nontoxic compounds than they are in water. To that degree the nontoxic compounds act as a reservoir for the toxic compounds and feed them slowly to the water. The distribution of the toxic compounds in the nontoxic compounds and in the water depends upon the relative solubility of these toxic compounds in the nontoxic compounds and in water, and upon the quantity of each present.

This theory is based largely on the fact that it was possible to obtain, by treating the 285–410° C. fraction of a high-boiling coal-tar creosote alternately with acid and alkali, a bright clear oil which failed to kill the test fungus *Fomes annosus*, even in a 20 per cent concentration. It is claimed that the fact that an oil of such a nature can be obtained from coal-tar creosote shows conclusively that there is in coal-tar creosote a nontoxic or barren oil.

More recently this theory of the mechanism of the action of coal-tar creosote as a wood preservative was further developed (3) to explain the relationship between the toxicity and permanence of coal-tar creosote and the amount injected.

The implications of such a relationship, especially because of the assumption that the toxic properties of coal-tar creosote are largely confined to the portion distilling below 270° C., are far-reaching.

A review of the literature on the subject shows that there is considerable disagreement among workers in the field on the existence in coal-tar creosote of a barren oil.

Nowotny (3) seems willing to accept not only Bateman's hypothesis as such, but all its implications. He explains the

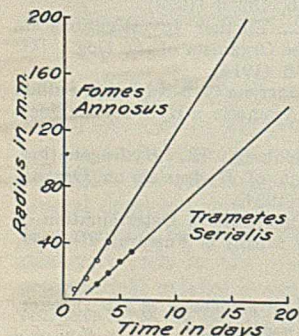


FIGURE 1. RADIAL GROWTH OF *Fomes annosus* AND *Trametes serialis* ON NUTRIENT MALT AGAR

inability of other investigators to obtain a nontoxic material from coal-tar creosote, through the removal of tar acids and bases, by assuming that the removal of these substances was not complete. However, Nowotny himself submits no experimental evidence in support of his views. He further seems to believe that tar bases, owing to their limited solu-

In coal-tar creosote there are substances varying greatly in their toxicity to wood-destroying fungi. Although there may be certain substances in coal-tar creosote which are essentially nontoxic, the presence of large amounts of nontoxic substances has not yet been demonstrated.

So-called barren oil cannot properly be considered as nontoxic to wood-destroying fungi. Although high concentrations of barren oil do not completely inhibit their growth, even relatively small amounts exert marked toxic effects.

bility, may play an important part in prolonging the toxicity of coal-tar creosote.

Moll (?), on the other hand, does not believe that the barren oil theory fully explains the toxic action of coal-tar creosote. He believes it to be quite possible that the so-called barren oil was not unchanged in the process of its preparation. Attention is also called to the fact that little is known concerning the nature

of these oils or the effects of condensation, polymerization, or oxidation on their toxicity. Moll, like Nowotny, gives no experimental data in support of his conclusions.

Dehnst (6) has recently published some results of a study of the toxic properties of coal-tar creosote that are apparently contradictory to those obtained by Bateman. Dehnst believes the observed differences to be due to the use of a different test fungus. Despite the fact that *Fomes annosus* may differ greatly from *Coniophora cerebella* in its tolerance towards various toxic substances, this may not be the most important cause for the marked differences in the results obtained. Dehnst claims to have followed the methods proposed by Bateman for the preparation of the barren oil. Although Bateman is somewhat ambiguous in his statements of how the barren oil was actually prepared, a careful study of Dehnst's paper shows clearly that Bateman's methods were not followed even in so far as they were clear. Little would be gained by comparing the results of these two workers. Suffice it to say that Dehnst concludes the toxicity of coal-tar creosote towards *Coniophora cerebella* is not greatly changed by the removal of the tar acids, tar bases, naphthalene, raw anthracene, the oils boiling below 285° C., and the water-soluble products.

Because of the fact that so much importance, direct and implied, is now attached to the presence or absence in coal-tar creosote of a nontoxic or barren oil, it appeared desirable to obtain additional information concerning the existence in coal-tar creosote of such an oil.

A sample of coal-tar creosote was therefore separated into several fractions. These were treated in approximately the manner described by Bateman in his work on barren oil. The toxicity to wood-destroying fungi of these fractions before and after treatment was determined by means of standard toximetric tests.

In the following discussion is included a detailed description of these experiments and of the results obtained from them.

MATERIALS USED

The sample of coal-tar creosote used in this study had the following characteristics:

Specific gravity at 38° C.	1.063
Fluidity at 38° C.	Liquid
Sulfonation residue (fraction 300-360° C.), %	0.8
Benzol-insoluble, whole creosote, %	0.09
Water content	None
Tar acids (fractions up to 300° C.), %	0.2

FRACTIONAL DISTILLATION

FRACTIONAL RANGE ° C.	WEIGHT OF DISTILLATE Grams
0-170	...
170-200	...
200-210	1.24
210-235	6.69
235-245	7.02
245-270	19.53
270-285	9.05
285-300	8.00
300-315	6.79
315-360	18.27
Residue	23.04
Loss	0.37
Total	100.00

AMOUNT DISTILLING BELOW:

° C.	GRAMS OF 100-GRAM SAMPLE
200	None
210	1.24
235	7.93
270	34.48
285	43.53

METHOD OF SEPARATING COAL-TAR CREOSOTE SAMPLE INTO VARIOUS COMPONENTS. The coal-tar creosote was first separated into three fractions by distillation in a Hempel flask of 500 cc. capacity. The angle between the neck of the flask and the vapor tube was 75°; the point of attachment of the vapor tube was 77 mm. below the mouth of the flask; the total height of the neck was 146 mm. One fraction consisted of that portion of the oil distilling below 285° C. (no temperature correction was made for the emergent stem of the thermometer); one fraction included that portion of the oil distilling between 285° and 350° C.; and the third fraction consisted of the residue remaining in the distilling flask at 350° C.

The fraction of the oil distilling below 285° C. was alternately washed for 3-hour periods with 450 cc. of 30 per cent sulfuric acid solution in water, and with a 15 per cent sodium hydroxide-water solution. The flask containing the oil and the extracting solution was placed in a boiling water bath. A reflux condenser was attached to the flask. The oil and extracting solution were continuously agitated by bubbling air through the liquid. After ten washes (five with acid and five with alkali) the oil was dried and redistilled. That portion of the oil not distilling below 285° C. was discarded. A clear yellowish oil was thus obtained. On chilling this oil, a white crystalline precipitate was formed (probably largely naphthalene) which was separated from the oil and tested for toxicity. A sample of the oily liquid after the removal of the solid was also set aside for toxicity tests.

The remainder of the oil distilling below 285° C. was extracted five more times, alternately with acid and alkali for 3-hour periods as above described. The oil was again dried and redistilled. Three hundred cubic centimeters of methanol, in which approximately 100 grams of mercury bichloride were dissolved, were added to the oil, and the mixture was vigorously shaken. The methanol was removed through evaporation and the oil distilled from the mercury bichloride. During this distillation some of the mercury bichloride decomposed to form mercury and hydrogen chloride. A light yellow oil was obtained which was subsequently treated with metallic sodium and redistilled. It was then washed thoroughly with hot distilled water and dried. The toxicity to wood-destroying fungi of this oil was determined.

The fraction distilling between 285° and 350° C. was treated in an almost identical manner to that just described. The fraction was cooled and filtered to remove a bright yellow precipitate which formed on cooling. After five washes each with acid and alkali, the oil was redistilled. A sample of the oil was retained to determine its toxicity, and the remainder alternately washed five more times each with acid and alkali, and then redistilled. After treatment with methanol and mercury bichloride, the oil was again distilled, and then once more distilled from metallic sodium. A part of the fraction, now distilled below 285° C., was retained to determine its toxicity. A clear bright yellow oil distilling between 285° and 350° C. was thus obtained, which, on being again chilled, yielded a small amount of yellow precipitate. This precipitate was removed

from the liquid by filtering and was discarded. Toxicity tests of the filtrate were subsequently made.

It is not intended to imply that these lowered temperatures resulted in a complete separation of solids. Further cooling undoubtedly would have yielded additional precipitate.

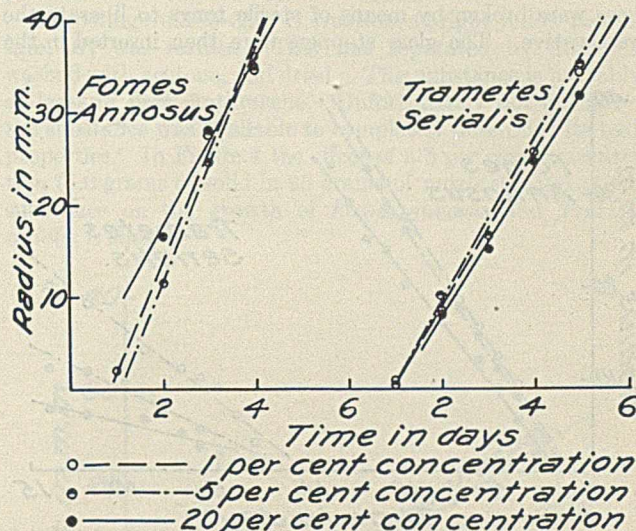


FIGURE 2. RADIAL GROWTH OF *Fomes annosus* AND *Trametes serialis* ON NUTRIENT AGAR CONTAINING COMPARATIVELY LARGE AMOUNTS OF PETROLATUM

The residue above 350° C. was a viscous liquid at room temperature. This material received no further treatment. Its toxicity to wood-destroying fungi, however, was determined.

The sample of coal-tar creosote was separated in the manner described into eleven component parts as follows:

DESIGNATION	METHOD OF PREPARATION
A	Original oil
B	Fraction below 285° C.
C	Fraction between 285-350° C.
D	Residue above 350° C.
FRACTION DISTILLING BELOW 285° C.	
E	B after 5 alternate washes each with acid and alkali, redistn., cooling, and removal of solid
F	Solid removed from E through cooling (probably largely naphthalene)
G	E after 5 addnl. washes each with acid and alkali, redistg., treatment with methanol solution of mercury bichloride, treatment with metallic sodium, redistg., and washing with water
FRACTION DISTILLING BETWEEN 285-350° C.	
H	Solid removed from C through cooling and filtering
I	C after cooling and removal of solid (probably largely anthracene)
J	I after 5 alternate washings each with acid and alkali, redistg., cooling, and removal of yellow ppt.
K	Fraction distg. below 285° C. in prepn. of J
L	J after 5 addnl. alternate washings with acid and alkali, treating with methanol soln. of mercury bichloride, treating with metallic sodium, redistg., washing with hot water, chilling, and removal of solids thus pptd.

For the sake of brevity and clarity these various component parts of the coal-tar creosote will be referred to in this discussion by the designation A, B, C, etc.

METHOD OF MAKING TOXICITY TESTS

The toxicity of the various component parts of the coal-tar creosote samples was determined by the agar plate method (11).

The nutrient agar consisted of:

Difco bacto-agar	15 grams
Trommers plain diastasic extract of malt	25 grams
Distilled water	1000 cc.

The amount of nutrient agar necessary to make a definite concentration of preservative in agar was placed in a 250-cc.

glass-stoppered Erlenmeyer flask and sterilized. In the preparation of the concentrations below 1.0 per cent, the preservative was placed in sealed glass ampoules. Concentrations of 1.0 per cent and above were prepared volumetrically.

In either case the toxic material was added to the nutrient agar after it was sterilized. When glass ampoules were used, these were broken by means of sterile tongs to liberate the preservative. The glass stoppers were then inserted in the

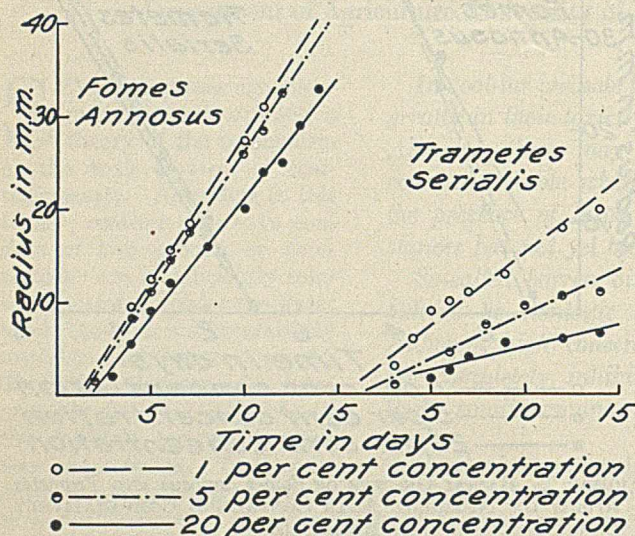


FIGURE 3. RADIAL GROWTH OF *Fomes annosus* AND *Trametes serialis* ON MIXTURES OF NUTRIENT AGAR AND SUBSTANCE D

neck of the flasks and the contents were violently shaken to emulsify the mixture as completely as possible. When about ready to gel, the contents of each flask was poured in approximately equal portions into four sterile dishes. Two Petri dishes were implanted with *Fomes annosus* and two with *Trametes serialis*. The Petri dishes were then covered with a bell jar to reduce the rate of loss of moisture and preservative, and incubated at 28° C. The growth of the test fungi was measured and recorded from time to time. If no growth occurred within 14 days, the transplants were transferred back to nutrient agar slants to determine if the fungus actually had been killed or growth merely inhibited.

EXPERIMENTAL RESULTS

In order to compute the inhibiting influence of a toxic substance on the growth of a test fungus, it is necessary to know how rapidly the test fungus grows when not so influenced. The normal rate of growth at 28° C. of *Fomes annosus* and *Trametes serialis* on nutrient malt agar was determined.

The growth rates of the test fungi are shown in Figure 1. Because of the fact that both test fungi grew rather rapidly on nutrient agar, it is necessary to extend the growth curves a considerable distance beyond the experimental data in order to get an approximation of the growth in 14 days. Such an extension of curves involves certain errors which in the present instance are considered relatively unimportant.

The toxicity to wood-destroying fungi of many of the creosote ingredients was low, and hence it was necessary to determine their inhibiting effects at high concentrations. In order to determine whether part of the inhibiting effect noted under such conditions might not have been due, in part at least, to actual dilution of the nutrients in the nutrient agar, the effects on the growth rate of the test fungi of comparatively large amounts of petrolatum were studied.

In Figure 2 is shown the growth of *Fomes annosus* and *Trametes serialis* in nutrient agar containing 1, 5, and 20 per

cent petroleum. It is obvious that the addition of even 20 per cent petrolatum to nutrient malt agar did not materially influence the growth rate of either *Fomes annosus* or *Trametes serialis*. Such differences in growth rate as are noted are no greater than might be expected on duplicate cultures on the same concentration of petrolatum or on plain nutrient agar. It would appear, therefore, that the slowing up of the growth rate of the test fungi on nutrient agar containing high concentrations of substances of low toxicity cannot be explained on the basis of dilution of nutrient materials. The slowing up of the growth of the test fungi is undoubtedly due to the toxicity of the substances added.

In Table I a summary of the results of the toxicity tests is given. In general, the results obtained with *Fomes annosus* and *Trametes serialis* are quite similar. Some of the differences that are noted are more apparent than real. For example, in the case of I it required a concentration of over 10 per cent of the substance to inhibit the growth of *Fomes annosus*, whereas the growth of *Trametes serialis* was inhibited at a concentration of 1.0 to 2.0 per cent. On 1.0, 2.0, and 5.0 per cent concentrations *Fomes annosus* grew slightly on the inoculum only, no growth occurring on the culture medium as such. If the incubation period had been lengthened, it is not unlikely that *Trametes serialis* might also have grown on these concentrations. In neither case did a 20.0 per cent concentration of substance I kill the test fungus.

TABLE I. TOXICITY TO *Fomes annosus* AND *Trametes serialis* OF COAL-TAR CREOSOTE AND VARIOUS SUBSTANCES SEPARATED THEREFROM

TOXIC SUBSTANCE	<i>Fomes annosus</i>		<i>Trametes serialis</i>	
	Inhibiting concn. %	Killing concn. %	Inhibiting concn. %	Killing concn. %
A	0.1-0.2	0.9-1.0	0.1-0.2	1.0-2.0
B	0.02-0.04	0.04-0.06	0.02-0.04	0.06-0.08
C	5.0-20.0	Above 20.0	1.0-5.0	Above 20.0
D	Above 20.0	Above 20.0	Above 20.0	Above 20.0
E	0.05-0.07	0.05-0.07	0.05-0.07	0.07-0.2
F	0.02-0.04	0.02-0.04	0.02-0.04	0.02-0.04
G	0.01-0.04	0.02-0.04	0.01-0.02	0.01-0.02
H ^a	Above 5.0	Above 5.0	Above 5.0	Above 5.0
I	10.0-20.0	Above 20.0	1.0-2.0	Above 20.0
J	Above 20.0	Above 20.0	Above 20.0	Above 20.0
K ^a	Above 5.0	Above 5.0	Above 5.0	Above 5.0
L	Above 20.0	Above 20.0	Above 20.0	Above 20.0

^a Not enough of this substance was available to completely determine its toxicity.

The original coal-tar creosote used in this study is moderately toxic. A concentration of 0.1 to 0.2 per cent completely inhibited the growth of both test fungi for a period of 2 weeks. A concentration of 0.9 to 1.0 per cent killed *Fomes annosus* under the experimental conditions, and a 1.0 to 2.0 per cent concentration was required to kill *Trametes serialis*. This difference in toxicity toward the two test fungi is not as great as it appears. It happened that the transplants of *Fomes annosus* were killed on a 1.0 per cent concentration of creosote in nutrient agar, although they were not killed on a 0.9 per cent concentration. *Trametes serialis*, on the other hand, was not found to have been killed at a 1.0 per cent concentration. The next higher concentration used was 2.0 per cent which killed the inocula of *Trametes serialis*.

As expected, the fraction of the coal-tar creosote distilling below 285° C. was far more toxic than the original oil, the fraction distilling between 285° and 350° C., or the residue above 350° C.

Also, as might have been logically expected, the fraction distilling between 285° and 350° C. was somewhat more toxic than the residue above 350° C.

Although a 20.0 per cent concentration of the residue above 350° C. in nutrient agar did not completely inhibit the growth of the test fungi, it is an overstatement of the observed facts to say that this residue is nontoxic to wood-destroying fungi.

Even a 1.0 per cent concentration of the residue above 350° C. exerted a marked inhibiting influence on the growth rate of the test fungi. This inhibiting effect is not greatly increased by increasing the concentration of the residue in nutrient agar to 20.0 per cent.

In Figure 3 is shown the effect of different concentrations of *D* (residue above 350° C.) in nutrient malt agar on the growth rate of *Fomes annosus* and *Trametes serialis*. No great accuracy is claimed for these curves, but they are accurate enough for the use here made of them.

In 5 days on nutrient agar containing 1.0 per cent of substance *D*, *Fomes annosus* had an average radius of 12.5 mm.; on nutrient agar containing 5.0 per cent *D*, the average radius was 11 mm.; and on nutrient agar containing 20 per cent *D*, the average radius was 8 mm. If this growth is compared with that made by the test fungus on nutrient agar, it becomes apparent that the growth rate of the test fungus on mixtures of nutrient agar and *D* was considerably reduced. For example, the radial growth of *Fomes annosus* on nutrient agar containing 1.0 per cent *D* was only about 23 per cent of the growth of the fungus on nutrient agar. The radial growth of *Fomes annosus* on nutrient agar containing 20 per cent *D* was only about 19 per cent of the growth of the fungus on nutrient agar alone. In other words, in the latter case the growth rate of *Fomes annosus* was inhibited about 81 per cent.

The growth rate of *Trametes serialis* on mixtures of nutrient agar and *D* was also materially reduced. On nutrient agar containing 1.0 per cent *D*, only about 22 per cent of the normal growth occurred; the addition of 20 per cent *D* to nutrient agar permitted but 7 per cent of the normal growth. In other words, in the latter case the growth of *Trametes serialis* was inhibited 93 per cent.

Attention has already been called to the high toxicity of the fraction distilling below 285° C. (*B*). Washing this fraction alternately for 3-hour periods with 30 per cent sulfuric acid and a 15 per cent solution of sodium hydroxide, and removing a white crystalline material which formed on cooling, did not greatly change its toxicity. This substance is now known as *E*. If anything, toxicity of *E* is slightly less than that of *B*. Whether this reduction in toxicity was caused by the partial removal of tar acids and tar bases or by the removal of the crystalline material formed on cooling is not clear. Neither is it clear how much emphasis should be placed on the differences in toxicity between *E* and *B*; these may be at least partly due to experimental error.

After substance *E* was again washed five times alternately with acid and alkali, treated with a methanol solution of mercury bichloride, and distilled from metallic sodium, the toxicity of the resulting substance (*G*) seems to be slightly increased over that of *E*. Here again it is not definitely known whether these differences in toxicity are significant, owing to experimental error, or owing to chlorination of the oil as a result of the decomposition of the mercury bichloride.

It seems clear, however, that the removal from the fraction below 285° C. of tar acids, tar bases, and the crystalline material which formed on cooling did not greatly change the toxicity of that fraction to wood-destroying fungi. This statement does not mean that the removed tar acids, tar bases, and crystalline materials were not toxic. Their combined toxicity must have been about equal to that of the residual substance *G*, which was highly toxic. In this connection, however, it should be remembered that the original creosote sample had a tar acid content below 300° C. of only 0.2 per cent.

The crystalline material (*F*) which formed, as previously noted, on cooling the 285° C. fraction is surprisingly toxic. This substance was undoubtedly naphthalene, but it is far more toxic than pure naphthalene. Its high toxicity is probably in large measure due to the impurities it contains.

On the whole, *G* is the most toxic substance separated from the creosote sample. The inhibiting concentration for both test fungi is between 0.01 and 0.02 per cent. A concentration between 0.02 and 0.04 per cent killed *Fomes annosus*. *Trametes serialis* was killed at a concentration between 0.01 and 0.02 per cent.

On cooling the 285–350° C. fraction, a bright yellow precipitate, *H*, was formed. This was separated by filtration, washed with acetone, and dried. This substance is probably, at least in part, anthracene. Unfortunately not enough of the substance was available to completely determine its toxic properties. In Figure 4 the effect of a 5 per cent concentration (5.0 grams of solid in 95 grams of nutrient agar) of this substance on the growth of *Fomes annosus* and *Trametes serialis* is shown.

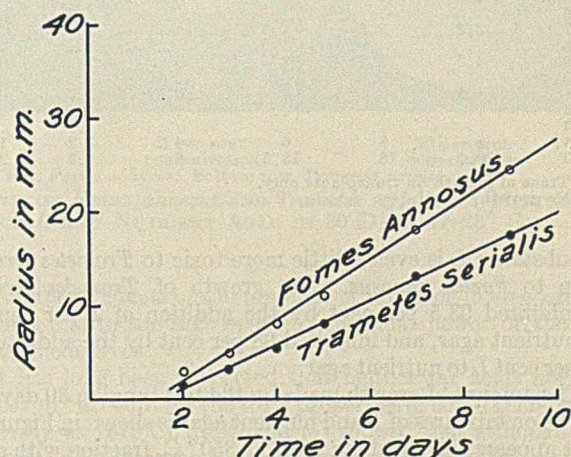


FIGURE 4. RADIAL GROWTH OF *Fomes annosus* AND *Trametes serialis* ON A 5 PER CENT MIXTURE OF *H* IN NUTRIENT AGAR

Although *H* is not highly toxic, it cannot properly be considered nontoxic. A 5 per cent concentration of the substance in nutrient agar inhibits the growth rate of *Fomes annosus* about 72 per cent, and the growth rate of *Trametes serialis* about 68 per cent.

The removal of the solid, *E*, from the fraction distilling between 285–350° C. (*C*) did not materially affect the toxicity of the residual substance *I*.

Washing the 285–350° C. fraction after the removal of the solid *E* five times each with dilute sulfuric acid and alkali seemed to somewhat reduce the toxicity of this substance.

Substance *K* was separated from *J* through fractional distillation. Both substances had received the same treatment. Essentially *K* was that portion of *J* which distilled below 285° C. after five acid and five alkali treatments. Not enough of this substance was obtained to make a complete study of its toxicity. Nevertheless, the data that were obtained clearly show that *K* is more toxic than *J*. In other words, the substance having the lower boiling point is more toxic.

The toxicity of *L* is of particular interest. This substance is essentially similar to the so-called barren oil of Bateman (1, 2).

The effect of *L* on the growth of *Fomes annosus* and *Trametes serialis* is shown in Table II. These data are plotted in Figure 5.

A comparison of the growth of *Fomes annosus* and *Trametes serialis* on mixtures of *L* and nutrient agar with the growth of these fungi on nutrient agar alone clearly brings out the fact that substance *L* was toxic to the test fungi. In 14 days the average radius of a colony of *Fomes annosus* on nutrient

agar containing 1 per cent *L* was approximately 8 mm.; on a 20 per cent mixture, the average radius was approximately 6 mm. In other words, 1 per cent of *L* in nutrient agar inhibited about 95.6 per cent of the radial growth, while a 20 per cent concentration inhibited it about 96.5 per cent.

TABLE II. RADIAL GROWTH OF *Fomes annosus* AND *Trametes serialis* ON DIFFERENT CONCENTRATIONS OF *L* IN NUTRIENT MALT AGAR

TIME Days	AVERAGE RADIUS OF COLONY					
	<i>Fomes annosus</i>			<i>Trametes serialis</i>		
	Percentage concentration:			Percentage concentration:		
	1	5	20	1	5	20
	Mm.	Mm.	Mm.	Mm.	Mm.	Mm.
1
2
3	0.5	a	a	a	a	a
4
5	2.5	2	a	0.5	a	a
6
7	3.2	2.7	1.5	1.2	0.5	a
8	4.5	4.5	3	3	2	0.5
9	4.5	4.5	3	3	2	0.5
10
11	6.5	6	4	3.7	2.7	0.7
12
13
14	8	8	6	4.2	3.2	1.2
30	20.5	18	18.5	6	4.5	2.0

a Trace of growth on transplants only.
b No growth.

Substance *L* is even a little more toxic to *Trametes serialis* than to *Fomes annosus*. The growth of *Trametes serialis* is inhibited 93.5 per cent by the addition of 1 per cent *L* to nutrient agar, and inhibited 98 per cent by the addition of 20 per cent *L* to nutrient agar.

The amount of growth made by the test fungi in 30 days at 28° C. on mixtures of *L* and nutrient agar is shown in Figure 6.

It appears that washing the 285–350° C. fraction with acid and alkali reduces its toxicity. Substance *J* is less toxic than the original 285–350° C. fraction, and *L* is somewhat less toxic than *J*.

If substance *L* had been chlorinated owing to the decomposition of the mercury chloride occurring during the separation of the oil from the bichloride, and if the chlorinated derivatives are more toxic than the original substance, then substance *L* should have been more toxic than substance *J*—provided, of course, that the increased toxicity of the chlorinated derivative was greater than the reduction in toxicity caused by five additional washings each with acid and alkali.

One might argue that practically all soluble substances inhibit the growth rate of fungi if the concentration is high enough. Even sugar, common salt, etc., are toxic at high concentrations. Substance *L*, however, was not toxic in this sense. Although a 20 per cent concentration of *L* did not entirely inhibit the growth of the test fungi, a 1.0 per cent concentration inhibited about 95 per cent of the normal growth. Is such a substance toxic or nontoxic? The answer is apparent.

In Figure 1 of Bateman's paper (2), growth of *Fomes annosus* for 2 weeks on nutrient agar containing 20 per cent barren oil is pictured. Neither the exact size of the colony nor the temperature at which the culture was incubated are given in the discussion. However, as nearly as can be estimated, the test fungus grew approximately 7 mm. in 2 weeks.

In the present studies *Fomes annosus* cultures on nutrient malt agar incubated at 28° C. had an average estimated radius of 170 mm. If this is considered the normal growth rate of the test fungus, the inhibiting influence of 20 per cent barren oil can be calculated. Such a calculation shows that the test fungus in Bateman's experiments grew only 4 per cent of the normal growth rate. In other words, a 20 per cent concentration of the nontoxic or barren oil caused a 96 per cent inhibition of the normal growth of the test fungus.

A 20 per cent concentration of substance *L* in nutrient

agar also permitted approximately 4 per cent of the normal growth rate of *Fomes annosus* or, in other words, caused a 96 per cent inhibition of the normal rate growth. In a 20 per cent concentration substance *L* and Bateman's barren oil were about equally toxic.

DISCUSSION OF RESULTS

The question of the value or purpose of studies such as are here reported may logically be raised. From a purely scientific point of view they can be justified, because they contribute to the knowledge or understanding (fragmentary though that knowledge or understanding may be) of the toxic action of coal-tar creosote.

The confusion that has apparently resulted from toxicity studies of one kind or another has been caused by an effort to apply them to wood-preservation practice without proper regard for their extremely fragmentary nature. Actually, little is known concerning the mechanism of plant or animal poisons. It would seem advisable, therefore, to recognize clearly that a bare start has been made on the study of the toxic action of wood preservatives. The number of interesting facts already brought to light point clearly to the desirability of additional experimental work, but at present it hardly seems wise for this reason to materially alter established wood-preserving practices, the results of which are certified by use of the treated product for many years.

It seems strange that the work of Zehl (12) has not received more attention by investigators of the toxicity of coal-tar creosote. Coal-tar creosote is a complex mixture of a large number of substances. Some of these substances are highly toxic, others less so. Zehl studied the toxic effects on *Aspergillus niger* of a large number of organic and inorganic substances. He also studied the combined effect of two inorganic

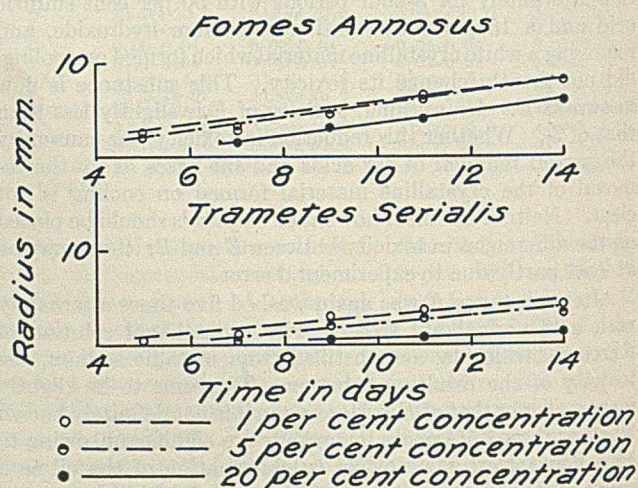


FIGURE 5. RADIAL GROWTH OF *Fomes annosus* AND *Trametes serialis* ON MIXTURES OF NUTRIENT AGAR AND SUBSTANCE *L*

substances, two organic substances, and one organic and one inorganic substance. The results obtained from the study of organic mixtures are of particular interest here. It was found, for example, that when vanillin and acetanilide were both added to nutrient agar the toxic effect on *Aspergillus niger* was the summation of the effects exerted individually by the substances. On the other hand the toxic effects of combinations of chloral hydrate and sodium benzoate, chloral hydrate and picric acid, and chloral hydrate and antipyrine were greater than the summation of the effects exerted by these substances individually. If this is true, it appears that an exact picture of the toxicity of coal-tar creosote may never be

obtained by separating it into its separate components. The results of Zehl's work are of sufficient importance to justify repeating the entire study to determine their accuracy.

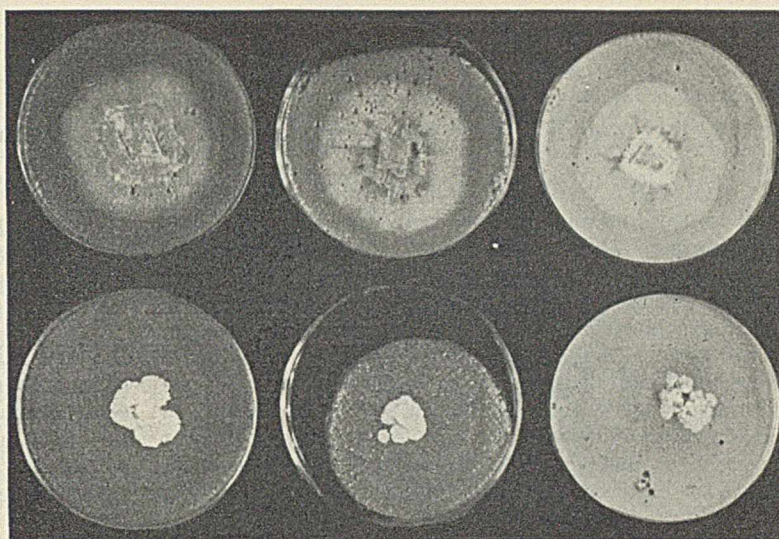
Bateman and Henningson (4), on the other hand, have published some results of more recent work which indicate that the toxic effects of mixtures of two or more hydrocarbons is the same as if one worked independently of the other. In this study the toxic effects of mixtures of acenaphthene and diphenyl, acenaphthene and durenene, and diphenyl and durenene were determined. It was found that the effect of combining two compounds is greater than either of the compounds alone, but it is not the sum of their respective retardations. The percentage growth of a fungus subjected to a mixture of hydrocarbons appeared to be the product of the percentage growths of the fungus when subjected to each component separately.

A very interesting, if somewhat speculative, paper has recently been published by Quastel (9). He raises some points which may have an important bearing on the explanation of the mechanism of the toxic action of coal-tar creosote. A systematic study of the effects of various reagents on *B. coli* lead Quastel to conclude that the dehydrogenations of the cell are associated with definite areas or particles of the surface, these particles possessing specificity of action or the power of discrimination between substrates. The selective action of the general poisons, according to this investigator, points to the existence in the total active surface of areas of varying chemical structures and potentialities. Centers of activity, each center exhibiting a unique or specific behavior, seem to exist. Probably most interesting of all is Quastel's suggestion that some substances appear to act as "poisons" simply by competing with the substrate for the space available for absorption at the centers. The poison and the substrate apparently compete with each other for absorption on fairly equal terms. Perhaps a similar mechanism is involved in combined effects of several poisons. Quastel's proposals are, as he himself suggests, highly speculative. They are nevertheless enlightening; and, if the study is continued, it may greatly contribute to a better understanding of the toxic action of wood preservatives.

Rhodes and Gardner (10) have approached the toxicity problem from a different angle. The tar acids and tar bases were removed from coal-tar creosote by twice extracting creosote with a 10 per cent solution of sodium hydroxide and twice with a 30 per cent solution of sulfuric acid. The final extracted oil was washed exhaustively with several portions of a 10 per cent solution of sodium hydroxide and with a 30 per cent solution of sulfuric acid in order to insure complete removal of acid and basic materials, and was then separated into ten fractions by distilling through a 10-inch (25.4-cm.) Hempel column.

The tar acids and tar bases were recovered from the acid- and alkali-extracting solutions, and after drying were also separated into ten fractions by fractional distillation.

A study of the toxicity of the individual fractions of the dead oil, tar acids, and tar bases showed that within each group of compounds the fungicidal power decreases as the boiling point increases. The neutral hydrocarbons were found to be fully as effective as the phenolic compounds of similar distillation ranges, while the tar bases were found to be only comparatively slightly toxic. The authors believe that



1 per cent concentration 5 per cent concentration 20 per cent concentration
Top row, *Fomes annosus*; bottom row, *Trametes serialis*
FIGURE 6. GROWTH OF *Fomes annosus* AND *Trametes serialis* ON MIXTURES OF SUBSTANCE L AND NUTRIENT AGAR IN 30 DAYS AT 28° C.

the desirable effects of the presence of tar acids in creosote oil are not due to the high specific fungicidal power of the tar acids themselves.

It has long been suspected that neither tar acids nor tar bases fully account for the toxic properties of coal-tar creosote. As early as 1912 Charitschkoff (5) showed that although the phenol and nitrogenous compounds occurring in coal-tar creosote by themselves are quite toxic, their presence in creosote only slightly increases the antiseptic power of the latter.

On the whole, only a comparatively small amount of work has been done to explain the toxic action of coal-tar creosote to wood-destroying fungi. Much of this seems to be highly contradictory. The need for additional experimental work on the subject is clear. Clearer still, however, is need for caution in the interpretation and application to wood-preserving practice of the incomplete data now available.

ACKNOWLEDGMENT

The original analysis of the coal-tar creosote samples was made by the standard American Wood-Preserver's Association method by John Burnes of the Page and Hill Company, St. Paul, Minn.

The original culture of *Fomes annosus* was obtained from the Forest Products Laboratory, Madison, Wis., and of *Trametes serialis* from W. H. Snell of Brown University.

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Tarnish-Resistant Silver Alloys

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ORDINARY sterling silver is an alloy of silver and copper containing 92.5 per cent silver and 7.5 per cent copper. However, any silver alloy containing 92.5 per cent silver is of sterling quality. The beautiful white color and high luster of the polished surface of pure silver is retained in copper sterling silver and, in addition, the presence of the copper makes the sterling silver much harder than pure silver without materially decreasing its malleability. The one undesirable property of copper sterling silver is its inability to retain the luster of its polished surface in the presence of sulfur or any of its compounds. Black silver sulfide is formed which destroys the beauty of the metal. This tarnish develops less readily in pure silver than in copper sterling silver, and it is possible that a silver alloy can be developed that will be entirely nontarnishing under ordinary conditions. An ideal silver alloy, in addition to having the hardness and malleability of copper sterling silver, would retain its high luster at all times. With silver at its present low price, such an alloy would find extensive use.

Much less work has been done on the development of tarnish-resisting silver alloys than their importance would warrant. As early as 1906, an English patent (2) was granted for making tarnish-resisting silver by coating its surface with a metal which would alloy with silver and form a white sulfide. Among the more recent patents issued for tarnish-resistant silver alloys may be mentioned several held by the Oneida Community Company, Ltd. These include: exposing silver to mercury vapors and obtaining a surface amalgam containing at least 90 per cent silver (3); exposing the silver to either chlorine, bromine, or iodine vapors (11); and the addition of 0.25 to 3 per cent silicon to 90 per cent silver, the remaining material not being specified (4). A United States patent (1) has also been granted for an alloy which contains, besides silver, 1.5-6 per cent silicon together with cadmium, aluminum, zinc, and antimony, as well as one (10) for an alloy containing 93 per cent silver, 6.5 per cent zinc, and 0.25-0.50 per cent sodium. It is claimed that the tarnish which forms on this alloy is easily rubbed off. While these patented alloys may have a higher resistance to tarnish than the copper sterling silver, they are not entirely stainless by any means, and some of them are of doubtful value.

Jordan, Grennell, and Herschman (6) made a rather comprehensive investigation of tarnish-resisting silver alloys, both binary and ternary. From the results of this work they conclude that tin, antimony, cadmium, and zinc increase tarnish-resistance when added to silver, while other metals decrease it. They discovered no nontarnishing alloys and express very little hope that a stainless silver alloy, especially of sterling quality, will ever be found.

Leroux and Raub (8) studied silver-copper base alloys containing zinc, cadmium, and nickel. They found that most of these alloys could be age-hardened, but they do not discuss the tarnish resistance of these substances.

The purpose of this investigation was to continue the study

of the alloys of silver with the various metals, in order to discover, if possible, an alloy having the intrinsic value, hardness, and malleability of copper sterling silver and, in addition, having a very high resistance to tarnish.

EXPERIMENTAL PROCEDURE

The metals used in the preparation of the alloys were pure silver shot, electrolytic copper, the c. p. grade of zinc, 99 per cent aluminum, ordinary crystalline silicon and chromium, and beryllium as an 80 per cent beryllium-20 per cent copper alloy. After the investigation of a series of alloys, the silver was recovered electrolytically and re-used.

Fifty-gram samples of the alloys were prepared by melting the carefully weighed metals in small fire clay crucibles in a gas-fired furnace. A small amount of sodium carbonate or borax was used as a flux. The melted alloy was cast into steel molds, the ingots formed being 1 sq. cm. in cross section and about 10 cm. in length.

EXAMINATION OF ALLOYS. The hardness, malleability, constitution, and tarnish resistance of all of the alloys made

were studied. The hardness of the alloys as cast, and also after annealing, was measured by both the Brinell and the Rockwell hardness testers. However, since many of the alloys were too soft for the standard Rockwell B scale, only the Brinell hardness numbers are given, using 500 kg. pressure and 10 mm. ball. The malleability of the cold alloys was determined by rolling tests. The alloy to be tested was rolled on electrically driven rolls until the piece fractured, or until it was rolled to a thickness of about 0.5 mm. Nineteen passes rolled a 1-cm. square ingot to 0.5 mm. in thickness, and its length was increased about 2000 per cent. While the decrease in thickness was proportional to the number of passes through the rolls, the increase in length was not. Twelve passes increased the length of the alloy 100 per cent, fifteen passes increased it 250 per cent, and eighteen passes increased it 1000 per cent. Thus, alloys differing only slightly in malleability may vary greatly in percentage elongation. The results in all cases are given as percentage of elongation produced by rolling until fracture occurred. The constitution of the alloys was studied by means of cooling curves and microscopic appearance.

In taking the cooling curves, the temperature was automatically recorded at 15-second intervals by a Brown recording pyrometer using a chromel-alumel thermocouple. An electric tube furnace was used to melt the samples, about 50 grams of the alloy being used for each determination. Fire-clay crucibles were used. No reducing gases were used to prevent oxidation, since the alloys oxidized but slightly even at their melting points. These slowly cooled alloys, after proper polishing and etching, were used in studying the microscopic structure. The best etching agent was found to be sodium cyanide with hydrogen peroxide, although dilute nitric acid was used in some cases.

The resistance to tarnish was the main object of the experi-

The silver-zinc-aluminum system containing from 75 to 100 per cent silver is investigated. Several alloys of silver with chromium, zinc, aluminum, beryllium, silicon, copper, tin, and barium as binary, ternary, and quaternary alloys are studied. An attempt is made to nitride the various alloys with gaseous ammonia at a somewhat elevated temperature in the hope that a tarnish-resistant case will be formed.

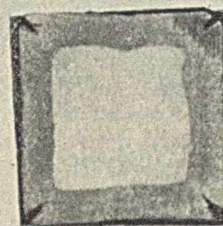
mentation. No exact test could be devised, but comparative results were obtained for each run. The method used was to place a drop of ammonium polysulfide solution on the polished surface of the alloy for a definite length of time, ranging from 0.5 to 3 minutes, to wash it off with distilled water, and to compare the degrees of tarnish. This operation was repeated several times on the same spot. The tarnish was then polished off and the test repeated. It was found that in some cases the result of the first test was different from those made later. If the alloy was polished only until the tarnish was gone, it tarnished more readily the second time than it had before. It was necessary to continue the polishing for 2 or 3 minutes so that the entire surface was removed if the results obtained were to be considered valid. In the tables the most readily tarnished alloy is given as number one; the higher the number, the more tarnish resistant the alloys are. The numbers correspond roughly to the time required to develop a certain degree of tarnish; the amount of tarnish developed by 0.1 *N* ammonium polysulfide solution in 1 minute on copper sterling silver, as cast, is taken as unity. The ammonium polysulfide solution had a composition corresponding roughly to $(\text{NH}_4)_2\text{S}_2$. This method of testing the tarnish resistance of the alloys was not good, since it was impossible to differentiate between samples having about the same tarnish resistance; nevertheless, it was the best method that could be devised.

SILVER-RICH ALLOYS OF THE SILVER-ZINC-ALUMINUM SYSTEM

The silver-zinc-aluminum system above 75 per cent silver was first studied. According to Jordan, Grennell, and Herschman (*6*) zinc confers upon silver the greatest tarnish resistance of any common metal, but the resultant alloys are not much harder than pure silver. Aluminum, although not increasing the tarnish resistance, increases the hardness of silver alloys. At room temperature, zinc and silver form α -solid solutions up to 25 per cent zinc (*1*). Aluminum and silver form α -solid solutions up to 4 per cent aluminum. At about 8 per cent aluminum the compound AlAg_3 is formed, and at 11 per cent the compound AlAg_2 is formed. AlAg_3 and AlAg_2 form solid solutions with each other. At room temperature, aluminum and zinc alloys consist of γ -solid solutions up to 2 per cent aluminum, α -solid solutions above 82 per cent

The results of the study of the silver-zinc-aluminum alloys are summarized in Table I.

HARDNESS. Table I shows the hardness of the alloys studied. It should be noted that increasing the amounts of aluminum increases the hardness very rapidly. Zinc alone added to silver has little effect on hardness. However, maximum hardness is attained when both aluminum and zinc are present.



SILVER 92, TIN 6, SILICON 2 PER CENT ($\times 3$)
Chill-cast followed by nitriding at 650° C. for 15 hours; etched with nitric acid. (Note dark case and cracks in four corners.)

MALLEABILITY. The malleability of the alloys is given in Table I. Silver-aluminum alloys containing much more than 4 per cent aluminum are not malleable because of the presence of the intermetallic compound, AlAg_3 . Hence, as expected, when zinc is added to a 4 per cent aluminum-96 per cent silver alloy, it becomes brittle unless the percentage of aluminum is decreased. The brittle alloys are probably solid solutions of intermetallic compounds. No silver-zinc-aluminum alloy with a hardness equal to the hardness of copper sterling silver is very malleable.

CONSTITUTION. Table I shows the constitution of the various alloys. A thermal diagram could not be made because an insufficient number of alloys were studied. Starting with an α -solid solution of a 4 per cent aluminum-96 per cent silver alloy, the following relation is approximately true: In order to maintain an α -solid solution, the zinc may be increased 6 per cent for each 1 per cent the aluminum is decreased.

TABLE I. PROPERTIES OF SILVER-ZINC-ALUMINUM ALLOYS

COMPOSITION			BRINELL HARDNESS AS CAST	MALLEABILITY ^a %	TARNISHABILITY ^b Minutes	SOLIDIFICATION		CONSTITUTION
Ag	Al	Zn				Begin	End	
(Copper sterling)			63	>2000	1
100	0	0	25	>2000	4
96	4	0	60	>2000	2	835	775	α -Solid solution
92	8	0	70	5	2	760	740	Solid solution of compounds
88	12	0	180	5	2	710	700	Intermetallic compounds
94	4	2	67	300	3	796	755	α -Solid solution
88	8	4	120	20	6	740	720	Solid solution of compounds
82	12	6	200	10	11	695	675	Solid solution of compounds
94	2	4	52	>2000	5	853	820	α -Solid solution
88	4	8	78	150	10	765	745	Solid solution of compounds
80	8	12	195	35	14	710	690	Solid solution of compounds
92	2	6	47	>2000	8	830	795	α -Solid solution
84	4	12	180	10	10	740	725	Solid solution of compounds
76	8	16	215	5	17	690	680	Solid solution of compounds
95	0	5	34	>2000	7	915	900	α -Solid solution
90	0	10	37	>2000	12	860	830	α -Solid solution
85	0	15	42	>2000	16	795	750	α -Solid solution
80	0	20	45	>2000	18	763	725	α -Solid solution
75	0	25	48	>2000	20	735	706	α -Solid solution
91	1	8	43	>2000	9	838	800	α -Solid solution
83	2	15	68	200	15	762	732	Solid solution of compounds
76	4	20	220	5	19	728	725	Two phase

^a Elongation by rolling.

^b Approximate time required to develop unit tarnish.

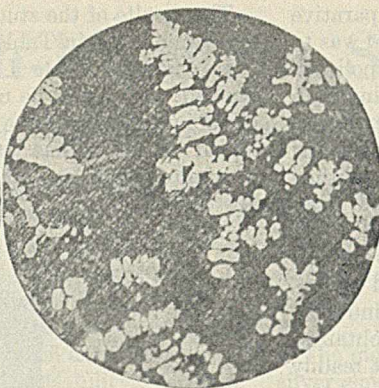
aluminum, and a mixture of α - and γ -solutions when the amount of aluminum is between 2 and 82 per cent. Thus, one would expect that all silver-aluminum-zinc alloys that contained from 0 to 4 per cent aluminum and from 0 to 25 per cent zinc would be α -solid solutions. These alloys should be fairly hard and somewhat resistant to tarnish.

TARNISH. Resistance to tarnish, as shown by Table I, increases as the percentage of zinc increases. Increasing the percentage of aluminum when zinc remains constant appears to make the alloys more resistant to tarnish, although the increased resistance is almost negligible. Even the least readily tarnished alloy is by no means stainless.



A. SILVER 76, ZINC 20, ALUMINUM 4 PER CENT ($\times 100$)

Slowly cooled; two-phase; etched with nitric acid.



B. SILVER-CHROMIUM-ALUMINUM ALLOY ($\times 100$)

Chill-cast; light is chromium phase; dark is silver phase; etched with nitric acid.

ALLOYS OF SILVER WITH OTHER METALS

The alloys of silver with a large number of other metals, as binary, ternary, and quaternary alloys, were tried with the hope that a satisfactory tarnish-resisting alloy would be found. Most of those metals which were reported to increase the tarnish resistance of silver (as well as many metals which very easily become passive, such as chromium and beryllium) were tried. The component metals were chosen with the idea of obtaining solid-solution alloys if possible. The metals tried in these alloys were chromium, nickel, beryllium, barium, zinc, aluminum, silicon, tin, and mercury.

SILVER-CHROMIUM BASE ALLOYS. Silver and chromium are practically insoluble in each other in both the liquid and solid state (5). At 465° C. chromium is soluble in silver to the extent of 3.3 per cent. The solubility decreases with decrease in temperature. Jordan, Grennell, and Herschman practically confirm this and report their inability to get silver to alloy with much chromium. An alloy made by them at 1200° C. contained 0.14 per cent chromium. They also tried to make ternary silver-chromium alloys containing 5 per cent of either zinc, tin, antimony, or cadmium, but the attempts met with only fair success, the alloys usually containing about 0.2 per cent of chromium. Chromium melts at 1615° C. which is about the boiling point of all the other metals tried, except silver and tin.

Since aluminum and chromium alloy with each other forming both solid solutions and compounds, an attempt was made to make an aluminum-chromium-silver alloy. Equal amounts of aluminum and chromium were mixed and heated to about 1800° C. with silver in an induction furnace. The result-

TABLE II. HARDNESS, MALLEABILITY, AND TARNISHABILITY OF BERYLLIUM-SILICON-SILVER ALLOYS

COMPOSITION		BRINELL HARDNESS AS CAST	MALLEABILITY ^a %	TARNISHABILITY ^b				
Ag	Zn				Al	Cu	Si	Be
91	5	2	2	0.1	...	60	>2000	5
96	0.4	1.8	...	77	5	5
97.1	0.6	...	2.3	55	15	3
93.3	5.5	...	1.2	60	40	3
91.7	8.3	...	103	5	2
92	6	2	...	164	10	2
91	5	2	2	95	30	2
92.5	5.5	1	0.5	...	0.5	48	5	4
90.5	6	...	3	0.5	...	90	>2000	5
93.7	6.3	35	>2000	6
91	6	...	3	55	>2000	5

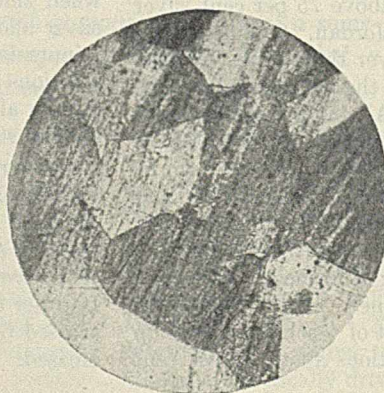
^a Elongation.

^b Pure silver, 4; sterling silver, 1.

ing alloy was two phase, even in the liquid state. The silver phase of the solid alloy contained about 13 per cent aluminum and some segregated chromium-rich phase. The alloy was too brittle and porous to have any value. An alloy of nickel, aluminum, and silver behaved somewhat similarly and was not investigated further.

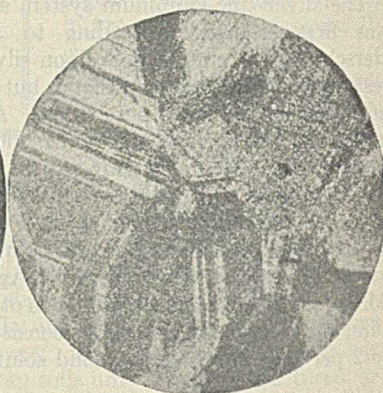
BERYLLIUM-SILICON-SILVER BASE ALLOYS. According to the thermal diagrams given in International Critical Tables, both silicon and beryllium form eutectic alloys with silver. However, these metals are mentioned in some of the patented tarnish-resisting silver alloys, but Jordan, Grennell, and Herschman report that silicon does not increase the tarnish resistance, and that beryllium actually seems to decrease the tarnish resistance of silver. They report that both elements increase the hardness and decrease the malleability of silver.

Since both beryllium and silicon are difficult to alloy with silver, owing to their high melting points and their strong tendencies to become covered with an infusible film of oxide, a small amount of beryllium-silver alloy, as well as a small amount of a silicon-silver alloy, was first made at a high temperature in an induction furnace. After analysis, these alloys were used instead of the pure elements for making the alloys to be tested.



C. SILVER 92.5, TIN 5, ZINC 2.5 PER CENT ($\times 100$)

Chill-cast followed by annealing at 700° C. for 1 hour; homogeneous α phase; etched with sodium cyanide and hydrogen peroxide.



D. SILVER 88, TIN 10, ZINC 2 PER CENT ($\times 100$)

Chill-cast and cold-worked; annealed at 700° C. for 1 hour; etched with sodium cyanide and hydrogen peroxide. (Note twinned solid-solution crystals.)

Table II shows the hardness, malleability, and tarnishability of the silver-silicon-beryllium alloys tested. Silicon and beryllium have a marked hardening effect on silver alloys, but even in small amounts they render the alloy nonmalleable. Beryllium causes brittleness in smaller amounts than does silicon. As tarnish-resisting elements in silver alloys, silicon and beryllium are valueless, since they have no outstanding effect on tarnishability.

SILVER-TIN BASE ALLOYS. At room temperature, tin forms α -solid solution with silver up to 19 per cent tin (12). Jordan, Grennell, and Herschman found that silver alloys containing tin were almost as tarnish resistant as those containing an equal amount of zinc. In addition, tin-silver alloys are harder than zinc-silver alloys.

Table III shows the hardness, malleability, and tarnishability of the alloys studied. In silver alloys, tin increases the hardness more than an equivalent amount of zinc. At the same time, the malleability decreases faster than in corresponding zinc-silver alloys. Low-tin alloys are more

tarnish resistant than corresponding zinc-silver alloys. Increasing the percentage of tin from 5 to 10 per cent does not materially affect tarnishableness, while in zinc-silver alloys the tarnish resistance in the alloys studied is proportional to the percentage of zinc present.

TABLE III. HARDNESS, MALLEABILITY, AND TARNISHABILITY OF TIN-SILVER ALLOYS

COMPOSITION						BRINELL HARDNESS AS CAST	MALLE- ABILITY ^a %	TARNISH- ABILITY AS CAST ^b
Ag	Sn	Zn	Cu	Al	Si			
95	5	40	>2000	11
90	10	58	150	12
90	5	5	47	>2000	10
87	5	5	3	54	>2000	8
88	10	2	..	75	40	9
80	10	10	78	60	7
92	6	2	75	40	6

^a Elongation.

^b Pure silver, 4.

OTHER ALLOYS. Many miscellaneous silver alloys were made and tested. Barium-silver and strontium-silver alloys were made by electrolyzing a fused bath of the alkali earth chloride in an iron dish using molten silver as the cathode. The alloys were hard, nonmalleable, and easily tarnished when the alkali earth metal was present to the extent of 10 per cent or more. These alloys appeared to have no value, either alone or as ternary alloys with tin or zinc.

An amalgam of the type used by dentists for filling cavities in teeth, consisting of 50 per cent mercury, 34 per cent silver, 14 per cent tin, and smaller amounts of zinc and copper, appeared to be exceedingly resistant to tarnish, but was entirely nonmalleable. When the composition was modified sufficiently to give malleability, the resistance to tarnish was greatly decreased.

NITRIDING WITH GASEOUS AMMONIA

It was thought that perhaps ammonia at high temperatures might case-harden silver alloys similar to the manner in which it case-hardens certain steels. Several elements that alloy with silver form stable nitrides (9). Aluminum nitride, ranging in color from pale yellow to black, forms when ammonia is passed over pure aluminum at 700° C. Copper, as copper oxide, will form copper nitride at 250° C. in ammonia gas, but it decomposes near its temperature of formation. Zinc forms a number of nitrides between 400° and 600° C. which range in color from gray to black. All of these decompose slowly at the temperature of formation. Tin decomposes ammonia but does not unite with it; silicon forms a number of nitrides which are grayish white powders. Pure silver does not form a stable nitride with ammonia gas, although a nitride is known which is explosive.

TABLE IV. PHYSICAL PROPERTIES OF ALLOYS NITRIDED FOR 15 HOURS AT 650° C.

