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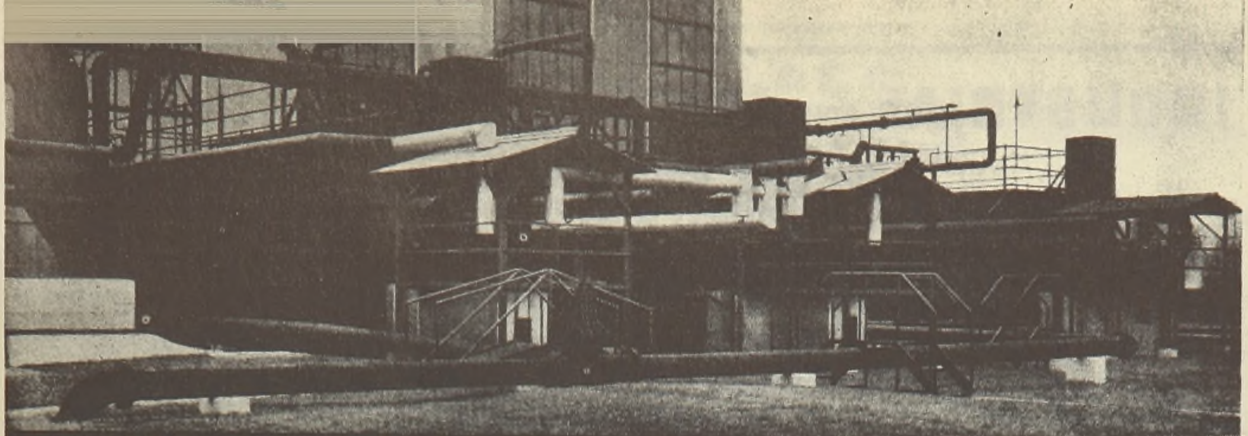

INDUSTRIAL AND ENGINEERING CHEMISTRY • INDUSTRIAL EDITION

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Fuel savings are made in the plant of Texas Gulf Sulphur Company (see photograph above) by passing incoming water through economizers which extract heat from the waste flue gases.

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DEPARTMENTS

TECHNICAL ARTICLES

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INDUSTRIAL AND ENGINEERING CHEMISTRY
REPORTS
ON THE CHEMICAL WORLD TODAY

Technology

Atom Items. No sooner had the atom bomb explosion become news than phones began to ring in the office of Lieutenant Colonel C. Consodine, Corps of Engineers in Washington. For five days and nights the Colonel and his staff continuously remained on duty answering questions, clearing stories, and arranging interviews about the event. Sleeping on the floor to answer inquiries coming in at any hour does not improve one's disposition, but some of the incidents provided laughs which helped put the development in a different light. Phone calls averaged four hundred and fifty a day, and two extra phones, in addition to the many already in the office, had to be installed. The United States reacted as only she could.

First a radio station requested the War Department to repeat the explosion so that the sound might be picked up by strategically placed microphones. A letter was received from an ex-sailor who wanted to be dropped with an atomic bomb and radio equipment in order to give a play-by-play description of what happened.

Another task of Consodine's was clearing credits. A fertilizer company which had put material on the lawn of one hospital of the plant in Tennessee wanted to tell the public of its important part in making the atom bomb. Another fertilizer company wanted clearance on an advertisement which proclaimed that, of the thousand-odd industrial companies in upper New York state which assisted in making the bomb, they alone had nothing to do with it. A letter of congratulation arrived which, in addition, pointed out two further goals to be reached by the atom bomb group—overcoming gravity so that airplanes could not fall, and making commercial the cold light of the firefly.

The newspapers reported on the farmer who wanted to purchase some atom bombs to discourage insects from bothering his crops, but they missed the prospector who claimed to have discovered a lode of valuable high-grade ore 25 feet below the surface of some rock. Would the War Department please oblige by dropping a bomb to strip off the overburden?

During the recent hurricane the mayor of a Florida city wanted a bomb dropped in the middle of the storm to turn it away from his metropolis. While on the subject of weather, there was the mother who had heard that the climate would be affected by all these atoms; would Consodine's office please tell her whether it would become colder, in order to give her a chance to make suitable clothing for her children?

While we were interviewing the Colonel, a Senator called to ask how he could obtain permission for a constituent to visit the site of the bomb explosion in New Mexico; the constituent, a doctor, wanted to camp there with his wife and children for a two-week vacation.