Ag	COMPOSITION						BRINELL HARDNESS		TARNISH- ABILITY ^a		APPEARANCE AFTER NITRIDING
	Zn	Al	Cu	Si	Be	Sn	Before nitrid- ing	After nitrid- ing	Before nitrid- ing	After nitrid- ing	
91	5	2	2	0.1	60	60	5	5	Dark gray
92.5	5.5	1	0.5	..	0.5	..	48	39	4	5	Gray
90.5	6	..	3	0.5	90	45	5	6	Grayish brown
93.7	6.3	35	28	6	6	White
91	6	..	3	55	34	5	5	White
95	40	29	11	12	White
90	5	58	45	12	11	White
90	5	5	47	34	10	9	White
87	5	..	3	5	54	48	8	7	White
88	..	2	10	75	67	9	8	Very light gray
80	10	10	78	54	7	10	White sparkle
92	2	..	6	75	40	6	5	Light gray

^a Pure silver, 4.

The samples were heated in a cylindrical electric tube furnace. The temperature was kept constant with a Leeds-Northrup controlling potentiometric pyrometer. The gaseous

ammonia was obtained from a cylinder and passed directly into the furnace. After passing through the furnace, the ammonia was absorbed in water.

The results of the nitriding under various conditions are given in Table IV. The alloys are softened because of the high temperature. Their resistance to tarnish is not markedly affected, and it is doubtful if any nitrated case is formed except in a few instances.

SUMMARY AND CONCLUSIONS

1. None of the metals studied gave binary alloys with silver that were satisfactory in every respect as regards hardness, malleability, and tarnish resistance.

2. Aluminum alone did not increase the tarnish resistance of binary silver alloys. It hardened the alloys materially and made them brittle when present in amounts beyond 4 per cent. Its malleable alloys were not as hard as copper sterling silver.

3. Zinc had the greatest tarnish-resisting effect in silver alloys of any of the metals studied. The resistance to tarnish was nearly proportional to the amount of zinc present. Zinc did not increase the hardness sufficiently to be used alone. The alloys containing up to 25 per cent zinc were malleable.

4. Chromium did not alloy with silver in amounts sufficient to have much effect upon its resistance to tarnish.

5. The barium-silver and strontium-silver alloys studied were brittle and were as readily tarnished as copper sterling silver.

6. Silicon had a marked hardening effect on silver alloys but could not be used in amounts much above 0.5 per cent, or brittleness resulted. It had no marked effect on tarnish resistance.

7. Appreciable amounts of beryllium made silver alloys hard and brittle, and decreased tarnish resistance.

8. Tin-silver alloys containing 5 per cent tin were the most tarnish resistant of any 95 per cent silver alloy studied, although only slightly better than the corresponding silver-zinc alloy. Increasing the amount of tin beyond 5 per cent did not increase tarnish resistance materially, while increasing the amount of zinc in silver-zinc alloys did increase tarnish resistance.

9. Nitriding with ammonia at either 500° or 650° C. was of no value for case-hardening or increasing the resistance to tarnish of silver alloys. Alloys containing aluminum and silicon were darkened, owing to the formation of an aluminum nitride and silicon nitride case, while the color of the other alloys was not materially affected. Cast alloys were softened because of the high temperature.

10. While many of the silver alloys studied were more tarnish resistant than copper sterling silver, and had sufficient hardness and malleability, none was found that could be considered entirely nontarnishing or stainless.

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Compression Stress Strain of Rubber

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By inflating a hollow thin-walled sphere of rubber, it is possible to determine stress-strain curve without resort to actual compression. Difficulties and errors inherent in direct compression tests are avoided. The method depends on the relation existing between a compressive force and the tensiles employed in two-dimensional stretching that would effect the same deformation in the rubber as the compressive force. The method assumes negligible volume change in the rubber.

The inflation of a hollow sphere is a convenient way of applying under accurate controls the tensiles for two-dimensional stretching. The experimental quantities determined on the inflating sphere are gas

pressure and dimensional measurements. Typical results on cold-cured pure-gum balloon stock are cited, including breaking point of the compression curve, energy of compression, and hysteresis.

Data for compression and for ordinary one-dimensional extension strongly indicate that these two operations are continuous, and that the stress-strain curves for the two constitute a single continuous curve. Based on such continuity being a fact, the main features of the complete stress-strain curve for rubber are described. Stress conditions at a point in deformed rubber are discussed, and attention is drawn to the analogy with pressure at a point in a fluid.

THE physics and the physical testing of rubber have received much attention. This naturally has centered in the property for which vulcanized rubber is notable among materials—its high elastic deformability. For the most part, this property has been studied through stretching tests by extending the specimen in one direction and diminishing it in the two transverse directions.

Much less attention has been given to the compression characteristics. The reason probably lies more in the difficulties of carrying out a compression test than in less importance attaching to compression phenomena. Mechanical rubber goods, such as automobile rubber shackles, universal joints, and shock absorbers on railway coaches, are regarded conventionally as proper subjects for compression studies. That, in actual service, compression plays a prominent part hardly needs to be emphasized. Tire treads, inner tubes, and rubber heels and soles are among stocks used in large volume which are subjected to compression in service or which undergo the one-dimensional decrease and two-dimensional increase in size, characteristic of compression. Indeed we may regard this sort of deformation as decidedly more common in the usage of rubber goods than the one-dimensional increase and two-dimensional decrease in size employed in the more usual stretching tests.

Although the importance of the compression stress strain is obvious, its accurate determination over its entire course has presented formidable difficulties which no doubt have retarded progress. These difficulties reside in the frictional forces which develop between the faces of the rubber and the compressing surfaces, and in nonuniform deformation of the rubber specimen. The former prevent one from knowing what force is expended on the compression itself, and the latter means that the *sine qua non* of any determination of stress and strain relationship is wanting. Errors arising from these sources become greater as the degree of compression increases.

Birkitt (4) reviews work on the compression characteristics of rubber down to 1925. The early studies of Clapeyron (8) and of Lundal were concerned with volume compressibility as distinct from alteration of shape under compression (with volume substantially constant), which is the sense in which "compression" is used in the present paper. Later Boileau, Heinzerling and Pahl, Stévant, Breuil (6), and Van Heurn

studied compressibility as we understand it here. They used machines by means of which the test specimen was compressed between parallel plates. Birkitt (4) used such a machine and reported analogies between the elongation-stress and the compression-stress curves. In a later paper Birkitt and Drakeley (5) showed that more consistent results are obtained by lubricating the rubber-metal interface, petrolatum being preferred.

Hippensteel (10) described tests on the cutting resistance of rubber insulation, which he subsequently (11) pointed out could be adapted to compression tests of a more general nature. His machine was used later by Ingmanson and Gray (12) in a study of compression and shear resistance of rubber stocks. They showed the marked effect of lubrication of the rubber-metal surface. Abbott studied resistance to flexure under compression (1) and described a "compressometer" for making compression tests (2). Church (7) studied the compression stress strain of sponge rubber. Ariano (3), pressing molded cylinders of rubber between parallel plates, obtained compression stress strains up to 55 per cent compression. The latter author also has made an elaborate mathematical analysis of the compression stress strain. Recently Jacobs (13) and Douglas (9) have published compression results obtained by the parallel plate method, apparently without lubricant; the work of Douglas bears more particularly on compressions at low temperatures.

We may summarize this previous work on the compression characteristics of rubber by saying that it has comprised (1) tests of a practical type which apparently did not aim at establishing a pure compression-stress relationship, and (2) tests having such a relationship as their objective, and that in the latter class of tests the technic has been that of directly compressing the specimen between parallel plates, either with or without the aid of a lubricant. We may conclude also that, where a lubricant has been used, it has alleviated the difficulties of direct compression mentioned above but has not removed those difficulties or the error resulting from them.

It is the purpose of the present paper to outline a method of determining the compression stress strain of rubber which is free from error due to friction or to nonuniform deformation. The method is an indirect one and consists of substituting for a compressive force two transverse stretching forces and of calculating from these what the corresponding compressive

force would have to be in order to cause the same degree of shortening in one direction. The method of the present authors does contain the possibility of error from another source—namely, neglect of such volume change as may occur in large deformations—though it is not the intention herein to treat in detail of this source of error. Before discussing how best to apply tensile forces so as to bring about two-dimensional stretching, the relation existing between such tensile forces and the equivalent compressive force will be shown.

COMPRESSIVE FORCE AS FUNCTION OF STRETCHING FORCES

Suppose, as in Figure 1, that we have a cube of unstressed rubber, *A*, of unit length. Let this be compressed so that it assumes the shape *B*, in which the height of the specimen has been diminished to the distance, *y*, which is less than unity. Let the new value for each of the two lateral dimensions be *x*. Then *x* will be greater than unity and, assuming that the volume of the rubber has not changed, will be equal to $y^{-1/2}$.

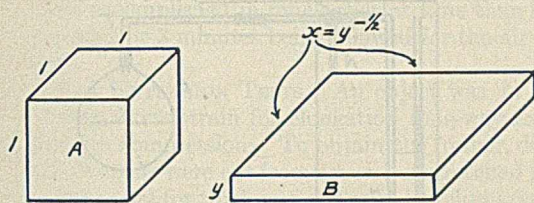


FIGURE 1. UNSTRESSED RUBBER CUBE AND STRAINED RUBBER CUBOID

It is clear that, in so far as the application of external forces to the specimen is concerned, there are two ways in which this deformation can be effected. One is to compress the specimen by applying a compressive force in the vertical direction; the other is to apply two tensile forces perpendicular to each other and also perpendicular to the direction of compression in the first case. Obviously, when mutually perpendicular tensiles are applied, they stretch the specimen in the two lateral directions and diminish it in the third; and, if one gives appropriate values to these tensiles, they can be made to bring about exactly the same change in shape as a single compressive force (any volume change being neglected).

Now a given deformation in a given specimen of rubber is effected by doing a given amount of work on the rubber. The work done, partly expended on overcoming internal friction in the rubber but mostly stored as potential energy, is independent of whether the external forces are tensions or compressions (its amount depends only on the degree of deformation). The work done to change the unstressed cube, *A*, to the strained cuboid, *B*, is the same whether the rubber has actually been compressed in one direction or whether it has actually been stretched in two directions. The same principle holds for the work done to impress an additional strain on an already strained specimen—the amount of additional work depends on the magnitude of the strain increment and is independent of the nature of the impressing forces. This principle enables the relationship between compressive force and the equivalent tensile forces to be determined.

Suppose the strained specimen, *B*, is under the compressive force, *P*. Let it be compressed through the further small distance, *dy*. The small increment of work is

$$dW = Pdy \quad (1)$$

Again, considering the strained specimen, *B*, let the compressive force, *P*, be replaced by two tensile forces, *T*, which are perpendicular to each other and to *P*. Let the forces, *T*,

be of such magnitude that they maintain the shape of the specimen as it was when compressed by *P*. Now let *T* be slightly increased so as to bring about the same increment of strain as in the former case—that is, so as to diminish *y* by *dy*, or so as to increase *x* by *dx*. Then the increment of work done on one of the two lateral faces that are moved by a force is

$$dW' = Tdx$$

and the work done on both faces which move simultaneously under a force is

$$2dW' = 2Tdx \quad (2)$$

But since the work done by the first method of increasing the deformation is equal to that done by the second,

$$\text{Since } Pdy = 2Tdx \quad (3)$$

$$x = y^{-1/2}$$

$$dx = -\frac{x^3 dy}{2}$$

Therefore

$$Pdy = 2T\left(-\frac{x^3 dy}{2}\right)$$

$$P = -x^3 T \quad (4)$$

$$P = -y^{-3/2} T \quad (5)$$

Equation 4 defines the compressive force as a function of the equivalent tensile and of the new (diminished) length in the direction of compression when the original (unstrained) specimen is a cube of unit length; Equation 5 defines the compressive force in terms of the equivalent tensile and of the new (augmented) length in the directions of expansion. It should be emphasized that *P* and *T* do not both act at any one time on the specimen; they are the alternative forces, either of which may be employed to get the same result as far as degree of deformation of the specimen is concerned, and they are called "equivalent" in the sense of their equal effects on deformation.

In computing the compression stress-strain data from measurements of tensiles in two directions, it may be more convenient to measure the expanded lengths, *x*, and to calculate the diminished length, *y*, than to measure the latter directly. If so, from Equation 3 we obtain:

$$y = x^{-2} \quad (6)$$

P and *y* are the quantities which, for various degrees of compression on a specimen, constitute the compression stress-strain data. Either Equation 4 or 5, therefore, may be used to compute *P*, and Equation 6 to compute *y* from measurements on a two-dimensional stretching operation

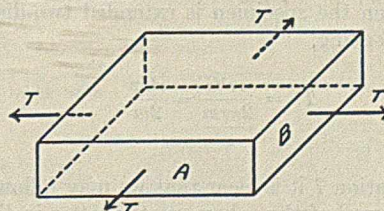


FIGURE 2. SLAB OF RUBBER STRETCHED IN TWO DIRECTIONS

which involves no direct measurements of compressive force, and which in fact does not subject the specimen to actual compression. The negative sign in Equation 4 or 5 arises from the circumstance that *P* is a pressure and *T* a tensile, and means that these forces are exerted in opposite directions as regards the specimen; *P* is directed toward and *T* away from the specimen.

HOLLOW SPHERE AS TEST SPECIMEN

We must now consider how we may apply tensiles in a two-way stretching operation, and do so without encountering

difficulties as great as those associated with actual compression. The question is: How shall we apply tensile forces in two mutually perpendicular directions, have them act uniformly over the faces to which they are applied, and accommodate themselves to the continuously changing shape of those faces? As a slab of rubber is stretched in two directions (Figure 2), the faces *A* and *B*, across which the tensiles act, become longer and narrower; it is clear that the difficulties become greater as the degree of extension increases.

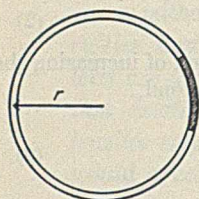


FIGURE 3. DISTENDED HOLLOW SPHERE OF RUBBER

Prache (14) tried various expedients to overcome the obvious difficulties which arise when a flat sheet is employed as specimen. He did not, however, succeed in showing how such a sheet may be subjected to high extension in two directions simultaneously with a uniform distribution of stress and strain. While Prache had the determination of the two-way extension stress strain in mind (as distinct from the present purpose of computing the compression stress strain from measurements on two-way extensions), nevertheless it is obvious that, as a step in computing the latter relationship, the method of stretching a plane slab in two directions simultaneously can be no more accurate than it is as a direct measure of the former relationship.

What is necessary, in order that the *P-T* relation of Equation 4 or 5 may be used, is a technic that will permit of the following: (1) stretching of a portion at least of a sample of rubber uniformly in two directions up to the breaking point with uniform distribution of tensile force over the progressively changing faces; (2) convenient measurement of tensiles and elongations. The inflation of a hollow sphere of rubber having a thin and uniform wall fulfils this requirement perfectly. The wall of such a sphere comes under a two-way tension when the sphere is distended with gas pressure.

If, as in Figure 3, we have a distended hollow sphere of radius, *r*, filled with gas under a (differential) pressure, *G*, the total force borne by the wall across a circumference is $\pi r^2 G$. But we wish to know how much of this force is borne by that area in the cross section of the wall of the distended sphere which had unit area originally (before distension), for this is the tensile, *T*, of Equation 4 or 5. The original cross-sectional area presented by the wall of the sphere is $2\pi r m/x$, where *m* is original wall thickness and *x* has the meaning heretofore used—namely, the length to which a unit length increases when the specimen is extended two-dimensionally. From the foregoing,

$$T = \frac{\pi r^2 G}{2\pi r m} = \frac{r G x}{2m} \quad (7)$$

From Equation 7 it is clear that we may follow the tensile forces in the wall of the sphere, as the latter is distended, by measuring the original wall thickness, *m*, which is a constant for a given sphere, and taking readings at intervals on the variables *r*, *G*, and *x*. In the experimental trial of the method, *x* was determined by making a mark on the undistended wall of the sphere 1 inch (2.54 cm.) long and by measuring this at each degree of extension. Of course, in place of this, the original radius of the sphere can be measured, whereupon the ratio of the new radius to the original radius is the quantity *x*.

The equivalent compressive force, *P*, may be calculated directly from the experimental data, *r*, *G*, *x*, and *m*, without first calculating *T*, by combining Equations 4 and 7 thus:

$$P = - \frac{r G x^2}{2m} \quad (8)$$

EXPERIMENTAL PROCEDURE

In the experimental trial of these principles, rubber balloons¹ have been used since they afford a fair approximation to the spherical shape required in theory. The balloons were the usual cold-cured type; undistended they were about 5 cm. in diameter and their walls were about 0.03 to 0.04 cm. thick.

BALLOON INFLATION. Figure 4 shows the arrangement by which the balloon was distended and by which readings were taken. The neck of the balloon, *B*, is taped securely to a glass tube, *T*; the latter leads, through a three-way stopcock, *SC*, to an air inlet, *A*, and to a manometer, *M*. The balloons tend to be pear-shaped; but this deviation from the spherical was minimized by taping down most of the neck region.

Before a balloon was fastened to the tube, two bench marks (one vertical and one horizontal) were made in the equatorial region as shown in Figure 4. These marks were 1 inch (2.54 cm.) long and were the means by which the expansion of the balloon was followed. The thickness of the wall in the bench-marked region prior to inflation was determined on a

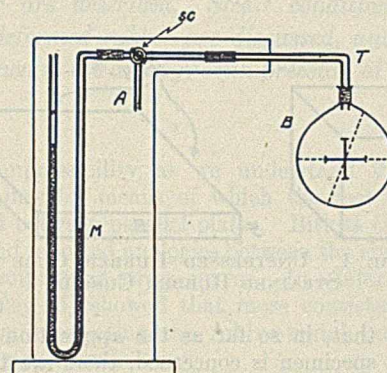


FIGURE 4. ARRANGEMENT FOR DISTENSION OF BALLOON

Randall and Stickney gage by measuring the folded stock and dividing the reading by two. The equatorial part was chosen as the place in which to observe the stress-strain properties because it was found most uniform in thickness; in particular, the pole opposite the neck was rejected on account of less consistent thickness and shape. It was considered better practice to take readings on a small area, marked as just described, than to consider the entire balloon as the test specimen. By confining readings to a small and well-chosen area, such variability in thickness and such imperfect sphericity as a balloon exhibited were made of less moment.

The liquid used in the manometer was a sulfuric acid solution of about 1.66 density; this was checked before each inflation experiment, in view of minor changes in density which occurred from day to day.

Each inflation was carried out according to a predetermined schedule. The schedules used on various balloons were such as to cause diminution of wall thickness at one or the other of the following rates, approximately:

- 0.0013 cm. (0.0005 inch) per minute
- 0.0025 cm. (0.001 inch) per minute
- 0.0076 cm. (0.003 inch) per minute
- 10 per cent of the actual (remaining) thickness per minute
- 20 per cent of the actual (remaining) thickness per minute
- 40 per cent of the actual (remaining) thickness per minute

The increments which the one-inch bench marks would have to show at fixed time intervals, in order that wall thickness should diminish at each of these rates, were calculated and the dilations were conducted accordingly.

In inflating a balloon, air was introduced at intervals of one minute. It was found more convenient to blow in air from the

¹ Balloons were supplied by the Eagle Rubber Company, Ashland, Ohio.

lungs than to use compressed air. With the stopcock turned so as to connect the balloon with tube A, air was introduced until the bench mark had increased as demanded by the inflation schedule for the balloon in question. Then the stopcock was turned so as to connect the balloon with the manometer, and the difference in height of the manometer arms was read. This difference in centimeters multiplied by the density of the manometer liquid yields the gas pressure values, G . At the same time, the bench marks and the circumference of the balloon in two directions were measured. The average of the two readings on the bench marks yields the quantity x , and the radius calculated from the average of the two circumference readings is the radius r of Equation 8. Of the circumference measurements, one was taken equatorially, the other almost vertically, but missing the immediate vicinity of the neck (as shown by the dotted lines in Figure 4). A balloon required altogether from 5 to 70 minutes for inflation, depending on the rate.

BALLOON DEFLATION. In the case of several balloons after they had been inflated nearly to the breaking point deflation data were taken in order to learn something of the hysteresis of the compression stress strain. The procedure used for inflation was followed, except that air was released a little at a time through the stopcock, measurements being taken on the pressure and on the bench marks at each step. The deflations were accomplished in much shorter time than the inflations, about 2 or 3 minutes being allowed for the air pressure to subside.

ONE-WAY EXTENSION TESTS. An object was to compare the ordinary stress strain for elongation (one-way extension) with that for compression. To obtain the former, dumb-bell shaped specimens were cut from several unstretched balloons. These were gaged for thickness and were bench-marked in the usual way. In order to make the rate of extension low (roughly comparable with the balloon dilations), the strips were tested by the dead weight method. One end of the specimen was fastened in a supporting clamp, and to the other end a pan was attached to which weights were added so as to give an extension of roughly 0.1 inch (0.25 cm.) per minute.

TYPICAL DATA ON BALLOON

Table I shows how the data for a balloon may be tabulated conveniently. It gives the original readings and the derived values for balloon 13. As this particular balloon was distended at a rather high rate, its stress strain was determined by fewer points than was the case with some of the balloons tested. This example, however, illustrates quite well how the compression stress strain data are derived in a particular case from the quantities measured on the expanding sphere.

The gas pressures as measured by the manometer for each step of the inflation are shown in column G . The radii in

the compressed thickness of what was a unit thickness before compression (given in the next column), are obtained from the x column through Equation 6. The P and y columns constitute the compression stress-strain data which it is the object to deduce. In the last column of the table the compression is expressed as a percentage, this being analogous to the way elongation is expressed in the ordinary extension stress strain of rubber. For example, 58.4 per cent compression means that a specimen originally 1 cm. thick has lost 58.4 per cent of 1 cm. (or 0.584 cm.); it therefore still retains a thickness of 0.416 cm. (as shown in the y column). Per cent compression has been used in plotting results in order to preserve the analogy with the conventional method of expressing elongations.

Table I shows that the rubber, before it broke, diminished in one direction to the extent of over 97 per cent of its original dimension. Perhaps this figure is in error, owing to the volume of the rubber actually increasing under tension, contrary to the authors' basic assumption. Even allowing for some error from volume increase, the result seems noteworthy, especially as 100 per cent compression corresponds with complete annihilation of the dimension in question. The calculated value for the force, P , which, if it had been applied as a pressure to a 1-cm. cube of the rubber, would have been required to compress the specimen to a residual thickness of 0.0257 cm. and to rupture it at that thickness, is the seemingly high figure of 9170 kg. In English units this corresponds to a breaking compressive force of about 130,000 pounds per square inch of original cross section. When, however, one considers how greatly the area is expanded over which this force applies (thirty-nine times the original cross section for 97.4 per cent compression), the compressive force does not seem unduly great.

The P and y columns in Table I show that P increases slowly at first, reaching only 47.4 kg. per square centimeter for a compression of 76.2 per cent. Towards the end of the compression, however, P increases very rapidly—so much so as to go from 5040 to 9170 kg. per square centimeter when the compression increases from 97.0 to 97.4 per cent. It is obvious that the results for the entire compression cannot be graphed advantageously on an equal division scale for stress. To display the compression data for the entire deformation graphically, one may break the curve into parts and use a suitable scale for each part. If one resorts to this expedient, the data must be broken into about four parts, and a separate graph for each must be made. It is better for most purposes to graph the stress logarithmically; even so, it is advisable to graph the early and later part of the stress strain with differ-

TABLE I. ORIGINAL AND DERIVED VALUES FOR INFLATION OF BALLOON 13

(Original wall thickness $m = 0.0305$ cm. Expansion in early part of inflation conducted so as to diminish wall thickness by about 0.00762 cm. per minute; later part of inflation involved faster rate)

GAS PRESSURE, G Grams/cm. ²	CIRCUMFERENCE		RADIUS, r Cm.	—ELONGATED-UNIT BENCH MARK—			CALCD. EQUIV. COMPRESSIVE FORCE, P Kg./cm. ²	CALCD. COMPRESSED THICKNESS OF ORIGINAL UNIT THICKNESS, y	COMPRESSION %
	Equatorial Cm.	Vertical Cm.		Horizontal	Vertical	Mean, x			
0		1.00	1.00	1.00	0	1.00	0
35.0	22.1	...	3.51	1.16	1.20	1.18	3.91	0.715	28.5
32.2	30.6	32.2	5.05	1.45	1.65	1.55	15.4	0.416	58.4
27.0	38.1	38.1	6.06	2.00	2.10	2.05	47.4	0.238	76.2
17.7	62.3	63.0	10.1	3.50	3.60	3.55	465	0.0794	92.1
13.0	95.5	100	15.6	4.90	5.20	5.05	2160	0.0393	96.1
18.0	101	114	17.6	5.50	6.00	5.75	5040	0.0302	97.0
18.7	117	130	19.6	6.00	6.50	6.25	9170	0.0257	97.4

column r correspond with the mean values for the equatorial and horizontal circumferences shown in the two preceding columns. The values of x are the means of the horizontal and vertical elongated bench-mark readings of the two preceding columns. The three variables, G , r , and x , together with m (the original thickness of the balloon wall), furnish, through Equation 8, the values of equivalent compressive force P which occur in the next column. The values of y ,

ent scales, so rapidly do the last few stress readings advance with increased compression.

The last point is illustrated by Figure 5 in which the stress-strain data of Table I are plotted. In this and all other graphs of compression data, the lower left-hand quadrant has been used; that is, compressive force P increases from top to bottom of the graph, and per cent compression increases from right to left. This is strictly analogous to the use of the

upper right-hand quadrant for plotting the ordinary elongation stress strain, when we consider that a pressure is a negative tension and a compression is a negative elongation. The convenience of this practice, especially when, as in the present case, an object is to correlate the elongation and compression curves as a single entity, will appear more definitely later.

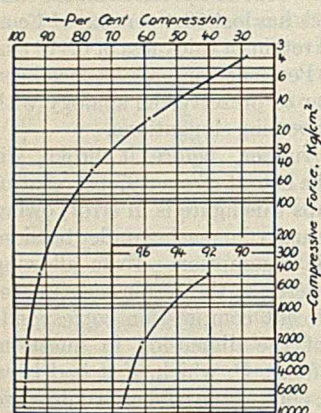


FIGURE 5. STRESS-STRAIN DATA OF TABLE I (BALLOON 13)

a given balloon, and the smooth curve enables corrected values to be read. In the case of balloon 13 the determined points are too far apart to afford corrections. Figure 6 plots the results for balloon 17 and is shown in order to illustrate a case involving more numerous points of determination. The deviation of the points from the smooth curve in this case is typical of tests where enough points were obtained to yield corrections. At the low-deformation end of the curve the points deviate from the smooth curve quite appreciably. This was generally true and perhaps followed from the technic involving higher relative errors in the measurement of the bench marks at low extensions. At any rate, the "zero end" of the compression stress strain cannot be considered very accurately delineated.

Balloon 17, as graphed in Figure 6, and several other balloons for which the data approach the zero end fairly closely, are of interest, however, in giving an indication at least of the course of the curve for small deformations—a matter of importance in attempting to correlate the compression and elongation stress strains. Balloon 17 was not distended to a break. It was inflated to a calculated compression of 97.0 per cent and a calculated compressive force of 5180 kg. per square centimeter which undoubtedly was close to rupture. At this stage, however, the balloon was deflated to obtain the hysteresis curve, and the latter likewise is shown in Figure 6.

RESULTS NOT INFLUENCED BY RATE OF COMPRESSION

Before starting the work, it was considered possible that the modulus of the compression stress strain and perhaps the end point would be influenced by the rate of deformation. Provision was therefore made for tests of various rates as previously defined. The results, however, do not disclose any influence of rate of compression. This is made clear by Table II in which moduli on each of nine balloons, compressed at various rates, are shown. These moduli, or compressive forces for given degrees of compression, show as much divergence between two balloons tested at a given rate as they show between one rate and another. It is evident that the variability of the balloons exceeds any influence which variable rate of compression may have entailed. This is borne out also by ordinary elongation tests on the stock of other balloons of the same lot, among which an equal, if not greater, variability was found. This is perhaps to be expected. For the

purposes of the present study it has been deemed sufficient, therefore, to base conclusions of a general nature on the approximate mean results of Table II.

The moduli of Table II are the corrected values obtained by reading from smooth curves similar to Figures 5 and 6 drawn through the original data. It is not inferred that greater changes in the rate of deformation than have been here employed would not have influenced the compression results. Such an influence, comparable with that which exists when rubber is elongated in one direction at various rates, is almost certain to exist for compressions (or for two-directional elongations) also, if the rate be sufficiently varied.

BREAKING-COMPRESSION DATA

Of the nine balloons summarized in Table II, only two were distended to rupture; the others were permitted to retract in order to obtain hysteresis data. No very accurate conclusions as to numerical values are justified from the data, particularly as to the breaking force. The breaking compression is indicated, with rather small variance, as about 97.3 to 97.4 per cent. The breaking force, however, is subject to marked variance, which is easily understood when the extreme slope of the stress-strain curve at high compressions is recalled.

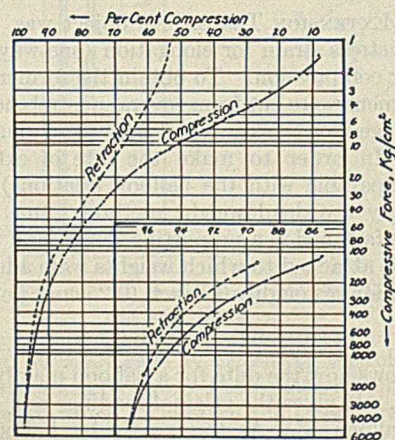


FIGURE 6. STRESS-STRAIN DATA FOR BALLOON 17

The breaking compressive force on this particular stock (a pure-gum cold-cured stock) may be taken as in the neighborhood of 6000 to 9000 kg. per square centimeter. It is probably not possible to obtain even rough approximations of the breaking point on compression by a technic involving actual compression of the specimen, for the latter is almost sure to be ruptured at some point prematurely by the ununiform stress which is engendered.

ENERGY OF COMPRESSION STRESS STRAIN AND HYSTERESIS LOSS

The energy of compression has been calculated for three balloons. The corrected stress-strain data, as read from smooth curves similar to those in Figures 5 and 6, were used as the basis. The corrected data were replotted on equal-division graph paper so as to permit of energy being computed by measuring the area between the stress-strain curve and the strain axis. It was necessary, as mentioned previously, to divide the graph into several parts. The authors found it desirable to make four such divisions with scales as shown in Figure 7, which plots the compression data for balloon 16. The four curves in solid line together constitute the stress-strain curve for this balloon. The energy corresponding to each portion of the curve was estimated by the "counting squares" method of determining subtended area. Due account must be taken, in the case of each curve portion, of its

TABLE II. SUMMARY OF COMPRESSION STRESS-STRAIN AND END-POINT DATA

BALLOON	APPROX. RATE OF COMPRESSION PER MIN.	COMPRESSION MODULI				HIGHEST VALUES OBTAINED ON:		
		P_{30}^a	P_{50}	P_{70}	P_{85}	Compressive force Kg./cm. ²	Compression %	BROKEN?
16	0.00127 cm.	4.58	16.4	276	1280	4950	96.9	No
17	0.00127 cm.	4.31	14.5	240	1080	5180	97.0	No
21	0.00254 cm.	4.11	14.5	230	1080	3050	96.8	No
13	0.00762 cm.	4.17	16.7	277	1220	9170	97.4	Yes
14	0.00762 cm.	..	14.6	235	1060	5650	97.3	Yes
15	0.00762 cm.	3.99	15.4	249	1170	6260	97.2	No
18	10%	4.93	17.3	280	1220	4390	96.8	No
19	20%	..	15.3	245	1040	2673	96.6	No
20	40%	..	14.4	242	1080	347C	97.0	No

^a P_{30} means compressive force at 30% compression on original cross section.

particular scales, since the energy equivalent of a unit subtended area depends on these and varies with each portion of the curve.

The energy required to compress one cubic centimeter of the stock in question close to, but not quite up to, the breaking point is thus estimated in the case of balloon 16 as 100 kg. cm. Further estimates of the energy of compression made from the data of balloons 15 and 17 are summarized in Table III. Considering the superficially enormous compressive forces involved, these energies are not high. This, of course, is because the distance through which compression progresses under very high stress is small.

TABLE III. SUMMARY OF ENERGY OF COMPRESSION AND OF HYSTERESIS

BALLOON	HIGHEST COMPRESSION REACHED	ENERGY OF COMPRESSION		ENERGY OF HYSTERESIS	
	%	Kg. cm.	Retraction	Loss	Loss
15	97.2	103	69	34	33
16	96.9	100	71	29	29
17	97.0	89	58	31	35

When the ordinary (one-way) elongation stress strain of stock from the same lot of balloons was determined by the dead weight method, as previously described, the energy capacity up to the breaking point ranged from 50 to 70 kg. cm. per cubic centimeter. In view of the higher energy figures obtained on compression than on elongation, and in view of the fact that the former does not include and the latter does include the breaking point, it would appear that the capacity of this stock to absorb energy on being compressed to rupture exceeds its capacity on being stretched to rupture. Whether this is a general rule or not is not known, but it is at least indicated that compression may permit of more energy absorption than does elongation. However, it would appear that the two energies are of the same order of magnitude.

We may well consider that energy is about the best common measuring stick to apply to both compression and extension deformations. A compression is not equivalent to an extension in any sense of the word when each involves the same stress or the same actual or relative change in any given dimension. Yet in a significant sense, a compression is equivalent to an extension on a unit volume of elastically deformable matter if equal amounts of work have been done to bring them about. From this standpoint, therefore, the stock of the balloons tested may be regarded as capable of withstanding more severe deformation when the change is a shortening in one direction and a lengthening in the other two than when it is an elongation in the one direction and a contraction in the other two.

This view is supported by elongation data for both types of deformation. In the usual type of one-dimensional extension, the breaking elongations on five test pieces ranged from 640 to 710 per cent. The two-dimensional elongations, on the other hand, on balloons 13 and 14 which were distended to rupture were 525 and 505 per cent, respectively. That these two-dimensional elongations imply a greater degree of strain than is implied by the superficially greater one-dimen-

sional elongation is clear when one recalls what is involved. In the case of stretching balloon 13, for instance, what has occurred amounts to this: A cube of rubber 1 cm. long has been stretched in one direction until it has elongated by 5.25 cm.; it becomes much reduced in the other two directions. Then, while the 5.25-cm. gain one way is maintained, the specimen is pulled out along one of the reduced dimensions until that also has increased by 5.25 cm. (attained 6.25 cm.). By this second stretching at right angles to the first, the third and remaining dimension becomes further reduced, reaching, in fact, the surprisingly small value of 0.0257 cm. A consideration of this sort fortifies the idea that the two-dimensional stretching, or the equivalent compression, conducted on the balloon stock imposed a greater strain than did the one-dimensional stretching.

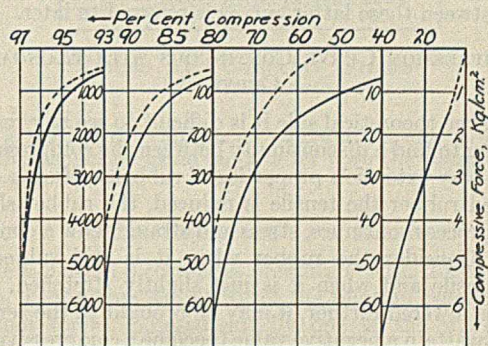


FIGURE 7. COMPRESSION DATA FOR BALLOON 16

Figure 7 shows the retraction stress strain by broken lines. The areas between these and the solid lines for compression together constitute the hysteresis loop. The energy lost by hysteresis as summarized in Table III amounts to about 30 to 35 per cent of the work of compression.

STRESS-STRAIN CURVE FOR TWO-DIMENSIONAL STRETCHING

While the present method of computing the compression properties involves stretching a specimen in two directions at once, the immediate data of that operation are in themselves of interest. These data are the elongations obtained simultaneously in the two directions together with their accompanying tensiles. Equation 7 gives the two-way tensile, T , as a function of the experimental quantities, and the two-way elongation is, of course, just another way of expressing the quantity x , for elongation equals $100(x - 1)$ per cent.

Figure 8 shows the stress-strain curve for two-way stretching superimposed by way of comparison on that for one-way stretching. The two-way values, identified by the symbols E and T , are shown by a solid line; the one-way values, identified by the symbols E' and T' , are indicated by a broken line. The $E'-T'$ line is the ordinary extension stress strain of the stock as determined by the dead weight method. The $E-T$ line represents a composite set of data based on balloons

13 and 17. Each curve is typical of the stock from the standpoint of the particular relation it depicts.

As might be expected, the E - T curve shows higher moduli than that for E' - T' . Energy of compression may, of course, be computed directly from the E - T curve, for the latter is but

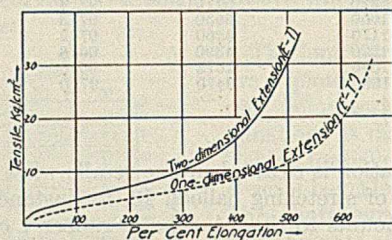


FIGURE 8. COMPARISON OF STRESS-STRAIN CURVES FOR TWO-WAY AND ONE-WAY STRETCHING

a different way of expressing the compression data. It should be recalled that, in computing energy of compression from the E - T curve, twice the area subtended must be taken, since two tensiles, each equal to T , are working simultaneously.

By no means are the E - T curve and the E' - T' curve two ways of expressing the same facts. They are unrelated, except empirically, as also are the ordinary elongation stress strain (the E' - T' curve) and the compression stress strain. The entirely empirical nature of any relation which may exist between these latter curves is referred to later.

COMPRESSION CURVE CONTINUOUS WITH ELONGATION CURVE

From the theoretical side it is difficult to see any reason for expecting to find a discontinuity between the compression and the one-way extension properties of rubber. If on a piece of stretched rubber the tensile is reduced, the rubber shortens. As the process continues, stress and strain follow a continuous curve. Consider the rubber when it is still subject to a small tensile and when it is just slightly stretched. If the tensile is lowered further, it may be brought to the zero point or it may attain a negative value (become a compressive force). If the tensile is carried to a small negative value, the elongation becomes slightly negative (becomes a compression). On going from a point on the extension curve in the neighborhood of the zero point to a neighboring point on the compression curve, the same change in properties is entailed as occurs when one proceeds down the extension curve toward the zero point—namely, elongation and tensile force suffer decrements in the algebraic sense. It is difficult to see in what respect any different thing is done in passing through the zero point and in passing from extension to compression, or vice versa, than is done in passing up or down either one of these curves without crossing the zero point.

These considerations have led the authors to expect that, when the compression data and the elongation data for the same vulcanizate are plotted together in analogous ways, they will produce a continuous curve. The experimental data on this are not conclusive, but they strongly support this view. In Figure 9 are plotted original data for extension and for compression in the neighborhood of the zero point. None of our determinations for either type of deformation was taken, unfortunately, as close to the zero point as might be desired in the present connection. The points in the elongation quadrant of Figure 9 are the original points determined in a representative stretching test. Those in the compression quadrant are the original points for the compression of the stock in balloon 17. Both sets of data are chosen for display because they show more than usual detail in the neighborhood of the zero point. These data seem to furnish fair, but not

quite conclusive, proof of continuity, and the authors hope to give this matter further study.

Considered somewhat more critically by plotting the points of Figure 9 on a larger scale (Figure 10), the compression points lead to a smooth curve which, on extrapolation, does not pass through the origin. It intersects the strain axis at about 0.7 kg. of compressive force. In fact, of course, the compression curve must, in the nature of things, pass through the origin; and, when our data lead to the smooth extrapolation thus somewhat avoiding the origin, there are just two possibilities. Either (1) the extrapolated part of the relation undergoes an unlikely sharp change of curvature near the origin which is quite unsupported by data and unaccounted for in theory, or (2) the entire set of compression results, near the top of the curve at least, are experimentally low on the graph. The latter is the more likely alternative. If the compression curve is lifted, without change in shape or direction so that its extrapolated end passes through the origin, it and the extrapolated end of the elongation curve will meet with the same slope within limits of the experimental accuracy.

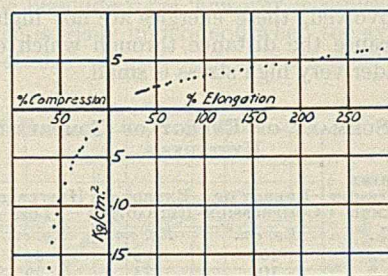


FIGURE 9. EXTENSION AND COMPRESSION NEAR ZERO POINT

The conclusion seems justified that any imperfection of the experimental data as evidence of continuity between compression and extension properties may be assigned to error. In Figure 10 the graph is on a large scale and is confined to a small region of the stress-strain results in close proximity to the origin. The data used are the same as in Figure 9. The extrapolated ends are shown in broken lines. The upper dotted curve in the compression quadrant coming away from the origin is the actual compression curve moved up to meet the origin but suffering no other change.

ANALYTIC FEATURES OF STRESS-STRAIN CURVE FOR RUBBER

If we accept the foregoing thesis of continuity of compression and extension, it alters our outlook on the much-debated equation of the stress-strain curve for rubber. The complete curve may be regarded as having a positive (extension) branch and a negative (compression) branch. Any equation which is proposed for the curve must fit both branches; it must be one which yields all values of stress and strain encountered experimentally and not just those of positive sign.

It is beyond the scope of the present paper to attempt any discussion of the equation for the curve. We may, however, ask: What are the analytic features to which the curve conforms and which will govern its equation?

1. The curve passes through the origin with negative curvature (convex upward).
2. The part to the lower left of the origin (compression branch) passes downward with increasing slope and is bound theoretically to have the vertical line representing 100 per cent compression as an asymptote. Experimentally also the curve is found to approach this vertical line asymptotically.
3. It is observed empirically that in a typical case the major portion of the part of the curve above and to the right of the origin (elongation branch) possesses positive curvature (concave upward).

4. It follows from 1 and 3 that a point of inflection must exist in the elongation branch; this is usually observed experimentally and occurs in the present results at or a little before 200 per cent elongation.

5. The elongation branch in its upper part is observed empirically to approach an oblique asymptote.

In Figure 11 the complete stress strain, including compression and elongation branches, is shown. This is drawn to conform to typical results of the present study. To bring the lower end of the compression branch with its high stress into the picture, it is necessary to break the scale and curve. The solid line represents the complete stress-strain data as usually expressed—namely, with stress calculated on the original cross section of the specimen.

When stresses are calculated to the actual cross sections, we have the curve shown by the broken line. The stress for a given strain based on the actual cross section is obtained by the well-known relation:

$$F_a = F_o \left(1 + \frac{\text{per cent elongation}}{100} \right)$$

where F_a and F_o = stresses based on actual and original cross sections, respectively.

Both branches of the stress-strain curve are elevated in the graph when stresses are based on actual as against original cross sections, and the curve passes through the origin with less curvature; this means increased values for tensile forces and decreased values for compressive forces. The apparently enormous compressive forces encountered become reduced to quite reasonable size when based on actual cross section. Thus the value 9170 kg. per square centimeter, determined on balloon 13, becomes 9170 (1 - 0.974) kg. per square centimeter = 238 kg. per square centimeter when figured on the actual cross section.

It is of interest to note that, notwithstanding the vertical shift which the curve undergoes when stresses are changed from the basis of original to actual cross section, the analytical features described above for the former hold also for the latter.

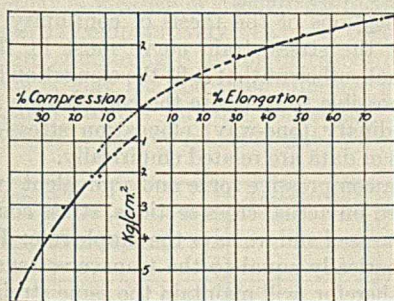


FIGURE 10. PLOT OF FIGURE 9 ON LARGER SCALE

The question of whether a point of inflection is always present in the stress strain for rubber has sometimes been discussed. If we accept continuity between compression and extension, then an inflection is an analytical necessity somewhere on the curve. It would have to exist in the compression branch, were it absent in the extension curve.

The authors believe attempts have been made to correlate the compression curve with the elongation curve on a theoretical basis, in the sense of deriving one as a mathematical function of the other. If the continuity theorem is correct, we have the following implications:

The elongation stress strain and the compression stress strain are but parts of one and the same curve.

The one will not be a function of the other in the sense of its being possible to calculate the compression stress strain from one-dimensional elongation stress-strain data, or vice versa.

On the contrary, the relationship of the compression branch to the elongation branch is entirely empirical, and it is necessary to learn the characteristics of each branch by operating on the rubber in the appropriate way—namely, by carrying out one-dimensional extensions (or two-dimensional contractions) to determine the elongation branch, and by executing one-dimensional contractions (or two-dimensional extensions) to determine the compression branch.

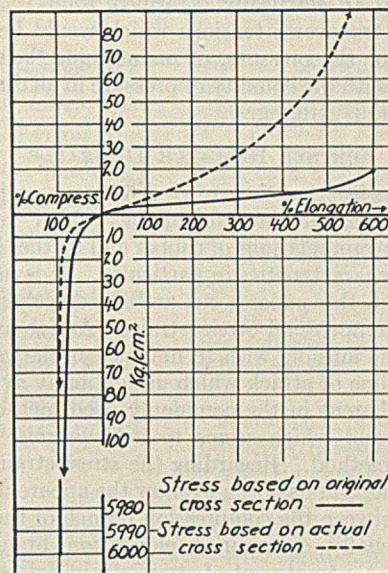


FIGURE 11. COMPLETE STRESS-STRAIN CURVE

If it is desired to establish an equation for the stress-strain curve, this should be based on data for both the elongation and compression branches.

STRESS RELATIONS AT A POINT

While Equation 5 correlates pressure P with the equivalent tensiles, T , the true simplicity of the relation between these equivalent forces, pointed out by one of the writers (15) in a previous paper, is not manifested in Equation 5. There forces are referred to the original (undeformed) cross sections; when forces are referred to actual (deformed) cross sections, the simpler relation appears.

Retaining the symbols P and T for forces based on original cross section, and distinguishing forces based on actual cross section by P_a for compressive force and T_a for equivalent tensile forces, we may show the relationship between P_a and T_a thus:

$$P = -y^{-3/2}T \quad (5)$$

where y = diminished length after compression of what was an undeformed cube of unit length.

Since we assume the volume of the rubber has not changed on compression, the area of the face perpendicular to the dimension y (the face on which P acts) is y^{-1} . Therefore,

$$\text{compressive force on unit area} = P_a = \frac{P}{y^{-1}}$$

$$P = y^{-1}P_a \quad (9)$$

or

As apparent from Figure 1, the area of the face on which T acts is $y \cdot y^{-1/2} = y^{1/2}$. Therefore,

$$\text{tensile force on unit area} = T_a = \frac{T}{y^{1/2}}$$

$$T = y^{1/2}T_a \quad (10)$$

or

From Equations 5, 9, and 10,

$$P_a = -T_a \quad (11)$$

Since P_a and T_a are forces on unit areas of actual cross section, Equation 11 expresses stress conditions at a point. It is evident that Equation 11 applies to a deformation in which the specimen lengthens in one direction and diminishes in two directions, as well as to a shortening in one direction and lengthening in two directions for which it has been proved. The following general rule expresses the foregoing: Pressure at a point in an elastically deformed solid is numerically equal to the transverse tensions which would be capable, if substituted for the pressure, of maintaining the same strain. The analogy with the equality of pressure in all directions at a point in a fluid is striking.

FURTHER RESEARCH DESIRABLE

The authors feel that their work will have been justified if it stimulates increased interest among rubber technologists in the stress-strain relations of rubber and further study of the compression characteristics in particular. It is not their aim to lay down in this paper a cut and dried technic for determining the compression stress strain. As far as technic is concerned, the authors wish to make clear the general principles of one line of attack which undoubtedly avoids certain difficulties inherent in the commonly used method of direct compression and which seems to hold promise of being a worth while method. Regarding the stress-strain properties themselves, the aim has been to show the apparent continuity of these as between the compression branch of the curve and the more usually determined elongation branch and to emphasize that a treatment of stress-strain data which takes cognizance of such continuity and which treats of the data in their entirety is more likely to result fruitfully than a treatment which deals with the elongation branch alone.

That full development and use of the ideas presented in this paper call for further research is apparent. For example, while it is satisfactory as a first approximation to consider the volume change of rubber nil, and to base, as has been done, all formulas and calculations on that assumption, it is most desirable that attention be given to whatever effect such volume change as actually occurs may have. The immediate purpose of the investigation has been satisfied by applying the technic of distending a hollow sphere to the most readily available and convenient specimens and these, as stated previously, were cold-cured toy balloons. Before the technic can be applied to any desired composition of rubber subjected to any desired hot cure, which is where its main usefulness will lie, it is necessary to construct a mold that will enable an accurately proportioned hollow sphere of rubber to be vulcanized. Further verification of continuity between the compression stress strain and the elongation stress strain should be obtained through a more minute experimental study of the zero ends of the two curves.

The authors purpose, as opportunity affords, to continue the study of the compression stress strain and suggest to those interested in the physics of rubber that a more intensive study of compression properties will round out the physics of rubber where it now lacks fullness and will promote the correlation of the elastic properties of rubber to ultimate structure.

SUMMARY

1. A relation of simple form between compressive force and equivalent two-way tensile forces is developed.

2. Based on this relation, a new method for determining the compression stress strain of rubber is outlined, which avoids difficulties and errors inherent in direct compression. It consists in applying tensile forces simultaneously in two directions, and, from these and the strained dimensions, in computing the compressive force that would have produced the same deformation.

3. The mode of applying the two-way tensiles is to inflate a

hollow sphere of rubber; the experimental data required to determine the compression stress strain are pressure of gas in, and dimensions of, the inflating hollow sphere.

4. The method has been applied to cold-cured pure-gum rubber in the form of toy balloons which, in its ordinary elongation stress strain, shows a breaking elongation of about 650 to 700 per cent and a tensile of 30 to 40 kg. per square centimeter. While the numerical values obtained on this stock have no special significance, as they will vary from stock to stock, the following are examples: breaking compression, about 97.3 per cent; breaking compressive force, 6000 to 9000 kg. per square centimeter (on original cross section); hysteresis, 29 to 35 per cent of work of compression to near rupture.

5. As a common measuring stick by which to gage degree of strain in deformations of different types—e. g., increasing one dimension (and diminishing the other two) as against diminishing one dimension (and increasing the other two)—energy seems the best. Energy at break for ordinary elongation stress strain was 50 to 70 kg. cm. per cubic centimeter, and for compression stress strain was 89 to 103 kg. cm. per cubic centimeter.

6. The compression stress-strain data may, if desired, be expressed in terms of two-way tensiles vs. two-way elongations. Energy of compression may be computed either as twice the area subtended between such a curve and the strain axis, or as the area between the compression stress strain and the strain axis.

7. It is strongly indicated that the compression stress strain of rubber is continuous with the ordinary elongation stress strain when both are plotted in the same units, and that the complete stress strain should accordingly be considered as a single continuous curve having an elongation branch and a compression branch with the origin as dividing point.

8. The analytic features of the complete stress strain are described.

9. Granting the observed concavity of the upper part of the elongation stress strain, and the thesis of continuity between elongation and compression, a point of inflection is bound to exist theoretically.

10. Implications of the thesis of continuity are: (1) An equation for the stress-strain curve must fit the complete curve; it is not sufficient that it fit the elongation branch only. (2) It is impossible to compute the compression stress strain from the ordinary (one-way) elongation stress-strain data. The two sets of data are related empirically.

11. When compressive force and equivalent two-way tensiles are based on actual cross sections, stress conditions at a point are expressed and we have the simple rule: Pressure at a point is numerically equal to the transverse tensions which, substituted therefor, will maintain the same strain.

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Effect of Calcium and Phosphorus on Adhesive Strength of Paper-Coating Casein

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DURING work on various caseins in regard to their coating properties, it was observed that samples high in ash were usually low in strength. It occurred to the authors that the adhesive strength of casein might be affected by the amount of calcium and phosphorus present. A search of the literature showed that no previous work on this specific relationship had been published.

This investigation was undertaken to determine to what extent it is desirable, from the standpoint of adhesive strength, to remove calcium and phosphorus in the manufacture of casein for paper coating.

EXPERIMENTAL METHODS

By the strength of casein is meant the value given by the so-called wax test. The procedure was essentially that described by Sutermeister (4) with the additional feature that the waxes were allowed to cool for 30 minutes in contact with the coatings before they were pulled. The same grades of paper, wax, and clay were used throughout the tests. It should be remembered that the strengths of caseins are designated by numbers which are in inverse proportion to the adhesive power of the caseins—that is, a casein of strength 8 is relatively strong, one of strength 11 comparatively weak. A coating prepared from a mixture containing 8 grams of casein of strength 8 per 100 grams of clay has the same adhesive strength as a coating prepared from a mixture containing 11 grams of casein of strength 11 per 100 grams of clay.

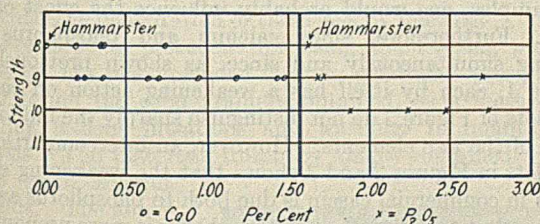


FIGURE 1. EFFECT OF ADDED CALCIUM AND PHOSPHORUS ON ADHESIVE STRENGTH OF CASEIN

The effect of calcium and phosphorus was studied by two general methods: first, by adding to equal portions of Hammarsten casein of previously determined strength, definite and increasing increments of calcium and of phosphorus compounds, and then determining the strength of the resulting mixtures when applied to paper; secondly, by analyzing the ash content of a considerable number of commercial caseins of different strengths for calcium oxide and phosphorus pentoxide.

In developing the first method, the casein solutions were prepared as follows:

Portions of Hammarsten casein were softened in water for 30 to 45 minutes, the calculated quantity of standard sodium

Calcium and phosphorus both reduce the adhesive strength of casein, but the latter has the greater weakening effect. The reason for this appears to be chemical rather than mechanical. None of the other inorganic substances present in commercial casein has an appreciable influence on its strength.

The estimation of calcium as sulfate and the direct precipitation and weighing of phosphorus as magnesium ammonium phosphate hexahydrate are reliable and comparatively rapid methods of determining these elements in casein ash.

hydroxide solution was poured in, and the definite amount of calcium or phosphate compound was added as required for each case. The mixture was then warmed on a steam bath with stirring to 55–60° C. until the particles of casein had disappeared. Water was then added so that the final concentration of the solution was such that each 5 grams of solution contained 1 gram of casein. This solution was then incorporated with the clay, following the usual strength test procedure.

For a basis of comparison in the strength tests, the strength of the Hammarsten casein in sodium hydroxide solution was determined carefully. It was found to be 8. Sodium hydroxide was used in the work with calcium in preference to other alkaline solvents in order to avoid as far as possible the precipitation of calcium. Weights of compounds furnishing amounts of calcium oxide equivalent to 0.18 to 1.48 per cent of the weight of the caseinate were added successively. The compounds used and their quantities are listed in Table I. These compounds were employed because they occur in paper-coating solutions, and because, therefore, it is desirable to know whether any of them exerts specific influences on adhesive strength. Such influences were not noted, however. The results on the effect of calcium addition on adhesive strength of casein are plotted in Figure 1.

TABLE I. EFFECT OF ADDED INORGANIC COMPOUNDS ON STRENGTH OF HAMMARSTEN CASEIN

(Weight values are per 10 grams casein)				
NaOH	ADDED COMPOUND	CaO ^a	P ₂ O ₅ ^{a,b}	STRENGTH
Gram	Grams	Gram	Gram	
0.3		0.019	...	8 ^c
0.3	0.025 Ca(OH) ₂	0.038	...	8
0.2	0.05 Ca(OH) ₂	0.038	...	8
0.3	0.05 Ca(OH) ₂	0.076	...	8
0.15	0.1 Ca(OH) ₂	0.152	...	8
0.1	0.2 Ca(OH) ₂	0.23	...	10
0.1	0.3 Ca(OH) ₂	0.072	...	9
0.25	0.25 CaB ₄ O ₇	0.072	...	9
0.35	0.25 Ca(C ₂ H ₃ O ₂) ₂ ·2H ₂ O	0.15	...	9
0.25	0.3 CaCl ₂	0.12	...	9
0.25	0.3 CaSO ₄	0.077	...	9
0.25	0.3 Ca(C ₂ H ₃ O ₂) ₂	0.098	0.012	9
0.25	0.3 CaHPO ₄ ·2H ₂ O	0.067	0.017	9
0.45	0.3 CaH ₂ (PO ₄) ₂ ·H ₂ O	...	0.033	10
0.3	0.176 Na ₂ PO ₄ ·12H ₂ O	...	0.12	9
0.3	0.3 K ₂ HPO ₄	...	0.069	10
0.3	0.35 Na ₂ HPO ₄ ·12H ₂ O	...	0.121	10
0.2	0.65 Na ₂ HPO ₄ ·12H ₂ O	...	0.148	10
0.2	0.79 Na ₂ HPO ₄ ·12H ₂ O	...	0.243	10
...	1.3 Na ₂ HPO ₄ ·12H ₂ O	8
0.3	0.3 KCl	8

^a Calculated.