Concessionaires began beating the tom-tom. Could they obtain the concession to the atomic bomb crater in New Mexico so that jewelery might be made of the stone which fused into green, hard pellets when the bomb exploded? They even had a name for it—"atomic jade".

Overnight the office of Colonel Consodine changed from a secrecy organization, bent on keeping atoms out of public information channels, into a publicity office, handling the biggest story ever encountered and trying to keep speculation, enthusiasm, and "guesstimations" within reason. One of the officers of the Department was in Switzerland when the bomb was dropped. Not being able to read the language but seeing unmistakable headlines about the event, he could only guess that the weapon had been used. Without the details he dared not question natives for fear it was not what he thought and his interest might provide an unwelcome leak.

A new shoulder insignia has been designed for those who worked on the project. Inside the top half of the shield, which has a blue background, is an Army service star Around the star is the loop of a question mark, the tail crossing the blue field in the form of a zigzag of lightning which travels to the bottom of the patch where it strikes a round golf ball (presumably an atom) and breaks it into three parts. This has become a collector's item, and at the time we were in the office, a letter came from a "four-star general", aged eleven, and adopted son of the Rainbow Division; he, with his "daddy" was running a race with the U.S.O. hostess in his town as to who would have the patch first. Would General Groves please oblige, etc.?

Then, too, there was the person who closed his letter with "Yours for the conquest of space"; as you can guess, it had to do with rocketing to the moon. Could he get the first permit to use atomic power for this purpose? Consodine answered this question easily by referring the writer to the Interstate Commerce Commission.

(Continued on page 8)

An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries

Lactic Acid Secret. The use of lactic acid in normal times for the manufacture of such essentials as leather, textiles, foods, and liquors does not explain the large increase in lactic production which took place during the war. The curtain on this mystery has now been partially lifted by military authorities, and we find that lactic performed one of the war's small but important jobs. It was used in a fire-quenching solution to prevent explosion and death in tank interiors.

Many tragedies had taken place inside of tanks when enemy shells pierced the armor and set fire to ammunition supplies. A number of remedies had been tried unsuccessfully until someone thought of the high surface activity and wetting properties of a solution of a lactic acid compound. In actual practice, the solution, Ammudamp, was jacketed around the tank's magazine, sides, and bottom, as well as in the spaces between the shell racks. An invading shell released the fire-quenching medium, and even if the ammunition was set ablaze, the resulting fire could be quickly brought under control.

In this manner a product normally used in the preparation of sauerkraut, pickles, and essences made one of chemistry's valuable contributions to warfare. The first shipment of this fire-eater was made on October 30, 1944, three months after the manufacturers had been asked by Army Ordnance to work with the Government on the problem.

Swords and Plowshares. The smoke generators which so effectively concealed U. S. troop movements may find a good postwar market. The Standard Oil Company of New Jersey is conducting experiments on the use of this generator in the citrus area. At present smoke pots are not efficient in preventing frost losses, but the smoke generator can create a dense blanket of smoke which might more fully protect the trees. This machine might also be used to disperse insecticides as a fine mist over large areas of orchards.

Absorbable Sponge. In I. & E. C. Reports for May, 1945 (page 5), we spoke of absorbable cellulose. Another physiologically absorbable product has now made its appearance, with the help of the Upjohn Company. It was reported by John T. Correll, Hazel R. Prentice, and E. C. Wise on the program of the Division of Medicinal Chemistry of the AMERICAN CHEMICAL SOCIETY's 1945 Meeting-in-Print. The new product, Gelfoam, is a sponge of partially denatured protein material. Although it was developed specifically as a medium for thrombin, the blood-clotting enzyme, it will probably have general application in surgery where a sponge that can be left in the body will be useful.

The effectiveness of thrombin was limited by the fact that it was applied as a fluid. A sponge that could be soaked in thrombin, squeezed out, and placed on the hemorrhage to absorb blood and hold the clot would facilitate its use. Sponges of fibrin, starch, and gelatin

(*Continued on page 10*)

were tried, but the gelatin sponge appeared to be the most satisfactory in regard to both physical properties and absorption. The gelatin sponge is prepared by air-drying a foam made from a specially prepared gelatin solution, and is light, tough, nonelastic, and porous. After the sponge has dried, it is packaged and sterilized by dry heat since autoclaving results in a complete loss of desired properties. It is not readily wet by water until it is kneaded to break the air cells, whereupon it will imbibe up to fifty times its weight and can be used repeatedly. It is not soluble in water, but a 1% solution of U.S.P. XII pepsin will digest a 100-mg. sponge *in vitro* in about 30 minutes at 37° C. Extensive clinical investigations on laboratory animals have demonstrated that it is absorbed in the body and that it disappears, with no antigenic manifestations, in 30 to 90 days.

Plastics by the Mile. The world was astounded when the late Thomas A. Edison succeeded in sending four Morse telegraphic transmissions over one line without interference. Today, thanks to continued scientific development of communications equipment, it is possible to use a single line for as many as 1440 two-way conversations. The coaxial cable is responsible and its success is ascribed to its high insulation properties. The insulating resin is polyethylene, a straight-chain thermoplastic polymer of liquid ethylene. Its low electrical losses and chemical and physical properties are ideal for this purpose.

As with many other recent discoveries, polyethylene demonstrated its value on a large scale in military equipment. Although manufactured in Britain on a modest scale, it is said that the I. G. Farbenindustrie obtained the plastic for use in undersea cables. When the war began in September, 1939, the British expanded polyethylene production for insulation in radar as well as in cables. In this country output of the resin was undertaken by two leading chemical manufacturers for such military applications as radar and shipboard communications.

Productive capacity created during the war for polyethylene is now available for many uses besides coaxial cables, although that field appears to be the most promising. Cables of this sort are necessary for linking together television stations, and the future may witness a wide use of polyethylene for this application alone. As insulation for ultrahigh frequencies it will play an important part in linking together a nationwide television network. As shunt losses are but one twelfth of those experienced with hard rubber, the telephone, also, is expected to make extensive use of this material.

Our Error. Plutonium changes to U-235 through emission of an alpha particle. Last month we blamed this transformation on the neutron in our report "Atomic Age". You will be glad to learn that the neutron does not have to worry about degrading plutonium and can devote all of its energies to splitting atoms.

(*Continued on page 12*)

I. & E. C. Report on the Chemical World Today

Economics

Fertilizer Goes West. Fifteen years ago the western states accounted for a very small part of annual United States fertilizer consumption. Since 1930 the use of fertilizers in the West and Midwest has expanded considerably.

The tonnage increases in fertilizer consumption since 1930, by areas, are shown in the following compilation prepared by the National Fertilizer Association:

	% of U. S. Consumption		% Increase in Tonnage
	1930	1944	
North Atlantic	14.3	13.9	33
East North Central	9.9	14.8	105
West North Central	1.3	2.7	172
South Atlantic	50.2	43.3	18
South Central	22.0	19.9	23
Western	2.3	5.4	222
United States	100.0	100.0	37

Thus, the use of fertilizer has gained most rapidly in the West, East North Central, and West North Central areas. National fertilizer consumption totaled 8,222,000 tons in 1930 and 12,072,000 tons in 1944.

The fact which partly explains this new trend is that corn has replaced cotton as the principal fertilized crop. One factor in this reversal is the wide adoption in the Midwest of hybrid corn which is being given generous tonnages of plant food.

Figures for tag sales during the prewar year 1939–40, compared with similar data for the fiscal year 1944–45, show that fertilizer sales in the Midwest rose from 561,000 to 1,208,700 tons. Very striking increases have taken place also in the use of fertilizer for fruits, vegetables, and grasslands. Pastures in several western sections are still in need of fertilizer.

A report from Iowa says that many so-called fertile soils in the West may not contain enough available phosphorus to produce maximum crop yields or good feed. Another from the University of Illinois shows that each ton of alfalfa hay represents a net removal from the soil of 18 pounds of nitrogen, 3.6 of phosphorus, 2.5 of potassium, and about 125 pounds of limestone. The same report contends that these elements might be replaced at a cost of about four dollars.

It is not surprising, then, that our fertilizer manufacturing industry is "going West" to supplement insufficient soil elements in those states. Probably for the first time in history, a manufacturing plant for fertilizers is being erected in Iowa to serve the Iowa and Minnesota sections. It is under construction by the International Minerals & Chemical Corporation at Mason City, and should be in operation in 1946.

Fertilizers, especially phosphates, are likewise needed on the West Coast. To meet this new demand another manufacturer, the Stauffer Chemical Company, is entering into additional long-term contracts for phosphate rock which will double its production of superphosphate in 1946. In this manner the fertilizer industry is correcting a supply situation which has been caused in the past by distribution inadequacies rather than by lack of sufficient capacity. Transportation and its costs have been more of a problem to agriculture in the West than to farmers in the Atlantic and southern states.