^b The average amount of P₂O₅ in Hammarsten casein (1.62%) is not included in the table although it has been calculated in the total percentage in Figure 1.

^c Standard.

The fixed amount of phosphorus pentoxide present in Hammarsten casein was taken as 1.62 per cent (5). Phosphates were added in such quantities as to give a range of 1.68 to 3.95 per cent, calculated as total phosphorus pentoxide. Trisodium phosphate was the compound used in most cases, although disodium and dipotassium phosphates were also employed. The effects of addition of phosphates on strength

of casein are shown in Figure 1. The previously mentioned experiments in which calcium phosphates were used furnished points for both the calcium and phosphate plots of Figure 1.

The amount of sodium hydroxide solution required to dissolve the casein was changed, when necessary, to compensate for the acidity or alkalinity of the added compound so that the range of pH values of the casein solutions was small. In some cases where trisodium phosphate was employed, no sodium hydroxide was necessary, the phosphate functioning as sole solvent.

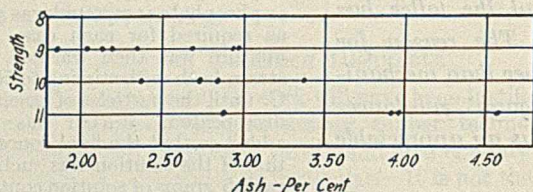


FIGURE 2. EFFECT OF ASH ON ADHESIVE STRENGTH OF CASEIN

The effect of added calcium salts on the apparent viscosity of casein solutions was very pronounced. A marked thickening took place, due probably to the formation of calcium caseinate. Sodium and potassium chlorides also had a somewhat thickening action, due possibly to a salting-out effect. The change in viscosity, however, was much less marked than in the case of the calcium compound.

The influence of potassium chloride on strength was determined because of its occurrence in poorly washed casein. No effect was demonstrated.

In attacking the problem by the second method, a considerable number of commercial caseins from widely different sources were analyzed for calcium and phosphorus, and the strengths of the samples were determined. Shaw's technic (3), with modifications, was used in the ashing procedure. The methods used for determination of calcium and phosphorus in the ash were modifications of that of Meigs, Blatherwick, and Cary (2), and the magnesium ammonium phosphate hexahydrate method of Fales (1).

The following principal adaptations were applied: Five-gram samples were used, nitric acid was added before charring and before ashing to prevent reduction of phosphates to phosphides, and calcium was determined by direct precipitation and weighing as sulfate. It was not necessary to reprecipitate the calcium as oxalate unless the precipitate obviously contained iron and other impurities.

Since the calcium had been removed previously, it was not necessary to resort to the molybdate separation. The phosphorus can be precipitated directly as magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4 \cdot 6H_2O$) and weighed as such. The precipitate of the hexahydrate is collected on a Gooch crucible. In this connection it might be mentioned that pads made of filter paper are especially satisfactory for the phosphate filtration, as they permit quick and thorough washing of precipitates and eliminate the tedious preparation of asbestos mats.

The results of the analyses of numerous commercial caseins are plotted against adhesive strength in Figures 2 and 3. The same group of caseins was used for each plot in these figures.

DISCUSSION OF RESULTS

The separate effects of calcium and phosphorus on the adhesive strength of casein are shown most clearly in Figure 1. Here, except for two points based on calcium phosphate additions, the percentage of calcium remained constant while that of phosphorus varied, and vice versa. It is ap-

parent that phosphorus has more of a weakening effect than calcium. It takes larger amounts of calcium to produce perceptible weakening, and even for the high amount of calcium the loss of strength is not so great as in the case of phosphorus. Whether the condition of the calcium and phosphorus as added to the Hammarsten casein is the same as that of these elements in commercial caseins is uncertain, and it was for this reason that it seemed desirable to attempt to duplicate these results by determinations on commercial caseins.

The question of the probable differences in the effects of organic and inorganic compounds of calcium and phosphorus has been brought to the attention of the authors. Since, in a well-washed acid casein, the calcium percentage approaches zero and the phosphorus pentoxide percentage approaches 1.62, the writers believe that organic compounds of calcium are practically absent from casein of this type, and that the phosphorus in organic combination is limited to the apparently constant amount in the casein molecule. If, by solution of the casein, the proportion of organically combined phosphorus or calcium is changed, the equilibrium attained should depend chiefly on the concentrations of hydrogen ions, calcium, and phosphorus. This being true, the amounts of calcium and phosphorus present would of themselves determine the proportions in organic combination, provided the pH values were uniform; this was true within narrow limits in the experiments described.

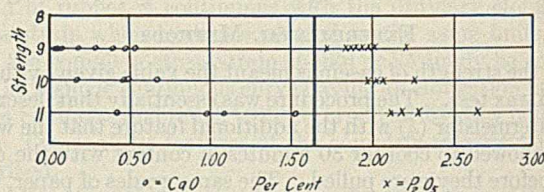


FIGURE 3. EFFECT OF CALCIUM AND PHOSPHORUS OF ASH ON ADHESIVE STRENGTH OF CASEIN

The ordinate figures in the plots represent the relative weights of caseins to give coatings of equal strengths. A casein with a strength of 8 is relatively strong; one with a strength of 11, relatively weak.

It will be seen from Figure 3 that an increase in either calcium or phosphorus percentage lessens the strength of commercial caseins. Since both these elements are present in the samples, one would probably influence the effect of the other. Furthermore, since calcium and phosphorus are varying simultaneously and since, as shown previously in Figure 1, each by itself has a weakening action on casein, the plots of Figure 3 do not distinguish sharply the individual effect of the two elements. However, an intercomparison of the plots in Figures 2 and 3 shows that the weakening effect of ash in commercial casein is due both to phosphorus and to calcium, but that the effect of phosphorus is more pronounced than that of calcium.

The two methods of attack have produced results that confirm each other.

These results show that, for the manufacture of casein of greatest strength, it is necessary to remove as much of the phosphorus and calcium as possible. This, of course, implies thorough washing.

Because of its marked weakening effect, the use of trisodium phosphate as a solvent for casein—except in cases where strength is not a factor—is to be deprecated. The weakening effect of trisodium phosphate has been observed repeatedly. Potassium chloride, another common ash constituent, is without effect on strength. This and other facts indicate that the reasons for the weakening effect of certain substances are chemical rather than mechanical.

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Dehydration of Zeolite Gels by Freezing

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Zeolite gels have been dehydrated by freezing, yielding a material of higher base-exchange value than similar oven-dried gels. A dynamic method of testing zeolites for capacity is described.

SYNTHETIC zeolites are becoming more important in the water-softening field because of their high capacity and proven ability to soften water satisfactorily. There have been many patents issued covering the manufacture of these products, all of which vary in detail but not in certain principles.

Artificial zeolites are often made by mixing a solution of sodium silicate with solutions of one or more aluminum salts which react to form a whole-volume gel. The two most widely used aluminum salts are aluminum sulfate and sodium aluminate. One or both may be incorporated into the reaction mixture. In order that a hard suitable product may be obtained, the water must be removed. This may be done by breaking up the gel, filter-pressing, and then drying, or by drying alone. The drying requires a large amount of heat, especially when the gel is not filter-pressed. After drying, the residue must be reduced to the proper size. This is accomplished by immersing the chunks in water, which causes the material to crack up or decrepitate into small particles. The decrepitated material is washed, dried, and screened before being packed.

FREEZING PROCESS

During the last few years a large amount of work has been done in this laboratory on the subject of zeolites, and in particular the dehydration of these gels by freezing.

There is some precedent for using the freezing process. Oakes (2) has recommended freezing gelatinous precipitates and filtering the solid granules obtained, as a method of avoiding tedious filtrations and washings in quantitative analysis. The materials frozen by Oakes contained a relatively small amount of solids. The anhydrous solids in the zeolite filter cakes comprised approximately 12 to 15 per cent of the total weight frozen. Freezing the zeolite gel, or filter cake, causes the solids to segregate into distinct clusters which are separated by clear ice. The water formed by melting the ice is allowed to drain away, carrying with it a large

amount of the free alkali and other soluble salts, leaving a deposit of suitably formed zeolite particles.

In these experiments the raw materials used were commercial sodium aluminate in solution and commercial sodium silicate. The aluminate solution was diluted with soft water to a strength of 0.20 mole of alumina per liter. Stiff whole-volume gels were made by mixing equal volumes of prepared sodium aluminate solution and sodium silicate solution. The concentration of the silicate solution was such that the resulting gel would have the desired mole ratio of silica to alumina. This gel was broken up, filter-pressed in a plate and frame press, frozen, thawed, washed, drained, dried, and tested for capacity or water-softening ability.

METHOD OF FREEZING

The gel or filter cake to be frozen was placed in 5-gallon ice cream containers which were immersed within about 10 cm. of the top in the brine tank of a refrigeration system. The mean temperature of the brine was -6.7°C . After 48 hours the cans were removed from the tank, washed with fresh water, and then inverted on the draining board. Soon after being inverted, the frozen mass would slide out. In a few hours the ice would melt, leaving behind moist zeolite particles.

METHOD OF TESTING

In order to obtain comparable results, the material was screened on Tyler standard screens. Commercial zeolites vary in size from 10 mesh (2.00 mm.) to 50 mesh (0.297 mm.). All zeolites tested were of the 28-35 mesh (0.589-0.417 mm.) size.

The testing apparatus consisted of a battery of thirty miniature water softeners. Each softener was made of a piece of glass tubing approximately 1.6 cm. in diameter, 38 cm. long, and fitted with a one-hole rubber stopper at each end. The glass tube was placed vertically in a rack. The upper stopper was connected by a small glass tube and a rubber tube to a pet cock on the common header. Over the bottom

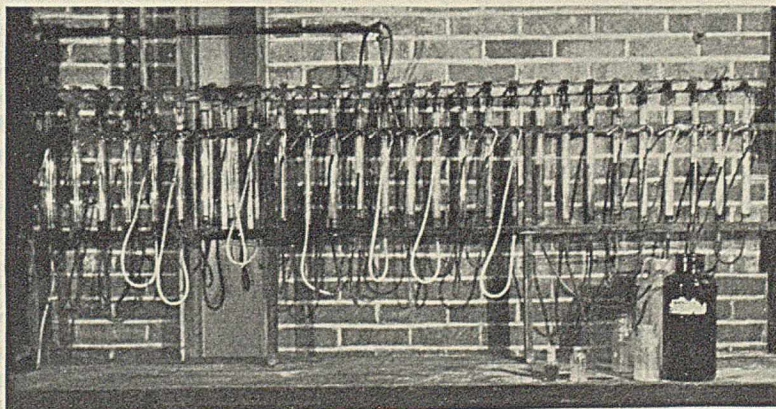


FIGURE 1. MINIATURE WATER SOFTENERS

stopper a disk of fine monel metal screen was placed. The disk fitted snugly against the walls of the tube. A small glass tube and about 50 cm. of rubber tubing were joined to the lower stopper.

Before testing a zeolite, the screened material was washed free of phenolphthalein alkalinity. The required amount was then placed in a softener so that a 20-cm. bed was obtained. At the start of each run, the material was backwashed to insure a uniform bed, after which 16 cc. of fine-grained salt were introduced into the top of the softener. The salt was slowly dissolved by passing water downward through the softener at such a rate that 20 minutes of salt contact were obtained with the zeolite. When soap tests indicated that the water issuing from below was soft, the water was run into a container. The exact amount of "zero" water obtained was caught and measured. The flow of water downward during the softening process was adjusted to a rate such that at the end of 4 hours the run would be complete. A run was considered complete when soap tests showed 17 p. p. m. of hardness. At all times during the backwashing, salting, and softening periods the bed of zeolite was kept below the water level in the tube. By measuring the volume of zeolite, the amount of water softened, and the hardness of the water, it was possible to calculate the softening capacity of the material tested. The laboratory water varies but little from a hardness of 376 p. p. m. The capacity was calculated as grams of calcium carbonate equivalent of hardness removed per liter of zeolite.

The method of testing a zeolite for capacity, as outlined, is a dynamic test but is very satisfactory for comparative purposes if all tests are run exactly alike. Such a test does not yield the absolute value of the exchange but is more valuable than an ultimate test, because it gives a better indication of what may be expected of a zeolite when put into a water softener. The amount of salt used in regeneration, the rate at which the water is run through the softener, the size of zeolite, time of salt contact, depth of the bed, hardness of the water, composition of the water, and perhaps the diameter of the tube—all seem to affect the results. This being the case, it is necessary to arbitrarily select the conditions of testing and to adhere to them.

As a check for comparison with results obtained in practice, some commercial zeolites of 28–35 mesh size were screened out on Tyler screens and tested as described. The average of ten runs for Doucil was 34.6, and for DeCalso, 34.4 grams of calcium carbonate equivalent per liter of zeolite. Two samples of each of the commercial zeolites were found to check within 5 per cent. Fine Doucil has been rated at approximately 27.5 grams per liter in commercial installations.

EFFECT OF FREEZING

The filter cake from several gels was divided into two portions. One portion was dried at 55° C., and the other portion was frozen at -6.7° C. It was found that freezing these gels resulted in a material having a higher capacity than when dried in the ordinary manner. Some typical examples are given in Table I. The values are the averages of ten runs.

TABLE I. EFFECT OF FREEZING FILTER CAKE

ZEOLITE	CAPACITY, CaCO ₃ EQUIV. PER LITER OF ZEOLITE	
	Frozen	Not frozen
	Grams	Grams
A	56.0	48.0
B	55.0	45.6
C	57.8	53.8

The compositions of the gels of zeolites A, B, and C were quite different as regards total alkalinity and silica-alumina ratio. It is not intended that the values given for Doucil and DeCalso should be compared with those given in Table I, as the materials made in the laboratory had a much lower

silica-alumina ratio than these proved commercial products. All of the testing was done at the same time and under the same conditions.

EFFECT OF FILTERING ON PARTICLE SIZE

In order to be a satisfactory zeolite, it is essential that the resulting material be of correct size, hard, and durable. The effect on particle size of filtering the gel before freezing is shown in Table II.

TABLE II. EFFECT OF FILTERING ON SIZE

Size Mesh	SCREEN Opening Mm.	Press cake 4.8 atm. %	AMOUNT RETAINED		Gel not filtered %
			Filter cake Büchner funnel %		
10	1.651	1.4	0.0	0.0	
14	1.168	7.3	0.0	0.0	
20	0.833	18.3	1.4	0.1	
28	0.589	21.6	8.8	0.6	
35	0.417	20.3	25.8	7.3	
48	0.295	11.6	27.0	22.4	
65	0.208	11.4	25.3	46.0	
100	0.147	2.6	4.7	10.8	
Passing 100 mesh		5.5	7.0	12.8	
Total		100.0	100.0	100.0	
Uniformity coefficient (β)		2.93	2.14	2.18	
Effective size, mm.		0.230	0.186	0.128	

The values given in Table II include all of the fines and dust passing a 48-mesh (0.295-mm.) screen, which amounted to about 19.1 of the total weight obtained from the press cake. Methods of reducing this loss are being studied.

DISCUSSION OF RESULTS

These experiments have been conducted on gels having a low ratio of silica to alumina. Colburn and Smith (1) have come to the conclusion that highest capacity is obtained with a ratio of 2.5 moles of silica to 1 mole of alumina. Since then, most of the work has been confined to gels having this composition. It should be pointed out that the range investigated by Colburn and Smith was rather narrow, 3.5 being the highest value recorded.

With this type of gel the experiments show that a material of the correct size may be obtained by freezing under the proper conditions. It seems that two factors affect the size—the amount of water in the material frozen and the rate of freezing. Qualitative observations indicate that rapid freezing is conducive to the formation of small particles.

The results indicate that freezing has a beneficial effect on capacity. Whether or not this increase is secured with gels having a higher silica-alumina ratio or having a different degree of alkalinity, is not known. However, there are some indications that high alkalinity increases the beneficial effect of freezing as regards capacity. These points are under investigation.

So far, freezing has not yielded a product having the desired hardness, unless the surface moisture is entirely removed by drying. The amount of drying to accomplish this is small. Exposure of a few hours to the open air was sufficient in the laboratory. If this method were put into practice, a drier would probably be required. As it is desirable to secure a harder product, the amount of dehydration obtained by freezing at lower temperatures is being investigated.

Many details must be worked out before a definite announcement of the commercial feasibility of this process can be made.

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Dehydration of Alcohols with Alkali Metal Alcoholates

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THE preparation of nearly anhydrous alcohol by fractionation of mixtures of aqueous alcohol and benzene, whereby the water is removed as a ternary azeotrope with alcohol and benzene, is well known and widely used on the large scale. A variety of other methods for the dehydration of alcohol have been proposed, such as the use of anhydrous calcium chloride, the use of glycerol alone or in combination with hygroscopic salts, the use of metallic calcium, aluminum, or magnesium, etc. None of these other processes has met with the success of the distillation method in the presence of a liquid which yields an azeotropic mixture owing to the economy of operation which the latter process permits. The distillation process, however, reaches its maximum efficiency only on very large-scale operation, where continuous operation and automatic control can be applied.

DEHYDRATION OF ALCOHOL BY ALKALI SALTS OF MONO- AND POLYHYDROXY ALCOHOLS¹

The work described here was done in an attempt to find a method more suitable for comparatively small-scale production than dehydration by means of benzene. Glycerol, potassium carbonate, triethanolamine, and ethylene glycol were all tried. Although the alcohol was increased in strength, none of these substances gave better than a 97.4 weight per cent alcohol on one treatment. A 98.6 weight per cent alcohol was obtained in two stages from 92.5 weight per cent alcohol, using glycerol and potassium carbonate.

It then occurred to the senior author to use the salts of higher alcohols or of the glycols as dehydrating agents. These salts were prepared by the usual method of mixing an excess of the alcohol with an alkali hydroxide and driving off the water (1-3). The aqueous ethyl alcohol was then mixed with the solutions of the anhydrous salts, and a portion was distilled off through a short column. The following salts were tried: sodium salts of glycerol, ethylene glycol, benzyl alcohol, methylcyclohexanol, *n*-amyl alcohol, xlenol, and phenol; the potassium salts of ethylene glycol and benzyl alcohol; and the calcium salts of ethylene glycol.

The reaction may be represented as follows:



where R = alkyl or aralkyl radical

X = an alkali such as sodium, potassium, etc.

The amount of the salt of the alcohol or glycol taken is in excess of that necessary to react with the amount of water present in the alcohol.

COMPARATIVE DEHYDRATION EFFECT OF VARIOUS SUBSTANCES

The efficacy of the various substances tried is compared in Table I. These tests were made by mixing the indicated amount of dehydrating agent with the indicated amount of weak alcohol. The mixture was then fractionated, using a 2-foot Vigreux column, and a first fraction was collected to the amount shown in the fifth column. The alcohol content was determined from the specific gravity and is reported as weight per cent.

In addition to the above dehydrating agents, the potassium

salt of ethylene glycol was prepared, but so much foaming took place while the water of reaction was being distilled that no further work was done with the potassium salt.

TABLE I. EFFICACY OF VARIOUS DEHYDRATING AGENTS

DEHYDRATING AGENT	AMOUNT USED	STRENGTH OF ALC. ADDED		STRONG ALC. RECOVERED	STRENGTH OF RECOVERED ALC.		REMARKS
		WEAK ALC. ADDED Cc.	OF ALC. ADDED %		CC.	%	
Glycerol	100 cc. (95%)	500	92.3	400	93.6	Glycerol not dehydrated before use	
Glycerol	70 cc. (95%)	350	93.6	260	94.6	Glycerol not dehydrated	
Glycerol	100 cc.	500	92.3	400	94.6	Glycerol dehydrated with toluene before use	
Glycerol	70 cc.	350	94.6	255	96.0	Dehydrated glycerol used	
Glycerol	250 cc.	500	92.3	400	95.8	Dehydrated glycerol used	
Glycerol	175 cc.	350	95.8	300	97.4	Dehydrated glycerol used	
Glycerol	100 grams	500	92.5	300	94.5	Distd. through 3-ft. column	
K ₂ CO ₃	80 grams	500	92.3	400	94.2	
K ₂ CO ₃	56 grams	350	94.2	348	95.3	
Triethanolamine	100 cc.	500	92.3	400	93.7	Triethanolamine dehydrated <i>in vacuo</i> to 130° C.	
Diethylene glycol	90 grams	360 grams	92.5	200	93.8	Diethylene glycol dehydrated by boiling <i>in vacuo</i>	
Ethylene glycol	200 grams	500	92.5	200	94.9	Ethylene glycol previously purified by fractionation	
Glycerol + K ₂ CO ₃	100 cc. (dry) } 100 grams (dry)	300	92.3	{ 200 65	97.1 94.3	
Glycerol + K ₂ CO ₃	100 grams (anhydrous) } 100 grams (anhydrous)						500
Glycerol + K ₂ CO ₃	100 grams (anhydrous) } 100 grams (1% H ₂ O)	500	92.5	465	97.2	Mixt. agitated during distn; distn. carried out in water bath; short fractionating column used	
Glycerol + K ₂ CO ₃	75 grams (anhydrous) } 75 grams (1% H ₂ O)						375
Glycerol + NaOH	368 grams } 80 grams }	600	92.5	500	96.5	Water removed from dehydrating mixt. by heating to 150-160° C. for 2 hours; mixt. had bad tendency to foam	
Ethylene glycol + NaOH	248 grams } 165 grams (48.4% soln.) }						500

¹ A patent application for this method is now pending.

TABLE I. EFFICACY OF VARIOUS DEHYDRATING AGENTS
(Continued)

DEHYDRATING AGENT	AMOUNT USED	STRENGTH OF ALC. ADDED		STRENGTH OF ALC. RECOVERED		REMARKS
		WEAK	STRONG	WEAK	STRONG	
		Cc.	%	Cc.	%	
Dry mixt. from previous expt.	260 cc.	375	97.6	{ 300 75	{ 99.2 94.7	Mixt. used dehydrated as above by distn. to vapor temp. of 180° C.
Benzyl alc. + Na salt of benzyl alc.	300 grams	350	92.5	300	96.0	Dehydrating mixt. prepared by mixing 4 moles benzyl alc. + 2 moles NaOH, and distg. to vapor temp. of 195° C.
Methylcyclohexanol + NaOH	295 grams } 78 grams } (48.4%)	238	92.5	200	95.3	Dehydrating mixt. prepared in manner similar to that used for Na salt of ethylene glycol; mixt. was dark brown after dehydration and practically insol. in alc.
n-Amyl alc. + NaOH	352 grams } 180 grams } (50%)	500	92.5	400	94.7	Dehydrating mixt. prepared by distn. through column and separating water from amyl alc.; mixt. distd. until vapor temperature reached 125° C.
Xylenol + NaOH	488 grams } 180 grams } (50% soln.)	500	92.5	400	94.9	Water removed from dehydrating mixt. by distn.; mixt. became dark on heating
Phenol + NaOH	376 grams } 178 grams } (50% soln.)	500	92.5	400	95.0	Water removed from mixt. by distn.
Benzyl alc. + KOH	432 grams } 112 grams } (dry)	500	92.5	400	95.7	Water of reaction removed from dehydrating mixt. by distn. to vapor temp. of 170° C.
Ethylene glycol + K ₂ CO ₃	100 grams } 100 grams }	500	92.5	470	96.1
Ethylene glycol + Ca(OH) ₂	248 grams } 55 grams }	450	92.5	400	95.3	Water of reaction distd. from dehydrating mixt. before use.

DEHYDRATING ACTION OF SODIUM ETHYLENE GLYCOLOXIDE

The three best dehydrating agents tried, as can be seen from Table I, were the mixtures of glycerol and potassium carbonate, of ethylene glycol and potassium carbonate, and of ethylene glycol and its sodium salt. All three of these gave strong alcohol in two steps starting with 92.5 per cent alcohol, but because there was decomposition of glycerol, the glycerol-potassium carbonate mixture was not tried out further. The mixture of ethylene glycol and its sodium salt showed promise of being a good dehydrating agent.

In order to determine whether the mixture of ethylene glycol and its sodium salt could be used repeatedly for alcoholic dehydration without any deterioration, a series of runs was made with the same batch of dehydrating agent. Two-hundred and forty-eight grams of ethylene glycol and 160

grams of 50 per cent sodium hydroxide were charged to a glass flask equipped with a Vigreux column, the water was removed by distilling to a vapor temperature of 180° C., and the cycle was repeated. The proportions of alcohol used contained water equivalent to 80 per cent of that which theory requires to react with the glycoloxide; previous experimentation had shown that this was the best proportion. The ethylene glycol which distilled with the water during the dehydrations was recovered by fractionation and charged back to the dehydrating mixture. The results on the series of ten batches run are given in Table II.

TABLE II. RESULTS OF REPEATEDLY DEHYDRATING ALCOHOL WITH MIXTURE OF ETHYLENE GLYCOL AND ITS SODIUM SALT

BATCH	DEHYDRATING MATERIAL	92.5% (WEIGHT) ALCOHOL CHARGED		STRONG ALCOHOL RECOVERED		COMPOSITION BY WEIGHT	WATER FRACTION
		Grams	Cc.	Cc.	%		
1	257	500	473	97.3	35		
2	257	500	470	97.0	40		
3	270	500	470	96.8	23		
4	260	500	470	96.8	42		
5	265	500	470	96.9	43		
6	262	500	470	96.9	44		
7	260	500	470	96.5	49		
8	263	500	470	96.6	40		
9	253	500	470	96.8	31		
10	250	500	470	96.8	..		

Before taking the water fraction from batch 1, there were added 20 cc. of glycol, which had been recovered by fractionation from the water removed from the initial preparation of sodium glycoloxide. Before taking the water fraction from batch 4, there were added 12 cc. of glycol, recovered from the water fractions of batches 1, 2, and 3. The same procedure was followed on batch 7, 14 cc. of glycol recovered from the water fractions of batches 4, 5, and 6 being added. Before starting batch 10, there were added 11 cc. of glycol recovered from the water fraction of batches 7, 8, and 9.

EFFECT OF METAL EQUIPMENT

In order to determine the effect of metal equipment on sodium ethylene glycoloxide, a series of runs similar to that described above was made in iron and in copper. In iron, the decomposition of the glycoloxide was quite rapid, and practically all of the glycol was decomposed after four successive batches. In the case of copper, the decomposition was less marked, but became apparent after about seven successive batches.

It was thought that this decomposition was accelerated by the high temperature which was required to dehydrate the glycoloxide. In order to obviate the use of a high temperature, a series of runs was made in copper similar to that described above, with the difference that the residue remaining after the strong alcohol had been distilled off was dehydrated under a vacuum in such a way that the temperature did not go over 150–155° C. A series of twenty-five batches was made in this way, with the following results:

Material charged	496 grams glycol 333 grams 48.1% NaOH 19775 grams 92.0% (by weight) alcohol
Material obtained	541 grams sodium ethylene glycoloxide residue 1591 grams water fraction 849 grams middle alcohol fraction (92.0% by weight) 17494 grams strong alcohol fraction (97.0% by weight)
Loss in 25 runs	129 grams

The glycol was recovered from the water fractions by fractionation, and from the glycoloxide residue by acidification and distillation. The total recovery was 416 out of 496 grams charged, or 84 per cent of the original charge. This apparent difference includes the unavoidable mechanical losses incurred in handling the recovered glycol over the whole

series of experiments. It is believed that consumption of glycol can be materially decreased in larger-scale operation.

ADAPTATION TO CONTINUOUS PROCESS

The dehydrations described previously were all made as separate batch experiments. Laboratory experiments were then made in order to determine whether this method of dehydration could be adapted to continuous operation. For this purpose it was necessary to add an excess of glycol to the glycoloxide in order to bring the crystallizing point of the glycol-glycoloxide mixture down below the boiling point of alcohol. A mixture of 5 moles of ethylene glycol to 2 moles of sodium hydroxide when dehydrated, crystallized at about 95° C.; a mixture of 6 moles of glycol to 2 moles of sodium hydroxide crystallized at about 60° C.; and a mixture of 7 moles of glycol to 2 moles of sodium hydroxide was still fluid at 40° C. The last named mixture was used in the continuous experiment.

Alcohol (92.5 per cent by weight) was boiled in a glass still, and the vapors were passed up a packed column 4 feet long. The dehydrating mixture was added to the column at a point about 1 foot from the top, at the rate of 150 grams for every 100 cc. of alcohol distillate collected. After a little time had been allowed for the system to reach equilibrium, two successive 100-cc. portions of the distillate were collected separately and analyzed. One of these was 99.5 per cent (by weight) alcohol, and the other was 99.2 per cent.

This experiment serves to show that 99 per cent alcohol can be obtained by a continuous process with sodium ethylene glycoloxide. In large-scale operation, of course, the aqueous alcohol would be fed to the column at a point near the bottom while a reboiler at the bottom of the column would supply the necessary heat. The dehydrating mixture would be continuously drawn off and dehydrated under vacuum in a separate system.

APPLICATION TO DEHYDRATION OF OTHER ALCOHOLS

The principle of dehydration with sodium ethylene glycoloxide was applied to *tert*-butyl alcohol and to isopropyl alcohol. In the former case, starting with commercial *tert*-butyl alcohol which had a specific gravity of 0.80560 at 25°/25° C., and which would not crystallize at 0° C., it was possible to obtain alcohol of crystallizing point 18° C. and specific gravity of 0.78254. Starting with isopropyl alcohol of specific gravity 0.80884 at 25° C., it was possible to obtain a dehydrated product with specific gravity 0.78714 at 25° C.

SUMMARY AND CONCLUSION

The alkali salts of high-boiling alcohols, glycols, and glycerol can be used for the dehydration of the lower-boiling alcohols which are difficult to dehydrate by ordinary means.

Sodium ethylene glycoloxide is an efficient dehydrating agent for aqueous alcohols, and has the merit that it can be readily regenerated for repeated use. The only feature which would apparently militate against its use on the large scale is the gradual decomposition which takes place in presence of some metals, resulting in ultimate loss of the glycol. This decomposition can be minimized by the avoidance of high temperatures in the dehydration, by the use of partial vacuum, or by operation in containers which do not have a catalytic effect on the decomposition of the alcoholate.

It is anticipated that the selection of the proper material for the construction of a plant employing this method will minimize the decomposition to a point where it would no longer be a serious cost factor.

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Corrosion of Bronzes by Vinegar

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A NUMBER of bronzes are used in the vinegar industry, but there has been little published to show the degree of corrosion of various bronzes by this medium under various conditions. According to St. John (5), a considerable amount of work has been done with wrought brasses, but information dealing with foundry brasses and bronzes is incomplete and unsatisfactory. Seiler (6) found that a phosphor-bronze, containing 90 to 91 per cent copper, 8 to 9 per cent tin, and about 0.25 per cent phosphorus, was resistant to corrosion by tan liquors provided the metal was free from iron, lead, and zinc. Philip (3) attributed the corrosion of common brass to local zinc-copper couples on the surface of the metal. Benik (1) stated that the corrosion product of an acid-resisting bronze was proportional to the time of immersion. Mrak and Cruess (2) found that a tin-copper bronze corroded faster in citric acid than in tartaric acid, and that corrosion in pure acids was faster than in tomato, lemon, or grape juices.

In order to determine the corrosion resistance of several bronzes that have been used or been recommended for use in the vinegar industry, eight bronzes and their chief components (copper, tin, and lead) were exposed under three sets of experimental conditions—namely, in still, aerated, and sprayed vinegar. These three test conditions were used, since Rawdon and Groesbeck (4) have shown that metals

corrode differently when exposed to different corroding conditions.

METHOD AND APPARATUS

The metals used were cut into strips 5.5 × 2.5 × 44.7 mm. The copper, tin, and lead strips were but 0.6 mm. in thickness. The metals were cleaned by burnishing with a cloth burnisher and then washing in ether and alcohol, after which they were dried in a desiccator over CaCl₂ and then weighed just before using in the corrosion tests. The composition of the bronzes used is given in Table I.

TABLE I. COMPOSITION OF BRONZES

BRONZE	METAL								
	Cu %	Sn %	Pb %	Zn %	P %	Fe %	Al %	Mn %	C
1	80.00	20.00
49	80.00	10.00	10.00
47	75.00	10.00	15.00
44	70.00	5.00	25.00
12	85.00	5.00	5.00	5.00
22	85.90	8.00	6.00	...	0.10
66	86.00	10.00	4.00	+
69	88.98	0.02	2.50	4.50	4.00	...

Cider vinegar, standardized to 4.27 per cent acid as acetic by the addition of distilled water or glacial acetic acid, was used in these tests.

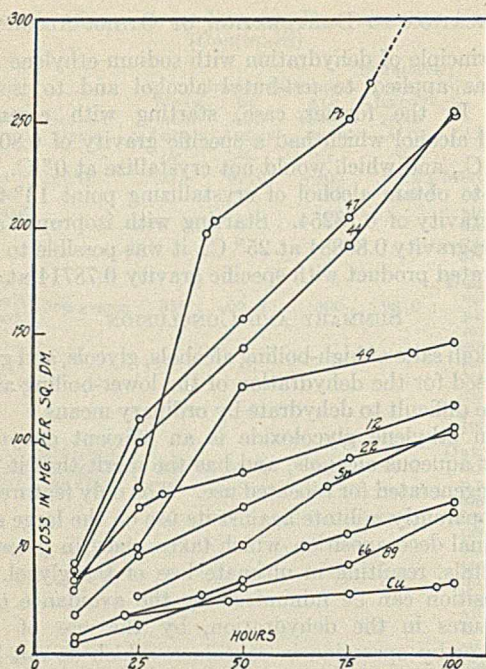


FIGURE 1. CORROSION OF BRONZES AND METALS TESTED BY SIMPLE IMMERSION IN VINEGAR

In the still or simple immersion tests, strips of metal were suspended in 325 cc. of vinegar in quart milk bottles and allowed to stand for the desired period. Aëration tests were conducted in similar manner, except that air was drawn through the vinegar at the rate of 50 cc. per minute by an aspirator.

The apparatus used in the spray tests was a modification of that used by Rawdon and Groesbeck. The metal strips were suspended in a bell jar near the top. The base of the bell jar stood in an enamel pan containing 1500 cc. of vinegar. An atomizer installed on one side of the bell jar near the base sprayed the vinegar into the jar, where it was distributed as a mist by the use of a baffle plate. An outlet at the top of the jar permitted the spray to move upward. The baffle plate acted as a receptacle to catch the liquid dripping off the metal strips. The concentration of spray was controlled by controlling the pressure of the air passing through the atomizer. In this test the vinegar was replaced every 24 hours.

When the corroded metals were removed they were washed in distilled water and alcohol and then dried in a desiccator several hours before weighing.

The data are expressed as loss of weight in milligrams per square decimeter of surface. Loss in volume of metal per given area of surface, or penetration in millimeters were not as reliable as loss in weight per given area, since the former two necessitated the use of the specific gravity of the metals. In the alloys the specific gravity may have changed because of selective corrosion.

TABLE II. CORROSION OF METALS UNDER VARIOUS TEST CONDITIONS

(In mg. per sq. dm. of surface for 100-hour period)

METAL	SIMPLE IMMERSION	AERATED VINEGAR	SPRAYED VINEGAR
Bronze 1	71.9	498.8	593.0
49	146.6	397.6	481.3
47	253.5	461.2	682.5
44	254.7	491.9	2607.0
12	116.9	402.0	580.9
22	103.2	334.3	478.7
66	67.0	273.0	709.0
69	68.6	298.2	852.6
Copper	33.6	212.0	837.1
Tin	106.5	349.0	41.9
Lead	324.7	1491.0	8826.8

All tests were conducted at a temperature of $20^{\circ} \pm 2^{\circ}$ C. All tests were made in duplicate and were repeated when

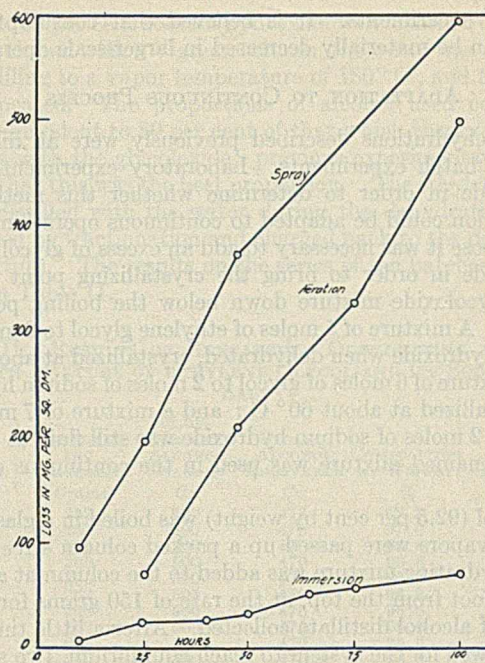


FIGURE 2. CORROSION OF BRONZE 1 UNDER THREE TYPES OF CORROSION TESTS

the duplicates did not check reasonably close. It was more difficult to obtain reproducible results in the spray than in the other tests; however, many of these tests were repeated a number of times, and the data given in Table II and Figures 1 and 2 are considered representative for corrosion under the given conditions.

DISCUSSION

The rate of corrosion was obtained for all the metals under the three types of conditions, and only the typical results are shown. Figure 1 is typical of the differences found between the rates of corrosion of the various metals under similar conditions. Figure 2 is typical of the difference found in the rate of corrosion under different conditions.

It is apparent from Table II that all metals tested, except tin, corroded most in the spray tests and least in the simple immersion tests. Tin, however, corroded most in the aërated vinegar and least in the spray tests. After 100 hours of exposure in the spray tests, tin maintained a smooth surface on which appeared a thin white film, whereas after the same exposure in the other tests the surface was considerably eroded and pitted. The presence of tin in bronze 1, however, did not seem to inhibit the increase in corrosion of this bronze in the spray. Rapid oxidation was undoubtedly responsible for the great increase in the corrosion of the metals in the spray tests. In the case of tin, this rapid oxidation probably favored the formation of a protective film.

Lead corroded more rapidly than any of the other metals tested. The presence of lead in bronze apparently decreased the resistance of bronze to attack by vinegar in the three tests used. In all tests the corrosion and lead content of bronzes 49, 47, and 44 varied in the order named at the end of the 100-hour period. No direct relation, however, between the lead content of the bronzes and its corrosion was found. These three bronzes, particularly 44, have been used in the vinegar industry primarily because of their supposed acid-resisting properties.

Bronzes 66 and 69 corroded with a clean surface when immersed in vinegar, but in the spray a dark scaly precipitate

formed on their surfaces. This material tended to flake off as corrosion proceeded.

All bronzes tested corroded sufficiently under all conditions used to cause considerable contamination of the vinegar with heavy metals. Since the contamination of foods with heavy metals is undesirable, it is inadvisable to use any of the bronzes tested in the vinegar industry, and it is particularly inadvisable to use the three containing a high percentage of lead.

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Some Studies in the Fat-Liquoring of Chrome Leather

II. Effect of Various Oils upon Oil Adsorption and Strength of Leather

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IN A previous paper the writers discussed the effect of hydrogen-ion concentration upon oil adsorption and showed that, as the pH value of the skin or fat liquor varied, the amount of oil adsorbed by the chrome leather varied also. It was further shown that each individual fat liquor gave a characteristic absorption curve over a pH range of 1 to 12. If a mixture of oils was used, the characteristic curve of the pure oil was changed in proportion to the mixture used.

The experimental work was extended to include the following effects: mixtures of raw and sulfonated oils upon oil adsorption and ultimate strength of the leather; moisture in leather before fat-liquoring upon oil take-up and strength of finished leather; and mixtures of different oils upon oil adsorption, strength of leather, and distribution of oil throughout the skin.

EXPERIMENTAL PROCEDURE

Chrome-tanned calfskin, direct from shaving, was cut into pieces, 2 × 4 inches, and fat-liquored in the oil emulsions to be noted at 120° F. (48.9° C.) and for 30 minutes. At the duration of the fat-liquoring period, the skin was removed and dried slowly (room temperature), and the oil adsorbed was determined, using low-boiling petroleum ether as the extractive. At the same time the tensile strength and the tearing strength of the fat-liquored leather were determined. The following systems were studied:

Characteristic oil-adsorption curves are obtained for various mixtures of raw and sulfonated oils used in the fat-liquoring of chrome-tanned calfskin. It is shown that the percentage of sulfonated oil added to raw oil drastically affects the amount of oil adsorbed by the leather. The effect of pH value, the oil concentration, and stability of the fat liquor upon the oil adsorbed during the period of fat-liquoring are given. A comparison, with relation to oil adsorption by the leather, of some sixteen different fat liquors is shown. The effect of moisture content of the chrome leather upon oil adsorption is given.

1. Raw neat's-foot oil and sulfonated neat's-foot oil, the mixtures varying from 100 per cent raw oil to 100 per cent sulfonated oil.
2. Raw cod oil and sulfonated cod oil.
3. Raw cod oil and moellon oil.
4. Raw neat's-foot oil and sulfonated castor oil, the fat liquors being adjusted to pH 4 and pH 9.
5. Raw cod oil and sulfonated castor oil, the resulting fat liquors being adjusted to pH 4 and pH 9.
6. Sulfonated cod oil and salted egg yolk, adjusted to pH 4 and pH 9.
7. Raw castor oil and sulfonated castor oil.

8. Raw neat's-foot oil and egg yolk.
9. Temperature of fat-liquoring upon oil adsorption and resultant strength of leather.
10. Comparison of sixteen different and varied fat liquors.
11. Effect of pH, oil concentration, and stability of fat liquor upon oil adsorption and ultimate strength of finished leather.
12. Effect of skin moisture and degree of washing before fat-liquoring upon oil adsorption.

When raw and sulfonated oils are mixed, and chrome leather is fat-liquored in such emulsions, the oil adsorption and strength of the leather varies with the mixture. Figure 1 shows the effect upon strength necessary for tear and upon oil adsorbed, of mixtures of raw and sulfonated neat's-foot oil. It is readily seen from Figure 1 that with raw neat's-foot oil alone the oil adsorbed by the chrome leather is very small, but, as the percentage of sulfonated oil added increases, the oil adsorbed becomes increasingly greater, probably because of the in-

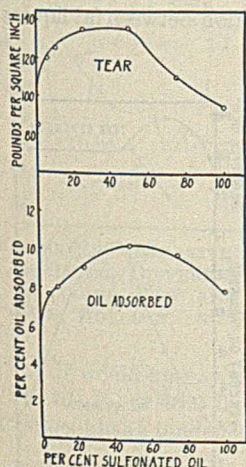


FIGURE 1. EFFECT OF MIXTURES OF SULFONATED AND RAW NEAT'S-FOOT OIL ON OIL ADSORPTION AND STRENGTH OF FINISHED LEATHER

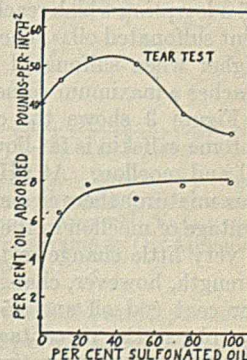


FIGURE 2. EFFECT OF MIXTURES OF SULFONATED AND RAW COD OILS ON OIL ADSORPTION AND STRENGTH (TEAR) OF LEATHER

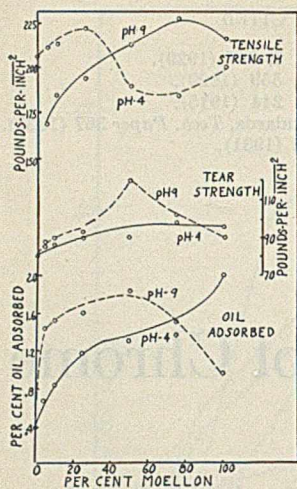


FIGURE 3. CHARACTERISTIC CURVES OF FAT-LIQUORING, USING RAW COD AND MOELLON OILS

creased stability of the emulsion formed, and of the combination of the evaporated oil with the leather. With regard to the strength of the leather under such treatment (measured by the tear test), the strength first increases, then decreases rapidly, until at 100 per cent sulfonated oil the leather strength is below that of 100 per cent raw neat's-foot oil, even though the percentage of oil adsorbed is greater at that point. This indicates that the amount of actual oil adsorbed is no criterion of ultimate strength of finished leather. When a mixture of raw cod and sulfonated cod oils are used in the fat-liquoring a somewhat different picture results (Figure 2). As in the case of the system raw neat's-foot oil-sulfonated neat's-foot oil, the addition of sulfonated cod oil results in an increased oil adsorption which reaches a maximum value at about 50 per cent sulfonated oil. The strength of the leather in all cases is higher when sulfonated oil is added to the fat liquor, but reaches a maximum value at 50 per cent sulfonated oil.

Figure 3 shows the characteristic curves obtained when chrome calfskin is fat-liquored in various mixtures of raw cod oil and moellon. At pH 4 (natural pH of the fat liquors of this mixture) there is a steady rise in oil adsorbed as the percentage of moellon in the fat liquor increases. At pH 4 there is very little change in the tear of the leather. The tensile strength, however, changes, rising to a maximum value at 75 per cent cod oil and 25 per cent moellon, then decreasing sharply as the percentage of moellon further increases. At pH 9, however, an entirely different system results, since the presence of alkali tends to disperse the oils more readily. The oil adsorbed rises to a maximum value of 50 per cent moellon and then decreases sharply. The strength of the leather, as measured by the tear test, follows the same general trend as that of the oil absorbed, rising to a maximum value of

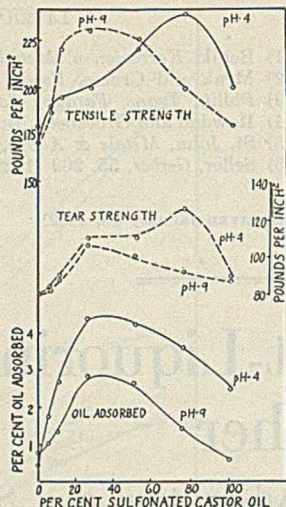


FIGURE 4. OIL ADSORBED, TEAR STRENGTH, AND TENSILE STRENGTH, USING SYSTEM NEAT'S-FOOT OIL-SULFONATED CASTOR OIL

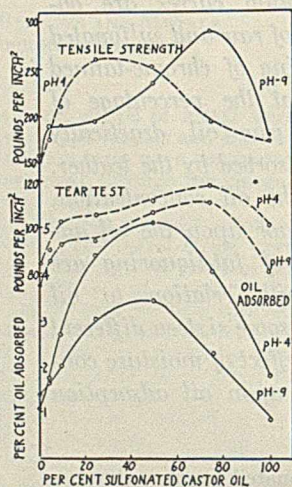


FIGURE 5. CURVES FOR SYSTEM RAW COD OIL-SULFONATED CASTOR OIL

50 per cent moellon. The tensile strength of the leather, however, attains its maximum value at 75 per cent moellon.

Figure 4 gives the graphical data obtained when mixtures of raw neat's-foot oil and sulfonated castor oil are used for the fat-liquoring of chrome leather. At both pH 4 and 9 the oil adsorbed rises to a maximum value at 25 per cent sulfonated castor oil. At pH 4 the oil adsorbed is greater than in the more alkaline system of fat liquors. The tear test is greater at pH 4 than at pH 9; in the case of the fat liquor at pH 4, this test shows a maximum value at 75 per cent sulfonated castor oil. With regard to the tensile strength of the leather, at high concentrations of raw neat's-foot oil, the fat liquor of the higher pH value shows the greater strength, while the reverse is true at higher concentrations of sulfonated castor oil. It would appear that the alkaline fat liquors, made up of mixtures of raw neat's-foot and sulfonated castor oils, show a lessened oil adsorption and tend to yield a somewhat weaker leather.

Figure 5 shows the data obtained using mixtures of sulfonated castor oil and raw cod oil. In this case, again, there is a greater adsorption using acid fat liquors than alkaline ones. In both cases the oil adsorption reaches a maximum value at a 50 per cent concentration. The tensile strength of the resulting leathers shows that the acid fat liquors are strongest when the raw cod oil predominates, while the alkaline fat liquors are strongest when the sulfonated castor oil is in excess. The tensile strength curves show that, in either acid or alkaline condition, mixtures of the oils are stronger than either single component.

When chrome leather is fat-liquored with mixtures of sulfonated cod oil and salted egg yolk, an entirely different picture results. In the first place, the addition of even very small amounts of egg yolk retards the adsorption of oil. There is little difference in oil adsorption between fat liquors

FIGURE 6. EFFECT OF ADDITION OF EGG YOLK TO SULFONATED COD OIL

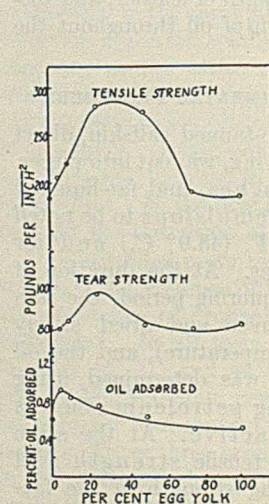


FIGURE 7. EFFECT OF ADDITION OF EGG YOLK TO NEAT'S-FOOT OIL

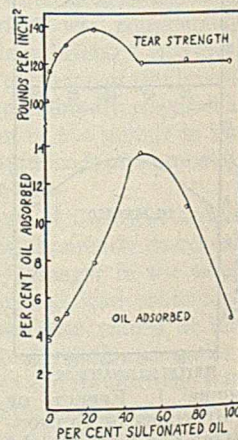


FIGURE 8. EFFECT OF ADDITION OF SULFONATED CASTOR OIL TO RAW CASTOR OIL

at pH 5 or 9. At pH 5 the strength of the leather (either tear or tensile) is constant, decreasing as the percentage of egg yolk increases. At pH 9, however, the strength of the resulting leather increases up to 50 per cent egg yolk. The data obtained are shown graphically in Figure 6. Figure 7 shows similar data for the system raw neat's-foot oil-egg yolk. In this case, again, egg yolk apparently retards the oil adsorption.

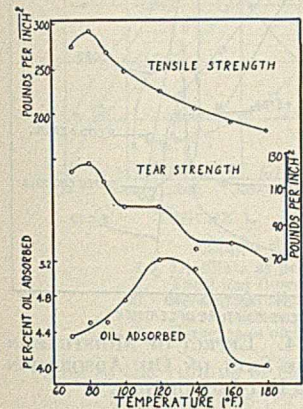


FIGURE 9. EFFECT OF TEMPERATURE ON OIL ADSORPTION

Figure 8 shows the adsorption of oil from mixtures of raw and sulfonated castor oils. As sulfonated castor oil is added, the oil adsorption increases to a maximum, and, as greater amounts of sulfonated oil are added, the oil adsorption decreases rapidly. The maximum tear strength is attained at 75 per cent raw and 25 per cent sulfonated castor oil.

EFFECT OF TEMPERATURE UPON FAT-LIQUORING

Chromed calfskin is usually fat-liquored at an initial temperature of 100° to 120° F. (37.8° to 48.9° C.), and it was of interest to determine just what role temperature plays with regard to oil adsorption and leather strength. Figure 9 shows the data obtained for a temperature interval ranging from 70° to 180° F. (21.1° to 82.2° C.).

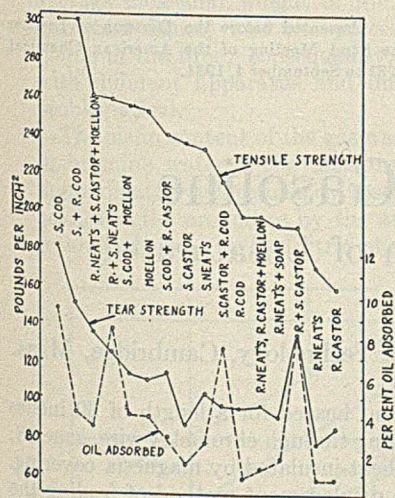


FIGURE 10. RELATIVE COMPARISON OF SIXTEEN DIFFERENT FAT LIQUORS, INCLUDING RAW AND SULFONATED OILS, MOELLON, AND SOAP

It would appear that increasing the temperature (up to 120-140° F., or 48.9-60° C.) favors oil adsorption, but such treatment has a tendency to give tender leather.

COMPARISON OF VARIOUS FAT LIQUORS

Some sixteen different fat liquors were used for a relative comparison of oil adsorption and resulting strength of leather. The fat liquors used were similar to those in regular use in tannery practice. Figure 10 shows the data obtained. The curves were plotted in relation to a decreasing tensile strength,

and it is to be noted that, in general, the oil adsorbed and the tear strength bear little relation to each other. It is generally found that leather fat-liquored with a sulfonated oil is decidedly stronger with regard to tear and tensile strength than a corresponding leather fat-liquored with the raw oil. Since it has been postulated previously that sulfonated oils actually combined with the collagen of the skin, it is possible that such combinations tend to give a stronger leather. It is to be further noted that sulfonated cod oil and moellon tend to give the strongest leathers, that the addition of either sulfonated or raw castor oil to a fat liquor tends to weaken the finished product, and that oil adsorption and strength of leather have little real relation.

Figure 11 shows a somewhat similar comparison, with the exception that the fat liquors were emulsified to a finer degree, using an acid emulsifier. In every case, where an emulsifier was used for stabilization, there resulted an increased oil adsorption and a stronger leather. These facts are particularly noticeable in the cases of moellon and linseed oils.

EFFECT OF EMULSIFICATION AND OIL CONCENTRATION

In a previous paper, characteristic curves were given for the oil adsorbed by chrome leather over a wide pH range of fat liquors. In this work only one concentration of oil was used. The data given in Figures 12 and 13 show these characteristic curves in two distinct ways: by concentration of oil from 1 to 5 per cent, and with and without the use of emulsifiers. It is readily seen that, when emulsifiers are not used, the curves obtained are of the same type, the oil adsorbed in each case being of a maximum value at pH 5. At this pH, however, the tensile strength of the leather is at a minimum value. When emulsifiers are used to cause a greater dispersion of the oil in the water, entirely new types of curves are obtained. The oil dispersed in an acid media (pH 3 to 5) in every case shows an increased absorption as the pH value of the fat liquor increases to pH 5, and, with the exception of 3 per cent oil, attains a maximum value at this point. In the cases of 1 and 2 per cent oil, minimum oil adsorption results at pH 6. In the case of 3 per cent oil neither a maximum nor minimum results, but only points of inflection at pH 5 and 7. For 4 and 5 per cent oil, there is shown a maximum oil adsorption at pH 5 and a minimum at pH 6. In all cases where the emulsifier is used, a greater oil adsorption results and a correspondingly greater leather strength.

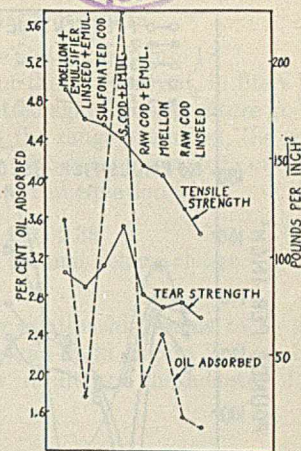


FIGURE 11. EFFECT OF EMULSIFYING AGENT ON OIL ADSORPTION

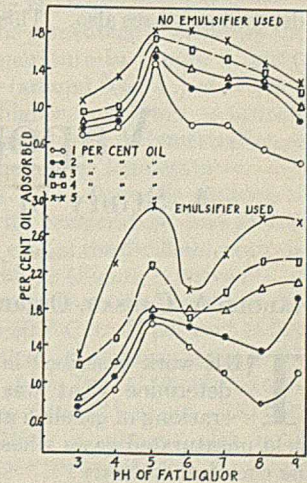


FIGURE 12. EFFECT OF OIL CONCENTRATION, EMULSIFICATION, AND pH VALUE OF FAT LIQUORS ON OIL ADSORPTION

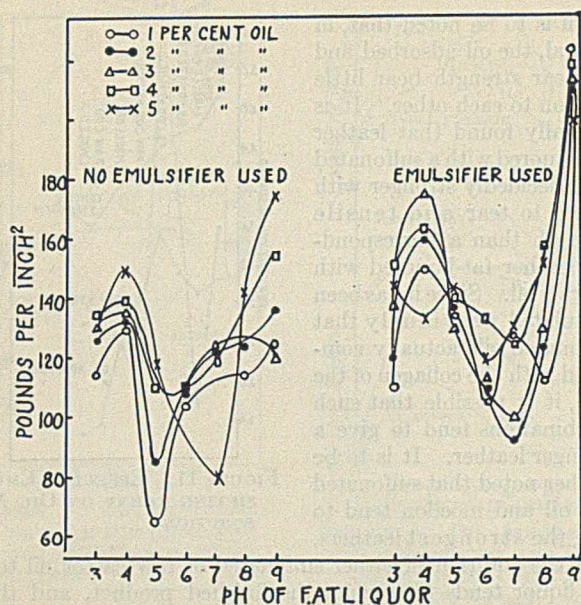


FIGURE 13. EFFECT OF OIL CONCENTRATION, EMULSIFICATION, AND PH VALUE OF FAT LIQUORS ON STRENGTH OF FINISHED LEATHER

EFFECT OF MOISTURE IN LEATHER

Chrome-tanned calfskin may be either fat-liquored and then colored, or the reverse, depending upon the individual manufacturer. In either case the skin contains a definite amount of water at the time of fat-liquoring. Figure 14 shows the oil adsorbed when chrome-tanned calfskin containing varying amounts of moisture is fat-liquored in various oils. From this figure it is seen that, in the cases of moellon, raw cod oil, cod oil and emulsifier, and moellon and emulsifier, the oil adsorbed decreases as the moisture of the leather increases. It is also seen that for sulfonated cod oil or for sulfonated oils in general, as the moisture of the leather increases, the oil adsorbed increases also. This fact is to be expected, since the

sulfonated oils emulsify readily with water, and the water present in the leather has no effect upon this emulsification. From Figure 14 it would appear that salted egg yolk is adsorbed as readily at any moisture content. The addition of emulsifier to a fat liquor containing moellon materially aids oil adsorption, giving a maximum adsorption at about 50 per cent moisture. For practical purposes, chrome-tanned calfskin, just after shaving, will attain between 50 and 60 per cent moisture when drummed for 30 minutes; thus, reading off values for the various oils at 50 per cent moisture will give an indication of the oil adsorbed under practical conditions.

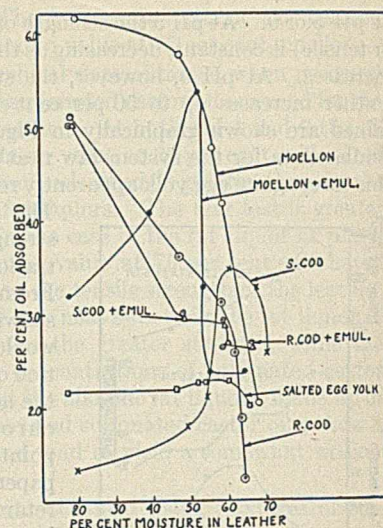


FIGURE 14. EFFECT OF MOISTURE IN CHROME SKIN ON OIL ADSORPTION DURING FAT-LIQUORING

ACKNOWLEDGMENT

The writers wish to acknowledge gratefully the support given this work by the Hunt-Rankin Leather Company, of Peabody, Mass., and to acknowledge their permission to publish the results of the investigation. The writers also wish to express their appreciation of the analytical work of Robert Stafford of the Hunt-Rankin Leather Company.

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Vapor-Phase Cracking of Gasoline

A Study of Optimum Conditions for Production of Unsaturated Gases from Gasoline

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THE work described in this paper was undertaken to determine what was involved in the vapor-phase cracking of gasoline at atmospheric pressures so as to yield unsaturated gases whose value is steadily increasing in the chemical industry.

The gasoline selected was an untreated straight-run distillate made from Pennsylvania crude. Its Engler distillation showed 34 per cent off at 212° F. (100° C.), and an end point of 410° F. (210° C.). The aniline point was 60° C.; hence it consisted mainly of paraffin hydrocarbons. This was also shown by its very low knock rating which was characteristic of straight-run distillates from this kind of crude. This type of gasoline was selected since its low knock rating makes it less valuable for use in automobiles than most gasolines.

EXPERIMENTAL PROCEDURE

The apparatus used consisted of a 3-foot (0.9-meter) length of 1-inch standard iron pipe, packed with pumice stone (1300

pieces per 100 grams) and heated for a length of 30 inches (76.2 cm.) by 1 kw. running through chromel A wire, gage 18; the whole was suitably heat-insulated by magnesia covering.

The mercury positive displacement method of feeding the gasoline into the apparatus was used. Temperatures were read by means of a thermocouple loosely slipped into a thermometer pocket at the exit of the tube; the gases and vapors produced were sent through a spiral condenser and receiver, the noncondensable gases being collected in two 20-liter glass carboys, graduated in liters and filled with water.

The temperatures experimented with ranged from 500° to 700° C., and the feed rates ranged from 40 to 240 cc. per hour. Standard Pyrex and combustion tubes were found unsuitable for the higher temperatures.

The volume of the 30 inches (76.2 cm.) of tube is 340 cc. All rates are reported as liquid time of contact, which figure takes care of the volume of the cracking tube used and the rate at which the gasoline was fed. Liquid time of contact is

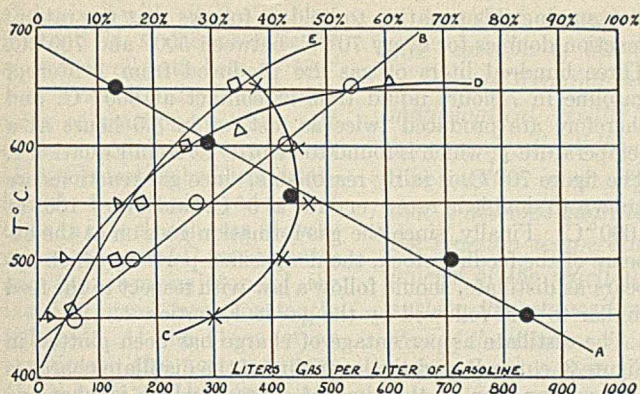


FIGURE 1. CONSTANT-RATE RESULTS

(Liquid time of contact, 5.66 hours)

- A. Distillate as percentage of charge (upper scale)
 B. Total gas (lower scale)
 C. Percentage olefins in gas (upper scale)
 D. Percentage aromatics in distillate (upper scale)
 E. Percentage olefins in distillate (upper scale)

equal to the volume of the hot tube (in liters) divided by the rate of feed (in liters per hour); since the figure has one dimension (that of time) cubic feet or centimeters can be substituted for liters and give the same figures. This method of reporting rates facilitates comparison with other investigations, as it does not involve the dimensions of the cracking tube used.

Thus Gault and Hessel (1) cracked hexadecane in a quartz tube, 2×64 cm., at the rate of 1 cc. per minute, corresponding to a liquid time of contact of 3.29 hours. At this rate they obtained 126 liters of gas per liter of feed at 615°C . Under similar conditions, Pennsylvania straight-run gasoline gave 230 liters.

A better index of rate from a theoretical standpoint would be the vapor time of contact. Unfortunately this involves the average molecular weight of the gasoline (a comparatively uncertain figure) and the percentage gasified at different points in the tube; consequently, for purposes of comparison with different apparatus and different stocks, its value is problematical.

The olefin content of the gas was determined by absorption in bromine water. The unsaturates in the distillate were approximately determined by absorption in 88 per cent sulfuric acid, and the aromatics by the aniline point method on the residue, checked by the nitric plus sulfuric method.

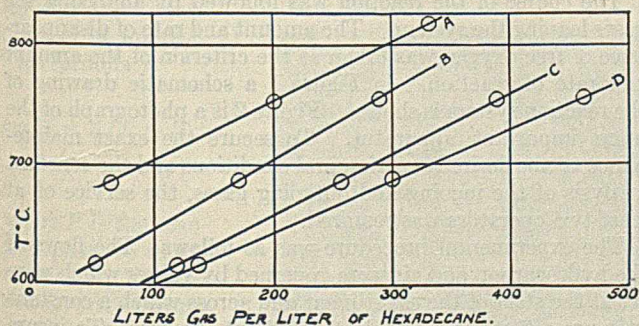


FIGURE 2. GAS EVOLVED DURING CRACKING OF HEXADECANE (1)

Curve	Liquid time of contact Hours
A	0.825
B	1.65
C	2.47
D	3.29

Two main series of runs were made: one at constant rate (60 cc. per hour, or 5.66 hours liquid time of contact) and at temperatures ranging from 500° to 700°C .; and the other at a constant temperature of 600°C . and at rates varying from 1.4 to 8.6 hours liquid time of contact.

CONSTANT-RATE RESULTS

The constant-rate results are plotted in Figure 1.

TOTAL GAS. The volume of the gas evolved, in liters per liter of gasoline charged, is plotted against temperature in $^\circ\text{C}$. (curve A, Figure 1). Within the range examined, the total gas evolved increases directly with the temperature and is a linear function of it. The empirical equation is

$$G = (T - 480) 2.38 \quad (1)$$

where G = volume gas evolved per unit volume charge
 T = temperature, $^\circ\text{C}$.

This simple empirical linear relationship seems to be generally true. Curves A, B, C, and D in Figure 2 show how some of Gault and Hessel's results on hexadecane form straight lines too.

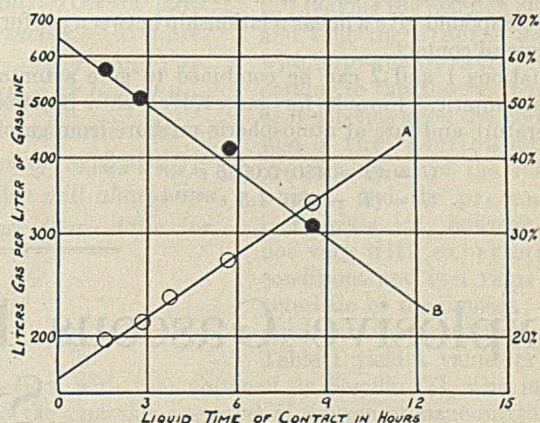


FIGURE 3. CONSTANT-TEMPERATURE RESULTS

- A. Total gas (scale on left)
 B. Distillate as percentage of charge (scale on right)

DISTILLATE CHARGE. The percentage of the charge that appears as distillate is plotted against temperature as curve B in Figure 1, and here, too, the relationship is linear.

UNSATURATES IN GAS. The percentage of olefins in the gas are plotted against the temperature in Figure 1, curve C; the olefins reach a maximum (around 600°C .) of 47 per cent, and diminish at both the higher and lower temperatures. This fact is almost certainly due to the polymerization of the unsaturates that occurs at the higher temperatures.

AROMATICS IN DISTILLATE. The aromatic content of the distillate increases rapidly with temperature, and at 700°C . has reached a figure of 60 per cent of the distillate, corresponding with 7.8 per cent of the charge (Figure 1, curve D).

UNSATURATES IN DISTILLATE. The olefin content of the distillate rises from 3 per cent at 500°C . to 35 per cent at 700°C . From the above it follows that, if a maximum gas volume is required, a temperature of above 700°C . should be adopted so that all the gasoline will be changed into gas—650 volumes per volume of gasoline. These conditions also hold for maximum olefins—220 volumes per volume of feed (Figure 1, curve E).

If a maximum olefin content in the gas is required—i. e., a gas as rich as possible in olefins (a condition sometimes demanded for economic treatment of the gas)—a temperature of 600°C . should be maintained, giving 45 per cent unsaturates or 135 volumes per volume of feed.

CONSTANT-TEMPERATURE RESULTS

The constant-temperature results are plotted in Figure 3. At a temperature of 600°C . the total gas evolved has been plotted against time of liquid contact in hours on semi-logarithmic paper; in curve A, Figure 3, the points lie on a straight line. The empirical equation is:

$$\ln_e G = H 0.0758 + 5.18 \quad (2)$$

where G = volume of gas per unit volume of feed
 H = liquid time of contact, hours

Differentiating,

$$\frac{dH}{dG} = 0.0758 G \quad (3)$$

or the gas formed per unit time is proportional to the quantity of gas already formed; this characterizes the reaction as autocatalytic. This would mean that a partially gasified stock should crack more readily than a virgin stock, and that cracked or recycle stock should be preferable to straight-run stock for producing gas. The liquid-phase cracking of gas oil runs in the same direction as far as the production of gas is concerned, although in the opposite direction, where the production of gasoline is examined, Gault and Hessel's results (1) with a single compound give a linear relationship between gas formed and time of contact.

Equations 1 and 2 can be combined to give a tentative general empirical formula for gas evolved as a function of temperature and rate at atmospheric pressure from gasoline:

$$G = (T - 480) 0.0085 e^{0.0758 H 5.18} \quad (4)$$

whence

$$G = (T - 480) 1.5 e^{0.0758 H} \quad (4)$$

Assuming this equation to hold, it follows that the rate of reaction doubles for every 70° C. between 500° and 700° C. Three hundred liters of gas are produced from 1 liter of gasoline in 7 hours liquid time of contact at 600° C. and therefore are produced twice as fast, or in 3.5 hours at a temperature T , which is found to be 670° C. from Equation 4. The figure 70° C. is fairly reasonable, since gas reactions are known to double in rate every 10° at 0° C. and every 100° at 1000° C. Finally, since the gas formation goes on at the expense of the feeding stock, the nongasified portion, which appears as distillate, should follow a law with respect to the feed similar to that followed by the gas in Equation 2.

The distillate as percentage of charge has been plotted in Figure 3, curve B , and the logarithm of the distillate charge is a linear function of the time of contact, which is what one would expect from the autocatalytic nature of the gas formation.

Numerous metallic oxides were tried as catalysts to modify the reaction but no marked effects were produced.

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RECEIVED January 6, 1932. The author's present address is Research Department, Sun Oil Co., Marcus Hook, Pa.

Explosive Gaseous Reactions in a Dynamic System

I. The Reaction of Oxygen and Propane

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IN THE course of an extended investigation on the oxidation of hydrocarbons conducted over a period of several years, certain observations were made which appeared to offer a means by which the mechanism of chain reactions or thermal explosions might be further elucidated. As a result special experiments were conducted with this object in view. These experiments and the deductions which followed therefrom are the subject of this paper. An incomplete but valuable bibliography on the subject of the oxidation of hydrocarbons is appended (1, 4).

PART I. EXPERIMENTAL METHOD AND RESULTS

In the majority of the experiments, mixtures of oxygen or air and a gaseous hydrocarbon were passed through a long tube of narrow diameter coiled in a molten bath. Commercial propane (99 + per cent C_3H_8) was the hydrocarbon employed in general. During the course of any experiment, the

pressure of the system, the composition of the ingoing gas mixture, and the rate of gas flow were maintained constant. In most cases, the reaction was conducted in Shelby steel tubes, although other materials were also employed. The length of the tube immersed in the heating bath was 350 cm. unless otherwise noted.

The course of the reaction was followed by analyzing the gases leaving the system. The amount and rate of disappearance of free oxygen was taken as the criterion of the amount and rate of reaction. In Figure 1 a schematic drawing of the reaction system is shown. Figure 2 is a photograph of the more important apparatus. To secure the exact maintenance of the desired experimental conditions and the constant analysis of the ingoing and outgoing gases, the service of at least two operators was required.

The experimental procedure was as follows: The flows of the hydrocarbon and air were governed by valves which were set at the start of the experiment and across which a constant pressure difference was held throughout the run. To insure uniform initial conditions, the hydrocarbon was evaporated

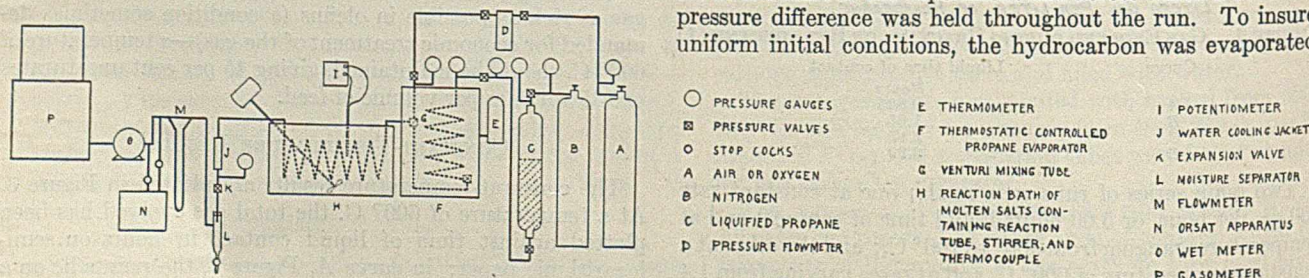


FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS

and mixed with air in a coil immersed in a thermostatically controlled oil bath held at 430° K. When the desired conditions of reaction pressure, rate of flow, and initial oxygen or air concentration had been established, the temperature of the reaction bath was slowly raised (about 1° C. per minute) and the composition of the issuing gases was constantly followed. At the close of an experiment the temperature of the bath was lowered, and unless the starting conditions were duplicated, the results were rejected.

Figure 3 expresses graphically the results of two typical experiments obtained by following the oxygen concentration as a function of the temperature of the heating bath. Curve A was obtained at 103 atmospheres pressure, whereas curve B was obtained at 52 atmospheres pressure. The reaction tube was 0.16 cm. in diameter. Curves obtained using tubes of this or a lesser diameter were precisely duplicated with both rising and falling bath temperatures. Reaction tubes of appreciably larger diameters showed a pronounced hysteresis effect, the curve obtained with a falling bath temperature lying considerably to the left of the curve obtained with a rising bath temperature. For purposes of subsequent discussion we shall arbitrarily define the bath temperature at which half the free oxygen has disappeared (under conditions of increasing temperature) as the "reaction temperature."

INFLUENCE OF PRESSURE ON REACTION TEMPERATURE

The data presented in Table I show that the reaction temperature decreases with increase of pressure.

The accurate representation of the data afforded by Semenoff's formula (5) for chain reactions is of interest. This formula is

$$\log \frac{P}{T} = A/T + B \quad (1)$$

where P is the reaction pressure in atmospheres, T is the reaction temperature in degrees absolute, and A and B are constants. According to this equation a straight-line relationship should be shown when $\log P/T$ is plotted against the reciprocal of the absolute tempera-

A method of mathematical treatment of explosive reactions of the hydrocarbon oxidation type in simple dynamic systems is presented. The mathematical results are in remarkably good agreement with all the experimental data obtained. The method is of very practical application in that it develops quantitatively the relation between the reaction temperature and the length and diameter of the reaction tubes, the pressure of the system, the composition of the mixture, the rate of flow of the mixture, etc.

It is quite probable that the same method of approach will be found equally effective for many other types of explosive reactions. On the other hand, certain types of chain reactions—e. g., reaction of hydrogen and oxygen—may require extended modification of this method, if indeed they are at all amenable to similar treatment. However, the extended application of explosive reactions by the chemical industry will almost inevitably involve dynamic rather than static (or "batch") systems.



agreement with that obtained by Sagulin (4), who investigated the explosion pressures of oxygen-propane mixtures at sub-atmospheric pressures by a static method, it is evident that the value of B is also dependent upon the rate of flow, or, reciprocally, the duration of heating, when the experiments are conducted by passing the reaction mixture through heated tubes.

The slope A is the most interesting term in Equation 1. According to Semenoff, A can be expressed in the case of thermal explosions in terms of E , the heat of activation of the primary or chain generating reaction, in the following manner:

$$A = 1/2 \cdot E/R \cdot \log e = 0.11 E \quad (2)$$

It is characteristic of explosions and many chain reactions

that unreasonably high values are obtained when an effort is made to calculate heats of activation by the methods commonly employed. Such would be the case if one were to use the data presented in the reaction curves shown in Figure 3. Semenoff's equation, however, at least yields plausible values for E . In addition, the results given in Table I show that the equation is applicable over extremely wide ranges of pressure.

That such is the case is shown by Figure 4.

Semenoff derived this formula theoretically both for "thermal explosions" and for chain reactions. It is characteristic of such reactions that the products of reaction are able to activate the reactants, and as a consequence abrupt changes of reaction velocity may occur. It is generally found that at some temperature, T , deactivation of the products does not occur as fast as they are formed (either by heat losses or by breaking the reaction chains), and thus the process occurs with auto-acceleration. According to this theory, the value of B depends upon the composition of the reaction mixture, the dimensions of the reaction vessel, and the presence of inert gases. A , however, does not vary with experimental conditions and is a value characteristic of the process. Inasmuch as the results given in Table I yield a value for A in

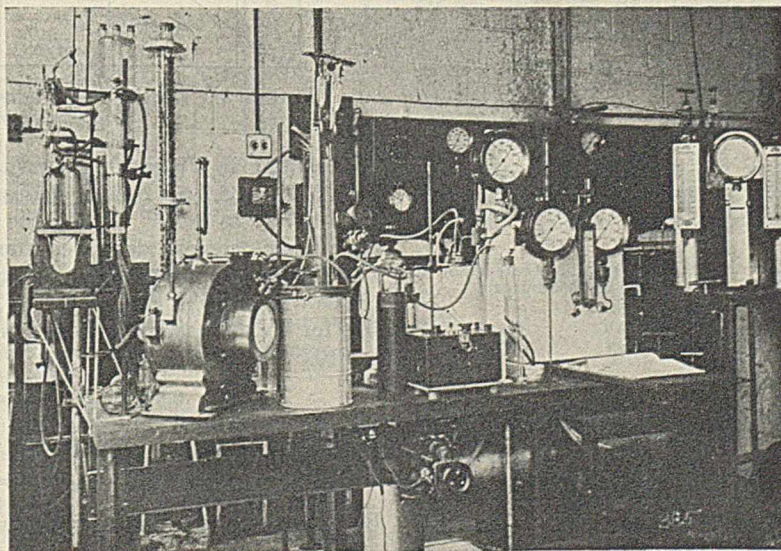


FIGURE 2. PHOTOGRAPH OF APPARATUS

Sagulin (4), who tested the validity of Semenov's equation for a number of explosive reactions at low pressures, found that the value of E for propane at temperatures below 680° C. was equal to 34.5 kg.-cal. per gram mole. The value calculated from our data is equal to 35.0 kg.-cal. Considering

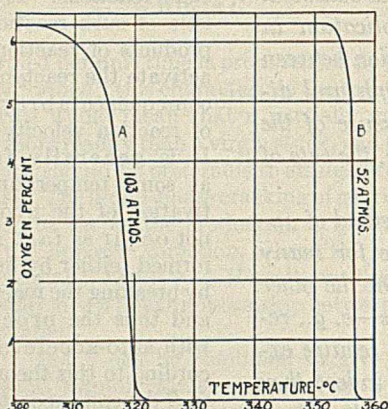


FIGURE 3. REACTION CURVES AT VARIOUS PRESSURES

the differences of experimental technic, pressure range, and concentrations, the agreement is at least interesting.

INFLUENCE OF AIR AND OXYGEN CONCENTRATIONS ON REACTION TEMPERATURE

As the air concentration is increased the temperature of reaction also increases. This is shown by the tabulated data and more explicitly by the family of reaction curves in Figure 5, where the broken line indicates the variation of reaction temperature with initial air concentrations. Oxygen concentrations are plotted; to get air concentrations, multiply the oxygen values by 4.76.

TABLE I. EXPERIMENTAL DATA

(Reaction system: Shelby steel tube, 350 cm. long and 0.159 cm. in diameter. Temperature of entering gases, 430° abs.)

EXPT. N.	RATE OF GAS FLOW AT N. T. P. (V) Liters/hr.	INITIAL O ₂ %	RE-ACTION TEMP. ° K.	PRESSURE (p) IN ATMOS.	REMARKS	
142	450	6.0	736.1	7.8	Variation of reaction pressure	
141	445	6.0	703.0	11.2		
139	453	5.9	670.2	18		
143	430	5.9	658.6	24.8		
138	448	6.0	644.2	35		
144	447	5.8	641.5	35		
137	441	5.5	621.8	52		
140	428	6.0	605.8	69		
145	442	5.5	580.1	120		
Av. 443 ± 7 5.8 ± 0.2						
127	447	1.25	610.5	52	Variation of initial air concentration	
126	432	2.4	612.5	52		
125	427	5.5	619.5	52		
128	442	10.0	625.5	52		
129	443	13.7	635.5	52		
Av. 438 ± 7						
136	450	2.4	607.0	52	Variation of initial pure oxygen concentration	
130	456	5.8	615.5	52		
135	456	8.2	615.0	52		
131	450	10.8	615.0	52		
Av. 453 ± 3						
149	175.5	5.7	607.5	52	Variation of rate of flow of reaction mixture	
174	215.1	5.7	608.0	52		
148	274.4	6.0	613.5	52		
172	430	6.2	618.0	52		
137	442	5.5	621.8	52		
150	620	5.9	627.5	52		
173	662	5.8	629.3	52		
155	668	6.2	633.0	52		
152	736	5.6	642.0	52		
151	948	5.8	644.5	52		
Av. 5.8 ± 0.4						
136	442	5.5	621.8	52		Tube diameter = 0.159
186	458	6.2	673.0	52	Tube diameter = 0.080	

The results on the variation of reaction temperature with the concentration of air or oxygen in the reacting mixture are of interest in that they can readily be formulated on the

assumption that the primary, chain-initiating reaction is unimolecular with respect to propane and is not affected by inert substances or oxygen. This represents the simplest mechanism, which can be ascribed to the primary reaction.



The rate of formation of C_3H_8' is presumably given by the following equation:

$$\frac{d(C_3H_8')}{dt} = k(C_3H_8) \quad (4)$$

Assume now that the rate of formation of C_3H_8' must attain a certain definite, though unknown value X before a sufficient number of reaction chains are initiated to bring about a spontaneous reaction. For values of C_3H_8' less than X , the reaction chains are broken as rapidly as they are formed, or the energy of the reaction is dissipated as rapidly as it is generated. It is to be noted that in small tubes the rate of reaction varied from zero (immeasurable) reaction to complete reaction for a temperature increase of 2 or 3 degrees. Consequently, one may conclude that the concentration and rate of formation of C_3H_8' necessary for explosion is extremely small. Hence the condition for explosive reaction is

$$\frac{d(C_3H_8')}{dt} = X = k(C_3H_8) \quad (5)$$

The variation of k with temperature is given by Arrhenius' equation

$$\frac{d \ln k}{dT} = \frac{-E}{RT^2} \quad (6)$$

E is taken as 35 Cal., the value obtained using Semenov's formula (Equation 2), on the assumption that the reaction is a thermal explosion.

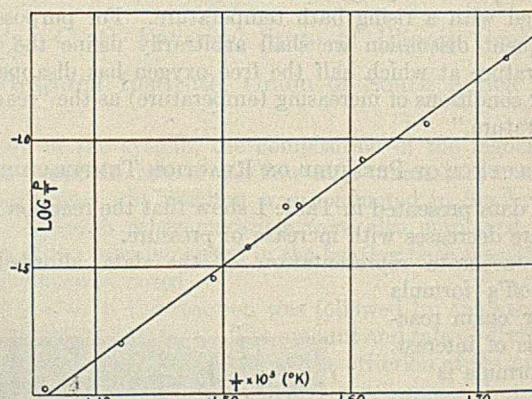


FIGURE 4. LOG P/T vs. RECIPROCAL OF ABSOLUTE TEMPERATURE

According to Figure 9, increasing the initial air content from 5.95 to 65.2 per cent increases the reaction temperature from 337.4° to 362.5° C. As the air content is increased, the propane content decreases from 94.05 to 34.8 per cent. It remains now to calculate whether the temperature increase will augment k to an extent just sufficient to compensate for the decrease in propane concentration. At 337.5° C. or 610.5° K.,

$$X = 0.9405 k_1 P \text{ or } k_1 = 1.064 X/P$$

At 362.5° C. or 635.5° K.,

$$X = 0.348 k_2 P \text{ or } k_2 = 2.873 X/P$$

By integration of Equation 6 we have,

$$\log \frac{k_2}{k_1} = \frac{E}{2.3 \times R} \left(\frac{T_2 - T_1}{T_1 \times T_2} \right)$$

Making the obvious substitutions, we have

$$\log 2.702 = 7655 \times \frac{T_2 - 610.5}{T_2 \times 610.5}$$

$$T_2 = 632.5^\circ \text{K.} = 359.5^\circ \text{C.}$$

The calculated value, although 3° low as compared with the experimental value, is considered satisfactory. Using values obtained for air, it is possible to calculate the values for pure oxygen-propane mixtures. For example, a 26.18 per cent air-propane mixture reacts at 619.5°K. ; at what temperature will a 5.8 per cent oxygen-propane mixture react? The calculated value is 614°K. , compared with an experimentally determined temperature of 615.5°K.

According to this formulation of the influence of concentration, the concentration-temperature curve of Figure 5 should be slightly convex to the temperature axis. Experimental evidence of this was found but, since the experimental conditions were somewhat different from those adopted as standard, they will not be given. This relationship proved to be useful in calculating the reaction temperatures of mixtures of propane containing excess nitrogen and even methane, which acts as an inert gas. The calculated results were in good agreement with those experimentally determined. Thus one mixture containing 49.7 per cent propane, 21 per cent methane, and 29.3 per cent air at a slow rate of gas flow (218 liters per hour) reacted at 353.9°C. The calculated reaction temperature was 353.3°C.

INFLUENCE OF RATE OF GAS FLOW ON REACTION TEMPERATURE

When all experimental conditions are held constant with the exception of rate of gas flow, it is found that the reaction temperature increases with the rate of gas flow. This is clearly shown by the data of Table I. A discussion of this phenomenon is given below.

INFLUENCE OF TUBE DIAMETER ON REACTION TEMPERATURE

The experiments undertaken to show the influence of tube diameter on reaction temperature were conducted somewhat differently from the standard procedure ordinarily used.

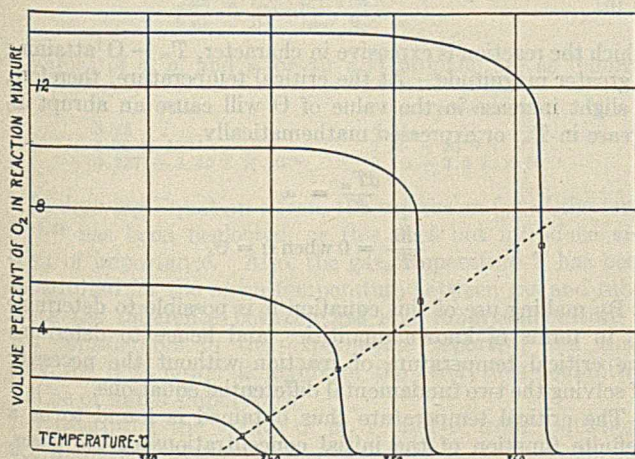


FIGURE 5. EFFECT OF AIR CONCENTRATION ON REACTION TEMPERATURE

An effort was made to obtain constancy in time of heating. To secure this, propane and air were heated separately in tubes of sufficient length to bring the gases up to bath temperature. They were mixed as they passed into the reaction tube. Reaction tubes of identical internal volume were used. Experiments were conducted at two different rates of flow.

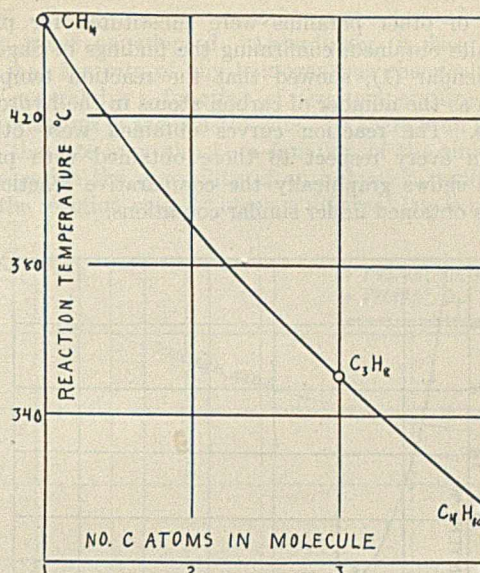


FIGURE 6. PARAFFIN HYDROCARBONS AT 52 ATMOSPHERES PRESSURE

The results are shown in Table II. Of significance is the fact that the narrower the tube, the higher is the reaction temperature.

TABLE II. EFFECT OF TUBE DIAMETER ON REACTION TEMPERATURE

FLOW	(Reaction pressure, 52 atmospheres)					
	INITIAL O ₂ %	TEMP. ° K.	TIME Sec.	TUBE DIAM. (d) Cm.	TUBE LENGTH (X) Cm.	
458	6.25	673.0	0.26	0.080	305	
433	6.15	643.6	0.27	0.159	76	
450	6.1	637.5	0.26	0.318	19	
Av. 447 ± 9						
317	6.1	666.3	0.38	0.080	305	
308	6.0	633.8	0.37	0.159	76	
314	6.1	631.5	0.37	0.318	19	
Av. 313 ± 3						

INFLUENCE OF LENGTH OF TUBE ON REACTION TEMPERATURE

It was naturally assumed that the seat of the reaction resulting in the disappearance of oxygen was located at the exit end of the tube when reaction began. This was proved by providing a reaction tube with lead-offs so that the treated gas mixture could be drawn off after passing through either 376 cm., 193.2 cm., or 101.6 cm. of the reaction tube. It was found that reaction began at 353°C. The analysis of a sample of gas drawn off at this temperature from the 193.2-cm. tap showed that no reaction was occurring before this point. The bath temperature was slowly increased, and when it reached 359°C. , a sample of gas at the 193.2-cm. tap showed reduction of oxygen. Further increase of the bath temperature moved the reaction toward the entrance end of the tube, as shown by the following table:

LENGTH OF TUBE Cm.	REACTION TEMPERATURE ° C.
376	353
193.2	359
101.6	369

Thus we observe that as the length of the tube decreases the reaction temperature increases.

REACTION TEMPERATURES OF OTHER HYDROCARBONS

In order to obtain comparative information on the reaction temperature of other hydrocarbons, experiments were conducted under identical conditions except that equal

volumes of other paraffins were substituted for propane. The results obtained, confirming the findings of Sagulin (4) and Callendar (1), showed that the reaction temperature increases as the number of carbon atoms in the hydrocarbon decreases. The reaction curves obtained were otherwise similar in every respect to those obtained with propane. Figure 6 shows graphically the comparative reaction temperatures obtained under similar conditions.

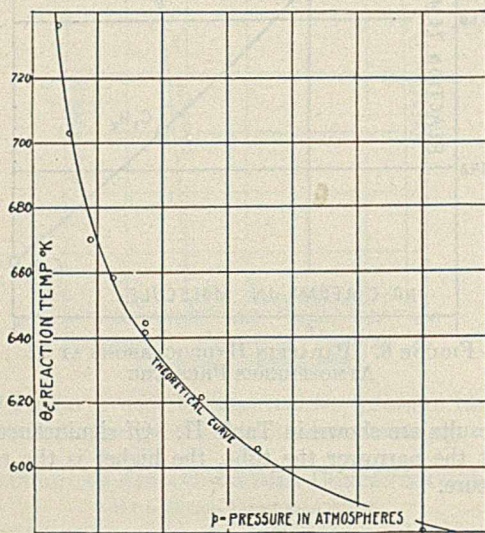


FIGURE 7. RELATION BETWEEN Θ_c AND p
 $v = 443$ $N_H = 0.72$ $D = 0.159$

[A few experiments were performed on unsaturated hydrocarbons (ethylene and propylene). The characteristics of the reaction curves were distinctly different from those of the saturated hydrocarbons and seemed to indicate that the mechanism of reaction of oxygen with saturated hydrocarbons does not involve the initial formation of unsaturated hydrocarbons.

PART II. THEORETICAL ANALYSIS

It was found possible to subject the experimental results which have been discussed to a further theoretical analysis. This analysis, amenable to mathematical formulation, has, in the authors' opinion, been of assistance in advancing our understanding of the reaction mechanism.

In all the experiments reported, the gas mixture enters the reaction tube at a fairly low initial temperature, T_i , but owing to heat transfer from the tube it is rapidly heated to within a few degrees of the bath temperature, Θ . If no reaction takes place and if, consequently, no heat is generated in the gas, it will attain the bath temperature asymptotically. In this simple case, the equation for the gas temperature can be obtained very readily from the differential equation which expresses the rate of heat transfer to the gas. The rise in temperature of the gas has a simple exponential form.

Let us now consider the case where chemical reaction does take place. By adding the rate at which heat is transferred to the gas to the rate at which heat is developed in the gas and equating the result to the rate of temperature rise in the gas, an equation is obtained connecting temperature, concentration, and distance along the tube. In addition, we have the equation which expresses the rate of reaction in terms of the temperature and respective concentrations of the gases constituting the mixture. If these two simultaneous differential equations can be solved, they will yield a precise knowledge of the temperature and the extent of reaction at every point along the length of the tube. Unfortunately, the differential equations descriptive of present concepts of

chain reactions are of such a nature that they cannot be solved by known methods, and we are thus forced to adopt some other means of arriving at the desired result.

If we assume that the reaction tube is sufficiently long, then it will readily be seen that the chemical heat liberated *may*, in due course, raise the temperature of the gas above that of the bath. If this occurs, it is evident that at some point the gas temperature must reach a certain maximum value, T_m , where the rate of heat liberation exactly balances the heat transferred to the bath. After this maximum has been reached, the temperature of the gas will sink steadily until it again approaches the final value Θ asymptotically. By equating the rate of heat liberation to the heat transferred by convection, the value of the maximum temperature, T_m , may be found in terms of Θ and the respective concentrations of the two gases, which at this point are as yet unknown. There is, however, a great difference in the ways in which the maximum temperature T_m can be attained. Either the reaction may proceed smoothly, the gas gradually attaining a maximum temperature only slightly above the bath temperature, or a point may be reached where the reaction takes place suddenly or explosively. Many explosive reactions, and certainly those studied in this investigation, exhibit the latter characteristic. In this case, the maximum gas temperature, T_m , appreciably above Θ , is attained suddenly. Our experiments are in agreement with the assumption that there is a certain critical bath temperature, Θ_c , below which reaction proceeds extremely slowly, $T_m - \Theta$ having a small value, and above

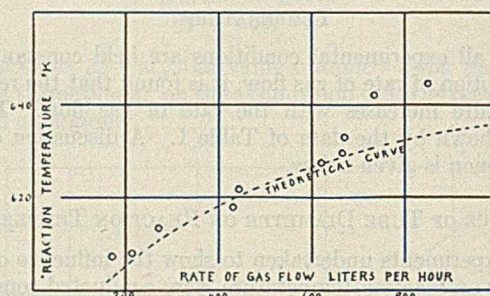


FIGURE 8. RELATION BETWEEN Θ_c AND V
 $p = 52$ $N_H = 0.72$ $D = 0.159$

which the reaction is explosive in character, $T_m - \Theta$ attaining a greater magnitude. At the critical temperature, therefore, a slight increase in the value of Θ will cause an abrupt increase in T_m , or expressed mathematically

$$\frac{dT_m}{d\Theta} = \infty$$

or

$$\frac{d\Theta}{dT_m} = 0 \text{ when } \Theta = \Theta_c$$

By making use of this equation it is possible to determine Θ_c in terms of known quantities, and hence to determine the critical temperature of reaction without the necessity of solving the two fundamental differential equations.

The critical temperature thus obtained is found to be a definite function of the initial concentrations of the gases, the pressure, the dimensions of the reaction tube, and the rate of flow, and it is therefore possible to test the theory with experiments performed when these factors are varied in turn.

The heat transmitted by convection across unit length of tube per second = $\pi D \alpha (\Theta - T)$.

According to definition, the heat developed in one mole of the mixture per second = $-Q dN_0/dt$.

Assuming that the mixture obeys the perfect gas laws, the heat developed per cm. length of tube per second is:

$$-Q \frac{dN_0}{dt} \frac{\pi D^2}{4 \times 22400} \frac{pT_0}{T}$$

The sum of these two heats must be equal to the mass of the gas per cm. multiplied by its specific heat multiplied by its rise in temperature in unit time

$$\text{i. e., } \frac{dT}{dt} = \frac{4\alpha T}{D\rho psT_0} (\Theta - T) - \frac{Q}{22400\rho s} \frac{dN_0}{dt} \quad (1)$$

But velocity $v = dx/dt$

$$\text{or } dt = \frac{dx}{v} \quad (2)$$

$$\text{Also } v = \frac{10VT}{9\pi D^2 p T_0} \quad (3)$$

Furthermore, the coefficient of heat transfer, α , for turbulent flow is given by Gröber (2) as

$$\alpha' = 22.5 Z^{-0.05} d^{-0.16} w^{0.79} p^{0.79} B_T$$

where

$$B_T = \frac{\lambda}{a^{0.79}}$$

α' = kg.-cal. per sq. m. per hour per ° C.

Z = distance in meters

d = diameter in meters

w = velocity in meters per sec.

λ = thermal conductivity in kg.-cal. per meter per hour per ° C. at N. T. P.

a = thermal diffusivity in sq. m. per hour at N. T. P.

From the table of values of B_T presented by Gröber, it is found empirically that

$$B_T = 0.171 \left\{ \frac{T_0}{T} \right\}^{0.59} \text{ for air}$$

If this value of B_T is substituted in the expression for α' , and if our units are employed, it will be found that

$$\alpha = \frac{CV^{0.79} \times 10^{-6}}{D^{1.75}} \left(\frac{T}{T_0} \right)^{0.23} \quad (4)$$

where $C = 3.25$ for air.

The value of C for any other gas is found from the equation

$$\frac{C_{\text{gas}}}{C_{\text{air}}} = \frac{(\lambda)}{(a^{0.79})_{\text{gas}}} \bigg/ \frac{\lambda}{a^{0.79}_{\text{air}}} \quad (5)$$

Values of c , ρ , and s for air and propane are as follows:

	AIR	PROPANE
c	3.25	5.81
ρ	1.29×10^{-3}	2.02×10^{-3}
s	$0.227 + 3.45 T \times 10^{-3}$	$0.10 + 9.2 T \times 10^{-4}$

In deriving Equation 4 from the expression for α' the term $Z^{-0.05}$ has been neglected, as this does not introduce any error of importance. Also, the gas temperature T has been substituted for the mean temperature between gas and tube. Since the difference between gas and tube temperature is not considerable in the experiments reported, and since only the 0.23 power is involved, the error thus committed will be of minor importance.

Substituting the values of dt , v , and α from Equations 2, 3, and 4 in Equation 1,

$$\frac{dT}{dx} = A (\Theta - T) - B \frac{dN_0}{dx} \quad (6)$$

$$\text{where } A = \frac{3.6 \pi C 10^{-6}}{\rho s D^{0.75} V^{0.21}} \left(\frac{T}{T_0} \right)^{0.23} \quad (7)$$

$$\text{and } B = \frac{4.46Q}{\rho s} \times 10^{-5} \quad (8)$$

In Equation 6 there are two independent variables, T and N_0 . Another equation is therefore required to obtain a

solution. To obtain this equation some law of chemical reaction must be adopted. Accordingly, it has been assumed that the rate of any homogeneous chemical reaction will in general be a function of the temperature and the partial pressures of the constituents. If there is an induction period, the rate may also be a function of the time, but in this discussion the possibility of an induction period during which the reaction velocity obeys a different law is neglected.

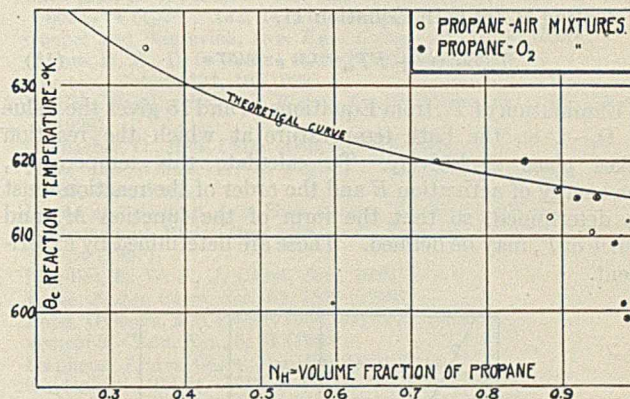


FIGURE 9. RELATION BETWEEN Θ_c AND N_H
 $p = 52 \quad V = 443 \quad D = 0.159$

It follows from the kinetic theory of reaction that the function expressing the reaction velocity may be written as the product of two functions, the first involving only the partial pressure of the constituents and the second involving only the temperature.

Furthermore, the temperature function according to the Arrhenius theory (6) is of the form

$$\left\{ \frac{T}{T_0} \right\}^n e^{-E/RT}$$

no matter what the order of the reaction may be. Hence we may write

$$\frac{dN_0}{dt} = -M \left\{ \frac{T}{T_0} \right\}^n e^{-E/RT} \quad (9)$$

where M may be a function of the partial pressures. By making use of Equation 2, we have

$$\frac{dN_0}{dx} = -\frac{M}{v} \left\{ \frac{T}{T_0} \right\}^n e^{-E/RT} \quad (10)$$

The simultaneous solution of Equations 6 and 10 will define the amount of reaction at all points in the reaction system. Unfortunately, this solution has not been found, but it is possible to determine the reaction temperature and to derive several valuable equations.

At the point in the reaction tube where the gas reaches its maximum temperature, $dT/dx = 0$, and thus it follows from Equations 6 and 10 that

$$T_m = \Theta - \frac{B}{A} \frac{dN_0}{dx} = \Theta + FT_m^{n-1.23} e^{-E/RT_m} \quad (11)$$

where

$$F = \frac{11.15 D^{2.75} p M Q}{C V^{0.79} T_0^{n-1.23}} \quad (12)$$

This equation gives the relation between the maximum gas temperature, T_m , and the tube temperature, Θ . Now it has been postulated that below a certain critical tube temperature, Θ_c , the reaction proceeds smoothly, but that above Θ_c it will take place explosively, with a consequent large increase in the value of T_m . At the critical temperature, therefore, a slight increase in Θ will result in a large increase in T_m . Hence

$$\frac{dT_m}{d\Theta} = \infty$$

or
$$\frac{d\Theta}{dT_m} = 0 \text{ at } \Theta = \Theta_c \quad (13)$$

Applying this to Equation 11,

$$1 = \left\{ \frac{n-1.23}{T_m} + \frac{E}{RT_m^2} \right\} (T_m - \Theta_c) \quad (14)$$

Writing Θ_c for Θ in Equation 11,

$$T_m = \Theta_c + FT_m^{n-1.23} e^{-E/RT_m} \quad (15)$$

Elimination of T_m from Equations 14 and 15 gives the value of Θ_c —i. e., the bath temperature at which the reaction takes place explosively. To calculate this temperature, the energy of activation E and the order of the reaction must be determined, so that the form of the function M , and hence of F , may be defined. These are determined by experiment.

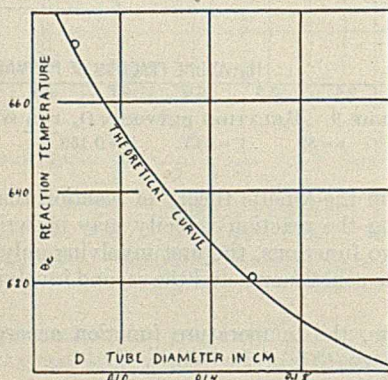


FIGURE 10. RELATION BETWEEN Θ_c AND D
 $p = 25$ $V = 443$ $N_H = 0.72$

It is to be noted that M involves the concentrations of the reacting constituents and, as reaction proceeds, these concentrations will change. However, in most cases and certainly under the conditions of our experiments, it may safely be assumed that the total reaction which has occurred up to the point of explosion is negligible. Therefore, in calculating the value of Θ_c from Equations 14 and 15, it is permissible to employ the initial concentrations of the constituents.

APPLICATION TO OXIDATION OF PROPANE

In accord with the data and discussion of Part I, it was assumed that the rate of reaction was directly proportional to the rate at which active hydrocarbon molecules are formed. If collision is held responsible for activation, then the rate of formation of active hydrocarbon molecules, and hence the rate of reaction, is directly proportional to the total number of collisions between hydrocarbon molecules and all the molecules in the gas mixture (θ). If N_0' , N_H' , and N_i' refer to the actual numbers of molecules per cc. of O_2 , hydrocarbon, and inert gases, respectively, then (θ),

$$\frac{dN_0'}{dt} = -k_0 Z e^{-E/RT}$$

where k_0 is a constant of proportionality and Z is the total number of collisions per second between hydrocarbon molecules and all the molecules of the mixture.

But (θ)

$$Z = k_1 N_H' (N_0' + N_H' + N_i') \left(\frac{T}{T_0} \right)^{1/2}$$

Hence, introducing the volume fractions N_0 , N_H , and N_i , where

$$N_0' = \frac{N_0 L p T_0}{T}, \text{ etc.}$$

L being Loschmidt's number, we have

$$\frac{dN_0}{dt} = k N_H p \left(\frac{T_0}{T} \right)^{1/2} e^{-E/RT} \quad (16)$$

Comparing Equation 16 with Equation 9, it is seen that

$$M = k N_H p \text{ where } k = k_0 k_1 L \quad (17)$$

$$\text{and } n = -1/2 \quad (18)$$

Equations 14 and 15, therefore, assume the forms

$$1 = \left(\frac{E}{RT_m^2} - \frac{1.73}{T_m} \right) (T_m - \Theta_c) \quad (19)$$

$$\text{and } T_m = \Theta_c + G T_m^{-1.73} e^{-E/RT_m} \quad (20)$$

$$\text{where } G = \frac{11.15 k Q T_0^{1.73} D^{2.75} p^2 N_H}{C V^{0.79}} \quad (21)$$

By experiment it was found that E is of the order of 35,000 and hence we can solve Equation 19 for T_m , and find

$$T_m = \Theta_c \left(1 + \frac{R\Theta_c}{E} \right) \quad (22)$$

where the second and higher powers of $R\Theta_c/E$ have been neglected. If this value is substituted for T_m in Equation 20, the following approximate result is reached, since $R\Theta_c/E$ is small:

$$\Theta_c^{3.73} = \frac{H p^2 D^{2.75} N_H}{V^{0.79} C} e^{-E/R\Theta_c} \quad (23)$$

$$\text{where } H = \frac{11.15 k Q T_0^{1.73} E e}{R} \quad (24)$$

Equation 23 may also be written

$$\frac{0.4343E}{R\Theta_c} = \log H + 2 \log p + 2.75 \log D - 0.79 \log V + \log \frac{N_H}{C} - 3.73 \log \Theta_c \quad (25)$$

Now from the experimental reaction temperature *vs.* pressure data, the following results are obtained:

$$\text{If } \begin{aligned} D &= 0.159 \\ V &= 443 \\ \frac{N_H}{C} &= 0.1415 \end{aligned}$$

$$\text{then } \Theta_c = 713 \text{ when } p = 10 \\ \Theta_c = 590 \text{ when } p = 100$$

From these results the numerical values of E and H were calculated to be

$$\begin{aligned} E &= 35,700 \\ H &= 4.47 \times 10^{24} \end{aligned}$$

The agreement of the value of the energy of activation, E , by this method of computation with that reported in Part I is significant. All the variables in Equation 25 are now known, and it is possible to calculate Θ_c for any set of conditions. Such calculations were carried out. The results are shown in the form of curves in Figures 7 to 10. The experimental data given in Table I, Part I, are plotted on the figures for comparison. The agreement is seen to be excellent.

In developing the theory, it was assumed that the reaction tube is of sufficient length so that in the absence of reaction the gas mixture would be heated to within 1 or 2 degrees of the bath temperature. If the tube is shorter, then it is to be expected that the bath temperature required for reaction to occur will be increased. This is confirmed by data shown in Part I. It must be borne in mind, therefore, that the equations developed are of strict application only when the tube

is of "infinite length"—i. e., about 300 cm. for rates of flow comparable with those recorded here.

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SYMBOLS

- $T_0 = 273^\circ \text{K.}$
 $T =$ temperature of gas mixture, $^\circ \text{K.}$
 $T_m =$ maximum temperature of gas mixture, $^\circ \text{K.}$
 $T_i =$ initial temperature of gas mixture, $^\circ \text{K.}$
 $\Theta =$ temperature of tube or bath, $^\circ \text{K.}$
 $\Theta_c =$ critical temperature of tube or bath, $^\circ \text{K.}$
 $N_0 =$ fraction of mole of first gas (O_2) in one mole of mixture (= $100 \times$ volume per cent)
 $N_H =$ fraction of mole of second gas (hydrocarbon) in one mole of mixture (= $100 \times$ volume per cent)
 $N_i =$ fraction of mole of third gas (inert—e. g., nitrogen) in one mole of mixture (= $100 \times$ volume per cent)
 $p =$ pressure of mixture in atmospheres
 $x =$ distance in cm. along tube measured from point of entrance of gas mixture
 $X =$ total length of tube in cm.
 $D =$ diameter of tube in cm.
 $V =$ flow of mixture in liters per hour measured at N. T. P.
 $Q =$ number of calories set free by reaction of one mole of first gas (oxygen)
 $R =$ gas constant
 $E =$ critical energy of activation
 $t =$ time in seconds
 $v =$ velocity of mixture in cm. per sec.
 $s =$ specific heat of mixture at constant pressure in cal. per gram
 $\rho =$ density of mixture at N. T. P., grams per cc.

$\alpha =$ constant of heat transfer by convection in calories per sq. cm. per sec. per $^\circ \text{C.}$

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Changes in Fats during Frying

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WITHIN recent years, the preparation of various foods, such as doughnuts, crullers, sea foods, etc., by means of frying in deep fat has become a standard method in nearly all bakeries, hotels, and restaurants. This method has become particularly attractive because of the widespread use of electrically heated frying equipment, which lends itself readily to automatic temperature control, economy, and ease of manipulation—three important considerations for a process of this type.

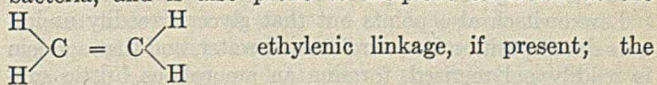
The practice of discarding used fat periodically has been followed by bakers and chefs in order to assure a product of the most pleasing taste and odor. With equipment formerly used, this waste was not particularly costly, as the usual gas-heated fry kettle for doughnuts, for example, contained but 10 to 15 kg. of fat, worth not more than four to five dollars. Discarding this every week or so was, therefore, of no particular concern.

However, with the advent of modern equipment in which much larger quantities—130 to 180 kg.—of fats were used, this waste was of some significance, particularly as it was found that in order to obtain food satisfactory in taste and odor it was necessary to discard and replace with fresh fat every 15 to 20 days. The necessity for discarding used fat is the development of some constituent which imparts an objectionable taste to food prepared therein. Acid constituents, oleic, linoleic, etc., were suspected and shown to be

present. How they were formed was not known. A survey of the literature did not yield worthwhile data or information applicable to the problem. A study was therefore made of the behavior of edible fats and oils when used as frying media.

HISTORICAL DATA

It has long been known that edible fats, especially when exposed to atmospheric conditions, undergo some chemical and physical changes. Hilditch (4) points out that fatty matter is an excellent medium for the growth of molds and bacteria, and is also prone to incipient oxidation at the



question of rancidity embraces a number of phenomena due to several distinct causes; and the main causes of rancidity may be assigned to two divisions, atmospheric oxidation and enzyme action (hydrolytic or otherwise). Indications are that atmospheric oxidation occurs at the unsaturated linkage, neither the glyceryl radical nor free carboxylic acid residue of a fatty acid being directly concerned. The progress of oxidation of heated oils is stimulated by the presence of free fatty acid and still more by the oxidation products or certain of them, whereas it is retarded by the presence of water vapor. This is also true for oxidation at ordinary temperatures. Initial products of oxidation which are

TABLE I. OVEN TEST AT 80 HOURS WITH AIR BUT NO LIGHT

FAT	TEMP. ° C.	ACID FORMED		COLOR	REMARKS
		%	Min. Sec.		
Animal	176.5	0.7	1 3	Faint brown	Considerable amount of dark brown gum formed at edge of fat and container
	232	1.4	1 15	Light brown	
Vegetable oil	176.5	0.8	1 12	Very light brown	Large amount of gum formed
	232	1.3	2 5	Light brown	
Hydrogenated vegetable fat 1	176.5	0.8	1 2	Faint brown	Considerable amount of gum formed
	232	1.1	1 25	Very light brown	
Hydrogenated vegetable fat 2	176.5	0.5	1 6	Faint brown	Small amount of gum formed
	232	1.4	1 20	Very light brown	
Hydrogenated vegetable fat 3	176.5	0.5	1 7	Faint brown	Small amount of gum formed
	232	1.4	1 15	Light brown	

TABLE II. DATA OBTAINED WITH NICKEL-PLATED COPPER KETTLE

FAT	TEMPERATURE		INPUT TO UNIT	ACID FORMED	VISCOSITY	COLOR	REMARKS
	Fat ° C.	Sheath ° C.					
Animal	176.5	190.5	40	1.0	1 25	Light brown	Considerable quantity of gum or wax formed at junction of surface of fat with container
	176.5	232	100	1.0	1 50	Light brown	
	176.5	357	400	1.3	2 10	Dark brown	
Vegetable oil	176.5	190.5	40	1.4	2 55	Dark brown	
	176.5	232	100	0.4	More than 5 min.	Dark brown	
	176.5	357	400	1.4	5 min.	Very dark brown	
Hydrogenated vegetable fat 1	176.5	190.5	40	...	1 55	Light brown	
	176.5	232	100	0.9	3 40	Light brown	
	176.5	357	400	0.9	4 10	Darker brown	
Hydrogenated vegetable fat 2	176.5	190.5	40	0.8	1 12	Light brown	
	176.5	232	100	1.2	2 5	Dark brown	
	176.5	357	400	1.7	1 42	Very dark brown	
Hydrogenated vegetable fat 3	176.5	190.5	40	1.2	1 55	Light brown	
	176.5	232	100	1.2	2 55	Light brown	
	176.5	357	400	1.4	2 30	Dark brown	

probably produced by direct addition of oxygen at an ethylenic linkage are broken up in the presence of moisture with scission of the aliphatic carbon chain, giving rise to the aldehydic derivatives of lower molecular weight which are characteristic products of rancidity.

Hilditch further points out that, when drying, oils are heated to about 260° to 270° C., air being excluded; the iodine number commences to fall rapidly—i. e., a certain number of the ethylenic linkage become saturated not by addition of hydrogen or oxygen, but by some kind of polymerization effect. Diminishing iodine number denotes diminishing unsaturation. Some acrolein and other volatile products of decomposition come away, but in the main the essential chemical structure remains unaltered.