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I. & E. C. Reports on the Chemical World Today

Commerce and Industry

Laboratory Rubber Goods. Soon after the start of the war, the composition of laboratory rubber goods was cut from 98 to 42% pure gum, with good-grade reclaim making up the difference; but it was not long before natural was eliminated altogether except in products for surgical use. For tubing, the first synthetic was neoprene which had come into use before the war; later GR-S was added, then the Buna N's, and finally Butyl rubber. Special-purpose synthetics are actually improvements over natural rubber. GR-S, the general-purpose rubber, however, is strictly a substitute that is tiding us over a critical period. The use of neoprene and Butyl in particular, and probably of the Buna N's, will continue regardless of the price of natural rubber. Neoprene is used where its oil- and ozone-resistant and noncracking properties are desired. It can also be made so that it will not support combustion. The Buna N's are characterized by extremely low swelling in oils. Butyl is inert to most chemicals, and its impermeability to air, which is four times that of natural rubber, recommends it especially for vacuum tubing. Most hand-wrapped tubing now being made is Butyl.

All rubber tubing is extruded, but a better product is obtained if it is hand-wrapped with cloth on a mandrel for curing. This accounts for the fabric pattern on most types of prewar tubing. Swelling is prevented and a denser tubing is obtained, but the demand for hand-wrapped tubing for aircraft use had created a manpower shortage in this item. Extruded tubing is simply dusted with talc before curing so it can be turned out with less labor. GR-S is being used for most extruded tubing.

Soybeans and the Future. The threefold increase in soybean production, from 62 million bushels in 1938–39 to nearly 200 million for every season since 1942, solved two problems. It provided edible oils for increased wartime needs and to fill the gap created by loss of imported oils, and it contributed to alleviating shortages in stock feeds. Industrial uses of soybean products have not played a significant part in this expansion, nor have they ever seriously affected the size of the crop.

As a result of wartime pressures and government subsidies, the soybean crop has been forced beyond its normal level. Soybean is known to be an eroding crop on rolling ground, and many producers are growing it on land which cannot support it. Many farmers have discarded their crop rotation programs to meet government requests for oil-producing crops. Although high prices aided in stimulating these increases, the patriotic appeal to serve the war effort by growing soybeans affected many farmers and contributed to increases in a way that prices alone could never have done. Therefore, declines may be expected from both these sources.

Although it did not figure largely in total production, soybean flour capacity was expanded some thirty fold during the war to 1.5 billion pounds in 1943. Ultimate production, however, never exceeded 400 million pounds, because neither Lend-Lease shipments, needs for rehabilitation feeding of occupied countries, nor domestic consumption to alleviate anticipated protein shortages

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assumed expected proportions. Postwar volume will probably be somewhat lower than the inflated production.

Industrially, soy is not a "wonder bean", no matter how useful this term may be in promoting its products. It is primarily a source of food products. Amounting to a meager 3% of total prewar output, the industrial uses of soybean products are not important in the over-all picture. Paint uses of soybean oil have declined because of greater demands for it as an edible oil. Soybean synthetic rubber was an interesting war-born development, but it had no special advantages to warrant the use of an edible oil for this purpose Soybean plastics are on the decline. They have water-sensitive characteristics and other shortcomings which cannot be offset by price advantages in certain applications. By now, plastics have gone beyond the soybean protein stage.

New industrial prospects for soybean products include isolated proteins for papermaking and other industrial uses and fractionated oils on which interesting work is now being done. Soybeans, however, will probably never figure prominently as an industrial raw material, simply because the farmer gets too much for his crop for it to compete against wood, coal, and petroleum. Soybean products are not by-products. Oil and meal will have to be codeveloped because the industry is not in a position to operate on a by-product basis. The postwar future of soybean products, therefore, will continue to be in edible products.