Hilditch also states that in pronounced cases of rancidity, short-chain acids, such as butyric, valeric, or capronic, make their appearance; also, aldehydic or ketonic compounds of a more volatile type are present from the earliest stages of rancidity.

Lewkowitsch (5) states that cottonseed oil, for example, contains glycerol and a mixture of acids which belong in most cases to the $C_nH_{2n}O_n$ series and can be more or less readily hydrolyzed by water. He further states that fatty acids are quite stable and are oxidized with difficulty. However, because of the presence of the carboxyl group, they readily undergo a variety of double decomposition.

Lewkowitsch also points out that glycerol readily undergoes decomposition into acrolein and water, and that acrolein is readily polymerized, forming an amorphous brittle substance named disacryl.

Abbott (1) states that he had noticed about 1920 that fats used in fry kettles attacked the steel sheath of electric heating units after a very short time in service.

MacLeod and Mason (6) state that fats hardened by hydrogenation have little tendency to become rancid by hydrolysis and may be heated to high temperatures without decomposition. They point out that in deep-fat frying there is danger of decomposition unless care is exercised to prevent overheating. The main reactions are hydrolysis and dehydration, the products being acrolein and fatty acid. As the fat decomposes, it smokes, the smoke being

filled with acrolein which "burns" the eyes and is unpleasant to smell. Once the fat has commenced to decompose, the acid formed hastens further decomposition.

Blunt and Feeney (2) give the order of decomposition of common fats as follows:

FATS	APPROX. TEMP. OF DECOMPOSITION ° C.
Cottonseed and corn oils	222-232
Hydrogenated fats	219-232
Leaf lard	214-221
Butter	208
Much used lard	190
Olive oil	167-175
Peanut oil	150-160

PERFORMED EXPERIMENTS

Two sets of experiments were made, one on a laboratory scale on the fats and oils alone, the other in a bakery under actual bakery conditions. The object of the laboratory experiments was threefold:

1. The effect on fat when kept at a constant temperature with no local heating.

This was accomplished by placing a glass beaker of fat in an electrically heated oven with an automatic control which maintained the oven temperature within $\pm 2^\circ$ C. Two tests were made, one maintaining a fat temperature of 176.5° C. and the other at 232° C.

2. The effect on fat when kept at a constant temperature, but with varied degrees of local heating.

This was accomplished by equipping a small nickel-plated copper fry kettle (approximately 1 kg. capacity) with an electric immersion heater unit having an exposed area of 25.8 sq. cm. and varying the impressed voltage while the fat temperature was held constant. Three separate tests were made, as follows:

(a) The voltage was regulated so as to dissipate 40 watts, giving a unit temperature of 190.5° C., which was just enough to maintain a fat temperature of 176.5° C. with the current on continuously.

(b) This test was a duplicate of test a except that the voltage was adjusted to give 100 watts. The fat temperature was maintained at 176.5° C. ($\pm 2^\circ$) by means of a thermostatic control. The resulting maximum unit temperature was 232° C.

(c) This test was a duplicate of test b except that the wattage was 400 and the maximum unit temperature was 357° C.

3. The effect on fat when kept at a temperature of 176.5 ± 5° C. and evaporating water added to it continuously.

This was accomplished by introducing continuously, by gravity feed, Chicago city tap water under the surface of the fat contained in a small kettle heated by means of electric immersion heaters.

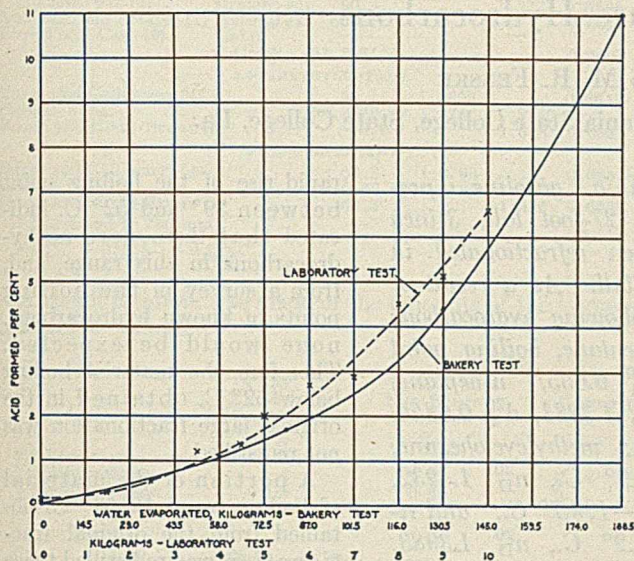


FIGURE 1. RELATION OF ACID FORMED TO WATER EVAPORATED

Analyses made on the fats to check decomposition were for acidity and viscosity. Acidity was determined by titration with standard alkali, using phenolphthalein indicator as outlined by Griffin (3). Calculations were made to oleic acid. Viscosity measurements were made with a Saybolt viscometer at 210° F.

FATS USED. Five commercial frying fats or oils in all were used, one animal fat, one vegetable oil, and three hydrogenated vegetable fats, having the following characteristics:

FAT	ACID %	VISCOSITY Sec.	COLOR
Animal	Trace	54	White
Vegetable oil	Trace	50	Pale yellow
Vegetable 1	Trace	52	White
Vegetable 2	Trace	60	White
Vegetable 3	Trace	56	White

EXPERIMENTAL DATA. The results in Table I show that only a small percentage of acid was formed in the fats during the oven test. There was a noticeable increase in viscosity in each fat, a slight darkening in color, and a gummy formation at the ring of contact of the exposed fat surface with the container.

TABLE III. WATER EVAPORATION DATA

WATER EVAPORATED Grams	ACID %	COLOR	REMARKS
000	0.11		
500	0.21	Slightly brown	
1500	0.29		
2500	0.62		
3500	1.20		
4500	1.44		
5000	2.00		Fat starting to foam and release volatile products which smart the eyes
6000	2.70		
7000	2.90		
8000	4.50		
9000	5.10		
10000	6.70		

The results of the reported tests in Table II show the formation of but little free acid, even with high unit temperature. The tendency is for an increase in acid content with increasing sheath temperature. In general, this also applies

to viscosity. The vegetable oil became very viscous, particularly with the higher sheath temperatures.

The results in Table III show that free acid was formed quite rapidly with evaporation of water. A curve using these data is plotted in Figure 1.

TABLE IV. BAKERY DATA

Kettle surface dimensions, cm. 61 X 86
 Fat, kg. 100
 Source of heat, five electric immersion units 3 kw. each
 Sheath temperature, ° C. 271
 Fat temperature, ° C. 176.5 to 199 (automatic control to ±3° C.)
 Food fried Doughnuts, 100 doz. per day
 Water evaporated from doughnuts, kg. 7.26 per 100 doz.
 Fat used Hydrogenated vegetable
 Daily make-up of fat, kg. 9.08

DOUGHNUTS FRIED Doz.	COLOR OF FAT	ACID AS OLEIC %	SAYBOLT VISCOSITY AT 210° F. Sec.	REMARKS
None	Lard white	Trace	52	Fresh fat
600	Light chocolate	Not detd.	54	
800	Chocolate	1.1	57	
1100	Chocolate	1.7	57	
1800	Chocolate	4.4	59	Fat smoking slightly; foaming slightly; objectionable flavor in food
2500	Chocolate	11.0	57	Fat smoking badly; much foaming; very poor flavor in food

The data of Table IV show a marked increase in acid formed. The viscosity increases somewhat to a maximum and then decreases. A curve using water evaporated and acid formed is shown in Figure 1.

CONCLUSIONS

The data indicate that little apparent breaking down occurs in the fats in question with heat alone under test conditions. There is a slight formation of acid, a noticeable increase in viscosity, particularly at the higher temperatures, and some gum formation presumably due to polymerization.

The data further show that the breaking down of fat involving the formation of acid is a direct result of a reaction with water at elevated temperatures. Both the experimental and bakery data show that up to approximately 0.75 per cent acid the rate of acid formation is comparatively small. Above that, the rate is considerably greater, presumably because of the acid acting as a catalyst to accelerate the reaction, as pointed out by Hilditch and others.

The breaking down of the fat is no doubt mainly due to hydrolysis to give glycerol and acid, the glycerol so formed undergoing further decomposition into acrolein and water, thus



The data also indicate that the per cent of free acid present in a used fat is a fairly reliable measure of the extent of its breaking down and of its objectionable quality of imparting a poor flavor to food fried therein. The baking data show objectionable flavor at about 4.4 per cent acid. Subsequent experiments, both bakery and laboratory, showed that above about 2.0 per cent acid (as oleic) an objectionable flavor could be noticed.

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Composition of Straight-Run Pennsylvania Gasoline

III. Isolation of Pure Hydrocarbons

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IN PREVIOUS articles (6, 7) the fractionation of Pennsylvania straight-run gasoline (end point 510° F. or 265.6° C.) in a 27-foot tall, 3-inch diameter packed column has been discussed. As a result of this fractionation, the gasoline was divided into 261 fractions, each of narrow boiling range. In order to identify the hydrocarbons in the gasoline and to determine their amounts and knock ratings, the fractions were redistilled. Since the original fractionation gave such an excellent separation, the refractionation should yield hydrocarbons in a greater state of purity than has heretofore been obtained from petroleum by distillation alone. No attempt was made to obtain the ultimate purity possible.

FRACTIONATING COLUMNS

Two columns were used for the refractionations. The first, column W, was made of brass pipe, 3/4 inch in diameter and 8.5 feet tall. The pipe was packed with 6 × 6 mm. brass rings and was insulated by magnesia pipe covering. The still was made of brass and was electrically heated. The column was operated with a total condenser and a variable take-off. Maximum reflux was attained by keeping the column just below the flooding point. The second column has been described previously (6). It was 52 feet tall and 3/4 inch in diameter, and was packed with alternate layers of glass rings and six-turn wire helices. It was operated at a 30-40 to 1 reflux ratio and a take-off rate of about 40 to 50 cc. per hour. While the 52-foot column was being constructed the refractionation was started in column W, and fractions up to 95° C.¹ were fractionated; from then on, the 52-foot column was used. The boiling points were taken in the column by means of a Bureau of Standards calibrated copper-copel thermocouple, and were checked in a Cottrell boiling-point apparatus. Refractive indices were taken on an Abbé refractometer held at 20° C. by means of a constant-temperature bath. Densities were taken at 20° C. in calibrated pycnometers.

ISOMERIC HEXANES

In the original fractionation a large amount of material was obtained at 34-36° C. The boiling point then rose very rapidly (13° in 250 cc.) to 52° and then somewhat more slowly to 56.8° C. From then on, it rose gradually to 70° C. Previous investigators (2) had established the material at 34-36° C. as a mixture of *n*-pentane and isopentane. The

¹ Since the large fractionation required several days, the barometer varied from 734-43 mm. Unless otherwise stated, the boiling points will be given in ° C. and at pressures between 734-43 mm.

*Straight-run Pennsylvania gasoline, previously fractionated in a 27-foot tall, 3-inch diameter column, has been refractionated in columns 8.5 and 52 feet tall. As a result of this refractionation, the following hydrocarbons were isolated: 2-methylpentane, boiling point 60.3° C., n_D^{20} 1.3722, d_4^{20} 0.655; *n*-heptane, boiling point, 98.4° C., n_D^{20} 1.3881, d_4^{20} 0.6844, freezing point, -91.2° C.; methylcyclohexane, boiling point 100.8-100.9° C., n_D^{20} 1.4232, d_4^{20} 0.7688, freezing point, -126.7° C.; and *n*-octane, boiling point 125.2° C., n_D^{20} 1.3983. *n*-Heptane and methylcyclohexane were not found to form a constant-boiling mixture.*

rapid rise of the boiling point between 39° and 52° C. indicated that there were no hydrocarbons in this range, and, from a survey of the boiling points of known hydrocarbons, none would be expected. Therefore the material boiling below 52° C. obtained in the original large fractionation was not redistilled.

A portion of the material of boiling range 52-66° C. obtained from the original fractionation was redistilled twice in column W with the following results:

B. P. (731-735 mm.) ° C.	n_D^{15}	n_D^{20}
20% distilled below 52
6% distilled from 57-58	1.3752-1.3760
46% distilled from 59-59.5	1.3744-1.3749	1.3721-1.3726
10% distilled from 61-62	1.3777-1.3780
15% distilled above 64

The major part of the material boiled at 59-59.5° C. and was 2-methylpentane. Small amounts of 2,3-dimethylbutane (57-58° C.) and 3-methylpentane (61-62° C.) were also found. No evidence was obtained of 2,2-dimethylbutane, boiling point 49.7° C. The amounts of 2,3-dimethylbutane and 3-methylpentane obtained were too small for further efficient fractionation. Since, however, there was a definite flat spot at each point, and since the boiling point and refractive index checked fairly well (considering the small amounts of the two hydrocarbons present and the subsequent futility of continuing the fractionation), there was no doubt as to the presence of small amounts of these two hydrocarbons in Pennsylvania gasoline.

The large amount of 2-methylpentane (59.0-59.5° C.) was remarkably pure, though it was fractionated but twice, as judged by boiling point, density, and refractive index. Density and refractive index are particularly good criteria of purity in this case since the hydrocarbons boiling 2° lower and 3° C. higher have considerably higher densities and refractive indices than 2-methylpentane, making a small amount of these hydrocarbons in the 2-methylpentane very easy to detect. As a further test, however, the entire fraction of 2-methylpentane was refractionated in column W. The first and last cuts had a slightly higher refractive index (n_D^{15} = 1.3746-1.3749) than pure 2-methylpentane, but the intermediate fractions were the pure hydrocarbon with a refractive index (n_D^{15}) of 1.3744-1.3746. Table I compares the 2-methylpentane results obtained above with those of other petroleum investigations and with the data compiled by Edgar and Calingaert (4) from a survey of the literature. For purposes of comparison, the data for 2,3-dimethylbutane and 3-methylpentane are given also.

TABLE I. COMPARISON OF PROPERTIES OF ISOMERIC HEXANES

REFERENCE	SOURCE	B. P. (760 MM.)	n_D^{20}	n_D^{25}	SP. GR.
° C.					
2-METHYLPENTANE					
Edgar and Calingaert (4)	Pa.	60.2	1.37445	0.654 ^b
Present work	straight-run	60.3 ^a	1.3745	1.3722	0.655 ^b
Bruun and Hicks-Bruun (3)	Okla.	60.4	1.373	0.658 ^b
Anderson and Erskine (1)	straight-run	60-61	0.661 ^c
Brown and Carr (2)	Cabin	61.1-61.2	0.660 ^d
2,3-DIMETHYLBUTANE					
Edgar and Calingaert (4)	58.1	1.3809	0.6618 ^b
Present work	58.3-59.0 ^a	1.3780	1.3740
Bruun and Hicks-Bruun (3)	58.0	1.378	0.668 ^b
3-METHYLPENTANE					
Edgar and Calingaert (4)	63.3	1.3793	0.6647 ^b
Present work	62.5-63.1 ^a	1.3780	1.3760
Bruun and Hicks-Bruun (3)	63.3	1.376	0.665 ^b

^a Corrected to 760 mm.

^b d_4^{20} . ^c $d_{15}^{15.5}$. ^d $d_{15}^{20.5}$.

A rough estimate was made of the amounts of the isomeric hexanes as follows:

	IN 510° F. END-POINT GASOLINE %	IN 400° F. END-POINT GASOLINE %	IN CRUDE OIL %
2,2-Dimethylbutane	Absent
2-Methylpentane	1.7	2.2	0.65
3-Methylpentane	0.5	0.65	0.2
2,3-Dimethylbutane	0.3	0.4	0.1

n-HEXANE FRACTION

The refractionation was continued with the material from the large fractionation of boiling range 65.7-71.8° C. This material was distilled but once, since it was realized that, with the gasoline becoming more complex and only the comparatively short column W available, a general idea of the constitution of the gasoline was all that could be expected. On redistillation of this fraction 75 per cent boiled from 66° to 69° C., and its refractive index (n_D^{20}) varied from 1.3820 to 1.3890. Pure *n*-hexane (11) has a boiling point of 68.7° C. and a refractive index (n_D^{20}) of 1.3751.

The high refractive index was proved to be due to the presence of benzene and a naphthene. The benzene was identified by a melting point and a mixed melting point of the dinitro derivative. Even after the removal of the benzene, however, the refractive index was too high for *n*-hexane, or any other paraffin boiling in this vicinity. The naphthene was probably methylcyclopentane (although ethylcyclobutane has practically the same physical properties), which boils at 72° C. and has a refractive index (n_D^{20}) of 1.4103. In order to prove that the high refractive index after nitration was not due to incomplete removal of the benzene, a sample containing only *n*-hexane and benzene was nitrated. It was found that all the benzene could be removed and the refractive index of the pure *n*-hexane obtained. Nitration of a fraction of 67.5° C. boiling point yielded practically pure *n*-hexane, but a fraction of 68.3° C. boiling point still had a high refractive index after nitration.

FRACTIONS NITRATED		n_D^{20}	After nitration and distillation	After renitration and distillation
B. P. (736 MM.) ° C.	n_D^{20}			
67.5	1.3820	1.3761	1.3761	1.3760
68.3	1.3866			

A quantitative estimate of the amount of the fraction with boiling point 66-69° C. follows:

IN 510° F. END-POINT GASOLINE %	IN 400° F. END-POINT GASOLINE %	IN CRUDE OIL %
3.1	4.0	1.2

Estimating 17 per cent of this fraction to be benzene and a naphthene:

	2.6	3.3	1.0
<i>n</i> -Hexane	0.5	0.65	0.2
Benzene and naphthene			

With the 52-foot column, it should be possible with the 3° C. difference in boiling point to separate *n*-hexane from methylcyclopentane, since in test runs the column has separated the isomers of diisobutylene boiling 3.3° C. apart. The *n*-hexane will, however, according to the literature, contain benzene because of a constant-boiling mixture. Young (14) gives a benzene-*n*-hexane constant-boiling mixture containing 19 per cent by weight of benzene. The data above show that a fraction containing considerable benzene has yielded a distillate containing *n*-hexane and from 4 to 8 per cent by volume of benzene (5 to 10 per cent by weight).

In this connection, the following experiment is cited: A 60-70° C. fraction of petroleum from the Vikings Products Company was distilled in the 52-foot column. *n*-Hexane was obtained with a boiling point of 68.9-69.3° C. (760 mm.) and a refractive index (n_D^{20}) of 1.3780-1.3785. The residue contained considerable benzene. The best cuts of the distillate, on refractionation through the 52-foot column, came off practically unchanged with a boiling point of 69.1° C. (760 mm.) and a refractive index (n_D^{20}) of 1.3780. On extraction with a nitrating mixture, the refractive index (n_D^{20}) of this distillate dropped to 1.3751. The distillate contained about 2.5 per cent by volume of benzene. The above data are contradictory, for, while the product appears to be a constant-boiling mixture, it does not show a minimum boiling point. There is something abnormal in the vapor pressure relations of these two liquids. However, Young's statement is undoubtedly incorrect and the constant-boiling mixture, if any, contains only about 2.5 to 4.0 per cent by volume of benzene. A further study of the separation of *n*-hexane and benzene and of their vapor pressure relations is being made and will be described later.

REFRACTIONATION OF MATERIAL WITH BOILING RANGE 71.8-95° C.

The refractionation was continued on the material, boiling between 71.8-95.0° C., obtained in the original fractionation. For the reasons given in the case of the *n*-hexane fraction, the material was distilled but once in column W. The boiling point rose very rapidly from 70° to 77°, then from 77° to 81° quite slowly. It then rose rapidly to 87° but from this temperature to 91° its rise was very gradual. From 91° to 96° the boiling point again rose very rapidly. The gasoline with the boiling range 71.8-95.0° C. is thus concentrated in two narrow-boiling fractions, one from 77-81° (734-736 mm.) the other from 87-91° C. (734-736 mm.).

The first fraction, 77-81°, is a mixture of benzene, a naphthene, and some paraffins. The presence of benzene and a naphthene was proved exactly as in the case of the *n*-hexane fraction. The naphthene is probably cyclohexane with boiling point of 81.4° C. and n_D^{20} of 1.4273. The second fraction, 87-91°, was apparently mainly a mixture of the isomeric heptanes. Since the refractive index was higher than the isomeric heptanes alone, a naphthene must have been present, as no aromatic hydrocarbons boil in this vicinity, and a nitration did not lower the refractive index of the fraction. The dimethylcyclopentanes boil from 88-95° C. (760 mm.). An estimation of the amounts of these two fractions follows:

FRACTIONS ° C.	IN 510° F. END-POINT GASOLINE %	IN 400° F. END-POINT GASOLINE %	IN CRUDE OIL %
77-81	1.0	1.3	0.4
87-91	3.5	4.5	1.4

From this point on, the 52-foot column was used for the redistillation, the fractions boiling between 96–126° C. from the original distillation being charged in at the proper boiling point. The results were so much better than in the distillations with column W that there was almost no comparison. The first distillate boiled below 96° and then the boiling point rose to 97° (739 mm.) and remained practically constant.

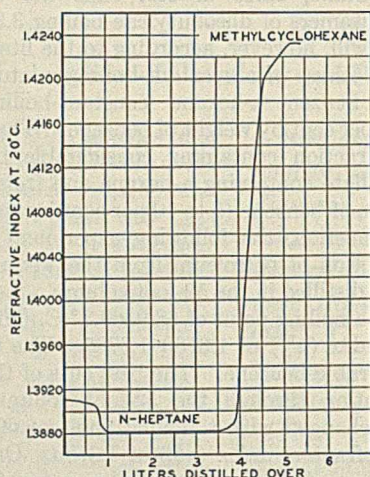


FIGURE 1. REFRACTIONATION OF MATERIAL BOILING BETWEEN 96.2° AND 99.1° C.

The material was *n*-heptane of high purity. A comparison of its physical constants with those of the known values for the pure hydrocarbon and those of other petroleum distillations follows:

REFERENCE	SOURCE	B. P. (760 MM.) ° C.	n_D^{20}	SP. GR.	F. P. ° C.
Edgar (5)	Jeffrey pine oil	98.4	1.38777	0.6836 ^a	-90.5
Shepherd (11)	Chlorosulfonic acid on gasoline	98.38	1.38775	0.68378 ^a	-90.67
Present work	Pa. straight-run gasoline	98.4	1.3883	0.6858 ^a
Anderson and Erskine (1)	Natural gasoline	98.2-99.3	0.7117 ^b
Brown and Carr (2)	Cabin Creek gasoline	98.6-98.7	1.4068	0.689 ^c
			^a d_4^{20} .	^b $d_{15.5}^{15.5}$.	^c d_{20}^{20} .

As the refractive index of the hydrocarbons 3° above and 7° below *n*-heptane is higher than the value for *n*-heptane, it is an excellent means of checking the purity, particularly since there is a rapid rise of boiling point from 91° to 97° C., and as the ability of the 52-foot column to fractionate substances 3° apart has been proved. The refractive index of the *n*-heptane was unchanged by treating with concentrated sulfuric acid and with a nitrating mixture, but fuming nitric acid lowered the refractive index (n_D^{20}) to 1.3880. There can be no doubt that *n*-heptane of high purity has been isolated from petroleum. Assuming the impurity to be methylcyclohexane, and calculating the percentage impurity from the refractive indices and densities, assuming linear relationships, the *n*-heptane is about 97–98 per cent pure.

FRACTIONATION OF AN 80–108° C. FRACTION OF STRAIGHT-RUN PENNSYLVANIA GASOLINE

The purity of the *n*-heptane obtained from the 510° F. end-point gasoline is limited by the fact that there is insufficient *n*-heptane to give the most efficient fractionation and to enable a refractionation to be made. The fractionation of a narrow-boiling cut should give *n*-heptane of much greater purity. With this object in view, 33.3 liters of a cut (boiling range 80–108° C.) from straight-run Pennsylvania gasoline obtained through the courtesy of the Kendall Refining Company was

fractionated in the 27-foot tall, 3-inch diameter column. A reflux ratio of about 25 to 1 was maintained.

The fractionation yielded 9315 cc. with a boiling range of 96.2–99.1° C. (729–731 mm.). This corresponds to 28 per cent by volume of the charge. The refractive index of the first part of the fraction (boiling range 96.2–99.1° C.) was as low as 1.3920 at 20° C., but the last part had a refractive index of 1.4179. These refractive indices are much higher than for pure *n*-heptane. Treatment with concentrated sulfuric acid and a nitrating mixture failed to change the refractive index, so that the amount of toluene present must have been very small. Further refractionation showed that the high refractive index was due to methylcyclohexane.

Seven thousand six hundred cubic centimeters of the above fraction were refractionated in the 52-foot column using a reflux ratio of 30–40 to 1; 6637 cc. of distillate were obtained. Table II gives a summary of the refractionation. A large amount of *n*-heptane was obtained and also a substance with physical properties similar to methylcyclohexane. Neither substance was pure, however.

TABLE II. REFRACTIONATION OF NARROW-BOILING CUT (96.2–99.1° C.) FROM 27-FOOT COLUMN

FRACTION	B. P. (735-737 MM.)	n_D^{20} ^a	AMOUNT	TOTAL
			Cc.	Cc.
Forerunnings	60	60
1	93.8-93.9	1.3910	215	275
2	93.1-96.0	1.3898	325	600
3	96.0-96.2	1.3910	295	895
4	96.2-96.8	1.3887	625	1520
5	97.0	1.3879	210	1730
6	1.3881	485	2215
7	1.3884	470	2685
8	97.1	1.3886	150	2835
9	1.3900	645	3480
10	97.2	1.3910	310	3790
11	1.3920-1.3950	240	4030
12	1.3950-1.4000	610	4640
13	1.4000-1.4050	165	4805
14	1.4050-1.4100	120	4925
15	1.4100-1.4200	657	5582
16	1.4200-1.4225	55	5637
Residue	99.7	1.4245	450	6087
Residue	1.4230	550	6637

^a Refractive index (n_D^{20}): *n*-heptane, 1.3878; methylcyclohexane, 1.4235

In order to purify the hydrocarbons, the material was again carefully refractionated in the 52-foot column using a reflux ratio of 30–50 to 1. Table III gives a summary of the refractionation. A large amount of very pure *n*-heptane was obtained. Some pure methylcyclohexane was obtained also but unfortunately the greater part of it (400 cc.) could not be distilled through the column as it constituted the residue in the still. Figure 1 shows how well the column separated the two hydrocarbons despite the fact that they boil only 2.4° C. apart.

TABLE III. REFRACTIONATION OF MATERIAL GIVEN IN TABLE II

FRACTION	B. P. (735-737 MM.) ° C.	n_D^{20}	AMOUNT	TOTAL
			Cc.	Cc.
1 Forerunnings	1.3918	60	60
2	93.8-93.9	1.3910	215	275
3	93.1-96.0	1.3905	515	790
4	95.8-97.0	1.3885	120	910
5	96.8-96.9	1.3882	120	1030
6	97.0	1.3881	195	1225
7	97.0-97.1	1.3881	2150	3375
8	97.1-97.15	1.3882	80	3455
9	97.15-97.2	1.3887	425	3880
10	97.15-97.90	1.3951	195	4075
11	97.9-98.6	1.4060	260	4335
12	98.6-99.35	1.4160	188	4523
13	99.35-99.45	1.4200	245	4768
14	99.45-99.55	1.4214	305	5073
15	99.55	1.4229	90	5163
16	99.55	1.4231	65	5228
17	99.55	1.4232	180	5408
18	Residue	1.4268	400	5808

The physical properties of the *n*-heptane obtained are as follows:

B. P. (760 MM.) ° C.	n_D^{20}	d_4^{20}	F. P. ° C.
98.4	1.388	0.6844	-91.2

Assuming the impurity in the *n*-heptane to be methylcyclohexane, and the refractive index and density to vary linearly between the two substances, the percentage of methylcyclohexane in the *n*-heptane can be calculated. It can also be calculated from the freezing point, using the value of 33.78 calories per gram for the heat of fusion of *n*-heptane obtained by Parks (10). Freezing points must be measured very accurately for an error of a few tenths of a degree makes a great difference in the amount of impurity actually present. Mole per cent impurity in *n*-heptane from petroleum calculated from refractive index is 0.9. Mole per cent impurity in *n*-heptane from petroleum calculated from density is 1.4. Mole per cent impurity in *n*-heptane from petroleum calculated from freezing point (1) using Edgar's value for *n*-heptane (freezing point, 90.5° C.) is 3.6; and (2) using Shepherd, Henne, and Midgley's value for *n*-heptane (freezing point, -90.65° C.) is 2.7.

As a further test of the purity of the *n*-heptane, 1100 cc. of the material, on which the above physical constants were measured, were fractionated in the 52-foot column using a reflux ratio of 32-36 to 1. Table IV shows the results of this fractionation. The entire amount, including residue, boiled within 0.3° C. and several cuts were obtained differing in refractive index by only one or two in the fourth place from the accepted value for *n*-heptane.

TABLE IV. REFRACTIONATION OF *n*-HEPTANE OBTAINED FROM PENNSYLVANIA PETROLEUM

FRACTION	B. P. (760 MM.) ° C.	n_D^{20}	AMOUNT Cc.	TOTAL Cc.
1	98.2	1.3884	20	20
2	98.2	1.3882	34	54
3	98.35	1.3881	40	94
4	98.4	1.3881	50	144
5	98.4	1.3879	40	184
6	1.3879	45	229
7	1.3880	50	279
8	98.4	1.3880	50	329
9	1.3880	50	379
10	1.3880	40	419
11	98.5	1.3880	40	459
12	1.3880	20	479
Residue	98.5	1.3882	415	894

The methylcyclohexane obtained corresponded to about 2 per cent of the original 80-108° C. cut. However, since only a relatively small number of the fractions containing methylcyclohexane were refractionated, the total amount of methylcyclohexane in this narrow cut is much greater than 2 per cent. The methylcyclohexane was of remarkable purity as the following comparison of its physical constants with those obtained by other investigators shows:

REFERENCE	B. P. (760 MM.)	REFRACTIVE INDEX	d_4^{20}	F. P. ° C.
Intern. Critical Tables	100.8	1.4235 ^a	0.764	-126.4
Timmermans (13)	101.2	1.4253 ^b	0.769 ^c	-126.4
Timmermans (12)	-126.85
Nagornov (9)	100.8	0.7696
Pa. petroleum	100.8-100.9	1.4232 ^a	0.7688	-126.7

^a n_D^{20} . ^b n_D^{15} .

^c Obtained by interpolation of values at d_4^{15} and d_4^{20} .

Young (15) gives a constant-boiling mixture of *n*-heptane and methylcyclohexane containing 20 per cent by weight of methylcyclohexane. No evidence of any such mixture has been found. The two hydrocarbons were practically completely separated despite the fact that the difference in boiling point is only 2.4° C. and that they have been regarded as impossible to separate by distillation alone, owing to the constant-boiling mixture. It is believed that the constant-boiling mixture has been regarded as such only because all previous fractionations were too poor to separate the constituents.

REFRACTIONATION OF MATERIAL OF BOILING RANGE 100-125° C.

In the refractionation of the 510° F. end-point gasoline, after the *n*-heptane had been obtained, the boiling point and refractive index rose gradually until a fraction was obtained with boiling point of 99.8-99.9° C. (739 mm.) or 100.8-100.9° C. (760 mm.), and refractive index of 1.4228-1.4234 at 20° C. The refractive index was unchanged by concentrated sulfuric acid and by a nitrating mixture. The material, however, reacted vigorously with fuming nitric acid. It is undoubtedly methylcyclohexane. An estimate of the amounts of *n*-heptane and methylcyclohexane follows:

	IN 510° F. END-POINT GASOLINE %	IN 400° F. END-POINT GASOLINE %	IN CRUDE OIL %
<i>n</i> -Heptane	3.1	4.0	1.2
Methylcyclohexane	2.9	3.7	1.15

After the methylcyclohexane was obtained, the boiling point and refractive index of the distillate rose rapidly. On treating with concentrated sulfuric acid, the refractive index was lowered considerably, indicating the presence of an aromatic. The latter was identified as toluene by a melting point and mixed melting point of the dinitro derivative. The amount of toluene in each fraction increased until 107° C.

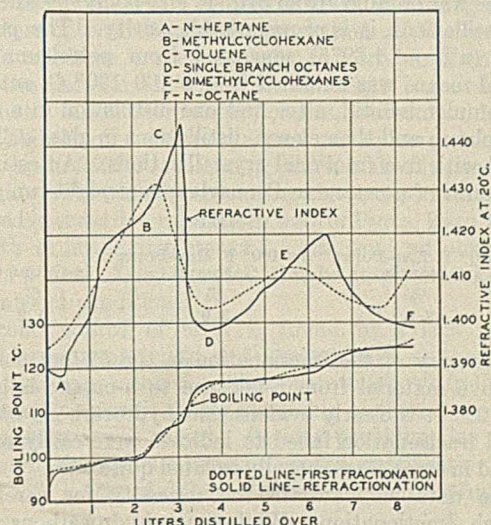


FIGURE 2. FRACTIONATION OF MATERIAL FROM *n*-HEPTANE TO *n*-OCTANE

(739 mm.) was reached, and then it dropped rapidly. The amount of toluene in the crude oil is estimated to be about 0.25 per cent. The boiling point in the meantime continued to rise rapidly to 114° C.; from this temperature to 118.8° C. it rose very slowly, and a large amount of material was obtained. From 114° to 117° C. the refractive index (n_D^{20}), 1.3980-1.4030, was near the values for the paraffins, but as the boiling point rose to 117-118.8° C., the refractive index became much higher (1.4030-1.4202). The refractive indices of these fractions were unchanged by concentrated sulfuric acid. The dimethylcyclohexanes of boiling point 119-124° C. (760 mm.) and refractive index (n_D^{20}) 1.4210-1.4312 are probably present. It was impossible in the one distillation to separate any constituent even in a semipure state. Since four of the isomeric octanes boil from 116° to 118.8° C. (760 mm.), the task is by no means easy. Approximately 20 per cent of the fraction 113-118.8° C. is of naphthenic character, and the rest is probably a mixture of the isomeric octanes. An estimate of the amount of the fraction 113-118.8° C. follows:

IN 510° F. END-POINT GASOLINE	IN 400° F. END-POINT GASOLINE	IN CRUDE OIL
%	%	%
4.3	5.5	1.7

From 118.55° C. the boiling point rose rapidly to 123° C., while the refractive index dropped steadily. A considerable fraction of *n*-octane was obtained at 123–125° C. As in the case of the *n*-heptane, the *n*-octane was practically pure. A comparison of its physical constants with the values obtained by other investigators follows:

INVESTIGATOR	SOURCE	B. P. (760 MM.) ° C.	n_D^{20}	SP. GR.
Edgar and Calingaert (4)	Data compiled	124.6	1.3980	0.702 ^a
Shepherd (11)	Chlorosulfonic acid	125.59	1.3976	0.70279 ^a
Mair (8)	Synthetic	125.7	1.3970
Leslie and Schicktanz (8)	Okla. straight-run (chlorosulfonic acid)	125.4	1.3970
Leslie and Schicktanz (8)	Okla. straight-run (crystallization)	125.5	1.3975
Present work	Pa. straight-run	125.2	1.3983
Brown and Carr (2)	Cabin Creek	124.3–124.4	1.4059	0.7123 ^b

^a d_4^{20} . ^b d_4^{20} .

The refractive index is again a good criterion of purity as the substances just above and below *n*-octane have a much higher refractive index than *n*-octane itself. The *n*-octane was unchanged by treating with concentrated sulfuric acid and with a nitrating mixture. Considering the fact that the *n*-octane was obtained from 510° F. end-point gasoline in only two distillations, it is of remarkable purity. The purest *n*-octane ($n_D^{20} = 1.3975$) separated from petroleum (8) by physical means was obtained from a 100–130° C. cut from a semi-commercial still, after first one distillation in a twenty-plate column and then eleven distillations in glass stills interspersed with five fractional crystallizations. An estimate of the amount of *n*-octane in Pennsylvania straight-run gasoline follows:

IN 510° F. END-POINT GASOLINE	IN 400° F. END-POINT GASOLINE	IN CRUDE OIL
%	%	%
3.0	3.9	1.2

A summary of the fractionation in the 52-foot column of the above material from *n*-heptane to *n*-octane is given in Figure 2. It is clearly evident that hydrocarbons which the original fractionation failed to indicate were easily recognizable and in some cases actually isolated quite pure.

These data substantiate the necessity for careful and thorough fractionation. While pure hydrocarbons can be isolated from petroleum by other physical or chemical means, it is desirable to know the separation possible using only distillation methods, and the facts so far obtained indicate that the limits of distillation have not yet been reached. A particularly effective fractionation at the start of a separation

is not only very helpful for further distillation, but it also effects rapid separation of materials, so that the use of other physical or chemical methods for purification is greatly simplified.

The results of this work have shown the need and possibilities of columns of even greater efficiency and capacity without losing the simplicity of operation. The need for increased efficiency is obvious, but it alone is not the solution to effective separation as the work here has been handicapped by the relatively small quantities of materials available. With columns of increased capacity and efficiency, the main obstacles to separation will have been overcome. Further work is being done on the design of columns which will fully meet these two requirements.

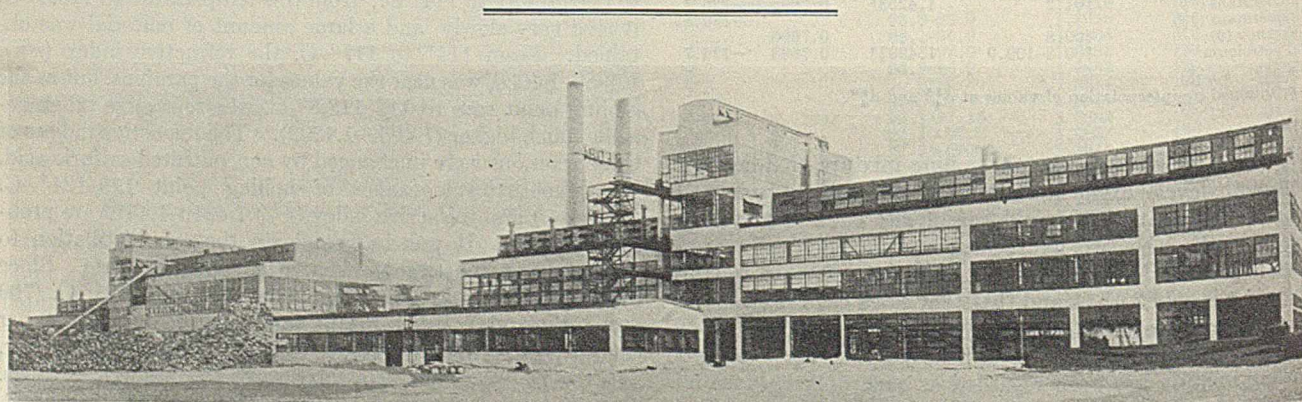
CONCLUSIONS

As a result of simply fractionating straight-run Pennsylvania gasoline in two distillations, 2-methylpentane, *n*-heptane, methylcyclohexane, and *n*-octane have been isolated, not only far purer than any previously isolated from petroleum by distillation alone, but in purity comparable to the synthetic hydrocarbons. It has been found that methylcyclohexane and *n*-heptane do not form a constant-boiling mixture. The constant-boiling mixture of benzene and *n*-hexane, if it does exist, has been found to be of widely different composition from the accepted value.

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FORD MOTOR COMPANY'S WOOD DISTILLATION PLANT, THE LARGEST AND MOST COMPLETE OF ITS KIND

Critical Temperatures of Petroleum Oils

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MANY commercial cracking processes are carried on at temperatures in the neighborhood of the critical for the oils used. A method of predicting the critical temperatures of these stocks will therefore be of service in studying the reaction mechanism by defining the phases present under various conditions.

The critical temperature of an oil may also be used in estimating various other properties which are themselves difficult to measure directly. Cope, Lewis, and Weber (2) have shown how this property may be employed in calculating the density of hydrocarbon vapors if the molecular weight and critical pressure are also known. Since the ratio $\frac{MP_c \text{ (abs.)}}{T_c \text{ (abs.)}}$ is roughly constant for the paraffin hydrocarbons, the critical pressure may also be roughly determined.

A refinement of Zeilfuchs' (11) method of determining critical temperatures of petroleum oils has been developed in order to increase the accuracy of this determination. This refinement consists in providing means for agitation of the oil sample contained in a thin-walled tube while it is being heated to the critical temperature.

A closer empirical relationship between critical temperatures and A. S. T. M. boiling points than that indicated by McKee and Parker (7) has been developed from experimental data, together with information from the literature on pure hydrocarbons. This was done by the introduction of a factor, depending on specific gravity, into the mathematical equation.

yielded discrepancies greater than possible experimental error. Figure 1 includes the experimental data together with data reported by McKee and Parker. The data on pure compounds are listed in Table III.

In view of the discrepancies shown in Figure 1, a study of critical temperatures was undertaken in order to develop an empirical method of estimating this property for wide- as well as narrow-boiling cuts with some accuracy.

EXPERIMENTAL METHOD

One of the most fruitful sources of error, in making critical temperature determinations by observation of the disappearance of a meniscus in a closed tube, is introduced when the walls of the glass tube in which the oil sample is sealed are so heavy that a lag in temperature occurs between the heating medium and the oil. Ordinary Pyrex tubing has considerable strength up to 950° F. (510° C.), which makes it possible to use a fairly thin-walled tube below this temperature. The tubes used in these determinations were of Pyrex, 25 to 40 mm. long, with an inside diameter of 3.5 mm. and an outside diameter of 5 mm. They were found to be amply strong except under unusual conditions.

A second source of error is found in a lack of true equilibrium between liquid and vapor phases as the critical temperature is approached. The apparatus shown in Figure 2 was designed to permit thorough mixing of the oil sample as the temperature was raised. Besides providing for vapor-liquid equilibrium, this mixing prevented stratification of the material into layers of different density, which confused the

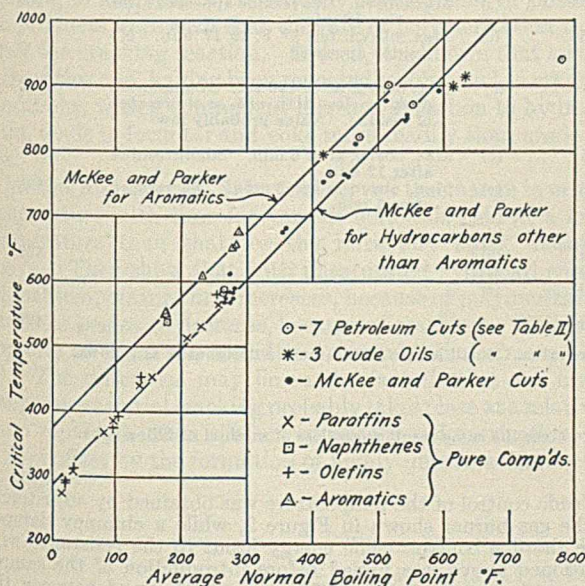


FIGURE 1. CORRELATION OF CRITICAL TEMPERATURES BY METHOD OF MCKEE AND PARKER

Watson (9) indicates that the critical temperature may be calculated if the molecular weight, normal boiling point, and liquid density at the boiling point are known. However, for a complex mixture such as any petroleum stock, it is probably simpler to determine experimentally the critical temperature than some of the other properties. McKee and Parker (7) present an empirical relationship between the critical temperature and the average boiling point. Some question as to the general applicability of this relationship was raised when actual determinations of the critical temperatures of various cuts were made in connection with work on total heat relationships (10). A comparison of the determined values with those calculated by the method suggested by McKee and Parker

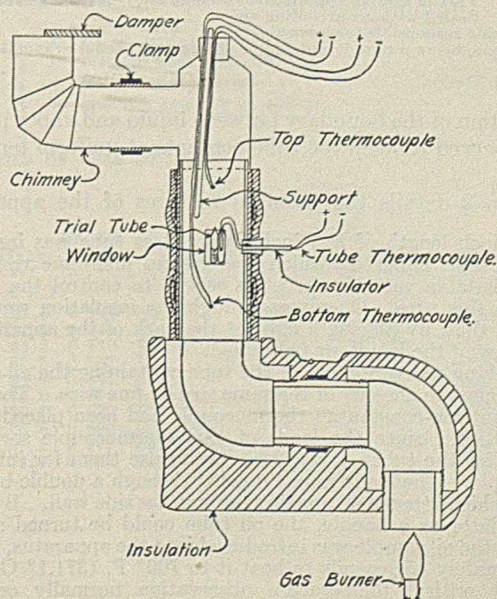


FIGURE 2. DIAGRAM OF APPARATUS

TABLE I. SUMMARY OF REPRESENTATIVE DETERMINATIONS

OIL	ESTD. PART OF TUBE FILLED			OBSERVED CRIT. TEMP. (t_c)	REMARKS ^d	BEST VALUE t_c FOR OIL ° F.	
	Before sealing %	After sealing %	At crit. temp. %				
No. 1 U. S. motor gasoline	37	37	80	584	(a)	584	
	39	39	85	584	(a)		
	38	38	85	584	(c)		
	48	37	80	605	(b)		
	37	34	60	599	(b)		
No. 2 U. S. motor gasoline	38	38	80	585	(c)	588	
	38	38	80	588	(a)		
	37	37	85	589	(c)		
	39	36	75	599	(b)		
	35	26	20	602	(b)		
	100	36	75	622	(b)		Tube filled and evaporated to 36%
No. 2 U. S. motor gasoline + bottoms	34	34	70	598	(c)	2% tar. All dissolved. No residue appeared during or after detn.	
	37	37	80	600	(a)		2% tar. All dissolved. No residue appeared
	38	38	60	611	(c)		5% tar. Small amt. not dissolved. Some residue at t_c and later at room temp.
	30	30	10	636	(c)		Same filtered. No residue appeared
Kerosene	34	34	60	766	(c)	Values given are maximum obtained in first 2-4 minutes	
	38	38	85	766	(c)		Prolonged heating caused t_c to fall slowly
	36	36	85	765	(c)		
Barbers Hill gas oil	35	35	80	820	(a)	Max. temp. obsvd.	
	34	34	80	820	(c)		First and max. obsvn. after 90 sec.
	33	33	80	822	(c)		
	38	38	95	822	(c)		First obsvn. after 150 sec.
East Texas gas oil	36	36	85	872	(c)	First obsvn. after 90 sec.	
	35	35	80	872	(c)		First obsvn. after 80 sec.
	38	38	85	(862) ^b	(c)		
Refractory cracking stock (De Florez furnace charge)	34	34	80	901	(c)	First obsvn. after 80 sec.	
	35	35	85	898	(c)		First obsvn. after 240 sec.
	37	37	90	901	(c)		
Lubricating oil (506 distillate)	37	37	85	941	(c)	First obsvn. after 120 sec. Cracked and darkened rapidly thereafter. Value probably low	
Synthetic crude (cracked Barbers Hill gas oil)	38	38	85	795	(c)	Max. obsvn. No residue appeared after heating 12 min.	
	39	39	85	795	(c)		Max. obsvn. fell 1° F. in 17 min. No residue appeared
Barbers Hill crude oil	40	40	90	913	(c)	Max. obsvn. after 120 sec. Sample too dark for close detn. of t_c or of presence of residue. Value probably low	
Spindletop crude oil	37	37	85	895	(c)	Max. obsvn. after 6 min. Slight residue after 12 min.	
	42	42	90	898	(c)		Max. obsvn. after 3 min. No residue after 6 min.
Benzene, c. p. (freezing point, 5.45° C.)	38	38	80	549	(c)	550	
	43	39	85	550	(b) ^c		
	30	30	10	549	(c)		
	40	40	85	550	(c)		
Chloroform	38	38	80	499	(c)	499	

^a Time of observation was measured from instant of insertion of oil sample into apparatus. Small letters in column are designated as follows:

(a) Evacuated and sealed in solid CO₂.

(b) Part of sample vaporized to exclude air. Gives high results.

(c) Sealed without excluding air.

^b Cracking responsible for low value.

^c Benzene, being a pure liquid, is not affected by partial evaporation and therefore gives the same result regardless of method of filling tube.

observation of the boundary between liquid and vapor phases. It also served to keep the tube contents at uniform temperature.

Figure 2 details the essential features of the apparatus.

A 12-inch length of 2³/₄ inch Pyrex glass tube was insulated with asbestos paper on which was wound nichrome resistance wire. Suitable variable rheostats served to control the energy input to this wire. Openings through the insulation were provided so that, by placing a light at the back of the apparatus, a clear view of the inside was obtained.

In making a determination, the tube containing the oil sample was attached to another of the same size by fine wire. The junction of an iron-constantan thermocouple had been placed in the second tube. Since the leads of this thermocouple served as support for the tubes, it was possible to use them for inverting the sample. The leads were threaded through a double-bore insulator which fitted in an opening through the side wall. By using the insulator as a handle, the oil tube could be turned at will.

When the oil sample was introduced into the apparatus, it took approximately 45 seconds to heat it to 700° F. (371.1° C.), and the first critical temperature observation normally occurred between 15 and 30 seconds later.

Crude control of the temperature was obtained by adjustment of the gas burner shown in Figure 2, while a chimney damper gave the fine control. The energy input to the resistance wire mentioned above was varied before introduction of the sample tube until no temperature difference was observed between the top and bottom thermocouples.

Several methods of sealing the sample tube were tried. The results are indicated in Table I. Practically no difference in critical temperature was observed between tubes sealed while still containing air and those evacuated and sealed with the liquid in the tube embedded in carbon dioxide snow. Most of the determinations were therefore made with tubes containing air.

The thermocouple used was calibrated carefully by comparison with an iron-constantan thermocouple previously calibrated by the Bureau of Standards. This couple itself had been compared to a platinum-platinum rhodium couple whose temperature-e. m. f. relationship was assumed to remain constant over long periods of time.

NECESSITY FOR MIXING

Zeitfuchs (11) and McKee and Parker (7) determined the critical temperature in tubes with no provision for stirring. They discussed in some detail the effect of volume of tube contents on the observation of the critical temperature, and found that the most accurate determinations were those where the tube was nearly full of liquid as the meniscus disappeared. This is in accord with observations by the present authors when static tubes were employed. However, it was found that, when the tube contents were continually agitated, no apparent difference in the critical point was recorded between a tube 70 per cent filled and one 95 per cent filled at the critical temperature. This fact was very helpful since the meniscus was much clearer in a tube with 70 per cent liquid than in one with 95 per cent liquid. It also lent strength to the argument that, with agitation of the sample, the necessary vapor-liquid equilibrium was obtained.

To the knowledge of the authors, there have been no determinations of the critical temperatures of petroleum stocks where mixing was employed.

CRITICAL TEMPERATURE AFFECTED BY CRACKING

Certain of the oils studied were held at the critical temperature for long periods of time and periodical observations recorded. The two lower curves of Figure 3 picture the normal decrease in critical temperature as the stocks continued cracking. The curve for the refractory gas oil, however, is unusual. This was the only stock to show a rise in critical temperature after the initial decrease. The reasons for this rise may only be surmised. It is possible that, after initial cracking to gas, with a consequent development of pressure, the products were such that the rate of polymerization to tar offset the cracking reaction. Indeed, it is known that a stock such as this one, having been repeatedly subjected to cracking conditions, with a consequent increase in carbon to hydrogen ratio, tends to form tar and coke more readily than crude gas oils.

McKee and Szayna (8) have observed the change in critical temperature with time for various materials held at a lower temperature than that for the refractory stock discussed above. They show that with unsaturated hydrocarbons the critical temperature first increases, because of polymerization, and later begins to decrease, because of cracking. This is the opposite of what was found to occur with the refractory gas oil. The difference may lie in the fact that at the higher temperature initial cracking probably takes place at a relatively more rapid rate than the accompanying polymerization, but is soon offset by the formation of highly unsaturated reaction products.

TAR IN SOLUTION

Table I includes several determinations where small amounts of tar were dissolved in a U. S. motor gasoline. A noticeable increase in critical temperature was observed, although the meniscus disappearance was just as sharp as with the pure gasoline. The tar, although of very much higher molecular weight than even the higher-boiling ends of the

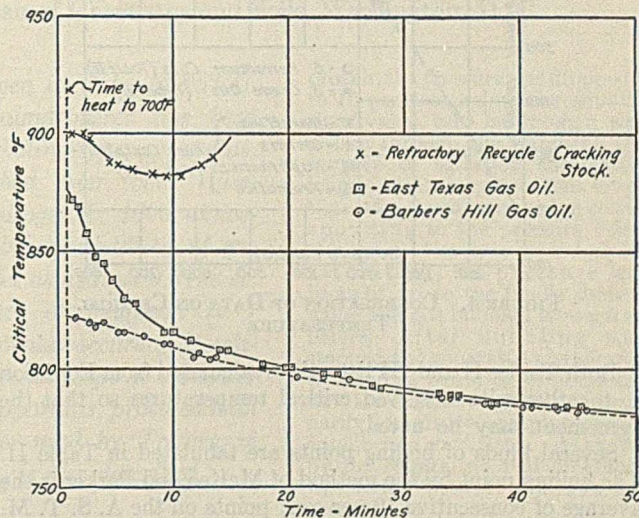


FIGURE 3. EFFECT OF CRACKING AT THE CRITICAL TEMPERATURE

gasoline, went easily into solution in the vapor. A marked darkening of the vapor was observed before the critical temperature was reached. These results are in agreement with similar determinations by McKee and Parker (7).

CORRELATION OF DATA

Essential physical data on the stocks studied are listed in Table II. An empirical equation for calculating critical temperatures was derived from the values shown here, together with data on pure compounds obtained from various sources in the literature. These sources are acknowledged in Table III.

The equation developed is as follows:

$$t_c = 180 + 1.75a - 0.00088a^2 \text{ for } ^\circ\text{F.} \quad (1)$$

where

- a = (t_b + 100) (S)
- t_c = critical temperature, °F.
- t_b = 50% boiling point (A. S. T. M. distillation)
- S = specific gravity at 60° F.

TABLE II. PHYSICAL CHARACTERISTICS OF OILS STUDIED

MATERIAL	BOILING POINT (A. S. T. M. DISTN.)					Method of McKee and Parker	Sp. Gr. AT 60° F.	COLOR N. P. A.	CRITICAL TEMPERATURE				
	Over ° F.	10% ° F.	50% ° F.	90% ° F.	Dry ° F.				Observed Temp. ° F.	Calculated Temp. ° F.	Dev. from obsvd. ° F.		
No. 1 U. S. motor gasoline	117	172	261	350	97% at 414	263	57.5	3/4	584	3	0	588	+ 4
No. 2 U. S. motor gasoline	116	174	260	356	97% at 412	264	57.9	W. W.	588	3	1	587	- 1
Kerosene	332	364	420	494	98% at 554	426	43.3	W. W.	766	3	0	760	- 6
Barbers Hill gas oil	396	440	471	502	98% at 526	471	33.7	0.857	822	4	1	824	+ 2
East Texas gas oil	486	528	554	584	97.5% at 600	555	36.4	0.843	872	2	0	877	+ 5
Refractory gas oil	394	448	497	626	95% at 640	514	16.0	0.959	901	3	1	892	- 9
Lubricating oil (506 distillate) ^a	600	717	785	853	97% at 890	785	20.7	0.930	941 ^c	1	...	1024	..
Synthetic crude oil ^b	146	236	453	528	95% at 582	419	32.6	0.862	795	2	0	814	+19
Spindletop crude oil ^a	201	400	580	895	92% at 920	625	27.1	0.892	899	2	1.5	918	+19
Barbers Hill crude oil ^a	171	341	590	975	93% at 990	649	29.5	0.879	913	1	...	918	+ 5

Average deviation = 8° F. ACCEPTED

Benzene (freezing point, 5.45° C.)	550	4	0.5	551	+ 1
Chloroform (c. p.)	499	1	...	500	+ 1

^a Distilled under 10 mm. Hg pressure, results corrected to atmospheric pressure.
^b Cracked Barbers Hill gas oil.
^c Value too low because of excessive cracking.

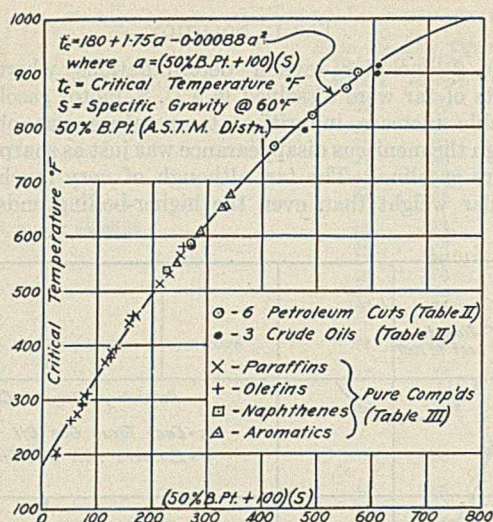


FIGURE 4. CORRELATION OF DATA ON CRITICAL TEMPERATURE

Both Tables II and III list values calculated from Equation 1, together with observed critical temperatures so that the agreement may be noted.

Several kinds of boiling points are tabulated in Table II. The boiling point by the method of McKee and Parker is the average of consecutive 10 per cent points on the A. S. T. M. distillation, while the integrated average boiling point is the average of consecutive 1 per cent points on the same distillation. It will be noted that these two methods give nearly identical values, which are sometimes quite different from the 50 per cent point. Use of the 50 per cent point, however, gives closer prediction of the critical temperature than either of the average boiling points, when the data on the two crude oils is included. If the two values for the crudes be elimi-

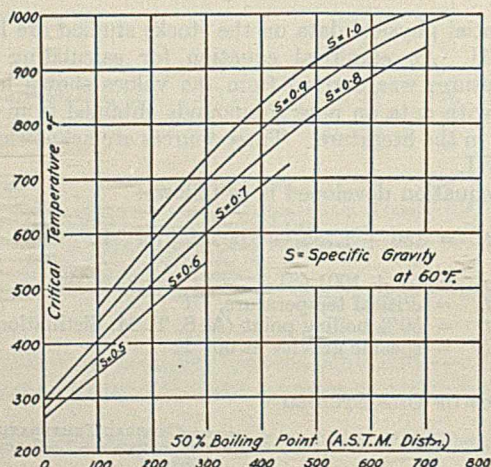


FIGURE 5. CHART FOR DETERMINING CRITICAL TEMPERATURES OF PETROLEUM OILS

nated from the correlation, use of the average boiling point gives slightly closer prediction than the 50 per cent point. However, in view of the greater simplicity of calculation, use of the 50 per cent point is justified, even for narrow cuts.

Figure 4 illustrates graphically the correlation between the data listed above and the equation. The curve fits the data closely for all pure compounds above the C_3 's on which information is available, the average deviation being $5.5^\circ F.$ ($3.0^\circ C.$), and the maximum deviation $+15^\circ F.$ ($8.5^\circ C.$). The agreement with the petroleum cuts is fully as good as it is for the pure compounds. The crude oils, however, including the cracked synthetic crude, show a critical temperature

slightly lower than the calculated value. On the whole, the agreement is good for all oils studied, except the Lube stock. The reported critical temperature of this oil is undoubtedly lower than the true value, owing to extensive cracking, but even so it is doubtful if the equation would apply to oils as high boiling as this one. No method of determining the critical temperature was developed where the temperature was so high that cracking occurred at a very rapid rate.

The stocks reported on are from crude sources which have quite different chemical and physical properties, and the recycle cracking stock in particular is a unique oil of entirely different properties from similar cuts of the ordinary crude oil source. The fact that the critical temperatures of all these oils, determined by an accurate method, are in close agreement with the equation developed, apparently justifies a confidence in the correlation for oils ordinarily met with.

Figure 5 is a reference chart which enables one to determine the critical temperature directly if the specific gravity and 50 per cent point on the A. S. T. M. distillations are known.

TABLE III. DATA ON PURE COMPOUNDS

COMPOUND Name	Formula	BOILING POINT ° F.	SP. GR. AT 60-68° F.	CRIT. TEMP. ° F.	DEV. FROM CRIT. LITERA- TURE	
					° F.	° F.
Methane	CH_4	-258.5 ^a	..	-116.5 ^b
Acetylene	C_2H_2	-118.5 ^a	..	+96.8 ^b
Ethylene	C_2H_4	-164.8 ^a	..	49.5 ^b
Ethane	C_2H_6	-126.9 ^a	0.377 ^b	89.8 ^b	163	..
Allylene	C_3H_4	-17.5 ^a	0.623 ^c	262.4 ^b	268	..
Propylene	C_3H_6	-52.6 ^a	0.523 ^c	198.2 ^b	223	..
Propane	C_3H_8	-48.1 ^a	0.515 ^d	204.1 ^b	226	..
α -Butylene	C_4H_8	+21 ^e	0.600 ^e	291.2 ^b	302	+11
β -Butylene	C_4H_8	34 ^e	0.613 ^e	311.0 ^b	318	+7
Isobutylene	C_4H_8	20.1 ^e	0.601 ^e	290.3 ^b	302	+12
n-Butane	C_4H_{10}	33.0 ^a	0.584 ^e	307.4 ^b	310	+3
Isobutane	C_4H_{10}	13.6 ^a	0.564 ^e	273.2 ^b	288	+15
Amylene	C_5H_{10}	104.0 ^a	0.651 ^e	394.2 ^b	397	+3
Isoamylene	C_5H_{10}	96.8 ^a	0.632 ^e	376.9 ^b	383	+6
n-Pentane	C_5H_{12}	97.0 ^a	0.631 ^e	386.8 ^b	383	-4
Isopentane	C_5H_{12}	82.4 ^a	0.621 ^e	368.8 ^b	367	-2
Benzene	C_6H_6	176.2 ^a	0.878 ^e	551.2 ^b	552	+1
Diallyl	C_6H_{10}	139.1 ^a	0.688 ^e	453.9 ^b	448	-6
Cyclohexane	C_6H_{12}	178.6 ^a	0.799 ^a	537.8 ^b	526	-12
n-Hexane	C_6H_{14}	156.2 ^a	0.660 ^a	454.6 ^b	451	-4
Diisopropyl	C_6H_{14}	136.6 ^a	0.666 ^a	441.3 ^b	434	-7
Toluene	C_7H_8	231.3 ^a	0.866 ^a	609.1 ^b	609	0
n-Heptane	C_7H_{16}	209.2 ^a	0.684 ^a	512.2 ^b	511	-1
o-Xylene	C_8H_{10}	287.6 ^a	0.879 ^a	676.9 ^b	674	-3
m-Xylene	C_8H_{10}	282.2 ^a	0.865 ^a	654.1 ^b	663	+9
p-Xylene	C_8H_{10}	278.6 ^a	0.861 ^a	651.9 ^b	657	+5
Octylene	C_8H_{16}	253.4 ^a	0.722 ^a	580.6 ^b	570	-11
n-Octane	C_8H_{18}	256.2 ^a	0.702 ^a	564.8 ^b	563	-2
Diisobutyl	C_8H_{18}	230.0 ^a	0.693 ^a	530.6 ^b	535	+4

Average deviation = $5.5^\circ F.$

^a International Critical Tables (4). ^d Dana, Jenkins, Burdick, and Timm (5)

^b International Critical Tables (5). ^e Coffin and Maass (1).

^c Maass and Wright (6).

^f McKee and Parker (7)

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Solubility of Hydrogen in Water at 25° C. from 25 to 1000 Atmospheres

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TWO papers on the solubility of gases at high pressures have appeared recently, which indicate the interest attached to the subject. Goodman and Krase (6) measured the solubility of nitrogen in water up to 300 atmospheres over a wide range of temperature, while Frolich and collaborators (5) obtained the solubility of hydrogen, nitrogen, and methane in water and other solvents at 25° C. up to approximately 150 atmospheres. The knowledge of the solubility of hydrogen and nitrogen in water is valuable in the operations leading to the synthesis of ammonia and in other related high-pressure processes.

With the exception of the work of Frolich and collaborators (5), all published work on hydrogen has been done at relatively low pressures. Tremearne, of this laboratory, using an apparatus to be described later, first attempted to measure the solubility of hydrogen in water up to 1000 atmospheres (8). However, owing to mechanical difficulties and to the time it would have required to establish equilibrium, his work was discontinued and the present method adopted.

APPARATUS AND EXPERIMENTAL PROCEDURE

The present apparatus and method are exceedingly simple. Figure 1 shows the steel cylinder in which the high-pressure saturation was effected. It is silver plated on the inside and has a capacity of 275 cc. of water.

For initial saturation, hydrogen at a pressure from 10 to 50 per cent higher than that to be finally required was passed into the cylinder at A, bubbled through the water, and expanded to the atmosphere through C and D (B and E being closed). After several hours, samples were taken to insure saturation above the finally desired value. At each pressure two approaches to equilibrium were then made. In the first, which will be called the high-pressure approach, the pressure was simply dropped to its final value and hydrogen bubbled through to aid in establishing equilibrium. In the other, the low-pressure approach,

The solubility of hydrogen in water at 25° C. and from 25 to 1000 atmospheres has been measured in a simple bubbling-type apparatus. Equilibrium is approached from both sides. When the pressure of hydrogen is 1000 atmospheres, water at 25° C. absorbs 15.20 cc. of gas (S. T. P.) per gram of water as against 0.0178 cc. when the partial pressure of hydrogen is 1 atmosphere. The experimental accuracy is estimated to be about 0.5 per cent except at the lower pressures. A solubility apparatus, provided with an externally driven stirrer used by Tremearne in some preliminary work, is also described.

the pressure was dropped 5 to 10 per cent below the equilibrium value, and hydrogen was passed through the water for the purpose of agitation sufficiently long to insure a gas content lower than the equilibrium value corresponding to the pressure being studied. After this period of desaturation, the pressure was brought up to the finally desired value and gas bubbled through as before. After bubbling was stopped, the apparatus was allowed to stand at rest 3 to 48 hours before the sample was taken. Ordinarily 2 hours were ample to insure equilibrium conditions. As shown by the results, no real difference was found between the two approaches.

Figure 2 shows the buret for the measurement of samples. The high-pressure valve is identical with valve E in Figure 1.

In the sampling procedure the high-pressure valve was opened slightly and a mixture of gas and water appeared. The water was measured in the 30-cc. buret, the bulk of the gas in the bulb volumenometer, and any amount smaller than 35 cc. in the 50-cc. gas buret. Measurements were made after no visible bubbles escaped from the water. The size of water samples ranged from 11 to 29 cc. The temperature of the buret was kept at 25° C. All burets had been carefully calibrated with water. The hydrogen used was 99.8 per cent pure according to combustion analyses, the impurity being nitrogen. Pressure measurements were made on two piston gages described by Bartlett and co-workers (2). The gages were connected directly to the top of the solubility apparatus (connection not shown in Figure 1) in order to prevent any pressure drop in this line during saturation.

DISCUSSION OF RESULTS

The experimental results are presented in Table I and Figure 3. The values for the two approaches to equilibrium

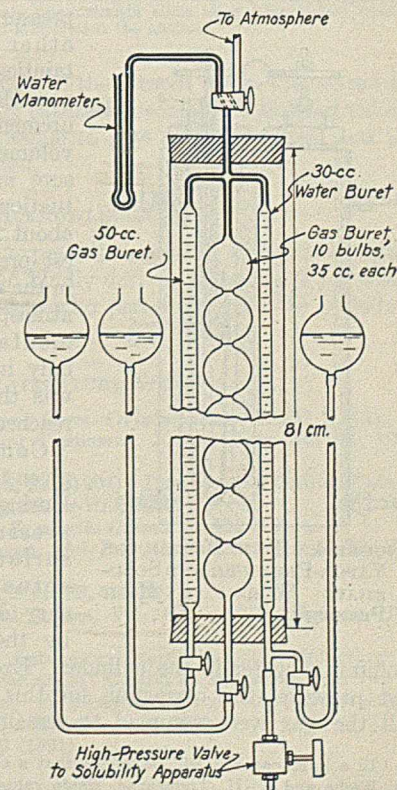


FIGURE 2. BURET SYSTEM FOR SOLUBILITY OF GASES IN WATER

FIGURE 1. HIGH-PRESSURE APPARATUS FOR MEASURING SOLUBILITY OF GAS IN WATER

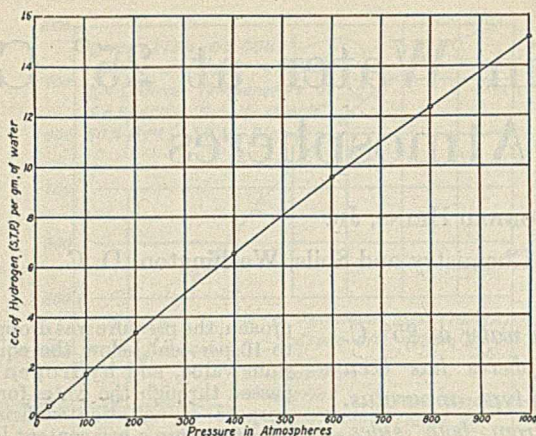


FIGURE 3. SOLUBILITY OF HYDROGEN AT VARIOUS PRESSURES

are tabulated separately. The agreement between the two sets of measurements at any pressure is satisfactory. In the average columns, the error stated is the probable error as given by equation

$$E = 0.674 \sqrt{\frac{\sum \Delta^2}{n(n-1)}}$$

of the average value. It will be noticed that the probable error so calculated is in some instances considerably smaller than the difference between the two average values, thus indicating the fact that reproducible values can be obtained at any point in the neighborhood of the particular equilibrium value when the process of saturation is dependent solely on diffusion from the surface of the liquid. A practical coincidence of the two average values could be obtained if more time had been taken in the establishment of equilibrium. The error of the final values was calculated from the average of the two average values, and a consideration of a possible effect of pressure fluctuation and other experimental uncertainties. The maximum possible error due to measurements of water and gas volumes, and due to pressure and temperature fluctuations is estimated to be about 2 per cent at the lowest pressures and 1 per cent in the range from 200 to 1000 atmospheres. The experimental results show that only in a few isolated cases was this possible maximum reached.¹

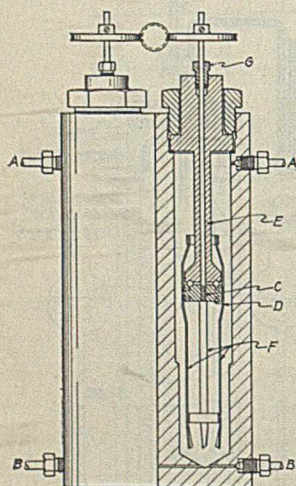


FIGURE 4. TWIN BOTTLE FOR VAPOR-PRESSURE AND SOLUBILITY WORK AT HIGH PRESSURES

Consideration was also given to the following points: During final saturation the pressure of the gas on the surface of the liquid was actually 20 mm. of mercury higher than indicated by the gage, owing to the

¹ In a later paper it will be shown that a shaking method, devised by R. Wiebe and T. H. Tremearne, yields values which are in agreement, within 0.1 per cent, with those obtained by means of the bubbling apparatus used here.

possibility of supersaturation of the water while in the buret was investigated. A 100 per cent supersaturation of the water in the buret for the 100-atmosphere run would produce an error of 1 per cent. That this was not anywhere near the case has been quite definitely established by taking samples at different partial pressures of hydrogen from 500 to 726 mm. in the buret, by evacuating the water initially in the buret and by varying the initial volume of water. The turbulence of the outcoming sample must effectively prevent supersaturation.

TABLE I. ABSORPTION COEFFICIENTS FOR HYDROGEN IN WATER AT 25 ± 0.1° C.

(In cc. of gas at S. T. P. per gram of water)

PRE-SURE	VALUES FOR LOW-PRESSURE APPROACH	AVERAGE	VALUES FOR HIGH-PRESSURE APPROACH	AVERAGE	FINAL VALUES
25	0.440	0.440
..	0.431	0.433
..	0.432	0.432
..	0.436	0.436
..	0.438	0.432
..	0.438	0.436 ± 0.001	0.438
..	0.435
..	0.435
..	0.440
..	0.433
..	0.437	0.436 ± 0.001	0.436 ± 0.008
50	0.869	0.872
..	0.868	0.864
..	0.866	0.873
..	0.863	0.865
..	0.870	0.872
..	0.860	0.860
..	0.862	0.868
..	0.867	0.875
..	0.864	0.866
..	0.863	0.869
..	0.866	0.865 ± 0.001	0.876
..	0.869
..	0.874	0.868 ± 0.001	0.867 ± 0.012
100	1.729	1.728
..	1.723	1.729
..	1.730	1.733
..	1.733	1.731
..	1.723	1.730
..	1.729	1.726 ± 0.001	1.735
..	1.732
..	1.728
..	1.727
..	1.726
..	1.728
..	1.730
..	1.736
..	1.732	1.730 ± 0.001	1.728 ± 0.017
200	3.386	3.402
..	3.381	3.393
..	3.380	3.401
..	3.373	3.399
..	3.378	3.400
..	3.399	3.377
..	3.390	3.396
..	3.401	3.414
..	3.388	3.397
..	3.389	3.385
..	3.387	3.410
..	3.382	3.386 ± 0.002	3.408
..	3.397
..	3.404
..	3.400	3.399 ± 0.002	3.39 ± 0.03
400	6.55	6.56
..	6.59	6.58
..	6.57	6.58
..	6.56	6.57
..	6.56	6.57
..	6.56	6.56
..	6.56	6.56	6.57
..	6.57
..	6.56
..	6.56
..	6.56
..	6.56
..	6.58
..	6.55
..	6.56
..	6.57
..	6.60
..	6.57
..	6.56
..	6.57
..	6.56	6.57	6.57 ± 0.04
600	9.57	9.56
..	9.59	9.59
..	9.57	9.57
..	9.59	9.58
..	9.56	9.58

TABLE I. ABSORPTION COEFFICIENTS FOR HYDROGEN IN WATER AT 25 ± 0.1° C. (Continued)

(In cc. of gas at S. T. P. per gram of water)					
PRES- SURE Atm.	VALUES FOR LOW- PRESSURE APPROACH	AVERAGE	VALUES FOR HIGH- PRESSURE APPROACH	AVERAGE	FINAL VALUES
...	9.60	9.58	9.59
...	9.55
...	9.58
...	9.59	9.58	9.58 ± 0.05
800	12.46	...	12.48
...	12.44	...	12.48
...	12.46	...	12.45
...	12.45	...	12.48
...	12.46	12.45	12.46
...	12.50
...	12.45
...	12.43
...	12.48
...	12.42
...	12.47
...	12.46
...	12.48	12.47	12.46 ± 0.06
1000	15.13	...	15.19
...	15.07	...	15.38
...	15.16	...	15.25
...	15.20	...	15.15
...	15.18	...	15.28
...	15.13	...	15.27
...	15.20	...	15.10
...	15.20	...	15.29
...	15.14	...	15.23
...	15.16	...	15.37
...	15.19	15.16 ± 0.01	15.23
...	15.26
...	15.14
...	15.23
...	15.30
...	15.11
...	15.16
...	15.20
...	15.24
...	15.31
...	15.20
...	15.23
...	15.26
...	15.18	15.23 ± 0.01	15.20 ± 0.08

The increase of the volume of water due to solubility of hydrogen in water at 1 atmosphere has been shown to be negligibly small by Ångström (1) as far as the present work is concerned. A slight error might possibly arise from the fact that there was a concentration gradient in the water of the gas burets. This effect, which would have been most noticeable in the first sample taken, was not observed.

Drucker and Moles (4) give as the average of the compilation of the "best" results for the Bunsen absorption coefficient 0.0178, which also agrees with the average obtained from the different K values in the International Critical Tables (7). Since the individual values for the Bunsen absorption coefficient at 1 atmosphere vary from 0.0175 to 0.0182, the average value is rather uncertain. Roughly, the present results would seem to favor the lower value, 0.0175, which was obtained by Winkler (9). Cassuto (3) obtained 0.150 for the Bunsen coefficient at 10 atmospheres. Since the value comparable to his obtained in the present work at 25 atmospheres is 0.0174, Cassuto's values must be too low, unless it is assumed that the solubility goes through a decided minimum below 25 atmospheres.

The following equation:

$$S = 0.0244 + 0.01712 p - 0.00000196 p^2 \quad (1)$$

where S = number of cc. of gas (S. T. P.) dissolved in 1 gram of water

p = partial pressure of hydrogen

fits the data from 50 to 1000 atmospheres within the estimated error but gives impossibly high values at lower pressures.

METHOD AND RESULTS OF TREMEARNE

Tremearne's apparatus, as shown in Figure 4, consisted of two internally connected cylinders drilled in one block.

Two externally driven stirrers provided agitation. The gas entered at A , and samples were taken at B . A hardened steel shaft, C , rotating in guide E , was at its lower end threaded into

steel plate D , to which the stirrer blades were attached. The steel plate, D , was forced upward against the ball bearings as indicated. The packing, consisting of shredded lead and flax, was adjusted by means of gland G . Since the space between the shaft and the stirrer guide was filled with water, the gas did not come in direct contact with the packing, and thus the leakage was kept down greatly, though it was impossible to keep the pressure constant overnight, which necessitated resaturation and gave no time for internal adjustment. Another mechanical difficulty was the twisting off of the stirrer shaft at the steel plate. In all runs, equilibrium was approached only from the lower side, and saturation was attempted solely from the surface through stirring. The necessarily slow rate of stirring and the great depth of the liquid made saturation extremely slow.

In Table II a comparison is made between the results obtained by Tremearne (8), those of Frolich and collaborators (5), the experimental values obtained in the present work, and the ones calculated from Equation 1.

TABLE II. COMPARISON OF RESULTS FROM SEVERAL SOURCES

(In cc. of gas at S. T. P. per gram of water)					
PRESSURE	TREMEARNE (8) ^a	FROLICH AND CO-WORKERS (5) ^b	WIEBE, GADDY, HEINS	CALCD. FROM EQ. 1	
Atm.					
25		0.436
50		0.86	0.867	0.876	0.876
100	1.64, 1.65, 1.67		1.72	1.728	1.717
	1.68, 1.68, 1.53, 1.74				
200	3.17, 3.24, 3.25				
	3.13, 3.24			3.39	3.37
300	4.50, 4.94, 4.74, 4.82, 4.85				4.98
	4.55, 4.58, 4.68				
400	5.74, 6.54				
	5.20, 6.11, 6.08, 6.54			6.57	6.56
	5.94, 6.28, 6.39, 6.21				
600	9.81, 9.52, 8.81, 9.14, 9.46				
	8.60, 9.76			9.58	9.59
	8.50, 9.46				
800	11.90, 12.28				
	10.97, 11.31, 11.75			12.46	12.47
1000	13.86				
	13.28, 13.11, 14.22			15.20	15.19

^a Values given in this column were from consecutive runs of a series including the highest obtained. The runs were selected from a total of over 500. The other results either form a gradually ascending series or are irregular and for the most part considerably lower. At 1000 atmospheres the shaft twisted off several times, and final results could never be obtained.

^b These values can be only approximate since they were taken from a blueprint which Frolich had kindly sent the authors.

As shown by the results of the present work, Tremearne did not succeed in reaching saturation except for isolated values. It was therefore impossible to give average values, and the above form was adopted.

ACKNOWLEDGMENT

The authors wish to express thanks to W. Edwards Deming, of this laboratory, who kindly derived Equation 1 for them, and to T. H. Tremearne who permitted them to include a discussion of his work.

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Iodine Number and Refractive Index of Perilla Oil

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ALTHOUGH perilla oil has only comparatively recently come into prominence, considerable and increasing quantities are now being imported into this country from the Orient. It is used chiefly in the paint and varnish and allied trades where its properties make it of particular value. The study of the constants of perilla oil as criteria of purity has not been carried as far as with some of the other oils, although its comparatively high price makes it a profitable field for adulteration. The more or less arbitrary standards now existing are perhaps somewhat open to argument.

review of the analytical results of perilla oil furnished by several laboratories, states in a summary concerning the iodine number, in substance as follows:

A survey of all the figures before us warrants the conclusion that very little, if any, pure perilla oil will have a Hanus iodine number lower than 195. Assuming this to be correct, we find that our extremes are about ten points, that is, from 195 to 205.

Referring to refractive index, he says:

There are very few determinations which are below 1.480 at 25° C. The highest figure listed is 1.4819, while the lowest one is 1.4794. We are inclined to believe, however, that no pure perilla oil would have a refractive index below 1.480 and, therefore, would set that as the minimum figure at 25° C. So far as our results go, we have but one which is above 1.4815. Therefore, it would seem that, if this figure were set as a maximum, no pure perilla oil would be excluded thereby.

TESTS ON ORIENTAL PERILLA SEED

An old importer of perilla oil on this coast, while recently traveling in the Orient, arranged to have some six grades of perilla seeds sent to this laboratory for experimentation. These seeds were hand-picked here, and all foreign seeds, chaff, dirt, or damaged seeds eliminated, the material pressed all being sound perilla seed of the grades designated. These were cold-pressed, though the modern practice is hot-pressing, which, however, should not appreciably affect the constants though it does the color. It is to be noted in Table I that there is quite a wide range between the minimum and maximum iodine numbers for these seeds of known purity (roughly 15 points). The accepted published minimum for the Hanus value would, on this basis, appear somewhat too high.

Based on the limited number of seed samples represented in this experiment, it would not be possible to prophesy what limitations of index of refraction or iodine value should be placed on a pure perilla oil, but it is evident that present accepted standards do not fully cover the practical facts in the case. As the refractive index and iodine value, more than anything else, tend to portray the purity of perilla oil, the subject should be given more thorough consideration, based on a greater variety of seeds of known purity and extended over a number of seasons. Such an investigation should establish a more definite knowledge of actual limitations of pure perilla oil.

In the course of regular routine work, this laboratory has been called upon to pass on the purity of a large number of shipments of perilla oil arriving at Pacific Coast ports. The shipments have arrived both in bulk and in drum lots, and

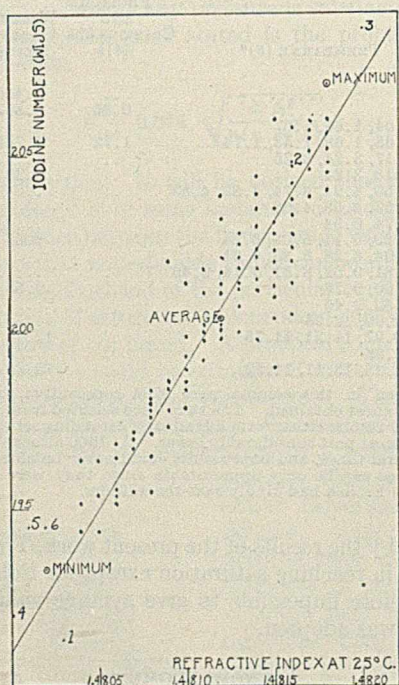


FIGURE 1. REFRACTIVE INDEX AND IODINE NUMBER OF PERILLA OIL

1. Manchurian greenish gray sample
2. Manchurian brown sample
3. Manchurian pale brown mixed sample
4. Korean No. 1 sample
5. Korean No. 2 sample
6. Korean No. 3 sample

The American Society for Testing Materials in its specification for raw or refined perilla oil (1) gives the iodine number (Hanus) minimum as 191.0 and does not mention the refractive index. Pickard (2), in a very interesting

TABLE I. ANALYSIS OF COLD-PRESSED OIL FROM HAND-CLEANED SEEDS

	(Clear settled oil used for analysis)					
	MANCHURIAN GREENISH GRAY	MANCHURIAN BROWN	MANCHURIAN PALE BROWN MIXED	KOREAN No. 1	KOREAN No. 2	KOREAN No. 3
Sp. gr. at 15.5/15.5° C.	0.9325	0.9342	0.9355	0.9324	0.9326	0.9326
Refractive index at 25° C.	1.4803	1.4816	1.4820	1.4800	1.4801	1.4802
Acid number	0.60	0.88	0.54	1.53	1.01	0.76
Saponification number	191.3	191.6	191.1	191.8	191.1	191.1
Iodine number	192.6	204.7	208.6	192.0	194.5	194.5
Iodine number (Hanus, 0.5 hour)	187.1	198.4	200.4	185.7	190.1	189.8
Difference between Wijs and Hanus ^a	5.5	6.3	8.2	6.3	4.4	4.9
Lovibond color:						
Yellow	40.0	30.0	30.0	40.0	40.0	40.0
Red	2.1	1.8	1.8	2.0	2.1	2.1

^a Average difference between Wijs and Hanus iodine numbers of the six samples = 5.9.

a large majority of them have been passed as pure. A detailed tabulation of all these results would require too much space, and therefore only a condensed summary of the iodine number (Wijs) and refractive index on approximately one hundred samples, passed as pure during the past few seasons, is included:

	MAXIMUM	MINIMUM	AVERAGE
Iodine number (Wijs)	207.0	193.3	200.4
Refractive index at 25° C.	1.4818	1.4802	1.4811

About 20 per cent of the oils included in the tabulation had indices higher than 1.4815, the limit suggested by Pickard, while none had indices below the lower limit.

During the course of the tabulation, several interesting points were brought to light. The interrelation between the refractive index and iodine number was noted, and the two were plotted against each other. As is shown in the graph, the figures, with very few exceptions, fall within two or three points of a straight line. It will be further noted that the constants on the oils of known purity previously mentioned

all fall on or near this line and, moreover, have values approaching both maximum and minimum figures.

Another interesting and extremely significant point is the fact that some of the highest figures were those obtained during recent months, when oil prices were at their lowest, and adulteration "to the analytical limit" was not worthwhile.

From the preceding, the rather contradictory conclusions are that, although in general the oils of highest quality have the highest iodine values and refractive indices, the constants of pure perilla oil (particularly the iodine value and refractive index) are subject to considerable variation, and low values do not necessarily mean adulteration.

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RECEIVED February 8, 1932.

Phenol-Acrolein Resins

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THE purpose of this work is to investigate McIntosh's reaction for the preparation of the resin "acrolite" (2).

The latter is prepared by heating for a long time at 160–180° C. a mixture of 100 grams of crystalline phenol and 70 grams of glycerol, 1 cc. of concentrated sulfuric acid being used as catalyst. Acrolites obtained in this way are almost black in acid media, purple in basic media, and highly hygroscopic.

The authors made attempts to improve the technical properties of acrolite, first by using another catalyst, and second by varying the proportions of glycerol and phenol. Comparative experiments for the condensation of phenol with glycerol were carried out in the presence of various catalysts, such as sulfuric acid, β -naphthalenesulfuric acid, acid potassium sulfate, and magnesium sulfate. The concentration of each catalyst varied from 0.02 to 0.5 per cent of the total weight of the reaction mixture. The concentration of the reagents varied in the following way: from 1 mole of phenol per 1 mole of glycerol, to 3 moles of phenol per 1 mole of glycerol. The resulting products were, however, darkly colored and highly hygroscopic in all cases.

In the process of the formation of acrolite, two main reactions seem to take place simultaneously: (1) Glycerol is converted into acrolein which then condenses with phenol; (2) glycerol is converted into polyglycerides which condense with phenol. Both suppositions are possible, since, under the influence of sulfuric acid, the formation of acrolein and the formation of polyglycerides take place simultaneously. Therefore, it is possible that acrolite is an intermediate form between phenol-acrolein resins and polyglyceride-phenol resins. Moureu has employed only basic catalysts in the condensation of phenol with acrolein, consequently the authors determined to study the influence of acid reagents on the condensation of phenol with acrolein.

The first experiments with phenol-acrolein resins were carried out by Moureu, together with Dufraisse (4). The authors used basic catalysts exclusively (3). Owing to their high elasticity, electrical stability, and the ease with which they

can be worked mechanically, these resins were recommended for the molding of all kinds of electrical and radio parts.

Kishi (1) condensed acrolein with phenol under pressure of 30 atmospheres in the presence of salts, such as zinc chloride, aluminum chloride, and other salts which, on being hydrolyzed, might give an acid reaction. Resins prepared by this method possess advantages over phenol-formaldehyde resin, in that they have greater elasticity and viscosity, and that their properties resemble those of synthetic rubber. On being mixed with oils, fats, and natural resins, they yield very viscous mixtures.

From the Japanese patent it is not clear whether the condensation of phenol with acrolein may also be carried out in the presence of acid catalysts under atmospheric pressure and, if so, what the resulting products would be. In this connection, it was decided in these experiments to compare the influence of acid and basic catalysts on the rate of condensation of phenol with acrolein, and to study the kinetics of the condensation process as influenced by time and temperature.

PREPARATION OF ACROLEIN

Acrolein was prepared in the following manner:

Five-tenths kilogram of finely powdered anhydrous acid potassium sulfate, 0.1 kg. of finely powdered anhydrous sodium sulfate, and 0.2 kg. of anhydrous glycerol were thoroughly mixed in a 5-liter cylindrical vessel made of copper. The vessel was closed, and the mixture allowed to stand for 24 hours at room temperature.

The reaction vessel contained three openings, one for a dropping funnel used for the addition of glycerol, the second for a mechanical stirrer propelled by an electrical motor, and the third for a condenser. The other end of the condenser was connected by means of an adapter to a large two-necked flask, heated on a water bath to 70–80° C. This flask was connected with another condenser, the second end of which was connected with another two-necked flask, used as a receiver for acrolein. The latter flask, through its second neck, was fitted with a reflux condenser, to the upper end of which a calcium chloride tube was attached.

In the first condenser the circulating water was heated to 40–50° C.; in the second, colder water (about 17–20° C.) was used. The mixture in the copper vessel (after standing for 20 to 24

hours) was heated on an air bath or oil bath to 195° C., and that temperature was maintained throughout the whole experiment. The temperature in both condensers and in the middle flask was so regulated that a mixture of condensed water and gaseous acrolein entered the flask, and chiefly gaseous acrolein left the flask. It was found that the best temperature to be maintained in the middle flask was about 70–80° C.

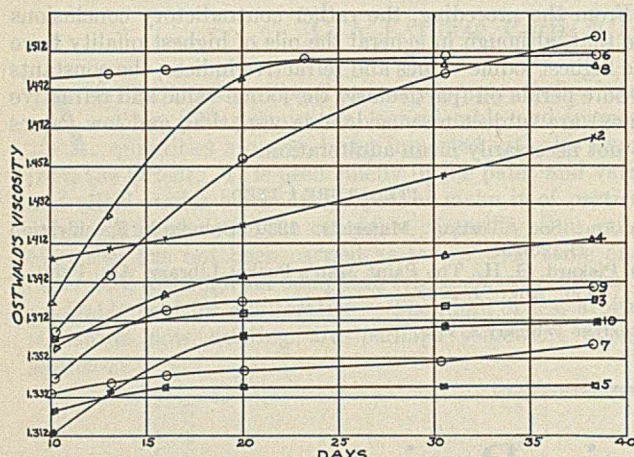


FIGURE 1. EFFECT OF CATALYSTS ON VISCOSITY OF PHENOL RESIN

(One mole of phenol per one mole of acrolein; catalysts, same as Table I)

The second two-necked flask (the receiver) contained two layers, the bottom layer consisting of water, saturated with acrolein, and the top layer of acrolein saturated with water. When only a small quantity of glycerol remained in the copper vessel, new portions were added from the dropping funnel so as not to slow up the distillation of acrolein. The quantity of the catalyst mentioned above was ordinarily sufficient for the conversion of 3 kg. of glycerol.

The yield of acrolein was as high as 65 per cent of the theoretical amount based on anhydrous glycerol. The acrolein from the receiver was redistilled by means of an efficient distilling column and was immediately used for condensation experiments.

CONDENSATION OF ACROLEIN WITH PHENOL

These experiments were carried on in the following way: a mixture of 10.2 grams of acrolein, 18.8 grams of crystalline phenol (1 mole of acrolein per 1 mole of phenol), and 0.1 gram of acid or basic catalyst was placed in a 100-cc. flask fitted with a stopper carrying a thermometer and reaching under the surface of the mixture. The flask while cooling was rapidly stirred and then placed on a water bath fitted with a stirrer; the temperature of the bath was maintained so as to keep the temperature of the mixture at 20° C. throughout the experiment. Every day or two, before the completion of the reaction (i. e., before the mixture was converted into an insoluble condition), the following measurements were made: rate of condensation, viscosity according to Ostwald, melting point according to Kraemer-Sarnow, and flow-point according to Ubbelode.

In order to determine viscosity, the product was dissolved in acetone (nine parts acetone, by weight, per one part resin). Measurements were made at 20° C., using an Ostwald viscometer. The results were found from the following relation:

$$n = n_0 \frac{St}{S_0 t_0}$$

where t_0 = time of efflux of acetone
 n_0 = viscosity of acetone

S_0 = gravity of acetone
 t = time of efflux of solution
 S = gravity of solution
 n = viscosity of mixture

The following catalysts were tested: acid potassium sulfate, β -naphthalenesulfuric acid, boric acid, potassium hydroxide, barium hydroxide, potassium carbonate, urea, pyridine, and hexamethylenetetramine. It was found that the reaction between acrolein and phenol may be carried out both in the presence of acid and basic catalysts. If the rate of condensation is to be judged by the increase in viscosity of a solution of the condensation product, the following catalysts may be considered most effective: acid potassium sulfate, β -naphthalenesulfuric acid, boric acid, phosphoric acid, and potassium hydroxide. Weak bases, such as barium hydroxide, potassium carbonate, pyridine, hexamethylenetetramine, and urea, influence the rate of the reaction to a much smaller extent (Table I).

TABLE I. EFFECT OF CATALYSTS ON VISCOSITY OF PHENOL RESINS

CATALYST	(One mole of phenol per one mole of acrolein)					
	VISCOSITY AFTER DAYS:					
	10	13	16	20	30	38
1. Acid potassium sulfate	1.360	1.397	1.404	1.458	1.502	1.521
2. Potassium hydroxide	1.403	1.406	1.413	1.421	1.448	1.470
3. Hexamethylenetetramine	1.360	1.361	1.362	1.378	1.380	1.382
4. β -Naphthalenesulfuric acid	1.358	1.375	1.388	1.395	1.407	1.413
5. Barium hydroxide	1.322	1.328	1.336	1.335	1.330	1.338
6. Boric acid	1.501	1.502	1.504	1.508	1.510	1.512
7. Potassium carbonate	1.332	1.336	1.342	1.336	1.348	1.361
8. Urea	1.382	1.427	1.423	1.502	1.507	1.508
9. Phosphoric acid	1.442	1.464	1.476	1.481	1.473	1.489
10. Pyridine	1.312	1.334	1.340	1.362	1.365	1.368

From Figure 1, where the abscissa represents time of condensation in days, and the ordinate the viscosity of acetone solution of the resin, it may be seen that the rise of the curves is particularly rapid for such catalysts as acid potassium sulfate, potassium hydroxide, β -naphthalenesulfuric acid, phosphoric acid, and boric acid; and less rapid for urea, barium hydroxide, potassium carbonate, and hexamethylenetetramine.

The other problems to be solved were: (1) to investigate how the rate of condensation, the color of the product, and

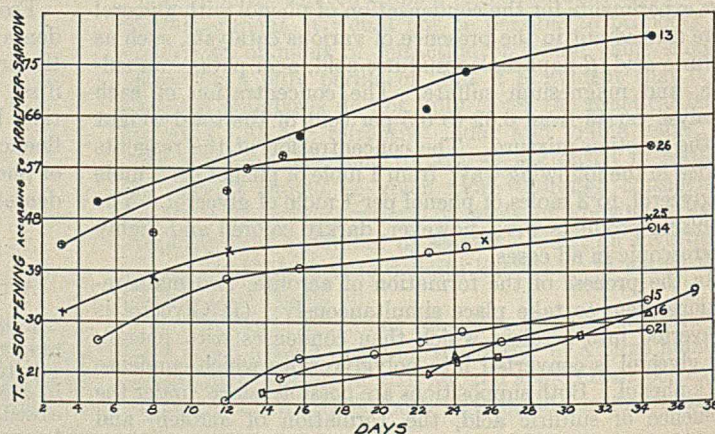


FIGURE 2. MELTING TEMPERATURES OF PHENOL RESINS

(Proportions same as Table II)

its technical properties depended on the mutual proportions of the reagents, if the same catalyst (acid or basic) was used; and (2) to investigate the influence of phenol, cresols, and xylenols on the rate of condensation and the properties of the final products. It was important to solve these questions both from the practical and theoretical points of view, as the solution might lead to the preparation of technically valuable phenol-acrolein resins. In the first series of experiments with

TABLE II. DETERMINATION OF MELTING POINTS OF PHENOL RESINS

RESIN	PROPORTION OF PHENOL TO ACROLEIN Moles	MELTING POINT ^a AFTER DAYS:													
		3	5	8	12	13	15	16	20	23	25	26	28	35	42
		° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
CATALYST, ACID POTASSIUM SULFATE															
15	1:1	16	..	20	24	..	27	29	34	..
14	1:1.5	..	27	..	38	40	..	42.5	44	47.5	..
25	1:3	32	..	37.5	43	44	..	45	..	49	..
26	1:4	44	..	46.5	..	58	60	61	62	..
13	1:5	51	52	..	54	..	60	63	..	69	76	82	..
16	1.5:1	22	26	32	33
CATALYST, POTASSIUM HYDROXIDE															
21	1:2.5	20	..	24	27	29	..
CATALYST, PHOSPHORIC ACID															
9	1:1	18	18	..	21	..	24	..	29	31	38

^a According to Kraemer-Sarnow.

TABLE III. DETERMINATION OF MELTING POINTS OF PHENOL RESINS

RESIN	PROPORTION OF PHENOL TO ACROLEIN Moles	MELTING POINT ^a AFTER DAYS:												
		4	8	12	15	17	20	23	24	26	28	30	35	
		° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	
CATALYST, ACID POTASSIUM SULFATE														
15	1:1	30	..	36	37	38	40	43
14	1:1.5	..	37	46	..	50	..	59	60	62
25	1:3	40	52.5	53	54	54.5	..	55.5
26	1:4	44	60.5	62	65	67	..	72
13	1:5	..	56	60	..	64	67	75	86
16	1.5:1	24	..	37	..	39	40	41.5
CATALYST, POTASSIUM HYDROXIDE														
21	1:2.5	24	..	29	..	30	..	31	32	34	..

^a According to Kraemer-Sarnow.

an acid catalyst (0.1 part by weight of acid potassium sulfate), the quantitative proportions of the reagents varied in the following order: 1, 1.5, 3, 4, or 5 moles of acrolein per 1 mole of phenol; and 1, 1.5, 2, 3.5, or 5 moles of phenol per 1 mole of acrolein. In the second series of experiments with a basic catalyst (0.1 part by weight of potassium hydroxide), the quantitative proportions of the reagents were the following: 1, 2.5, or 5 moles of acrolein per 1 mole of phenol; and 1, 1.5, or 2 moles of phenol per 1 mole of acrolein.

The mixtures, according to the above-mentioned quantitative proportions, were thoroughly shaken in air-tight flasks that were placed in a cooling bath where the temperature was regulated so as to keep the reaction mixture at 20° C. The rate of condensation was measured. The results are given in Tables II-IV.

These experiments show that the rate of condensation in the presence of acid potassium sulfate increases with the increase in the quantity of acrolein, and reaches its maximum when the proportion is 5 moles of acrolein per 1 mole of phenol. In the presence of potassium hydroxide the maximum is reached when the proportion is 2.5 moles of acrolein per 1 mole of phenol. With a further increase of acrolein from 2.5 to 5 moles per 1 mole of phenol, in the presence of potassium hydroxide, the rate of condensation decreases considerably, so that the resinous product even in a month's time is still half liquid with a sharp smell of acrolein. The color of the condensation product is also different, depending upon the mutual proportions of the reagents: products with an acid catalyst and 5 moles of acrolein, and products with a basic catalyst and 2.5 moles of acrolein stand out because of their lighter color; the darkest products were obtained when more than 1 mole of phenol was used per 1 mole of acrolein.

In Figure 2 the ordinates represent the melting temperatures according to Kraemer-Sarnow for products with an acid catalyst, and the abscissas the time of condensation in days. This figure shows that the curves rise rapidly with the increase of the quantity of acrolein per 1 mole of phenol; and, vice versa, with a decrease of acrolein they become more gradual. This same order may be observed in the temperatures of the falling of drops, according to Ubbelode (Figure 3).

The change in viscosity for products prepared in the presence of acid and basic catalysts is shown in Figure 4. The ordinates represent the viscosity of the solution of resins, and the abscissas, the time in days. It may be seen from Figure

4 that at first the curves rise more rapidly for products with an acid catalyst; but later, during the course of condensation, these curves become more gradual and almost parallel to the abscissa axis. The curves for basic catalysts at first rise more slowly, but, when the reaction is nearly ended, their steepness rapidly increases. Such results coincide with those obtained for phenol-formaldehyde resins by Novák and Cech (5).

It is interesting to note that the maximum rise with an acid catalyst may be observed in the curve for a resin prepared from 5 moles of acrolein per 1 mole of phenol, and with a basic catalyst for a resin prepared from 2.5 moles of acrolein per 1

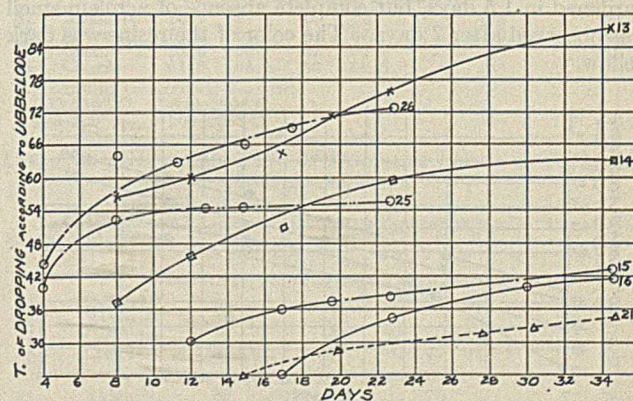


FIGURE 3. DRIPPING TEMPERATURES OF PHENOL RESINS
(Proportions same as Table III)

mole of phenol. The elementary composition of the resin, prepared by condensing 1 mole of phenol with 5 moles of acrolein in the presence of acid potassium sulfate, varied depending on the purification of the resin. A resin, twice precipitated by water from an acetone solution and dried at 50° C. under reduced pressure at 65 mm., showed the following composition: carbon, 56.20 per cent; hydrogen, 6.66 per cent; and oxygen, 37.14 per cent. The same resin precipitated by water from an alcohol solution and dried under the same conditions showed: carbon, 61.47 and 61.80 per cent; hydrogen, 6.32 and 6.32 per cent; and oxygen, 32.21 and 31.88 per cent. The resin residue insoluble in alcohol showed: carbon, 50.96 per cent; hydrogen, 6.96 per cent; and oxygen, 42.11 per cent.

CONDENSATION OF ACROLEIN WITH HOMOLOGS OF PHENOL

English tricresol was divided by distillation in two fractions, boiling at 195–200°, and 200–205° C., respectively. Resins were prepared from them by the same method as was used for phenol.

Thirty-three grams of acrolein (7 moles of acrolein per 1 mole of cresol), 12.96 grams of the cresol fraction, and 0.1 gram of acid potassium sulfate or potassium hydroxide were thoroughly mixed on a water bath, where the temperature was maintained so as to keep the reaction mixture at 20° C. to the end of the reaction, and a little longer for the time necessary to determine the melting point according to Kraemer-Sarnow and Ubbelode, and the viscosity in acetone solution.

The products with an acid catalyst hardened on the second day, but a complete absence of acrolein smell was observed only on the fifth day.

The products with a basic catalyst (potassium hydroxide) hardened in 1.5 days, but complete absence of acrolein smell was observed after 7 days. The color of the resins was dark yellow.

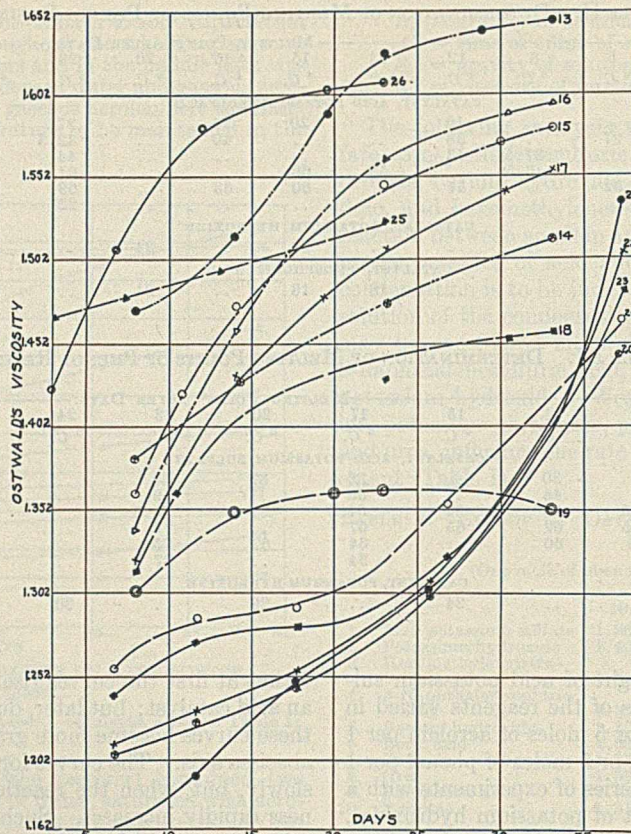


FIGURE 4. CHANGE IN VISCOSITY OF PHENOL RESINS
(Proportions same as Table IV)

The results of the determination of the melting points according to Kraemer-Sarnow for cresol resins are shown in Table V and Figures 5 and 6.

The mixture of xylenols was obtained from the higher fractions (boiling point, 185–250° C.) of purified phenols from coal tar. Purification consisted in treating the fractions with a small quantity of formaldehyde and sulfuric acid in order to get rid of thio-compounds, and then fractionating them between 190–250° C., the distillate being dissolved in a 10 per cent solution of sodium hydroxide and washed with ether and benzene to get rid of hydrocarbons. Free phenols were isolated by passing carbon dioxide through an alkali solution, and were separated, dried with sodium sulfate, and distilled.

The fractions boiling at 200–210° and 210–220° C. were condensed under the conditions previously mentioned. Mixtures of 14.32

grams of the xylene fraction and 33 grams of acrolein (5 moles of acrolein per 1 mole of xylene) with an acid catalyst were converted into a hard resin on the second day, the acrolein smell disappearing on the fifth day. The color of

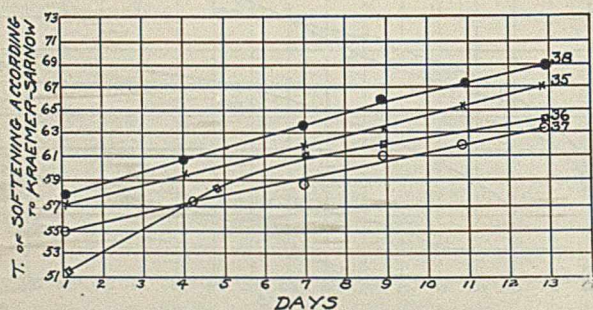


FIGURE 5. DETERMINATION OF MELTING POINTS OF XYLENOL AND CRESOL RESINS WITH ACID CATALYST
(Proportions same as Table V)

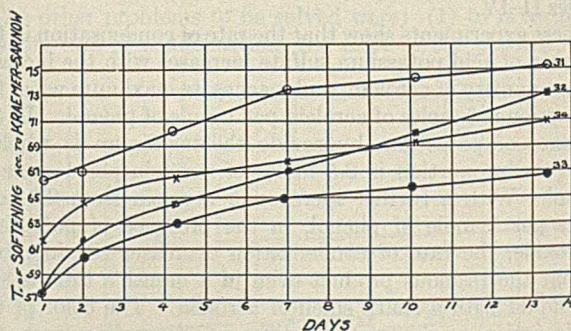


FIGURE 6. DETERMINATION OF MELTING POINTS OF XYLENOL AND CRESOL RESINS WITH BASIC CATALYST
(Proportions same as Table V)

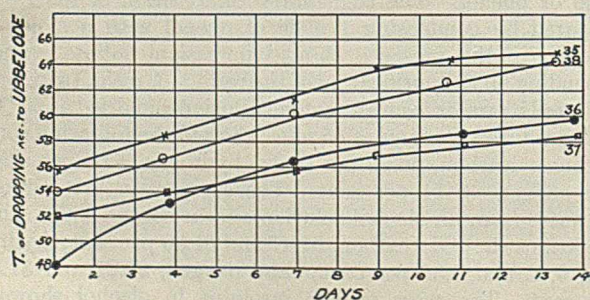


FIGURE 7. DETERMINATION OF DROPPING POINTS OF XYLENOL AND CRESOL RESINS WITH ACID CATALYST
(Proportions same as Table VI)

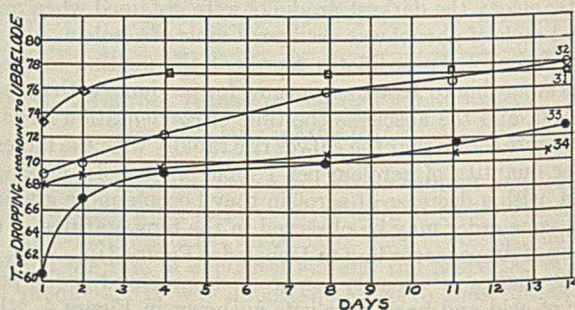


FIGURE 8. DETERMINATION OF DROPPING POINTS OF XYLENOL AND CRESOL RESINS WITH BASIC CATALYST
(Proportions same as Table VI)

TABLE IV. DETERMINATION OF VISCOSITIES OF PHENOL RESINS

RESIN	PROPORTION OF PHENOL TO ACROLEIN Moles	VISCOSITY AFTER DAYS:													
		3	7	8	10	12	13	14	18	20	23	27	28	30	33
CATALYST, ACID POTASSIUM SULFATE															
15	1:1	1.362	...	1.412	...	1.475	...	1.547	1.560	1.581	...
14	1:1.5	1.382	...	1.425	...	1.475	...	1.477	1.495	1.515	...
25	1:3	1.468	...	1.472	...	1.482	1.494	...	1.508	...	1.528
26	1:4	1.425	...	1.512	...	1.582	1.594	...	1.515	...	1.599	1.608
13	1:5	1.470	1.459	...	1.582	...	1.626	...	1.635	1.643
16	1:5.1	1.341	1.412	1.433	...	1.462	...	1.566	...	1.580	1.593
17	2:1	1.319	1.409	...	1.428	...	1.428	...	1.540	1.566
18	3.5:1	1.314	1.352	1.351	...	1.360	...	1.364	...	1.440	1.457
19	5:1	1.302	1.349
CATALYST, POTASSIUM HYDROXIDE															
20	1:6	...	1.214	1.234	1.255	1.314	1.420
21	1:2.5	...	1.161	1.201	1.259	1.316	1.521
22	1:1	...	1.221	1.242	1.263	1.319	1.498
23	1.5:1	...	1.250	1.281	1.291	1.336	1.470
24	2:1	...	1.266	1.296	1.304	1.368	1.452

the products was pale yellow. With a basic catalyst (potassium hydroxide) the product hardened in 1.5 days, and the acrolein smell disappeared after 6 days. The color of the products was pale yellow.

The results of the determination of melting points and viscosities of resins in acetone solution are shown in Tables V-VII, and Figures 5-10.

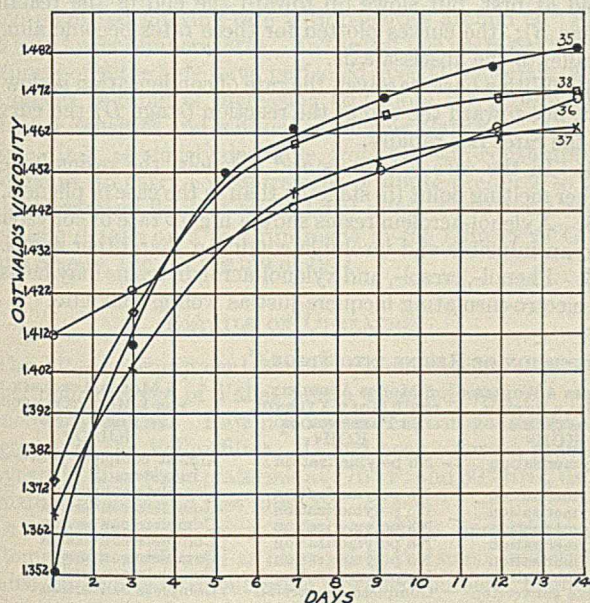


FIGURE 9. DETERMINATION OF VISCOSITIES OF XYLENOL AND CRESOL RESINS WITH ACID CATALYST (Proportions same as Table VII)

From these figures it may be seen that the maximum rate of condensation belongs to the resin prepared from acrolein and the higher-boiling fraction of xylene, and the minimum rate to the resin prepared from acrolein and the lower-boiling fraction of tricresol.

CHARACTERISTICS OF PRODUCTS

All the resins prepared, before gelatinization in stage A, readily dissolve in acetone, in benzene, and in a mixture of alcohol and benzene; partly dissolve in methyl and ethyl alcohols, and in ether; and difficultly dissolve in turpentine, flax oil, and aliphatic hydrocarbons. Like phenol-formaldehyde resins, these resins may be converted into an infusible and insoluble condition (stage C) only if the quantity of phenol does not exceed 1 mole per 1 mole of acrolein. The rate of conversion into stage C varies according to the kind of catalyst used and the proportions of phenol and acrolein, as shown in Table VIII.

The rate of polymerization was determined by heating resin

films on glass to 180-190° C. in a thermostat, and subsequently dissolving the film in a hot mixture of alcohol and benzene. In case of complete conversion into stage C, the film remained insoluble; in case of partial conversion, there was a partial solution. In this way it was found that the most rapid polymerization was shown by resins prepared from xylene when the proportion was 5 moles of acrolein per 1 mole of xylene, and when potassium sulfate was used as a catalyst. Phenol came next with the same catalyst and the same proportion of reagents. Polymerization is much slower for phenol when the proportion is 4 moles of acrolein per 1 mole

TABLE V. DETERMINATION OF MELTING POINTS OF XYLENOL AND CRESOL RESINS

RESIN	5 MOLES ACROLEIN PER 1 MOLE OF:	MELTING POINT ^a AFTER DAYS:							
		1	2	4	7	9	10	11	14
CATALYST, ACID POTASSIUM SULFATE									
35	Xylenol ^b	56	..	58	62	65	65.5	66	66
36	Xylenol ^c	48	..	56	57	58	59	59	59.5
37	Cresol ^d	52	..	56	56.5	57.5	..	58	59
38	Cresol ^e	54	..	59	61	64	64.5	..	65
CATALYST, POTASSIUM HYDROXIDE									
31	Xylenol ^c	66.7	67	69	74	..	75	..	76
32	Xylenol ^b	57.5	62	64	67	..	69	..	74
33	Cresol ^d	57.5	60	62	65	..	66	..	67
34	Cresol ^e	61.5	65.5	66	66.5	..	68	..	70

^a According to Kraemer-Sarnow.
^b 200-210° C. ^c 210-220° C.
^d 195-200° C. ^e 200-205° C.