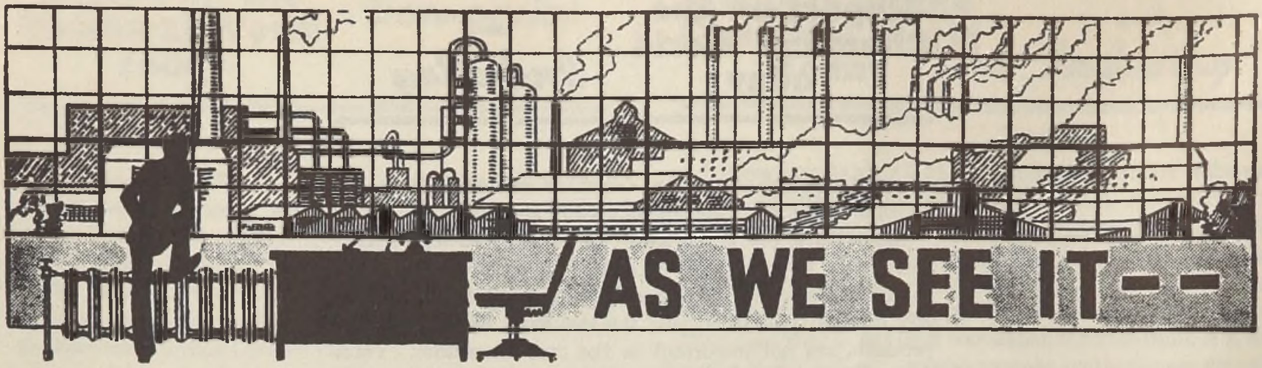
Italian Renaissance. Vitalization of the Italian chemical industry is one of the most important problems facing the Allied Military Government. Over 40% of the industrial plants of Italy had been damaged, mostly by bombing, but many also by German sabotage. Lack of coal has been the most serious raw material shortage, and only with great difficulty have most of the plants been made operable.

One of the first to be reopened was a chlorine plant, for reasons of health. The hemp industry has been brought to some degree of usefulness, mostly due to the financial stability given the market by the military officials.

The allied commission has started six cement plants capable together of turning out 10,000 tons per month. Superphosphate plants were badly damaged, owing to the fact that the cooling sheds were favorite military storage units and, consequently, favorite targets for planes. Today this industry, vital to agriculture, has been rehabilitated to the point where it is turning out about 200,000 tons per year. Many of the furnaces had been destroyed by the Germans and could not be used until plants making a certain refractory cement had been repaired and were producing.

Mercury mines were largely undamaged, and a store of 8000 flasks of mercury, hidden from the Germans, were uncovered. Copper sulfate for insecticides is being made again at a rate of 3000 tons per month; salvaged brass is the raw material.

Making nitrogenous fertilizer did not yield to an easy solution. The Germans had decamped with all the platinum catalyst from the Crotone plant.



Controlled Exchange. The application of controllers to chemical plant equipment is never easy, since the many factors affecting operation and response yield only to complex analysis or to trial and error. During the past few years, however, practical applications have been investigated with a view to applying complex theoretical analysis to the problems posed. A major stumbling block has been difficulty in the application of controls to heat exchangers. More, Quail, and Bain have, in this issue, described some of their pioneering work in this field. See "Application of Automatic Controllers to Heat Exchangers".

Out of Hiding. Censorable articles which are finding their way into the lives of the Editors are being welcomed with open arms because these contributions can now be put in print instead of being hidden in the safe. One article recently out of the censored status is that of Linn and Grosse entitled "Alkylation of Isoparaffins by Olefins in Presence of Hydrogen Fluoride". This process is important in the manufacture of aviation gasoline, and we are pleased to make the knowledge available. As information becomes further declassified, more on this subject will be spread before you.

Explosive Waste. Despite the modern techniques for eliminating all residual TNT from liquids emanating from shell-loading plants, it was found that 100 parts per million of TNT was not uncommon in the discharged waters. Since this was a nuisance of considerable magnitude for the streams into which the waste was dumped, research was instituted with the hope of finding an adequate answer. Ruchhoft, LeBosquet, and Meckler, of the United States Public Health Service, found that soil and activated carbon absorption bore most promise as a temporary war measure. Now, with the advent of peace, it may seem that such an article is of little immediate value. However the chemical plants of the nation are going to be faced with analogous disposal problems, and the results presented here will remain important long after the plants, for which the studies were made, are razed.

Bearing Up Well. Corrosion of bearings by chemical mechanisms is at present undergoing interpretive and exhaustive research. Prutton, Turnbull, and Frey, specifically studying the corrosion of lead by peroxides, have added to our knowledge of the basic corrosive reactions in lubrication systems. One of the important considerations in the evaluation of the corrosivity of an oil, according to the authors, is the thermal stability of the oxidizing agent.

Another Sell in Cellulose. Carboxymethylcellulose, made by reacting monochloroacetic acid on alkali cellulose, is now introduced commercially and has begun its career of usefulness to the chemical industry. Hollabaugh and Burt of the Hercules Powder Company, anticipating a need for information on this compound, have compiled a complete summary of its history, properties, and possible applications. Apparently research teams in many industries will spend much time on this substance, for the list of applications is lengthy.