TABLE VI. DETERMINATION OF DROPPING POINTS OF XYLENOL AND CRESOL RESINS

RESIN	5 MOLES ACROLEIN PER 1 MOLE OF:	DROPPING POINTS ^a AFTER DAYS:								
		1	2	4	7	8	9	10	11	14
CATALYST, ACID POTASSIUM SULFATE										
35	Xylenol ^b	56	..	58	62	..	64	..	66	69
36	Xylenol ^c	40	..	52	56	..	58	..	60	62
37	Cresol ^d	52	..	54	55	..	57	..	59	61.5
38	Cresol ^e	54	..	57	60	..	62	..	63	64
CATALYST, POTASSIUM HYDROXIDE										
31	Xylenol ^c	69	69.5	72	..	76	77	78
32	Xylenol ^b	73.5	76	76.5	..	77	..	77.5	..	78
33	Cresol ^d	60.5	67	68	..	69	..	70	..	73
34	Cresol ^e	68	69.5	70	..	71	71	71.5

^a According to Ubbelode.
^b 200-210° C. ^c 210-220° C.
^d 195-200° C. ^e 200-205° C.

TABLE VII. DETERMINATION OF VISCOSITIES OF XYLENOL AND CRESOL RESINS

RESIN	5 MOLES ACROLEIN PER 1 MOLE OF:	VISCOSITY AFTER DAYS:											
		1	3	5	7	9	10	11	12	14	14	14	14
CATALYST, ACID POTASSIUM SULFATE													
35	Xylenol ^a	1.352	1.410	...	1.466	1.470	1.476	1.483
36	Xylenol ^b	1.412	1.425	...	1.444	1.454	1.463	1.471
37	Cresol ^c	1.367	1.403	...	1.447	1.452	1.456	1.463
38	Cresol ^d	1.375	1.418	...	1.455	1.462	1.465	1.471
CATALYST, POTASSIUM HYDROXIDE													
31	Xylenol ^b	1.523	1.551	1.556	1.594	1.600	...	1.615
32	Xylenol ^a	1.481	1.491	1.492	1.513	1.520	...	1.546
33	Cresol ^c	1.402	1.472	1.480	1.495	1.501	...	1.527
34	Cresol ^d	1.412	1.505	1.522	1.545	1.551	...	1.565

^a 200-210° C. ^b 210-220° C.
^c 195-200° C. ^d 200-205° C.

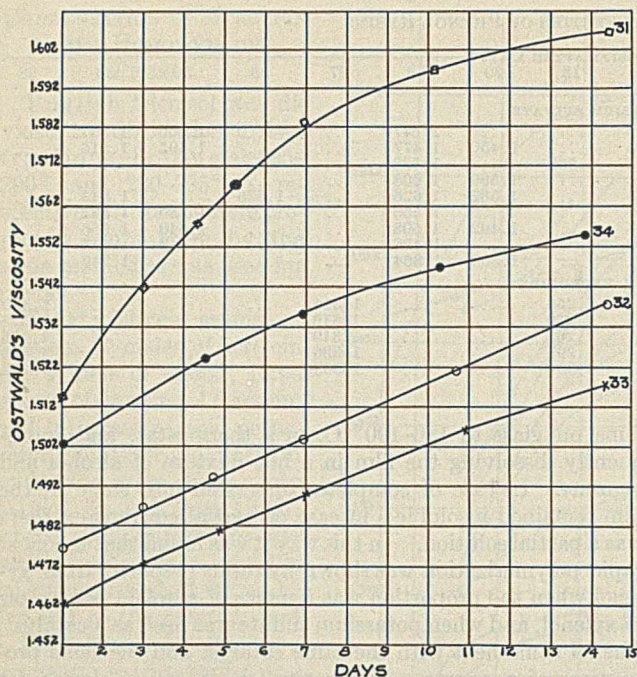


FIGURE 10. DETERMINATION OF VISCOSITIES OF XYLENOL AND CRESOL RESINS WITH BASIC CATALYST

(Proportions same as Table VII)

of phenol. When a basic catalyst (potassium hydroxide) is used, and the proportion is 2.5 moles of acrolein per 1 mole of phenol, polymerization goes on still more slowly.

Preliminary experiments showed that phenol-acrolein resins may be used for the preparation of insulating lacquers. The tensile strength and the volume and surface resistance of films

made of these lacquers are quite satisfactory, and, at any rate, are not worse than those made of Bakelite. A great deal depends on the method of preparation of the lacquers and on the solvent and plasticizers used. Table IX shows the results obtained in this laboratory with films of Bakelite, phenol-acrolein (resins 13, 25, 26), xylenol-acrolein (resin 31), and cresol-acrolein (resin 34). Cresol- and phenol-Bakelite resins were made using ammonia as catalyst. The data on electrical properties were determined from films (on cigarette paper) after drying at 80° C. (but not polymerization), and after complete polymerization (at 80° C.). Polymerized films were tested immediately after heating and after immersion for 24 hours in water, in ammonia solution (15 per cent), in hydrochloric acid solution (1 per cent), in potassium hydroxide solution (1 per cent), and after remaining in water vapor for 24 hours.

SUMMARY

1. The rate of condensation with an acid catalyst reaches its maximum when 5 moles of acrolein per 1 mole of phenol are used, and with a basic catalyst when 2.5 moles of acrolein per 1 mole of phenol are used.
2. With an acid catalyst, the course of condensation is rapid at first, but slows up toward the end of the reaction (stage B); the curves plotted for these rates become almost parallel to the abscissa axis.
3. With a basic catalyst, the rate of condensation is slow at first, but toward the end of the reaction (stage D) the curves for the rates rise rapidly.
4. In the case of cresols and xylenols, the resins have a higher melting point (in stage B) than in the case of phenols.
5. Xylenol-acrolein resins show a higher rate of conversion into an infusible and insoluble condition than other resins.
6. Phenol-, cresol-, and xylenol-acrolein resins may be used for electro-insulating lacquers just as well as Bakelite.

TABLE VIII. EFFECT OF CATALYST ON CONVERSION OF RESINS INTO STAGE C

TIME OF HEATING AT 180-190° C.	5 MOLES ACROLEIN PER 1 MOLE PHENOL IN PRESENCE OF KHSO_4^a	4 MOLES ACROLEIN PER 1 MOLE PHENOL IN PRESENCE OF KHSO_4^b	2.5 MOLES ACROLEIN PER 1 MOLE PHENOL IN PRESENCE OF KOH^c	5 MOLES ACROLEIN PER 1 MOLE XYLENOL IN PRESENCE OF KOH^d	5 MOLES ACROLEIN PER 1 MOLE XYLENOL IN PRESENCE OF KHSO_4^e
30 sec.	Partial conversion into stage C	No polymerization	No polymerization	No polymerization	Almost complete conversion into stage C
60 sec.	Complete conversion	No polymerization	No polymerization	No polymerization	Complete conversion
120 sec.	Complete conversion	No polymerization	No polymerization	No polymerization	Complete conversion
180 sec.	Complete conversion	No polymerization	No polymerization	No polymerization	Complete conversion
6 min.	Complete conversion	No polymerization	No polymerization	No polymerization	Complete conversion
10 min.	Complete conversion	No polymerization	No polymerization	No polymerization	Complete conversion
20 min.	Complete conversion	No polymerization	No polymerization	No polymerization	Complete conversion
40 min.	Complete conversion	No polymerization	Complete conversion	Complete conversion	Complete conversion

^a Resin 13. ^b Resin 26. ^c Resin 21. ^d Resin 31. ^e Resin 35.

TABLE IX. PROPERTIES OF RESIN FILMS

RESIN	AFTER DRYING AT 80° C. Ohms/cm. ²	AFTER POLYMERIZATION						
		Immediately after heating Ohms/cm. ²	After soaking in 1% HCl soln. Ohms/cm. ²	After soaking in 1% NaOH soln. Ohms/cm. ²	After soaking in 15% NH_3 soln. Ohms/cm. ²	After staying in water vapor Ohms/cm. ²	After soaking in water Ohms/cm. ²	
SURFACE RESISTANCE								
31	Xylenol-acrolein	3.52×10^{10}	8.2×10^{10}	2.37×10^{10}	2.76×10^{10}	1.79×10^{10}	7.12×10^{10}	3.56×10^{10}
34	Cresol-acrolein	1.14×10^{12}	2.3×10^{12}	2.42×10^{11}	1.24×10^{10}	1.54×10^{10}	3.86×10^{10}	1.08×10^{10}
25	Phenol-acrolein	6.07×10^{12}	9.4×10^{12}	2.23×10^{11}	1.09×10^{10}	2.9×10^{10}	4.75×10^{10}	9.06×10^{10}
13	Phenol-acrolein	3.99×10^{12}	6.7×10^{12}	2.64×10^{11}	1.09×10^{10}	1.13×10^{11}	1.11×10^{11}	1.42×10^{11}
26	Phenol-acrolein	1.74×10^{10}	4.2×10^{11}	1.4×10^{11}	4.37×10^{10}	4.4×10^{11}	2.58×10^9	1.97×10^{12}
..	Cresol-Bakelite	1.14×10^{12}	2.14×10^{12}	1.01×10^{11}	1.34×10^{10}	6.54×10^{10}	4.38×10^{11}
..	Phenol-Bakelite	1.9×10^{13}	4.2×10^{12}	1.1×10^{11}	8.14×10^{10}	7.25×10^{10}	38×10^{11}
VOLUME RESISTANCE								
31	Xylenol-acrolein	1.22×10^{10}	3.1×10^{11}	1.4×10^{10}	Deterioration	1.51×10^{10}	1.83×10^{10}	1.36×10^{12}
34	Cresol-acrolein	2.25×10^{11}	3.2×10^{11}	4.55×10^9	Deterioration	5.88×10^9	6.6	6.11×10^{10}
25	Phenol-acrolein	1.35×10^{11}	2.3×10^{11}	4.18×10^9	Deterioration	1.28×10^{10}	3.46×10^9	6.23×10^{10}
13	Phenol-acrolein	1.06×10^{12}	5.3×10^{12}	1.35×10^{11}	4.55×10^9	4.18×10^{11}	1.83×10^{12}	9.5×10^{11}
26	Phenol-acrolein	3.4×10^{11}	3.96×10^{10}	4.08×10^9	Deterioration	3.98×10^9	9.5×10^{10}
..	Cresol-Bakelite	8.46×10^{12}	4.2×10^{12}	1.33×10^{11}	Deterioration	3.75×10^{10}	3.5×10^{11}
..	Phenol-Bakelite	1.68×10^{11}	3.7×10^{11}	3.93×10^9	Deterioration	6.94×10^9	3.22×10^{10}
DIELECTRIC STRENGTH ^a								
		Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.
31	Xylenol-acrolein	36.6	38.1	32.1	30.2	30.3	31.3	30.3
34	Cresol-acrolein	38.2	38.6	36.1	31.0	30.8	30.2	31.2
25	Phenol-acrolein	31.0	32.3	26.1	20.0	21.0	22.1	22.5
13	Phenol-acrolein	47.6	48.1	46.1	40.3	41.2	40.0	42.3
26	Phenol-acrolein	37.2	39.0	35.4	32.0	33.1	34.1	31.8
..	Cresol-Bakelite	30.5	37.5	30.2	27.0	30.1
..	Phenol-Bakelite	31.9	36.1	36.1	26.2	34.2

^a K/V.

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RECEIVED June 30, 1931.

High-Density Filtration

JOHN P. GREVEN, Godchaux Sugars, Inc., Reserve, La.

IN THE old days of the sugar industry the mechanical filtration of sugar liquors was accomplished with various types of gravity filters, such as bag filters, Danek filters, etc. The use of filter aid was unknown, and, as a consequence the rate of flow was rather slow and could be maintained only by carrying proper dilution, usually around 55° Brix, and high temperatures, usually around 190° F. When the various types of pressure filters came into use, filter aids were developed subsequently, which made it possible to obtain a very much increased filtering rate with densities around 60° Brix and with lower temperatures. In the last few years the manufacturers of filter aids have perfected special materials, with the object in mind of increasing still more the rate of flow at higher densities and without sacrificing clarity.

Since it is obviously desirable, from a steam-consumption standpoint, to carry concentrations of dilute products to the highest practical limit, it might be of interest to submit some operating details on a test run made in the refinery of Godchaux Sugars, Inc., in the fall of 1931.

DETAILS OF OPERATION

The filtering equipment at that plant consists of the so-called refinery type of Vallez filters, supplied with 70 × 80 monel wire screens. Raw liquors and centrifugal sirups are filtered over the Vallez filter. It had been common practice for years to filter these materials at 176° F. and 60° Brix, using a mixture of slow and fast filter aid.

In explanation, it may serve to state here that the diatomaceous earth used as filter aid in the sugar industry is graded, according to its filtration efficiency, as slow, medium, and fast. Slow and fast filter aids were mixed in order to obtain proper clarity and speed combined. The slow filter aid gives the maximum clarity and minimum filter speed, and the fast filter aid, the minimum clarity with maximum speed. It was common practice to use the slow filter aid for the preliminary coating of the press screens and then follow this with fast pressure filtration, and fast filter aid.

In September, 1931, a test was made covering approximately one month of operating time, during which the fast filter aid was used exclusively. An orifice plate, 1 inch in diameter, was installed in all 4-inch liquor inlet lines to the Vallez filters in order to insure a very gradual pressure increase in the filters during the filtering cycle. This point is essential in obtaining satisfactory results from heavy-density filtration. Beyond that, no mechanical changes were made. Nothing but fast filter aid was used, and the density of the filtrate was increased to 66.5° Brix.

Temperatures of the filtrate remained the same (176° F.), and pH was maintained at 7.1 as formerly. Maximum pressure on the Vallez filters at the end of the cycle was 40 pounds, which was slightly in excess of former pressures obtained. Clarity of the filtrate was up to normal standards as measured by a modification of Tyndall's turbidimeter. The following tabulation indicates the advantages obtained:

VALLEZ FILTERS	NORMAL DENSITY	HEAVY DENSITY
Cycles per 24-hour day	38	11
Average filtering time per cycle	2 hr., 46 min.	8 hr., 55 min.
Raw sugar per cycle, tons	27	85
Filter aid per ton melt, pounds	8.27	6.21
Corrected Brix of filtrate	60	66.5

Since the resulting mud cake sluiced from the Vallez filters is being refiltered over a set of secondary filter presses, designated as mud presses, a brief tabulation shows results obtained there:

MUD PRESSES	NORMAL DENSITY	HEAVY DENSITY
Press cycles per day	15.2	11
Average filtering time per cycle, hours	3.86	6.62
Press mud per ton melt, pounds	20.67	11.87
Sucrose loss per ton melt, pound	0.14	0.10

Here again the advantage of heavy-density filtration shows up clearly in an extension of press cycles, with resulting reduction in sugar losses and production of light sweet water.

Following the changes produced through subsequent char filtration, it was noted that, owing to the heavier concentration carried, it was possible to handle the same volumes of melt over one less char filter, making this char filter available for other purposes. Ash and color removal in char showed an increase with heavy-density filtration, as might be expected because of higher concentration of nonsugars. An increase was noted in the time required to sweeten off the char filters, owing to heavy-density filtration, resulting in an excess production of concentrated sweet water per ton melt. This was particularly noticeable in the fine grist char.

SUMMARY

1. Raw liquor can be safely filtered, using high speed filter aid exclusively, at 66–67° Brix density without a sacrifice of clarity.
2. Advantages of high-density filtration are:
 - a. Economies resulting from reduction in fuel used, reduction in filter aid used, reduction in sucrose losses, and reduced maintenance of filter equipment.
 - b. Increased capacities of mechanical filtration, char filtration, and subsequent evaporation processes.
3. The disadvantage of high-density filtration is the increased sweet water production in the char house, but this is not sufficient to offset the advantages obtained.

ACKNOWLEDGMENT

The author is indebted to Roy D. Elliott, filtration expert with Johns-Manville, Inc., for his suggestions and advice in connection with this experiment.

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AMERICAN CONTEMPORARIES

Percy Hargraves Walker

FOR a number of years this part of our Journal has been one of its most diverting features. These ante-mortem obituaries are informative and inspirational. The subject learns what one of his fellows dares to say about him in print, and the writer has a fine chance to air his opinion of his colleague. Meanwhile the editor rides his hobby. Few activities are so universally pleasing.

From "Who's Who" one can find out that Percy Hargraves Walker was born in Alabama, July 6, 1867. Although his sixty-fifth anniversary comes this year, he is really not so old as that—at least not in spirit, nor evidently in the flesh.

After the usual preparatory schooling, Walker went to the University of Virginia, where he was a student in 1885-87, and 1889-90. A man's college is truly his Alma Mater, his bountiful mother of pleasant memories. Walker still talks about his student days and speaks of Professor Mallet in a way that shows his deep respect and affection, which one can well understand who ever heard that fine old man give a lecture. Some of his accounts of life at Charlottesville indicate that the students indulged in other sports than athletics.

In the fall of 1892 Walker went to the University of Iowa, where he was instructor in chemistry and mineralogy until 1896. Meantime, in 1895 he received the degree of master of science. After a semester at the University of Heidelberg, immediately followed by one at the University of Berlin, he returned to Iowa, where he stayed until 1899. An associateship in chemistry and physics at the University of Arkansas, 1900-2, ended his teaching career; for ever since he has been a federal employee.

During the years up to the last date mentioned, Walker was engaged in various other enterprises. For a time he was a partner in a commercial laboratory at Nashville, Tenn., where all sorts of chemical work was done. The most important was making fertilizer analyses for the state Department of Agriculture; partly as a result of this, the laboratory played a prominent part in the development of the phosphate rock industry in Tennessee. For a time he had a field laboratory for testing phosphate rock. He also worked in laboratories in the Birmingham, Ala., district, analyzing iron ores, pig iron, fluxes, slag, and other materials. After this he went to Scranton, Pa., as an assayer connected with the International Correspondence Schools. He had a share in writing some of their books on chemical technology.

This brings us to the Bureau of Chemistry, United States Department of Agriculture, where he became an assayer in 1902. The bureau was then under Harvey W. Wiley. The writer has never seen an assayer actually at work, which probably accounts for his strongly alchemical mental image of an assayer. That is not at all Walker's type, so it is not surprising that in 1906 he became chief of the Contracts Laboratory of the bureau, a position he held until 1914.

The writer became acquainted with Walker some time in 1904, probably while spending a day in Washington, sight-seeing. Memory can be tricky, and can tell apocryphal tales. Walker may not have been the chemist whose picture comes to mind, but he might have been, and there can be no doubt about what the chemist was doing. Remember this was twenty-eight years ago.



P. H. WALKER

Some higher-up in the Government was giving a dinner and, to show his Americanism, only California wine was to be served. The sting to this is that he had his doubts about the wine and was having it analyzed by the Contracts Laboratory. The point to be settled was whether the wine had been colored artificially. Although this research was being conducted along strictly scientific lines, the visitor was hospitably urged to make a service test.

In those days Uncle Sam, not content with his other sources of revenue, eked out his income by the sale of olive oil and wine, both being what remained of samples that had been analyzed and passed as unadulterated. It was a curious sight to behold a handful of people standing outdoors behind the old building of

the Department of Agriculture, while an auctioneer faced them with partly filled bottles of oil or wine in his hands. Somehow, the whole proceeding had a furtive clandestine appearance.

In the Contracts Laboratory many different kinds of supplies were analyzed and tested. As the methods employed were of interest to the contractors, as well as to other chemists, Walker wrote Bulletin 109, Testing of Miscellaneous Materials. Several years later it was partly revised and issued as Miscellaneous Paper 15 of the Bureau of Standards. This paper represents only one phase of Walker's work on standardization in the purchase of supplies as we shall see farther on. A much more important paper, written in 1906 in collaboration with L. S. Munson, was on the Unification of Methods for the Determination of Reducing Sugars. As Fehling's solution was the reagent used, this involved making a vast number of careful analyses of solutions of a wide range of concentrations. The tables are still standard. Other papers on work done or directed by him appeared while he was in the Bureau of Chemistry.

One paper that deserves to be remembered because it was the pioneer on the subject, and because of its ultimate direct and indirect results, was on Platinum Laboratory Utensils. With F. W. Smither he made a study of platinum crucibles and dishes, and showed convincingly that their quality left much to be desired. The metal fell far short of what was claimed for it by the manufacturers of the ware. This was in 1910. The next year a committee of the AMERICAN CHEMICAL SOCIETY, under the chairmanship of Dr. Hillebrand and with Walker as a member, issued a report that was in full harmony with the earlier findings. This started led to a great deal of further work in one laboratory or another, and eventually brought about a great improvement in the quality of the ware now sold.

In those days there were three government laboratories in Washington whose work overlapped or conflicted here and there. There were the Contracts Laboratory, the laboratory of the Supervising Architect of the Treasury Department, and part of the Chemistry Division of the Bureau of Standards. The scarcely veiled rivalry between the three laboratories led to an amusing situation in 1908 when the General Supply Committee began to function as a general contracting agency for the departments in the District of Columbia. The laboratories were invited to send representatives to the large room occupied by the committee, where thousands of bid samples were arranged in groups on the floor, waiting to be carried away and tested. Each of us knew that

there were plenty of samples that had to be tested somehow and by somebody. It was more than evident that there were enough to go around; yet the three of us staged the pleasing one-act play of grab, each fearful that the other would get more than his share of the samples and, ultimately, too much of the supposititious credit for doing the work. At times the situation became more than usually tense, and our language to one another severely and insultingly polite. The funny side of all this did not strike us until later, and that one experience was enough for all of us.

In 1914 Walker and most of the chemists in the Contracts Laboratory were transferred to the Bureau of Standards. The chemists in the Technologic Branch of the Geological Survey had already been transferred to the bureau when the branch was expanded into the Bureau of Mines. All of us were under the chief chemist, W. F. Hillebrand.

At present Walker is in charge of the work on paints, varnishes, and similar protective coatings, and on bituminous materials except as they are used for road-making. As assistant chief of the Chemistry Division he exercises a mild supervision over some of the work in which he is not otherwise directly interested. He is also in charge of all correspondence for which the division is responsible. He does not exercise this function in a careless perfunctory way, but reads outgoing letters before approving them. Every now and then he asks that some particularly choice letter be rewritten, because what it says is incorrect or of doubtful advisability. For all that, some of the most scathing letters that go out are his—not dictated but written and revised until all parts are at the desired temperature.

Although born so near the Gulf, Walker is not a "professional southerner," nor lazily indolent, nor a fire eater. Whatever tendencies in the last direction he may have inherited are not displayed, but are merely hinted at by the delight he takes in argument. The topic may be almost anything, provided it is one on which it is easy to disagree. When the debate is over, his spirit of opposition lies dormant. As readily as anyone he will shift to a jocular mood. He enjoys amusing stories—including his own—and his hearty laugh rings out with slight provocation. This recalls the Bureau of Chemistry. It was not permitted to smoke in the old building, which was a fire trap, to say nothing of its decrepitude. So at lunch time the smokers gathered on the outside and discussed all the topics—some called it gossip—of the day. Of this group, known as the Liars' Club, Walker was both an honorary and a regular member. It is not for me to suggest why he attained this double distinction.

Probably every large testing laboratory is asked from time to time to write specifications for various materials, and neither the Bureau of Chemistry nor the Bureau of Standards is an exception. However, it was not until the establishment of the Federal Specifications Board a few years ago that the writing of specifications became a major activity of either bureau. Before the board came into being, Walker worked off that kind of steam in committees of the American Society for Testing Materials. He still maintains his interest in that society, and is active in its work, in spite of having a great deal of similar work nearer at home to keep him busy. He is a member of several of the technical committees appointed by the board to write specifications for various kinds of supplies. He is not content with being just a member of a committee, but attends the meetings and takes an active part in the discussions. His disposition to continue a meeting until something definite has been accomplished and to argue his side of all questions that arise, has caused much good-natured banter on the part of the other members. For all that, they respect his opinions and hold him in high esteem.

An unfortunate feature of committee work is that the chairman, like the general of an army, gets the credit for whatever is accomplished, unless the accomplishment happens to be a specification, in which case nobody seems to get any credit. A specification is the perfection of anonymity. Yet into any specification goes a measure of precise knowledge. Somebody, usually the

chairman, has made a study of the material in the laboratory and elsewhere, and has become so familiar with it that he is able to set down what he knows in precise language. Walker is chairman of the technical Committee on Paints and Oils. He is well prepared for this task, because his work in the Contracts Laboratory not only made him familiar with the subject, but also gave him a clear understanding of standardized purchasing of supplies. He knows paint as a laboratory sample and on the test fence. He has no zest for selling talk. His committee has written about thirty specifications, and all of them are largely his work.

At meetings of other committees than the one of which he is chairman, he does not sit back and vote for a specification just because it is carefully worded and neatly typed. There must be in it some evidence of thoughtful preparation and detailed knowledge of the material. The writer once asked his opinion of the first draft of a specification and was told that it took a great many words to say that so-and-so of good quality was desired. Having this trend of mind and the courage of his convictions, he actively discusses specifications when they are under consideration and usually succeeds in improving them. He has had a share in the writing of about one hundred specifications promulgated by the board.

It is not unreasonable for a buyer of paint to expect it to last at least two or three years outdoors. A chemical analysis cannot tell the whole story, and, if an actual service test were to be made, the most indifferent purchasing agent would begin to ask about that delayed laboratory report long before the test was completed. Paint is something that lends itself admirably to an accelerated aging test because in a few years, at most, it is possible to compare the character of the breakdown of the film in the laboratory with the behavior of a duplicate film exposed to the weather. Many have worked on this problem, and it seems fair to say that the accelerated test, described in print by Walker a few years ago, is one of the best that has been devised. The paint films break down in the laboratory in the same way that they do outdoors. Varnishes can be tested equally well, or to even better advantage, because their analysis is hardly worth the time spent on it.

Much more might be said about Walker's efforts and accomplishments in the chemical field, but space is lacking. This is not a bibliographic sketch, but biographic, and our editor asked for a word picture showing the man as he appears to the writer.

If his home life can make or mar a man, Walker cannot ascribe the blame for his derelictions to domestic troubles. He does not have the usual annoyances of the hobby-rider, because he has no hobbies except his pipe and books that are worth reading. He enjoys a game of bridge, and seems to be an accomplished back-seat driver when his wife or daughter is at the helm.

He is no longer a member of the Liars' Club, but belongs to the Cosmos and Federal Clubs in Washington. He has been a member of the AMERICAN CHEMICAL SOCIETY since 1893, and was president of the Washington Section in 1909. He became a member of the American Association for the Advancement of Science in 1905, and a fellow in 1908. Since 1907 he has been a member of the American Society for Testing Materials, and served on their Executive Committee in 1924.

Without the cheerful cooperation of F. W. Smither, a colleague of Walker for three decades, many parts of this sketch would perforce have been omitted.

C. E. WATERS

THE DEVELOPMENT OF SELF-SUFFICIENT CHEMICAL INDUSTRIES in countries which were formerly dependable outlets for German chemical products is an outstanding factor in the decline of the German chemical industry during the last two years, according to the Commerce Department. Intensified competition by the other large chemical-producing countries has also been severely felt by German producers. The possibility of these developments was overlooked or ignored while the German industry was expanding and rationalizing after the war on a gigantic scale, calculated in many instances to supply the world.

NOTES AND CORRESPONDENCE

Toxicity of Ethylene and Propylene Glycols

Editor of Industrial and Engineering Chemistry:

Your belated publication of Reid Hunt's letter concerning the toxicity of the ethylene and propylene glycols [IND. ENG. CHEM., 24, 361 (1932)] neglects references to published papers on the actions of these compounds from our laboratory during the interim. These papers report extensive pharmacological data which, it is believed, give a fair cross section of the actions and toxicity of these two glycols. The papers referred to are entitled "General Properties, Irritant and Toxic Actions of Ethylene Glycol," by P. J. Hanzlik, M. A. Seidenfeld, and C. C. Johnson [*J. Pharm.*, 44, 387 (1931)], and "The General Properties, Actions and Toxicity of Propylene Glycol," by M. A. Seidenfeld and P. J. Hanzlik [*Ibid.*, 44, 109-21 (1932)].

Our results on acute and chronic toxicities in animals indicate that the margin of safety in the internal administration of ethylene glycol is vastly greater than has been sometimes erroneously supposed from the older investigations. Some older investigators pointed out that the undesirable and injurious effects occurred only after very large doses outside the therapeutic range, and this we were able to confirm. We, too, found propylene glycol comparatively much less toxic, as did Hunt. On the other hand, propylene glycol appears to be somewhat more irritating locally in injected tissues than ethylene glycol, a fact of importance in connection with the choice of suitable vehicles for the hypodermic and intramuscular administration of medicinal agents. Whether the glycols, either ethylene or propylene, might be useful as, or in, foods is a matter that has not been given special consideration in our studies.

P. J. HANZLIK

STANFORD UNIVERSITY SCHOOL OF MEDICINE
SAN FRANCISCO, CALIF.
March 24, 1932

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Editor of Industrial and Engineering Chemistry:

Hanzlik and I have been interested in ethylene glycol from very different points of view. He was especially interested in the possible injurious effects of very small amounts (2 cc., for example) when used as a solvent for a powerful antisiphilitic drug. I did not question the safety of such use; as a member of the Council on Pharmacy and Chemistry of the American Medical Association, I voted to approve his preparation, although I did express the hope that, for reasons given below, a different solvent might ultimately be found. My letter to you was written before I knew of Doctor Hanzlik's interest in the subject, and it referred entirely to the suggested use of glycol in food products and flavoring extracts. Having been a witness of the disastrous results which, about 30 years ago, followed such use of methanol (which had been pronounced harmless on the basis of certain experiments on animals and also on man), I was interested in whether somewhat similar results might occur if ethylene glycol were used in a similar way. It had been suggested for such use in about forty food and flavoring products. Of course, I recognized that there would be less temptation to drink a product containing the glycol than one containing alcohol, but the idea that flavoring extracts are potable beverages is widespread. The same is true of antifreeze preparations,

as shown by the considerable number of deaths from methanol from the drinking of such preparations. At least seven deaths have resulted from the thirsty drinking an antifreeze containing ethylene glycol.

That ethylene glycol is, from this standpoint, a distinctly toxic substance cannot be doubted. The fatal doses found by Hanzlik, Seidenfeld, and Johnson agree very closely with those I had found. Hanzlik found 80 per cent of rats injected intravenously with doses of 2.8, 3.3, and 3.8 grams per kilo to die; I found 2.8 grams per kilo to kill about 50 per cent of the rats injected and 3.2 grams to kill about 90 per cent. I obtained similar results from intraperitoneal injections and from oral administration. My method of interpreting these results differed from that of Hanzlik and his co-workers. They remark, "Transferring the results on rats to adult men of 70 kg. . . . a fatal dose (of the glycol) would be about 308 grams, or more than half of a pound," and again: "It would seem that 77 grams might be injected intravenously without demonstrable effects in a 70-kg. man. Dr. Mehrtens has injected 2 and 3 cc. quantities in 3 adult men without demonstrable symptoms of any kind" (*italics mine*). It seems to me that such reasoning is not convincing. I found, for example [*New Engl. J. Med.*, 198, 230 (1928)], that rats would survive 11.6 cc. of methanol per kilo *per os*. Applying Hanzlik's argument, a 70-kg. man should survive 812 cc. of methanol *per os*. There have been so many deaths in men from the drinking of methanol that the probable fatal dose of this for man is fairly well known; it is about 120 cc., or about one-seventh of what would be considered a fatal dose according to the above line of reasoning.

It seemed to me that in the case of two poisons like methanol and ethylene glycol, a closer approximation to the possibly dangerous doses for man might be obtained by first determining the relative toxicity of the two upon animals. I did this with various animals and found that in the case of the rat 3.2 grams per kilo of the glycol were usually fatal, but that rats would almost invariably survive a dose of 9.3 grams of methanol. Thus the glycol was almost three times as toxic as methanol. Knowing that 120 cc. (96 grams) of methanol are a dangerous, and frequently fatal, dose for man, we might be justified in fearing that 32 grams of the glycol would at least be dangerous. However, the very scanty data available would suggest that the fatal dose of the glycol for man would be considerably larger than this. Thus Hansen (*Sammlg. Vergiftsfälle*, p. 175 (1930)) reported two very severe cases of poisoning in which two men drank the ethylene glycol contained in a pocket flask. He estimated that the flask contained about 200 cc. of the glycol. Both men were in a comatose condition for several days but, in the opinion of the author, their lives were saved by a surgical decapsulation of the kidney. These cases would suggest that 100 cc. of the glycol would frequently be very near a fatal dose for man, but this is not much more than a third of what Hanzlik argues would probably be fatal.

I fail to see that this recent work "indicates that the margin of safety in the internal administration of ethylene glycol is vastly greater than has been sometimes erroneously supposed;" any compound more poisonous than methanol will continue to be regarded as a potentially dangerous ingredient of food and beverage products, and it was only such use that I had in mind. I also found that the toxicity of the glycol was greatly increased in some conditions of malnutrition (vitamin A deficiency, for example), and that the fatal dose of both the glycol and of arsphenamine was lowered when the other was present.

When I wrote that letter in June, 1930, I did not know that anyone was contemplating recommending the intramuscular injection of ethylene glycol. I had in mind only the proposed use of the compound in food and beverage products, a matter to which Hanzlik states that he has not given special consideration. The chief reason why the letter was not published earlier seems to have been because some who had contemplated using the glycol in food products promptly abandoned the plan when told of my results. Pressure of other work and rather prolonged visits abroad prevented my carrying the work as far as was desirable. It would be very important, for example, to have more information as to exactly what happens to the compound in the body. It seems to be largely destroyed. It has been definitely shown that it is not converted into glycogen, in this respect differing markedly from propylene glycol which has been found by Salter here to form glycogen and so to have true food value. One of the questions which arises in connection with ethylene glycol is whether there may not be formed toxic intermediary products. There seems to be evidence that in the case of methanol, formaldehyde is produced as an intermediary product. It may be that the toxic action of the glycol is due to such intermediary products rather than to the comparatively small amount of oxalates which appear in the urine.

The extraordinary contrast between the toxicity of ethylene and propylene glycol suggests that in the case of the former some toxic product is formed which is later destroyed or has not been detected. In this connection I may remark that my observations of the effect of the glycol upon the kidney were somewhat more disquieting than were those of Hanzlik. The kidneys of rats which had received for 15 days doses of ethylene glycol which had not checked the growth or produced obvious symptoms of any kind, were described by Tyzzer as follows: "Macroscopically the kidneys were mottled as though sprinkled with fine sand; microscopically, sections presented the following appearance: There is extensive loss of parenchyma, the convoluted tubules being reduced to small areas. The cortex is thus largely replaced with connective tissue and the remaining tubules are distended. There are widespread accumulations of crystals of various types and a considerable number of the tubules are filled with polynuclear leucocytes."

Hanzlik found that the drinking by rats of a 1 per cent solution of glycol caused distinct pathological changes in the kidneys. But he argues that the "equivalent for a 70-kg. adult would be about 154 grams (more than a quarter of a pound) taken for about 6 or 7 years." It is interesting to recall what actually happened to Hansen's patients who took a single dose of about 100 cc. of the glycol; the quantity mentioned by Hanzlik would probably kill more than 2000 persons.

I desire to repeat, however, that although protests have been made to such use, I see no objections to the addition of the glycol to the antisiphilitic remedy, but the people should be protected against the promiscuous use of the compound in food products. Vastly more poisonous substances (strychnine, for example) are in constant use by physicians, but this does not justify the addition of strychnine to a great variety of patent medicines and even to beverages (as has occurred in the past). The trouble is that there are too many totally incompetent individuals dabbling in this field, as was well illustrated by the appalling results in the "ginger paralysis" episode.

REID HUNT

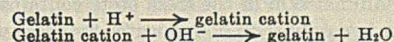
HARVARD MEDICAL SCHOOL
BOSTON, MASS.
April 4, 1932

Dilatometric Measurement of Hydration

Editor of Industrial and Engineering Chemistry:

In a recent paper [IND. ENG. CHEM., 23, 1298 (1931)] Gustavson has criticized the improved dilatometric method of measuring the potential hydration capacity of proteins in general, and of gelatin and animal skin in particular. Gustavson, in his comprehensive criticism of our hydration work, maintains that our measurements bear no relation to the actual hydration of the proteins. He bases his contentions, at least to some extent, upon work done by other workers sometime after the papers in question were turned over to the publishers of our work. Gustavson's criticisms are apparently directed toward the effect of hydrogen-ion concentration upon what we have been pleased to call "relative hydration."

In the light of Gustavson's comments, let us consider the mechanism occurring when isoelectric gelatin is placed in a solution of hydrochloric acid having a pH value of 4.7. Considerable swelling of the gelatin occurs. This swelling taking place at the isoelectric point cannot be attributed to any osmotic effects and cannot therefore be explained by the Donnan membrane equilibrium theory, as outlined by Procter and Wilson and by Loeb. If the change in volume of this isoelectric system (gelatin-solution) is considered, it is found that a net contraction occurs, and such contraction cannot be explained in the light of the Zwitterionic theory:



since for this explanation we have assumed isoelectric gelatin in a hydrochloric acid solution at pH 4.7 (isoelectric point of the gelatin). In this isoelectric system, none of the ionic reactions (outlined above) given by Gustavson can take place, and here the net contraction of the system must be attributed to the adsorption and compression of water molecules by the hydrophilic substance—gelatin. Likewise, the swelling or increase in the volume of the gelatin itself must be due to this addition of water molecules or hydration, as distinguished from osmotic swelling in which the water is considered mechanically held.

This fundamental idea upon which our studies of hydration (decrease in net volume of system) are based seems to have escaped our critic. The reactions which are proposed cannot explain a net contraction of the system, but only an expansion. When the gelatin is hydrated in an isoelectric solution and is then transferred to a more acid or more alkaline solution, a net expansion in volume does occur which we attributed to decreased hydration, but this net expansion in volume may be interpreted in terms of the reactions which Gustavson presents. Our measurements certainly show, under these conditions, the release of water molecules indicated by the increase in volume of the system. It may be held that these reactions result in the production and elimination of water molecules, which is in the strict sense of the word, dehydration. Although we did not attempt to explain why gelatin is less hydrated on either side of the isoelectric point, the obvious inference is that the effect must be due to the combination of the gelatin with H^+ and OH^- ions as the case may be. This inference is not contrary to the contentions of Gustavson. However, as we pointed out in the article on gelatin, these effects are completely reversible, and the curve, as shown in that article, may be obtained either by hydration of dry gelatin or by dehydration of the completely hydrated isoelectric gelatin. Such behavior of the system suggests an adsorption equilibrium rather than a definite chemical reaction.

A further point which in our minds seems particularly incompatible with Gustavson's explanation of our work (and which has been overlooked by him) is the influence of temperature upon

the volume change. In the articles on gelatin and animal skin, it was shown that when the measurements of this net contraction of the systems were made at different temperatures an increased contraction results at the lower temperatures. This is what one should expect if dealing with an adsorption phenomenon, but, if the volume change were attributed to chemical action only (as the Zwitter-ionic concept postulates), the volume change of the system should have been the same for all of the temperatures used as the same pH value obtained at equilibrium in every case. In the case of the volume change for animal skin, the net contraction at 37.5° C. was only 10 per cent of that at 0° C., which would indicate that forces other than primary chemical ones play a role in our measurements.

At pH values less than 3.5, it has already been pointed out by us that "at higher concentration of acid, effects other than hydration become important," and again, "at the higher concentrations of acid, chemical changes may take place" [IND. ENG. CHEM., 22, 68 (1930)].

Gortner, in his classical work on vegetable proteins, has demonstrated the presence of bound and free water and has shown that these play an important role in the life cycle of winter wheat. In this work, he has shown that lower temperatures favor an increase in the so-called "bound water"—this bound water in our minds being practically what we have been pleased to call "hydration." In a former paper we have postulated, "The water of hydration that exists in animal skin at any process period can be compared to water bound by the tissue (and this binding of water in this state cannot be explained by the second law of thermodynamics). Animal skin in the fresh state contains both bound and free water in equilibrium bound water \rightleftharpoons free water. During processing this equilibrium is altered, usually in favor of the bound water. The binding of water in the soak water can be changed about by the action of various chemicals, etc." [J. Am. Leather Chem. Assoc., 26, 360 (1930)].

In summation, we would state again that hydration as measured by us (net contraction of the entire system) is different from the forces set up during swelling. In the first place, there are those forces of chemical attraction between the molecules of water and certain of the groups of the protein. In the case of gelatin, these forces cause the solution of the gelatin in water when the forces of cohesion between the gelatin molecules forming the gel can be overcome. The take-up of water at the isoelectric point is in our minds primarily due to residual valency forces and in no way connected with direct chemical reaction such as the Zwitter-ionic concept. At other points, on the acid or alkaline side of the isoelectric point, these forces which evidence themselves at the isoelectric point are undoubtedly present and active and must be responsible at least to some degree for the water bound at other than the isoelectric point. At other than the isoelectric point of the protein, it is entirely possible that our results can be interpreted to some degree by the Zwitter-ionic concept, but not entirely so in view of the many changes in protein structure which may take place in solutions of acids or alkalis.

EDWIN R. THEIS
HARVEY A. NEVILLE

LEHIGH UNIVERSITY
BETHLEHEM, PA.
January 29, 1932

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Editor of Industrial and Engineering Chemistry:

In the paper on "Dilatometric Measurement of Protein Hydration" [IND. ENG. CHEM., 23, 1298 (1931)], I pointed out that the dilatation of the total volume of a fully hydrated protein system in an electro-neutral state, which is observed upon the addition

of acids and alkalis, is quantitatively accounted for by the removal of the highly hydrated H^+ and OH^- ions from the system by their combination with the amphoteric-ionic proteins. The independence of protein hydration from its degree of ionization—i. e., the pH values of the medium—has been amply demonstrated by means of widely different technics by Sørensen, Meyerhof, Weber, and others in contributions appearing years before Theis's experimental work was initiated. But these workers' testimonials are evidently a *terra incognita* to Theis. Recently, in an investigation by Weber and Versmold [Biochem. Z., 234, 62 (1931)] utilizing Polanyi's "nonsolvent space" technic in a modified form, the hydration of egg albumen is shown to be the same within such a wide pH range as from 3.1 to 10.3. How is it possible in light of these overwhelming evidences still to maintain that the volume change in the pH range from 2 to 9 is a measure of the degree of hydration of the protein?

The contention of Theis and Neville that an adsorption process is indicated by the fact that their "hydration" curve may be obtained either by hydration of dry gelatin or by dehydration of the fully hydrated electro-neutral gelatin, only demonstrates an extraordinary lack of familiarity with the amphoteric-ionic concept. Their statement has no basis in fact as a proof of an adsorption process and a demonstration of the inapplicability of the Zwitter-ionic concept upon the reactions taking place in the pH range from 2 to 9.

The present author never objected to the use of total volume measurements as a *relative* indicator of the degree of hydration of water-soluble proteins, as that of gelatin, in systems with constant H-ion concentration. But even in the latter instance an uncritical extension of the dilatometric technic to such heterogeneous systems as those of rawhide, with hair and impurities present, is doomed to be a failure. The reader is referred to a discussion of this phase of the problem in the chapter on "Leather" in the forthcoming Volume VI of "Annual Survey of American Chemistry."

Theis's data of the pH factor in the hydration of gelatin, with the resulting unwarranted conclusions of a maximum degree of hydration of the gelatin in its isoelectric state, are untenable. His measurements have nothing whatsoever to do with the actual hydration of the protein in systems in which the condition of a constant pH is not fulfilled. It is evident that the main object of Theis's investigations is to establish the changes in the "hydration" of hide proteins taking place in shifting the "neutral" hide substance to acidic or alkaline media, as in the work processes of pickling, liming, and chrome tanning. Furthermore, even the fixation of oils and soaps from fat emulsions is measured by the very same, evidently very versatile technic, but a change in nomenclature is introduced—i. e., "oilation." Theis has collected an enormous amount of data and hydration curves of apparently very uncontrollable behavior, which, in fact, only show the vicissitude of H^+ and OH^- ions on their reactivity with the hide. Their behavior is very simple when compared to basic chromic salts containing highly hydrated complexes and to oil emulsions, which are all "explained" by a radical simplification of problems.

The question of the different temperature functions of the swelling and hydration processes has no bearing upon the problem under discussion. It may be said, however, that it is a well-known story. Stiasny and Meunier, among others, have repeatedly emphasized this fact, but their statements evidently have escaped Theis's attention.

What the authors have to say about the reactivity of Zwitter ions in the isoelectric zone makes any discussion of this question futile.

K. H. GUSTAVSON

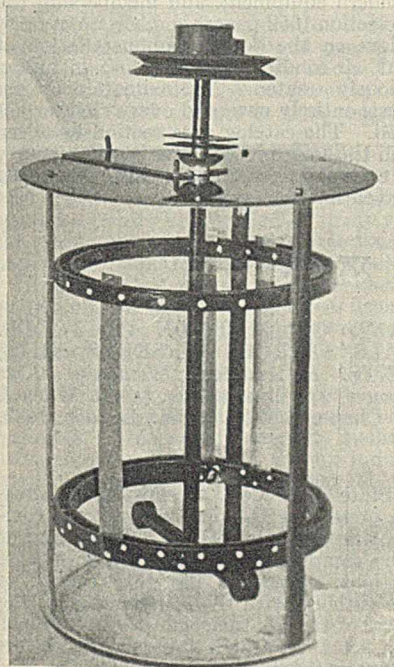
ÖREBRO, SWEDEN
March 25, 1932

Corrosion of Metals by Milk

Editor of Industrial and Engineering Chemistry:

A paper on "Corrosion of Metals by Milk" [IND. ENG. CHEM., 24, 339 (1932)] deals with the effects of operating conditions on the behavior of nickel, copper, and some alloys. The corrosion of milk at different rates of flow was studied; for this purpose, tests were made with a rotating spindle machine, the specimens being suspended in stirrups attached to the moving arm of the apparatus.

In Germany, however, we consider an arrangement like this not quite reliable. For, if the specimens are moved, as is done in the above-mentioned investigation, a state may be reached when the attacking agent is moving with nearly the same velocity as the specimens themselves. In order to avoid this uncertainty, we keep the specimens still, and agitate the solution instead. In most instances a stirring apparatus, such as is shown



STIRRING APPARATUS

in the accompanying photograph, is used. The specimens are fastened to a cage, the solution being moved by a stirrer. The data derived from such stirring tests give results in good accord with practical experience.

Figure 2 of the above paper, representing the effect of velocity on corrosion, shows a curve which increases slightly from 20 to 130 meters per minute, but then drops. The use of the rotating machine perhaps affords an explanation for this behavior. At a velocity of 20 to 130 meters per minute

the specimens are rotating in a quiescent solution; with increasing velocity, however, the agent itself begins to move, thus lowering the velocity of the specimens.

In evaluating the results, the authors of the paper took only the change of weight into consideration. According to our experiments, the judgment of the corrodibility based only on the change in weight does not always suffice. It may be sufficient with even attack, but in case of pittings and, above all, of intergranular deterioration the rate of corrosion cannot be calculated from these data. They should be supplemented by investigations of structure and physical properties of the specimens before and after the corrosion test.

Further details about corrosion tests in Germany may be found in the tentative standards elaborated by the German Reichsausschuss für Metallschutz, translations of which have already been published in English and American journals [*Metal Progress*, 20, No. 4, 91 (1931); *Ind. Chemist*, 7 (80), 379 (1931); *Aircraft Eng. (London)*, 3, No. 30, 195 (1931)].

GEORG GOLDBACH

DEUTSCHE VERSUCHSANSTALT FÜR LUFTFAHRT E. V.
BERLIN-ADLERSHOF, GERMANY
April 28, 1932

Editor of Industrial and Engineering Chemistry:

The arrangement with rotating specimens is, in general, not more satisfactory in the United States than in Germany. This is also pointed out in our paper in the second paragraph on page 341 where we say: "Because of the uncertainty in regard to velocity and aëration in the above experiments, another experimental procedure was tried." We then proceed to describe our continuous flow method which we believe is much more satisfactory than the method described by Goldbach.

The rotating spindle experiments were included in our paper only because they represent a condition which may sometimes be found in a plant, and also because we were rather surprised to find that reproducible results could be obtained by such a crude and simple method of adjusting velocities.

Goldbach's note regarding weight loss determination *vs.* visual examination is correct in so far as the change in weight does not by any means always suffice to judge about corrodibility. However, it did suffice in our work, because corrosion was surprisingly even. To include the results of visual examination in our tables would have complicated the paper tremendously without contributing anything to bring out the point of the effects of operating conditions on corrosion in various parts of pasteurizing equipment. It would have shown numerous small pits with high corrosion rates of nickel, no pitting at low corrosion rates of nickel, and no pitting with any of the other metals tested.

Other changes in structure and physical properties were not investigated, as they could hardly be expected in such short tests as ours. In spite of the fact that the pitting was of no particular importance, a note should possibly have been added to explain this, and we are grateful for this occasion to do so.

H. A. TREBLER

NATIONAL DAIRY PRODUCTS CORPORATION, INC.
BALTIMORE, MD.
May 14, 1932

The Yellowing of Oils

Owing to an unfortunate misunderstanding, Morrell and Marks, in condensing their original manuscript criticizing Elm's publications on the above subject, changed the sense of their criticism materially by omitting a number of essential points to which reference is made in Elm's reply, printed at the same time [IND. ENG. CHEM., 24, 593 (1932)]. Elm's reply, however, was printed in its original form. This explains fully the apparent lack of connection between these two notes.

A. C. ELM

THE NEW JERSEY ZINC CO.
PALMERTON, PA.
May 25, 1932

Hydrolysis of Starch by Carbonic Acid

In commenting on the article by M. A. Dewey and N. W. Krase [IND. ENG. CHEM., 23, 1436 (1931)], it should be said that the saccharification of starch by carbonic acid under pressure has some advantages over the usual hydrolysis by hydrochloric acid. A pure-tasting liquid is obtained; and the removal of the salts, obtained in the neutralization process, is avoided at the plant. On the other hand, however, the equipment is larger and the reaction lasts longer. In both methods it seems that the decoloration and subsequent filtration are not to be avoided. The method is, moreover, not entirely new, for in 1877 Bachel and Savalle, and in 1883 Jacob W. Decastro applied for patents. In the meantime, no practical application of these protected methods has been reported.

A. P. SCHULZ

FORSCHUNGSANSTALT FÜR STÄRKEFABRIKATION
SEESTRASSE 13, BERLIN N65, GERMANY
April 13, 1932

BOOK REVIEWS

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. VOLUME IX. Edited by C. Ainsworth Mitchell. 5th edition. 617 pages. P. Blakiston's Son & Co., 1012 Walnut St., Philadelphia, 1932. Price, \$7.50.

THE last edition of this volume was published nineteen years ago. The new edition has been very largely rewritten, and several subjects that were included in preceding editions have been omitted and are reserved for a later volume. This volume consists of a series of monographs by authorities in their respective fields, and consequently there is some overlapping.

The first monograph, on proteins of plants, contains 34 pages and deals with the protein content of various plant materials, including cereals, legumes, nuts, oil seeds, roots, tubers, fruits, and vegetables. The plant proteins are classified and their distribution in the various plants discussed. The determination of amino acids in the proteins is given, as well as their biological value. The proteins of the individual cereals are discussed in some detail, especially those of wheat and flour.

The next three monographs of 31, 29, and 111 pages, respectively, deal with the proteins of milk, milk, and milk products. The nature and composition of milk, factors affecting its composition, and methods of analysis are discussed. Methods are given for the manufacture and analysis of various dairy products, such as casein, cheese, whey powder, lactose, condensed milk, milk powder, infants' foods, and specially treated milks.

The final monograph of 385 pages consists of a complete discussion of the various types of meat and meat products. The methods of analysis and composition of beef, veal, pork, mutton, lamb, the various cured meats, fish, poultry, sausage, meat extracts, eggs, and fish roe are given. The enzymes of meat are discussed in relation to their action on meat during storage. Various methods of preserving meat, as by desiccation, heat sterilization, curing, and cold storage, are considered in their relation to effect on the physical and chemical properties of the meat. The proteins of meat, as well as the nitrogenous and nonnitrogenous extractives, are classified, and methods are given for their determination.

This book should be of value not only to the analyst but also to those interested in the biochemistry of the products considered. The volume contains many references to the original work.

A. H. JOHNSON

THE DEGRADATION OF SCIENCE. By T. Swann Harding. 386 pages. Farrar and Reinhart, Inc., on Murray Hill, New York, 1931. Price, \$3.00.

IN THIS volume an effort has been made to gather together criticisms of the unscientific procedures of business, education, social science, journalism, religion, politics, law, dentistry, pharmacy, medicine, research, scientific specialization, and living. The unscientific procedures are listed and discussed. Quotations are given in great numbers from first-class periodicals side by side with some from journals which may not be in the same category. It is a fertile field, for there is no question but that most of the failings related are real, but it must have been depressing to wade about in the cesspool so long. These matters should be brought to our attention, and the volume provides interesting reading.

The author claims that "instead of having utilized scientific knowledge for the social good we have shamelessly abused and unscrupulously exploited it. For, in spite of the fact that we have produced the body of precise and useful knowledge called science, our social, economic, and political beliefs remain predominantly in what might not inaptly be called a magical or, at least, a religious stage of development." He admits that he does not provide a remedy, but claims that he does give some suggestions here and there. In general, he does not advise how business, education, and all the rest should proceed to be strictly scientific, but he does tell decidedly how they are not at present following scientific procedures. The author lays the blame for the neglect of scientific methods mostly upon our profit system and economic individualism. The individual financial returns degrade scientific thought so that it cannot assert itself.

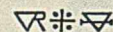
It is to be regretted that unnecessary statements are made in the volume which will cause lack of confidence in the author and what he writes. For example, he praises very highly the Soviet system in earlier chapters; in the last chapter, apparently fearing that he has gone too far, he criticizes the Soviet for being opposed

to what it does not like. He criticizes the AMERICAN CHEMICAL SOCIETY severely, finding fault with its workings, but he does not seem to be a member of the SOCIETY and he is evidently ignorant of what he is writing about in this case. It is unfortunate that a good idea and a great amount of work are marred and rendered far less valuable by these defects.

J. N. SWAN

AMERICAN SOCIETY OF HEATING AND VENTILATING ENGINEERS GUIDE, 1932. VOLUME 10. 956 pages. American Society of Heating and Ventilating Engineers, 51 Madison Ave., New York, 1932. Price, \$5.

THE 1932 Guide is the tenth anniversary volume and differs from earlier volumes in being larger and having an attractive new binding. It contains four major sections—text, manufacturers' catalog data, index to modern equipment, and membership roll of the society. The text section (552 pages) is made up of forty chapters of important data on the design and installation of heating, ventilating, and air-conditioning systems, including many subjects not previously treated. Approximately 50 per cent of the subject matter is entirely new, and every chapter has been rewritten and revised. The catalog data section has been carefully coordinated with the text and contains supplementary information on specific materials, equipment, and accessories available for heating and ventilating service.



THE STRUCTURE AND COMPOSITION OF FOODS. VOLUME I. CEREALS, STARCH, OIL SEEDS, NUTS, OILS, FORAGE PLANTS. By Andrew L. Winton and Kate Barber Winton. 710 pages, 274 illustrations. John Wiley & Sons, Inc., New York; Chapman & Hall, Ltd., London, 1932. Price, \$8.50.

THE authors, "Sometime State and Federal Chemist and Microscopist," respectively, are presenting the first volume of a comprehensive work, emphasizing the interrelation of structure or the optical science to the composition or chemical science of foods. Previous publications, especially the "Microscopy of Vegetable Foods," by the authors, with the collaboration of the late Professor Moeller, head of the Pharmacognostic Institute of the University of Vienna, set a very high standard which has been upheld in this new augmented work.

Brief statements concerning the chief structural elements, their terminology, reagents, and the character of the chemical constituents precede the detailed discussion. The individual descriptions are helpful in their clearness and scholarly completeness. With the increased interest in microchemical application we, no doubt, shall see this phase more emphasized in the forthcoming volumes. A reference to the remarkable chemical differentiation of *Cruciferae* on the basis of the composition of the volatile oils of mustard-like products, etc., would also seem worth while. As a rule, the fine drawings are magnified at the same (160) diameter, thus permitting a quick judgment of the relative sizes.

While students generally prefer less elaborately treated books for class work, the student or laboratory worker finds in the new Winton an indispensable guide, serving him well in any work on food, feed, and vegetable waste products.

ARNO VIEHOEVER

CHEMICAL CALCULATIONS. By J. S. Long and H. V. Anderson. 3rd edition. 259 pages. McGraw-Hill Book Company, Inc., 370 Seventh Ave., New York, 1932. Price, \$1.75.

THE changes which characterize the third edition of this book include additional methods of molecular weight determination, some rearrangement and enlargement of the chapters on gas analysis and volumetric analysis, and a brief discussion of pH values. A few topics are given more emphasis than in the usual texts of general inorganic chemistry. These include gas analysis, calorific power and intensity, volumetric analysis, common ion effect, and solubility product. The 15 chapters and more

than 800 problems offer considerable freedom of choice of problem material. As valuable as problem work is known to be, comparatively few courses in elementary general chemistry permit as much time as is necessary to cover the entire book. The theoretical discussion is quite full and complete so that the book may be used with practically any type without danger of omissions. For this reason it would seem that the authors might have gone a little farther and covered such topics as the factors which govern the choice of an indicator, the magnitude of errors possible with unsuitable indicators, and the shortcomings and limitations of the solubility product, particularly as applied to sulfides. There is also a question as to the value of calculating calorific intensity, since such temperatures are not realizable in practice. On the whole, the book is a most valuable source of problem material for college courses.

W. T. READ

ANNUAL REPORTS OF THE SOCIETY OF CHEMICAL INDUSTRY ON THE PROGRESS OF APPLIED CHEMISTRY. VOLUME XVI, 1931. Edited by *T. F. Burton* with numerous contributors. 748 pages. Society of Chemical Industry, Central House, 46, 47 Finsbury Square, London, 1932. Price to members, 7 s. 6 d.; to others, 12 s. 6 d.

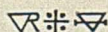
ONE result of the mass production in the field of chemical literature has been the formation and growth of chemical reviews that appear annually. The Reports on the Progress of Applied Chemistry is undoubtedly the outstanding review in this particular field. The 1931 volume is even more comprehensive than its predecessors.

It is difficult to suggest methods of improving this report. It might be mentioned, however, that, if the first chapter dealing with chemical engineering unit operations could be expanded, it would be greatly appreciated by many readers. The addition of the patent literature covering fractionating column design, especially in the petroleum industry, would be welcome.

In recent years chemical engineers have attempted to transfer equipment operations and processes from one industry to another, with, of course, certain definite modifications. Therefore, there has been considerable interest shown by chemical engineers working in one industry as to what was occurring in another. It would be a very worthwhile undertaking if these reports would include a subject index on what might be termed "chemical unit" processes. This would materially facilitate the location of pertinent references throughout various industries which covered one specific operation such as oxidation, chlorination, hydrogenation, etc.

A work such as this requires an enormous amount of time and energy to maintain its present standard, and it certainly deserves a better binding. The additional cost would be gladly borne by the appreciative reader, who will have frequent occasion to use its pages.

D. B. KEYES



BERICHTE DER GESELLSCHAFT FÜR KOHLENTCHNIK. BAND III, HEFT V. Pages 466-543. Gesellschaft für Kohlentechnik, Dortmund-Eving, Germany, 1931. Price, 7 marks.

THIS is a continuation of a series of similar publications wherein are reported the results of both laboratory and industrial investigations concerning the coal industry and its allied fields.

The present number is divided into two parts. The first division deals with a new method for desulfurizing a gas whereby there can be obtained not only ammonium sulfate but also ammonium nitrate and the primary and secondary ammonium orthophosphates. The method consists in removing the sulfides by converting them into ammonium thiosulfate through a washing and oxidation process, followed by interaction with ammonium sulfite in solution. The ammonium thiosulfate is subsequently decomposed to the desired salt by the action of sulfuric, nitric, or orthophosphoric acids. The laboratory experiments in connection with the development of this process are described in detail, and all the essential data are reported in the usual manner. Also, a large-scale experiment at the Victoria gas works (Lünen) is described. An excellent treatment of the properties of ammonium thiosulfate with special reference to its preparation and purification is included; this should be of special interest to inorganic and physical chemists.

The second division is concerned with methods for the removal and subsequent recovery of carbon monoxide from industrial gases. Valuable data are given concerning the carbon monoxide

absorptive capacity of the following solutions: those containing no copper salts, ammoniacal solutions of cuprous salts, aqueous solutions of cuprous salts containing organic bases, nonaqueous solutions of cuprous salts containing organic bases, and acid solutions of cuprous salts. The experimental procedure used in these investigations is described in detail. The last chapter of this second division deals entirely with the development and construction of the carbon monoxide washing apparatus. The increasing importance of carbon monoxide as an agent in the formation of methanol and higher alcohols makes this treatise most valuable at this time.

The present number is a distinct contribution because of the invaluable data presented therein. However, the commercial aspects of the two processes (gas desulfurization and carbon monoxide recovery) cannot be viewed with alarming expectations.

IRVIN LAVINE

MUCKENBERGER'S HANDBUCH DER CHEMISCHEN INDUSTRIE DER AUSSERDEUTSCHEN LÄNDER. 7th edition. 1077 pages. Verlag von Urban & Schwarzenberg, Berlin and Vienna, 1932. Price, 60 marks.

THIS directory of the chemical industries of the world (Germany excepted) is essentially what its name implies. It is divided into two parts. The first consists of a list of chemical works, alphabetically arranged for the countries of the world outside of Germany, and a separate list of export and import houses, wholesale houses, and agencies, also arranged by countries and in alphabetical order, with addresses and a brief statement of the nature of the business of each. This latter list includes German houses. If the list of the other countries is in as good form as that for America (there is every reason to believe this to be the case), the directory will be found of real value to any one who wishes to communicate with the world's chemical industries.

The second part is arranged alphabetically on the basis of chemicals, raw materials, and wholesale wares, and articles required in chemical works, with the firm producing these in each country.

It is unfortunate that no book of this character has been compiled for America alone in our own country, and that we must go for important information of this kind to a German publication.

CHARLES L. PARSONS

VON DEN KOHLEN UND DEN MINERALÖLEN. EIN JAHRBUCH FÜR CHEMIE UND TECHNIK DER BRENNSTOFFE UND MINERALÖLE. BAND IV. Published by Verein Deutscher Chemiker. 234 pages. Verlag Chemie, Berlin, 1932. Price, paper, 16 marks; bound, 18 marks.

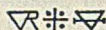
THE book contains the proceedings of the Section of Fuel and Petroleum Chemistry at the general meeting of the Society of German Chemists, Vienna, June, 1931. Fischer and Pichler describe the influence of pressure on some reactions of water gas. It was found that diminished pressure lowers the reaction temperature and greatly increases the reaction velocity of the decomposition of methane by steam or carbon dioxide. The mechanism of the combustion of gaseous fuels with regard to Haber and Bonhoeffer's explanation of the combustion process is discussed by Farkas. Rosin shows that in the combustion process the attack of a solid fuel by the air proceeds in a way analogous to the solvation of a lump of salt. Müller and Jandl give an improvement of the well-known method of determining the reactivity of coke, and describe the dependence of the reactivity on time and temperature of coking. Melzer reports on the technic of the determination of the ignition point of coke. A new method for determination of the iodine number of mineral oils is described by Galle. Schaarchmidt deals with the separation of branched-chain aliphatic hydrocarbons in hydrocarbon mixtures by antimony pentachloride.

Kiemstedt reports on the harmful sulfur in motor fuels and on the behavior of sulfur in the production of benzene. A new method by Conrad is described for the determination of the boiling range of liquid fuels, consisting of continuous control of the weight of the distillation flask filled with the fuel and placed on a scale.

Grote outlines the production of high-antiknock gasoline by means of the Edeleanu process, and Schmidt points out the relations between the chemical structure and knocking properties of motor fuels. A description of the Linde process of the separation of benzene from coke-oven gas at low temperatures is given by Schuftan. Terres reports on his research work of many years upon the mechanism of combustion in the engine and the six-cycle principle.

The yearbook gives a good review of the kind of work that is being done in the German fuel laboratories, and it can be recommended to all who are interested in fuel research.

H. TROPSCH



BERL-LUNGE CHEMISCH-TECHNISCHE UNTERSUCHUNGSMETHODEN. VOLUME II, PART 1. Edited by *Ernst Berl*. 8th edition. LX + 878 pages. 215 figures, 115 tables. Julius Springer, Berlin, 1932. Price, 69 marks.

THE first part of the second volume of Berl-Lunge is fully up to the standard set by the appearance of the first volume of the new edition. As in the first volume, each chapter is written by an expert in his special field. It is a valuable treatise on industrial analytical chemistry, dealing with the products of every phase of the manufacture of basic chemicals.

The specifications and methods of analysis of the raw material entering the plant are first described in detail. The composition and analysis of the finished products are then treated. The plan of the book is best illustrated by the following list of chapters: Solid and Liquid Fuels, Motor Fuels, Physical and Chemical Examination of Boiler Waters, Examination of Potable Waters, Waste Liquors and Sewage, the Air, Manufacture of Sulfurous Acid, Manufacture of Nitric Acid, Manufacture of Sulfuric Acid, Manufacture of Hydrofluoric Acid, Manufacture of Sodium Sulfate and Hydrochloric Acid, Manufacture of Soda, the Chlorine Industry, Liquefied and Compressed Gases, and Potassium Salts.

The text is very clear and each subject is exhaustively treated. Numerous up-to-date references are given, some from American literature. Analytical methods for the examination of products resulting from the very latest industrial developments are included. In the chapter on Motor Fuels, for instance, procedures for the examination of the newer fuels such as Ethyl gasoline, Motalin, and Motyl are discussed. However, no reference is made to the Ethyl Gasoline Corporation's method for the determination of tetraethyllead, which was published by Edgar and Calingaert in 1929. The chapter also includes the motor fuel specifications of most of the European countries, as well as those of the United States and Mexico.

The chapter on Boiler Waters gives, besides the analytical methods, a discussion of the treating processes necessary for the various types of water. Typical analyses are given as examples, and the amounts of the treating chemicals calculated. The numerous special methods include the analysis of smoke and dusts and the determination of minute traces of impurities in the air, such as hydrogen peroxide, sulfurous acid, hydrogen sulfide, mercaptans, aniline, nitrobenzene, and numerous other compounds.

This is a masterful treatise on the subject. It contains a most complete collection of the latest methods of analysis of the products mentioned. This book should represent a very valuable addition to any library; it will be particularly useful to the industrial and consulting chemist. E. L. BALDESCHWIELER

DIE CHEMISCHE WAFFE IM WELTKRIEG UND—JETZT. By *Ulrich Müller*. 152 pages. Verlag Chemie, Berlin, 1932. Price, 5.50 marks.

THE preface states that the author has taken an active interest in chemical warfare since 1915. It further says that the book is free from any *Politik*, and stands on the firm basis of facts, and that the author has striven to give, in a fundamental and easily understandable manner, a picture of reality in order that those interested may have a concept of the future possibilities of chemical weapons and defense against them. The book, on the whole, substantiates these statements.

Part I is devoted to gas warfare. Cloud attack, projector attack, and the use of chemical agents in artillery shell, airplanes, *minenwerfer*, and hand grenades are discussed. The possibility of airplane gas attacks on cities is considered quantitatively and the conclusion drawn that incomparably greater effects may be attained by the use of high explosive and incendiary bombs, but that some gas will be used to increase panic and hinder repair work. The best defense against such an attack is an effective anti-aircraft service and an airplane force sufficiently strong in cooperation with it to repel an attack and to carry out retaliatory attacks.

The discussion of agents is good. From the statement of basic principles governing the selection of agents, it is readily understood why only thirty out of three thousand materials considered were used in the field, and why only about twelve of these have

sufficient value for future use. A notable feature of the book is the table on pages 113-14 giving the volatility, the threshold irritation concentration, the intolerable concentration, and the estimated concentration to produce death in one minute.

Part II gives a good discussion of screening smokes, including colored smokes.

The final section on the future of chemical weapons is brief and written with the restraint of one who has a technical and military knowledge of the subject. Experience has shown that the technic of any war is similar to that of the preceding one. New chemical warfare agents of exceptional activity are not to be expected. Screening smokes will probably be more highly developed in peace time than the physiologically active materials.

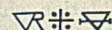
DUNCAN MACRAE

HYDRIERUNG DER KOHLEN, TEERE UND MINERALÖLE. TECHNISCHE FORTSCHRITTSBERICHTE. BAND XXVII. By *Ernst Galle*. 111 pages, 16 illustrations, 28 tables. Theodor Steinkopff, Dresden and Leipzig, 1932. Price, paper, 9 marks; bound, 10 marks.

THIS volume is interesting reading; it would probably appeal equally well to one interested in pure chemistry or chemical technology. It gives the professional as well as the layman a comprehensive picture of the great industry being built around the hydrogenation of coal, tar, and mineral oil. The work is well organized and developed chronologically. There are numerous literature references, and a large number of patents are listed, together with a brief indication of their contents. These two items alone make this volume valuable to anyone wishing to begin study in this field, or to expand or refresh his existing knowledge. There is a considerable discussion of catalysts and the part they play in the process.

The volume is divided into three parts. Part I is the introduction with a discussion of the economic aspects of the problem and the research accomplished up to 1918. Part II gives the results on hydrogenation of coals, tars, and mineral oils since 1918. This section is divided into results (1) without catalysts at atmospheric pressure, (2) without catalysts at high pressure, (3) with catalysts at atmospheric pressure, (4) with catalysts at low pressures, and (5) with catalysts at high pressure. Part III deals with the present economic, scientific, and technical aspects of the problem.

M. R. FENSKE



DIZIONARIO DI MERCEOLOGIA E DI CHIMICA APPLICATA. VOLUME IV. SENAPA-ZUCCHERO. By *G. Vittorio Villavecchia*. 5th edition. 1205 pages. Ulrico Hoepli, Milan, 1932. Price, 80 lire.

WITH the appearance of Volume IV, the fifth edition of this authoritative and comprehensive reference work is complete. The usual high standard of the previous three volumes which have been reviewed in previous issues [*IND. ENG. CHEM.*, 21, 393 (1929); 22, 406 (1930); 23, 725 (1931)], has been maintained. This volume treats in an unusually complete manner such products as silk, medicinal specialties, animal and vegetable fibers, wines, sulfur, and sugar. It also contains a general alphabetical index of 278 pages in Italian, French, German, English, and Spanish.

The reviewer wishes to reiterate that this reference work is not a mere dictionary but includes valuable statistical data on production, import and export custom duties, manufacturer's tax, transportation, and sanitary laws as they apply to the raw and manufactured products of the chemical, pharmaceutical, metallurgical, food, textile, and agricultural industries. It is, therefore, an invaluable addition to any library. PETER MASUCCI

DIE BRENNSTOFFE UND IHRE INDUSTRIEN. By *M. Dolch*. 200 pages, 71 illustrations. Akademische Verlagsgesellschaft, Leipzig, 1932. Price, bound, 14.50 marks.

THIS last contribution of one of Germany's leading teachers of fuel technology was completed just before his untimely death. It is a compact textbook written for industrial engineers who wish to instruct themselves in the broad field of fuels, fuel technology, and fuel economics.

The properties, composition, and classification of solid, liquid, and gaseous fuels are given in an introductory chapter. The next chapter on combustion and its fundamentals includes the subjects of calorific value, combustion temperature, heat exchange,

and types of furnaces and stokers. The third chapter on the transformation and processing of fuels covers the subjects of drying, briquetting, gasification, carbonization, and liquefaction of brown coal and bituminous coal. This chapter, which occupies more than half the book, is followed by a short chapter on petroleum, its refining, and its products. A final 2-page section on natural gas completes the book. In each of these chapters the author presents a well-digested critical outline of scientific fundamentals and their industrial application. Competent judgment is shown in selecting and describing commercial processes that illustrate present-day trends and sound practice in fuel technology. Although some space is given to the low-temperature carbonization of German brown coals, the author dismisses low-temperature carbonization of bituminous coal with the statement that for Germany it has not proved commercially profitable.

The book is recommended for those who desire a compact, well-balanced textbook on fuels and fuel technology in the German language. It is not a reference book.

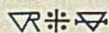
A. C. FIELDNER

VOM WASSER. EIN JAHRBUCH FÜR WASSERCHEMIE UND WASSERREINIGUNGSTECHNIK. BAND V. Published by Verein Deutscher Chemiker. 268 pages. Verlag Chemie, Berlin, 1931. Price, paper, 20 marks; bound, 22 marks.

This fifth volume contains 24 papers and some discussions delivered before the Section of Water Chemistry at the meeting of the German Chemical Society, Vienna, June, 1931. Several papers deal with methods to determine and soften water, especially with trisodium phosphate, for boiler purposes. The general conclusion is that phosphate additions are warranted for special purposes but are as a rule too costly. Studies on iron and manganese removal indicate that treatment with lime and removal of carbon dioxide alone were ineffective, and additions of potassium permanganate were best. Preparation of so-called black sand was inadvisable. The questions of oxygen and oil in water used for boilers are discussed only in general. Work on the effects of chlorine and chlorocompounds when the water is strongly agitated is of general interest. Studies by Jan Smit and his assistants on the self-purification of polluted water as affected by sedimentation, light, temperature, chemical composition of water, competition among bacteria, bacteriophages, and protozoa, using *B. coli* and *B. typhi* and *paratyphi* as indices, are of great interest to the specialist. The effects of paper waste and chlorinated sewage effluent upon aquatic and fish life show that although the oxygen content of the water may be sufficient, and although the carbon dioxide, alkalinity, and pH may be normal, fish are killed rapidly. The causes appeared to be rosin-like substances in solution which are not measured by the ordinary chemical methods employed. Results obtained with activated sludge experiments at Leipzig show production of thin sludge, poor settling, trouble with fungi, etc. No relation was found between numbers or types of protozoa and purification activities of the floc.

Several of the general papers have comparatively little value for the American reader interested in this field, but the majority are well worth reading and studying. Some of the 70 illustrations and curves are excellent.

W. RUDOLFS



KAPILLARCHEMIE. EINE DARSTELLUNG DER CHEMIE DER KOLLOIDE UND VERWANDTER GEBIETE. BAND II. By Herbert Freundlich, with the assistance of J. Bikermann. 4th edition. 955 pages. Akademische Verlagsgesellschaft, Leipzig, 1932. Price, paper, 60 marks; bound, 69 marks.

This volume completes the first thorough revision of Freundlich's classical work since 1922. The topical outline of the work remains substantially unchanged, but the text has been brought up to date by suitable omissions, condensations, or expansions in accordance with the progress of the last decade. Although the size of this volume is over 35 per cent greater than the corresponding part of the last edition, the amount of new material added is actually a good deal more. The bibliographic value of the work was maintained by the addition of many new references, even where the text was not modified. The most extensive changes and greatest expansion were made in connection with the coagulation of lyophobic sols, adhesion of colloid particles to walls, spontaneous and induced double refraction and the mesomorphic

state, viscous and elastic properties of sols, nonaqueous dispersions of high molecular weight materials such as rubber, polysaccharides and their derivatives, etc., colloidal behavior of proteins, freezing and swelling of gels, thixotropy, x-ray analysis of colloid systems, and determination of particle size with the ultracentrifuge.

As indicated by these topics, recent progress has been particularly marked along physical lines, and what is customarily called "colloid chemistry" has become in large part a question of colloid physics. With respect to many aspects of physical behavior, the distinction between lyophilic and lyophobic systems is not clearly evident, and the division of the whole discussion of sols according to their lyophobic or lyophilic character frequently separates what are basically similar, as Freundlich admits. It seems entirely likely that, by the time the next edition is prepared, this basis of subdivision can appropriately be discarded, or at least made much less prominent.

Without question, Freundlich's work remains the most useful, comprehensive, and systematic treatise on the subject. All those interested in any aspect of colloid science doubtless will join the reviewer in wishing that Professor Freundlich may long continue his literary activities.

E. O. KRAEMER

ARBEITEN ÜBER KALIDÜNGUNG. By O. Eckstein, A. Jacob, and F. Allen. 235 pages, 72 figures. Verlagsgesellschaft für Ackerbau, Berlin, 1931. Price, 6 marks.

The German Kalisyndikat established in 1929 an experiment station at Berlin-Lichterfelde. It was provided in the research program of the founders that the activities of the station deal with soil and plant nutrition problems, not alone in Germany, but in various soil regions of temperate, subtropical, and tropical countries. This book constitutes a report on the present status of the research activities of the station.

Four general topics are dealt with by the authors—namely, objectives of an experiment station specifically dealing with potash research, the physical plant and resources of the station, soil profiles and mapping of the land used by the experiment station at Berlin-Lichterfelde, and projects and results of the station. The latter is divided as follows: (1) laboratory studies of soils with special consideration of tropical soils; (2) comparative tests of different methods for the determination of soil potash readily assimilable by plants; (3) studies of the content of potash in plants and its chemical combinations; (4) the influence of fertilization with potash on the composition of crop products; (5) potash salts as protective agents of plants; (6) the physiological reaction of potash salts; (7) the fertilizer action of anions and other constituents of potash salts; (8) tests of the fertilizer action of different materials containing potash and magnesia; (9) studies of the compatibility in mixtures of different commercial fertilizers; and (10) investigations on the significance of potash for the animal organism. J. G. LIPMAN

DECHEMA MONOGRAPHIEN, BAND 4, NR. 38-47. TRENNEN FESTER UND FLÜSSIGER STOFFE. By the Deutsche Gesellschaft für chemisches Apparatewesen, E. V. 183 pages, illustrated. Verlag Chemie, Berlin, 1931. Price, 8 marks.

This book contains ten lectures on the general subject of the separation of solids and liquids, delivered by specialists in the construction and uses of new apparatus.

In the first lecture, P. H. Prausnitz, of the Jenaer Glaswerk Schott und Genossen, presents the method of preparation of sintered glass filters and their most promising applications. In the sintered glass filter, the glass itself is both filter body and binder. Breakage from chemical glassware (Jena glass 20) is powdered, sieved to definite grain size, sintered, and attached by melting to suitable shapes, such as china crucible walls, so that the glass forms the bottom. The grain size governs the pore size. The advantages of sintered glass filters are transparency, alkali-resistance, acid-resistance, control of pore size, and variation of pore size within wide limits. In the laboratory, for example, glass filters are ideal for the analysis of α -, β -, and alkali cellulose. They are well adapted also to the filtration of dyes from concentrated sulfuric acid media. The disadvantages are easy breakage and the low limiting temperature to which they can be heated (600° C.); indeed, they are most suitable for laboratory operations which require merely drying to constant weight in the oven. To give an idea of the pore sizes, filter G1 has coarse pores—500 μ ; G2 has the medium size—20 μ ; and G5 has the finest pores—colloidal dimensions, or $1/2 \mu$. (The figures for pore size are not given in just that way in the text,

but may be so interpreted from the context.) Such glass filters have been introduced in plant operations; the maximum size is 50 cm. in diameter.

In the second lecture, E. Kratz discusses new developments in ultra-filters and ultra-filtration, especially membrane filters for water filtration, and "cellafilters," for organic liquids.

Porous hard-rubber filter plates are discussed in the third lecture by E. Vossen. Such a filter is made as follows: Compounded rubber is rolled into sheets and heated just enough to produce incipient vulcanization. The soft mass so obtained may then be powdered, and the powder classified by sieving. To make the filter plate, the grains are heaped in a heated iron form, and pressed enough to retain the desired pore volume (total pore space). Next, vulcanization is completed by further heating. Pore size is determined by the size of the grain. Such porous hard-rubber plates are resistant to hydrofluoric acid, hydrochloric acid, phosphoric acid, alkalies, and salt solutions. They may be placed in filter presses, replacing the filter cloths.

The remaining subjects are: T. Steen, the clarification of muddy liquors; H. Manger, large-scale filtration with special reference to the suction rotary filter; H. Barkholt, the separation of liquids from solution by atomizing solutions; G. Quincke, wet and dry classification; H. Schranz, flotation of ores and coal; F. B. Krull, gas purification by adsorption with silica gel; E. Kirschbaum, new questions and recent advances in the rectification technic. Each one of these lectures is on the same high level as the first three. A short statement of the author's professional activities precedes each article.

The reading of this book leaves the impression that the authors are progressive scientists who seek and welcome new ideas and new procedures.

E. RAYMOND RIEGEL



FETTBERICHTE. GESAMTÜBERSICHT ÜBER DAS GEBIET DER FETTE, FETTPRODUKTE UND VERWANDTEN STOFFE FÜR 1927, 1928, 1929, 1930. By J. Davidsohn and K. Rietz. 458 pages. Ferdinand Enke, Stuttgart. Price, 47 marks; bound, 49 marks.

This volume, as indicated by the title, is an attempt to review for the years 1927 to 1930, inclusive, books and the more important literature dealing with fats, oils, waxes, and related products. It includes chapters on hardened fats, edible fats, fatty acids, glycerol, soaps, sulfonated oils, varnish, lacquer oils, leather fats and oils, and candles. The first 24 pages are devoted to recent works on these subjects, and the remainder of the book deals with the literature. Each subject, with a few exceptions, is subdivided into the following topics: physiology and biochemistry, chemistry, physics, analysis, technology, and patents. At the end is a subject, author, and patent index. The patents are listed under the titles of American, German, English, French, and various other countries.

This book furnishes a convenient source for references to articles on many subjects relating to fats and oils. However, the reviewer found that these abstracts are for the most part much shorter than those given, for example, in *Chemical Abstracts*. It was observed that the list of references under a given subject is in several instances not as complete as might have been expected. For example, under rancidity, mention is made of but eleven articles, whereas thirty-eight are given in *Chemical Abstracts*. Although the authors claimed to have reviewed all worthwhile articles on the subjects under discussion, the reviewer can scarcely agree with them in all cases.

R. S. MCKINNEY

DIE TROCKENTECHNIK. GRUNDLAGEN, BERECHNUNG, AUSFÜHRUNG UND BETRIEB DER TROCKENEINRICHTUNGEN. By M. Hirsch. 2nd edition. 484 pages, 336 figures, 3 folding charts. Julius Springer, Berlin, 1932. Price, 36 marks.

The first of the two parts of the book deals with the theoretical aspects of air-drying, and particularly with the construction and use of the humidity chart. The three large folding humidity charts for water vapor and air are carefully drawn and give the relations between temperature, vapor pressure, relative humidity, absolute humidity, and enthalpy, as ordinarily required in drying calculations. The adiabatic cooling lines are shown, together with a similar family of curves of slightly different slopes. The latter curves are used instead of the adiabatic cooling lines for wet- and dry-bulb hygrometry. The theoretical basis for these lines does not appear entirely sound. Numerical examples

are given illustrating the use of various formulas developed. Since absolute and relative humidities are dimensionless ratios, and since the other quantities are easily convertible to the English system, the charts may be used without great difficulty by engineers commonly employing English units.

The physics of the drying process, involving the movement of the liquid through the solid, and diffusion into the air stream, is touched on briefly, whereas it might well form the basis for a third section of the book. The quantitative treatment deals only with the evaporation of the moisture and its diffusion into the air stream, and not with liquid movement through the solid. The erroneous impression is conveyed that near the end of the drying process the rate of drying decreases solely because the vapor pressure of water over the solid is reduced at low moisture contents.

The second and larger section of the book discusses industrial drying and driers. A large number of sketches and diagrams make this section an excellent descriptive treatise. The basic principles of design and means for proper air circulation are described for numerous types of driers. However, few data are included on capacities or performance of the different types, or on the relative drying times of solids commonly dried industrially. Qualitative treatment is given to the requirements which must be met in drying various specific materials. At the end of the section is a chapter devoted to instruments.

T. K. SHERWOOD AND J. J. HOGAN

CHEMISCHE TECHNOLOGIE DER NEUZEIT. Edited by Otto Dammer. 2nd edition, revised and enlarged by Franz Peters and H. Grossman. VOLUME II: pages 689-876, price 1st part 7.40 marks, 2nd part 11.00 marks. VOLUME IV: pages 1-128, price 11 marks; pages 129-384 (in 2 parts), price 10.50 each part; pages 385-480, price 8.50 marks. VOLUME V: pages 1-128, price 11.00 marks; pages 129-256, price 11.00 marks; pages 257-384, price 11.00 marks; pages 385-512, price 11.00 marks. Ferdinand Enke, Stuttgart, 1932.

UNDER the direction of H. Grossman who succeeds Franz Peters, recently deceased, as editor of this encyclopedic work on chemical technology, the task of completing the second edition begun in 1926 is going rapidly forward, and the final sections of Volume II on metallurgy and Volumes IV and V on the organic industries are promised by 1933.

Installments of Volume II recently released by the printer are devoted mainly to the subjects of magnetic and electrostatic separation and to the furnaces and methods used in roasting and sintering ores. The latter topics are particularly well covered, and descriptions of all the important furnaces of both American and European design are presented in considerable detail with the help of more than 100 cuts.

The two final numbers of this 5-volume series embrace the organic section of the work. The reader will find in these, as well as in the earlier volumes, a wealth of general information, although he may be disappointed in its meagerness of technological detail. Thus, for instance, while Volume IV is encyclopedic in its discussion of the sources, physical properties, and methods of testing fats and oils, the subject of oil hydrogenation is given only 2 pages; of the two patents cited, the later is dated 1913. In all fairness, however, probably no other work on vegetable and animal oils approximating its size contains more valuable factual material or has it arranged in better form. Illustrations of modern oil and soap machinery are numerous and excellent. Additions to Volume IV include chapters on varnish and lacquer, the waxes and resins, sugar (beet practice mainly), starch from its many different sources, and, of especial importance because of the relative meagerness of other publications on the subject, a large section on the applications of yeasts, molds, and bacteria to organic manufactures in general and to the production of yeasts, vinegar, and alcohol in particular.

Volume V is a veritable handbook of the chemistry of dyes, which, with its copious references to the patent and journal literature and its graphic formulas of dye structures, should be of special value to the organic chemist. Additions to Volume V cover the field of the natural textiles—cotton, wool, and flax—with emphasis rather upon the mechanical aspects of processing and dyeing than upon the chemical principles involved. Finally, the subject of coal tar and its derivatives is given eminently satisfactory treatment.

The reviewer is impressed with the fact that, in the entire series, those chemical industries of major importance in Germany, or at least in Central Europe, are given the best and fullest discussion. But this is doubtless as it should be. The work is outstanding in the quality of its paper and printing and of its line drawings and half tones.

H. L. OLIN

MARKET REPORT—JUNE, 1932

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, JUNE 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

NEWER CHEMICALS			
<p>Acetaldehyde, drums, 10-l., wks.lb. .18½</p> <p>Acetaldol, 50-gal. drumslb. .27</p> <p>Acetylene tetrachloride, <i>see</i> Tetrachloroethane</p> <p>Acid, abieticlb. .12</p> <p>Adipiclb. .72</p> <p>Linoleiclb. .16</p> <p>Ammonium linoleate, drumslb. .11</p> <p>Amyl furoate, 1-lb. tinslb. 5.00</p> <p>Aroclorslb. .40</p> <p>Butyl carbitol, <i>see</i> Diethylene glycol monobutyl ether</p> <p>Cellosolve, <i>see</i> Ethylene glycol monobutyl ether</p> <p>Furoate, tech., 50-gal. drumslb. 1.00</p> <p>Carbitol, <i>see</i> Diethylene glycol monoethyl ether</p> <p>Cellosolve, <i>see</i> Ethylene glycol monoethyl ether</p> <p>Acetate, <i>see</i> Ethylene glycol monoethyl ether acetate</p> <p>Crotonaldehyde, 50-gal. drumslb. .32</p> <p>Dichloroethyl ether, 50-gal. drumslb. .06</p> <p>Diethylene glycol, drumslb. .14</p> <p>Monobutyl ether, drumslb. .24</p> <p>Monoethyl ether, drumslb. .15</p> <p>Diethylene oxide, 50-gal. drumslb. .50</p> <p>Dioxan, <i>see</i> Diethylene oxide</p> <p>Diphenyllb. .30</p> <p>Ethyl acetoacetate, 50-gal. drumslb. .65</p> <p>Carbonate, 90%, 50-gal. drumsgal. 1.85</p> <p>Chlorocarbonate, carboyslb. .30</p> <p>Ether, absolute, 50-gal. drumslb. .50</p> <p>Furoate, 1-lb. tinslb. 5.00</p> <p>Ethylene chlorhydrin, 40%, 10-gal. obyslb. .75</p> <p>Dichloride, 50-gal. drumslb. .05</p> <p>Glycol, 50-gal. drumslb. .25</p> <p>Monobutyl ether, drums, wks.lb. .24</p> <p>Monoethyl ether, drums, wks.lb. .17</p> <p>Monoethyl ether acetate, drums, wks.lb. .19½</p> <p>Monoethyl ether, drumslb. .21</p> <p>Oxide, cyl.lb. 2.00</p> <p>Furfuramide (tech.), 100-lb. drumslb. .30</p> <p>Furfuryl acetate, 1-lb. tinslb. 5.00</p> <p>Alcohol, tech., 100-lb. drumslb. .50</p> <p>Furoic acid (tech.), 100-lb. drumslb. .50</p> <p>Glyceryl phthallatelb. .26</p> <p>Glycol stearatelb. .18</p> <p>Isopropyl ether, drumslb. .10</p> <p>Lead dithiofuroate, 100-lb. drumslb. 1.00</p> <p>Magnesium peroxide, 100-lb. cs.lb. 1.15</p> <p>Methyl acetate, drumsgal. 1.20</p> <p>Cellosolve, <i>see</i> Ethylene glycol monomethyl ether</p> <p>Furoate, tech., 50-gal. drumslb. .50</p> <p>Paraldehyde, 110-55 gal. drumslb. .20½</p> <p>Phosphorus oxychloride, 175 cyl.lb. .20</p> <p>Propyl furoate, 1-lb. tinslb. 2.50</p> <p>Strontium peroxide, 100-lb. drumslb. 1.25</p> <p>Sulfuryl chloride, 600-lb. drums, crudelb. .15</p> <p>Distilledlb. .40</p> <p>Tetrachloroethane, 50-gal. drumslb. .09</p> <p>Trichloroethylene, 50-gal. drumslb. .10</p> <p>Triethanolamine, 50-gal. drumslb. .40</p> <p>Trihydroxyethylamine linoleatelb. .40</p> <p>Trihydroxyethylamine stearatelb. .35</p> <p>Vinyl chloride, 16-lb. cyl.lb. 1.00</p> <p>Zinc dithiofuroate, 100-lb. drumslb. 1.00</p> <p>Perborate, 100-lb. drumslb. 1.25</p> <p>Peroxide, 100-lb. drumslb. 1.25</p>	<p>Acetone, drums, wkslb. .10½</p> <p>Acetphenetidin, bbls.lb. 1.25</p> <p>Acid, acetic, 28%, c/l, bbls. 100 lbs. 2.75</p> <p>56%, c/l, bbls.100 lbs. 5.10</p> <p>Glacial, c/l, bbls.100 lbs. 9.14</p> <p>Glacial, U. S. P., c/l, carboys 100 lbs. 9.64</p> <p>Acetylsalicylic, bbls.lb. .75</p> <p>Anthranilic, 99-100%, drumslb. .85</p> <p>Benzoic, tech., bbls.lb. .40</p> <p>Boric, bbls.lb. .04</p> <p>Butyric, 100% basis, obys.lb. .80</p> <p>Chloroacetic, mono-, bbls., wks.lb. .18</p> <p>Di-, obys.lb. 1.00</p> <p>Tri-, bbls.lb. 2.50</p> <p>Chlorosulfonic, drums, wks.lb. .04½</p> <p>Chromic, 99%, drumslb. .13</p> <p>Cinnamic, bottleslb. 3.25</p> <p>Citric, U. S. P., cryst., bbls.lb. .30</p> <p>Cresylic, pale, drumsgal. .49</p> <p>Formic, 90%, obys., N. Y.lb. .10½</p> <p>Gallic, U. S. P., bbls.lb. .74</p> <p>Glycerophosphoric, 25%, 1-lb. bot.lb. 1.40</p> <p>H, bbls., wks.lb. .65</p> <p>Hydriodic, 10%, U. S. P., 5-lb. bot.lb. .67</p> <p>Hydrobromic, 48%, obys., wks.lb. .45</p> <p>Hydrochloric, 20%, tanks, wks.100 lbs. 1.35</p> <p>Hydrofluoric, 30%, bbls., wks.lb. .06</p> <p>60%, bbls., wks.lb. .13</p> <p>Hydrofluosilic, 35%, bbls., wks.lb. .11</p> <p>Hypophosphorus, 30%, U. S. P., 5-gal. demis.lb. .85</p> <p>Lactic, 22%, dark, bbls.lb. .04</p> <p>48%, light, bbls., wks.lb. .11</p> <p>Mixed, tanks, wks.N unit .07</p> <p>S unit .08</p> <p>Molybdic, 85%, kegs.lb. 1.25</p> <p>Naphthionic, tech., bbls.lb. nom.</p> <p>Nitric, c. p., obys.lb. .11</p> <p>Nitric, 36%, c/l, obys., wks. 100 lbs. 5.00</p> <p>Oxalic, bbls., wks.lb. .11</p> <p>Phosphoric, 50%, U. S. P.lb. .14</p> <p>Pieramic, bbls.lb. .65</p> <p>Picric, bbls., c/l.lb. .30</p> <p>Pyrogallollb. 1.50</p> <p>Salicylic, tech., bbls.lb. .33</p> <p>Stearic, d. p., bbls., c/l.lb. .07½</p> <p>Sulfanilic, 250-lb. bbls.lb. .14½</p> <p>Sulfuric, 66%, c/l, obys., wks. 100 lbs. 1.60</p> <p>66%, tanks, wks.ton 15.00</p> <p>60%, tanks, wks.ton 10.50</p> <p>Oleum, 20%, tanks, wks.ton 18.50</p> <p>40%, tanks, wks.ton 42.00</p> <p>Sulfurous, U. S. P., 6%, obys.lb. .05</p> <p>Tannic, tech., bbls.lb. .23</p> <p>Tartaric, U. S. P., cryst., bbls.lb. .23½</p> <p>Tungstic, kegs.lb. 1.40</p> <p>Valeric, c. p., 10-lb. bot.lb. 2.50</p> <p>Alcohol, U. S. P., 190 proof, bbls. gal. 2.44½</p> <p>Amyl, from pentane, tankslb. .176</p> <p>Amyl, imp. drumsgal. 1.75</p> <p>Butyl, drums, c/l, wks.lb. .123</p> <p>Cologne spirit, bbls.gal. 2.69</p> <p>Denatured, No. 5, comp. denat., c/l, drumsgal. .356</p> <p>4.00</p> <p>Isoamyl, drumsgal. 1.00</p> <p>Isobutyl, ref., drumsgal. .60</p> <p>Isopropyl, ref., drumsgal. 1.00</p> <p>Propyl, ref., drumsgal. 1.00</p> <p>Wood, <i>see</i> Methanol</p> <p>Alpha-naphthol, bbls.lb. .57</p> <p>Alpha-naphthylamine, bbls.lb. .32</p> <p>Alum, ammonia, lump, bbls., wks. 100 lbs. 3.30</p> <p>Chrome, casks, wks.100 lbs: 4.50</p>	<p>Potash, lump, bbls., wks.100 lbs. 3.35</p> <p>Soda, bbls., wks.100 lbs. 3.45</p> <p>Aluminum, metal, N. Y.100 lbs. 22.90</p> <p>Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.lb. .06</p> <p>Aluminum stearate, 100-lb. bbl.lb. .20</p> <p>Aluminum sulfate, comm'l, bags, wks.100 lbs. 1.25</p> <p>Iron-free, bags, wks.100 lbs. 1.90</p> <p>Aminoazobenzene, 100-lb. kegs.lb. 1.15</p> <p>Ammonia, anhydrous, cyl., wks.lb. .15½</p> <p>50,000-lb. tanks, wks.lb. .05620</p> <p>Ammonia, aqua, 26°, tanks, wks., contained NH₃.lb. .05½</p> <p>Ammonium acetate, kegs.lb. .33</p> <p>Bifluoride, bbls.lb. .21</p> <p>Bromide, 50-lb. boxeslb. .35</p> <p>Carbonate, tech., caskslb. .08</p> <p>Chloride, gray, bbls.100 lbs. 5.25</p> <p>Lump, caskslb. .10½</p> <p>Iodide, 25-lb. jarslb. 5.20</p> <p>Nitrate, tech., cryst., bbls.lb. .08½</p> <p>Oxalate, kegs.lb. .22</p> <p>Persulfate, caseslb. .26</p> <p>Phosphate, dibasic, tech., bbls.lb. .10½</p> <p>Sulfate, bulk, wks.100 lbs. 1.00</p> <p>Amyl acetate, tech., from pentane, tankslb. .157</p> <p>Aniline oil, drumslb. .14½</p> <p>Anthracene, 80-85%, casks, wks.lb. .60</p> <p>Anthraquinone, subl., bbls.lb. .45</p> <p>Antimony, metallb. .05</p> <p>Antimony chloride, drumslb. .13</p> <p>Oxide, bbls.lb. .08½</p> <p>Salt, dom., bbls.lb. .22</p> <p>Sulfide, crimson, bbls.lb. .25</p> <p>Golden, bbls.lb. .16</p> <p>Vermilion, bbls.lb. .38</p> <p>Argols, red powder, bbls.lb. .07</p> <p>Arsenic, metal, kegs.lb. .27</p> <p>Red, kegs, caseslb. .09½</p> <p>White, c/l, kegs.lb. .04</p> <p>Asbestine, bulk, c/l.ton 15.00</p> <p>Barium carbonate, bbls., bags, wks.ton 56.50</p> <p>Chloride, bbls., wks.lb. .03½</p> <p>Dioxide, drs., wks.lb. .12</p> <p>Hydroxide, bbls.lb. .05½</p> <p>Nitrate, caskslb. .07½</p> <p>Barium thiocyanate, 400-lb. bbls.lb. .27</p> <p>Barytes, floated, 350-lb. bbls., wks.ton 23.00</p> <p>Benzaldehyde, tech., drumslb. .60</p> <p>F. F. C., obys.lb. 1.40</p> <p>U. S. P., obys.lb. 1.15</p> <p>Benzidine base, bbls.lb. .65</p> <p>Benzol, tanks, wks.gal. .20</p> <p>Benzoyl chloride, obys.lb. 1.00</p> <p>Benzyl acetate, F. F. C., bottleslb. .75</p> <p>Alcohol, drumsgal. .75</p> <p>Chloride, tech., drumslb. .30</p> <p>Beta-naphthol, bbls.lb. .22</p> <p>Beta-naphthylamine, bbls.lb. .58</p> <p>Bismuth, metal, caseslb. .90</p> <p>Bismuth, nitrate, 25-lb. jarslb. .95</p> <p>Oxychloride, boxeslb. 2.95</p> <p>Subnitrate, U. S. P., 25-lb. jarslb. 1.10</p> <p>Blanc fixe, dry, bbls.ton 65.00</p> <p>Bleaching powder, drums, wks.100 lbs. 2.00</p> <p>Bone ash, kegs.lb. .06</p> <p>Bone black, bbls.lb. .08½</p> <p>Borax, bagslb. .018</p> <p>Bordeaux mixture, bbls.lb. .11½</p> <p>Bromine, bot.lb. .36</p> <p>Bromobenzene, drumslb. .50</p> <p>Bromoforn, jarslb. 1.80</p> <p>Butyl acetate, drums, c/l.lb. .159</p> <p>Cadmium bromide, 50-lb. jarslb. 1.40</p> <p>Cadmium, metal, caseslb. .55</p>	

CHEMICALS PREVIOUSLY QUOTED

Acetanilide, U. S. P., powd., bbls.lb. .22	
Acetic anhydride, 92-95%, obys.lb: .21	

Cadmium sulfide, boxes.....lb.	.60	Indigo, 20%, paste, bbls.....lb.	.12	Phosphorus, red, cases.....lb.	.42
Caffeine, U. S. P., 5-lb. cans.....lb.	2.40	Iodine, crude, 200-lb. kgs.....lb.	4.20	Phosphorus trichloride, cyl.....lb.	.18
Calcium acetate, bags.....100 lbs.	2.50	Iodine, resubl., jars.....lb.	4.85	Phthalic anhydride, bbls.....lb.	.15
Arsenate, bbls.....lb.	.05½	Iodoform, bot.....lb.	6.00	Platinum, metal.....oz.	37.50
Carbide, drums.....lb.	.05½	Iridium, metal.....oz.	160.00	Potash, caustic, drums.....lb.	.06½
Chloride, drums, wks., flake.....ton	21.00	Kieselguhr, bags.....ton	50.00	Potassium acetate, kegs.....lb.	.28
Cyanide, 100-lb. drums.....lb.	.30	Lead, metal, N. Y.....100 lbs.	3.00	Bicarbonate, casks.....lb.	.09½
Nitrate, bags.....ton	35.00	Lead acetate, bbls., white.....lb.	.10½	Bichromate, casks.....lb.	.08
Phosphate, monobas., bbls.....lb.	.08	Arsenate, bbls.....lb.	.10	Binoxalate, bbls.....lb.	.14
Tribas., bbls.....lb.	.11	Oxide, litharge, bbls.....lb.	.05½	Bromate, cs.....lb.	.35
Calcium carbonate, tech., bags,100 lbs.	1.00	Peroxide, drums.....lb.	.20	Carbonate, 80-85%, calc., casks.lb.	.04½
U. S. P., precip., 175-lb. bbl.....lb.	.06½	Red, bbls.....lb.	.06½	Chlorate, kegs.....lb.	.08
Camphor, Jap., cases.....lb.	.40	Sulfate, bbls.....lb.	.06½	Chloride.....ton	34.55
Carbazole, bbls.....lb.	.75	White, basic carb., bbls.....lb.	.07½	Cyanide, cases.....lb.	.55
Carbon, activated, drums.....lb.	.08	Lime, hydrated, bbls.....100 lbs.	.85	Meta-bisulfite, bbls.....lb.	.11
Carbon bisulfide, drums.....lb.	.05	Lime, live, chemical, bbls., wks.100 lbs.	1.05	Permanganate, drums.....lb.	.16
Carbon black.....lb.	.0275	Limestone, ground, bags, wks.....ton	4.50	Prussiate, red, casks.....lb.	.37½
Carbon dioxide, liq. cyl.....lb.	.06	Lithopone, bbls.....lb.	.04½	Yellow, casks.....lb.	.18½
Carbon tetrachloride, drums.....lb.	.06½	Magnesite, crude.....ton	32.00	Titanium oxalate, bbls.....lb.	.21
Casein, stand. gr., bbls.....lb.	.05½	Calined, 500-lb. bbls., wks.....ton	40.00	Pyridine, drums.....gal.	1.50
Cellulose acetate, bbls.....lb.	.80	Magnesium, metal, wks.....lb.	.30	Resorcinol, tech., kegs.....lb.	.65
Cerium oxalate, kegs.....lb.	.33	Magnesium carbonate, bags.....lb.	.06	Rochelle salt, bbls., U. S. P.....lb.	.15
Charcoal, willow, powd., bbls.....lb.	.06	Chloride, drums.....ton	36.00	R salt, bbls.....lb.	.42
China clay, bulk.....ton	8.00	Fluosilicate, cryst., bbls.....lb.	.10	Saccharin, cans.....lb.	1.70
Chloral hydrate, drums.....lb.	.70	Oxide, U. S. P., light, bbls.....lb.	.42	Salt cake, bulk.....ton	13.00
Chlorine, liq., c/l, cyl.....lb.	.04	Manganese chloride, casks.....lb.	.07½	Saltpeter, gran., bbls.....lb.	.06
Chlorine, tanks.....100 lbs.	1.75	Dioxide, 80%, bbls.....ton	80.00	Silica, ref., bags.....ton	22.00
Chlorobenzene, mono-, drums.....lb.	.10	Sulfate, casks.....lb.	.07	Silver nitrate, 16-oz. bot.....oz.	.22
Chloroform, tech., drums.....lb.	.15	Mercury bichloride, cryst., 50 lbs.lb.	1.51	Soda ash, 58%, light, bags, con- tract, wks.....100 lbs.	1.15
Chromium acetate, 20° soln., bbls.lb.	.05	Mercury, flasks, 76 lbs.....flask	58.00	Soda, caustic, 76%, solid, drums, contract, wks.....100 lbs.	2.50
Coal tar, bbls., wks.....gal.	.10	Meta-nitroaniline, bbls.....lb.	.67	Sodium acetate, bbls.....lb.	.04½
Cobalt, metal, kegs.....lb.	2.50	Meta-phenylenediamine, bbls.....lb.	.80	Benzoate, bbls.....lb.	.42
Cobalt oxide, bbls.....lb.	1.25	Meta-toluylenediamine, bbls.....lb.	.67	Bicarbonate, bbls.....100 lbs.	1.85
Cod-liver oil, bbls.....bbl.	30.00	Methanol, pure, synthetic, drums, wks.....gal.	.37½	Bichromate, casks.....lb.	.05
Copperas, c/l, bulk.....ton	14.50	Tanks, wks.....gal.	.35½	Bisulfite, bbls.....lb.	.04
Copper, metal, elec.....100 lbs.	5.50	Methyl acetone, drums.....gal.	.50	Bromide, bbls., U. S. P.....lb.	.31
Copper carbonate, bbls., 52/54%.....lb.	.16½	Salicylate, cases.....lb.	.42	Chlorate, kegs.....lb.	.05½
Chloride, bbls.....lb.	.22	Methyl chloride, cylinders.....lb.	.45	Chloride, bags.....ton	12.00
Cyanide, drums.....lb.	.39	Michler's ketone, bbls.....lb.	3.00	Cyanide, cases.....lb.	.16½
Oxide, red, bbls.....lb.	.15½	Naphtha, solvent, tanks.....gal.	.26	Fluoride, bbls.....lb.	.07
Sulfate, c/l, bbls.....100 lbs.	2.75	Naphthalene, flake, bbls.....lb.	.03½	Metallio, drums, 12¼-lb. briks.lb.	.19
Cotton, soluble, bbls.....lb.	.40	Nickel, metal.....lb.	.35	Metasilicate, bbls.....100 lbs.	2.85
Cream tartar, bbls.....lb.	.18	Nickel salt, single, bbls.....lb.	.10	Naphthionate, bbls.....lb.	.52
Cyanamide, bulk, N. Y.Ammonia unit	.97½	Double, bbls.....lb.	.10	Nitrate, crude, 200-lb. bags, N. Y.....100 lbs.	1.76½
Diaminophenol, kegs.....lb.	3.80	Niter cake, bulk.....ton	11.50	Nitrite, bbls.....lb.	.07
Dianisidine, bbls.....lb.	2.35	Nitrobenzene, drums.....lb.	.08½	Perborate, bbls.....lb.	.18
Dibutylphthalate, drums, wks.....lb.	.218	Oil, castor, No. 1.....lb.	.09	Peroxide, cases.....lb.	.21
Diethylaniline, drums.....lb.	.55	China wood, bbls.....lb.	.05½	Phosphate, trisodium.....100 lbs.	3.20
Diethylene glycol, drums.....lb.	.14	Coconut, Ceylon, tanks.....lb.	.03½	Picramate, kegs.....lb.	.69
Diethyl phthalate, drums.....lb.	.23	Cod, N. F., tanks.....gal.	.25	Prussiate, bbls.....lb.	.11½
Diethyl sulfate, tech., drums.....lb.	.30	Corn, crude, tanks, mills.....lb.	.02½	Silicate, drums, tanks, 40° 100 lbs.	.75
Dimethylaniline, drums.....lb.	.26	Cottonseed, crude, tanks.....lb.	.02½	Silicofluoride, bbls.....lb.	.06½
Dimethylsulfate, drums.....lb.	.45	Lard, edible, bbls.....lb.	.08½	Stannate, drums.....lb.	.17
Dinitrobenzene, drums.....lb.	.15½	Linseed, bbls.....lb.	.059	Sulfate, anhyd., bbls.....lb.	.02
Dinitrochlorobenzene, bbls.....lb.	.13	Menhaden, crude, tanks.....gal.	.14	Sulfide, cryst., bbls.....lb.	.02½
Dinitronaphthalene, bbls.....lb.	.34	Neat's-foot, pure, bbls.....lb.	.07½	Solid, 60%.....lb.	.03½
Dinitrophenol, bbls.....lb.	.23	Oleo, No. 1, bbls.....lb.	.05½	Sulfocyanate, bbls.....lb.	.28
Diphenylamine, bbls.....lb.	.34	Olive oil, denat., bbls.....gal.	.59	Thiosulfate, reg., cryst., bbls....lb.	.02½
Diphenylguanidine, bbls.....lb.	.30	Foots, bbls.....lb.	.04½	Tungstate, kegs.....lb.	.70
Epsom salt, tech., bbls., c/l, N. Y.100 lbs.	1.70	Palm, Lagos, casks.....lb.	.04	Strontium carbonate, tech., bbls.lb.	.07½
Ether, nitrous, bot.....lb.	.80	Peanut, crude, tanks.....lb.	.02½	Nitrate, bbls.....lb.	.09
Ether, conc., drums.....lb.	.09	Perilla, bbls.....lb.	.05½	Sulfur, bulk, mines, wks.....ton	18.00
Ethyl acetate, tanks, c/l.....lb.	.09	Rapeseed, bbls., English.....gal.	.37	Sulfur chloride, red, drums.....lb.	.05
Bromide, drums.....lb.	.50	Red, bbls.....lb.	.06½	Yellow, drums.....lb.	.03½
Chloride, drums.....lb.	.22	Soy bean, crude, tanks.....lb.	.028	Sulfur dioxide, commercial, cyl....lb.	.07
Methyl ketone, drums.....lb.	.30	Sperm, 38°, bbls.....gal.	.68	Sulfuryl chloride, drums.....lb.	.10
Ethylbenzylamine, 300-lb. drums.lb.	.88	Whale, bbls., natural, winter...gal.	.56	Thiocarbamid, bbls.....lb.	.26½
Ethylene dichloride.....lb.	.05	Ortho-aminophenol, kegs.....lb.	2.15	Tin.....lb.	.20½
Chlorohydrin, anhyd., drums.....lb.	.75	Ortho-dichlorobenzene, drums.....lb.	.08	Tin tetrachloride, anhydrous, drums, bbls.....lb.	1.465
Glycol, c/l, wks.....lb.	.25	Ortho-nitrochlorobenzene, drums.lb.	.28	Oxide, bbls.....lb.	.22½
Feldspar, bulk.....ton	6.50	Ortho-nitrophenol, bbls.....lb.	.85	Titanium dioxide, bbls., wks.....lb.	.19
Ferrie chloride, tech., bbls.....lb.	.05	Ortho-nitrotoluene, drums.....lb.	.16	Toluene, tanks.....gal.	.30
Ferrous chloride, cryst., bbls.....lb.	.06	Ortho-toluidine, bbls.....lb.	.20	Tribromophenol, cases.....lb.	1.10
Ferrous sulfide, bbls.....100 lbs.	2.50	Palladium, metal.....oz.	19.00	Triphenylguanidine, drums.....lb.	.58
Fluorspar, 98%, bags.....ton	31.00	Para-aminophenol, kegs.....lb.	.78	Triphenyl phosphate, bbls.....lb.	.60
Formaldehyde, bbls.....lb.	.06	Para-dichlorobenzene.....lb.	.15½	Tungsten, powder.....lb.	1.65
Formaniline, drums.....lb.	.37½	Para-formaldehyde, cases.....lb.	.38	Urea, pure, cases.....lb.	.11
Fuller's earth, bags, c/l, mines ton	15.00	Paraldehyde, tech., drums.....lb.	.20½	Whiting, bags.....100 lbs.	1.00
Furfural drums, tech., contract, works.....lb.	.10	Para-nitraniline, drums.....lb.	.48	Xylene, 10°, tanks, wks.....gal.	.26
Glauber's salt, bbls.....100 lbs.	1.00	Para-nitrochlorobenzene, drums..lb.	.25	Xylidine, drums.....lb.	.36
Glucose, 70°, bags, dry.....100 lbs.	3.14	Para-nitrophenol, bbls.....lb.	.45	Zinc, metal, E. St. Louis.....100 lbs.	2.80
Glycerine, c. p., drums.....lb.	.10½	Para-nitrosodimethylaniline, bbls.lb.	.92	Zinc ammonium chloride, bbls....lb.	.05½
G salt, bbls.....lb.	.42	Para-nitrotoluene, bbls.....lb.	.29	Chloride, granulated, drums...lb.	.05½
Hexamethylenetetramine, tech., drums.....lb.	.46	Para-phenylenediamine, bbls.....lb.	1.15	Oxide, Amer., bbls.....lb.	.05½
Hydrogen peroxide, 25 vol., bbls.lb.	.05½	Para-toluidine, bbls.....lb.	.40	Stearate, bbls.....lb.	.20
Hydroquinone, kegs.....lb.	1.20	Paris Green, 250-lb. kegs.....lb.	.23	Zinc dust, bbls., c/l.....lb.	.041
		Phenol, drums.....lb.	.14½		
		Phenolphthalein, drums.....lb.	.80		
		Phenylethyl alcohol, 1-lb. bot.....lb.	7.00		