Cracking Olefins. Greensfelder and Voge report again on the cracking of hydrocarbons. This time it is the olefins, and the work was done with a silica-zirconia-alumina catalyst. Results are reported and analyzed.

***Bacillus brevis,* Chemical Manufacturer.** The efficient growth of Bre'r *brevis* is becoming a first-class problem in chemical economics and manufacturing. *Brevis* is the chemical cow which gives the milk containing tyrothricin. Lewis, Dimick, and Feustel are wondering whether it cannot be done better in shallow-layer growth on a culture of juice made from asparagus butts—a waste product of food canning. According to this report, yields amount to as much as 2 grams per liter, which, they say, is greater than any reported so far.

Boil and Bubble. Liquids, like humans, boil at different degrees and for different reasons. Larson, in "Factors Affecting Boiling in a Liquid", investigates a phase of unit operations that has been somewhat neglected, and arrives at conclusions that will be helpful to the designers of heat exchangers. Worrying the facts of nucleate and film boiling, he built an apparatus for testing ebullators or bubble makers and found that metals of different composition seemingly produce different ebullition temperatures. One of his conclusions is that ebullition does depend upon an aid whose property determines the amount of superheat tolerated. Following the paper the same author investigates and discusses thermodynamically the reasons for bubble formation.

Design Data. Noting the increasing popularity of continuous solvent-extraction methods for vegetable oils, Pollard, Vix, and Gastrock, of the Southern Regional Research Laboratory, are publishing data on boiling points and densities of cottonseed and peanut oils mixed with hexane. This is important to the designers of vacuum evaporators and strippers used in the extraction processes.

Plastic Intermediate. Aconitic acid may be used in acrylic resins as a modifier; its esters enter a variety of chemical materials, and its decomposition product, itaconic acid, can, through esters, be used as a plastic. With all these uses, aconitic acid should be popular with the chemical fraternity; Umbdenstock and Bruins report on the catalytic dehydration of citric acid to make this intermediate.

With the Departments. Von Pechmann senses the confusion which has existed in many plants in the swing to peacetime production and suggests the planning of sound policies. Murdock examines the three areas available for the disposal of industrial wastes. Brown sees that many new wartime products will be important to industry in the postwar. Munch writes the chapter and verse on the application of strain gages to pressure measurement.

INDUSTRIAL AND ENGINEERING CHEMISTRY
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Editorials

WALTER J. MURPHY, EDITOR

A Scientific Credo

FOR years the editors of THIS JOURNAL have urged the chemists of the Nation to show an active and intelligent participation in the affairs of the world. Decrying the ivory tower of science, and begging the chemist to assume responsibilities in our everyday world, we have pointed out many, many times that the course of civilization could be better directed if the approach of science were among those many arts and diverse forces that today mold our public opinion.

Now we notice that the anthropologists, too, are beginning to become interested in this aspect of living and Dr. Gene Weltfish, of the Department of Anthropology at Columbia University, in the September *Scientific Monthly* has written a stirring and moving plea for cooperation by scientists in our everyday affairs. Miss Weltfish states that some years ago, while attending commencement exercises, she heard the medical graduates recite the Hippocratic oath. She was impressed by its solemnity, but even more striking was to her the fact that the only group of graduates that was asked to express any public responsibility were the physicians.

She abhors the disinterestedness of the scientists, stating that it amounts to a lack of evaluation of purposes, and that as a consequence the scientist can readily become the creator of havoc and destruction. For our reconstructed world she thinks that graduates should take cognizance of their responsibilities and the social consequences resulting from their use of scientific techniques. In order to make them conscious of their obligations she proposes a simple yet moving oath which she titles "The Scientist's Oath", and which we pass on to you because of its importance in the thought currents that are stirring us today.

"I pledge that I will use my knowledge for the good of humanity and against the destructive forces of the world and the ruthless intent of men; and that I will work together with my fellow scientists of whatever nation, creed, or color, for these, our common ends."

This is an important suggestion. Perhaps what is needed is some simple impressive ceremony which will bring to our scientists a deep understanding of their responsibilities and their great potentialities.

Mankind has had a narrow squeak in the war that has just ceased. Under the wrong sponsorship, science had become, in the totalitarian countries, something awful to behold. Without proper guidance from men of generous outlook, science can become, in any part of the globe, a force of evil.

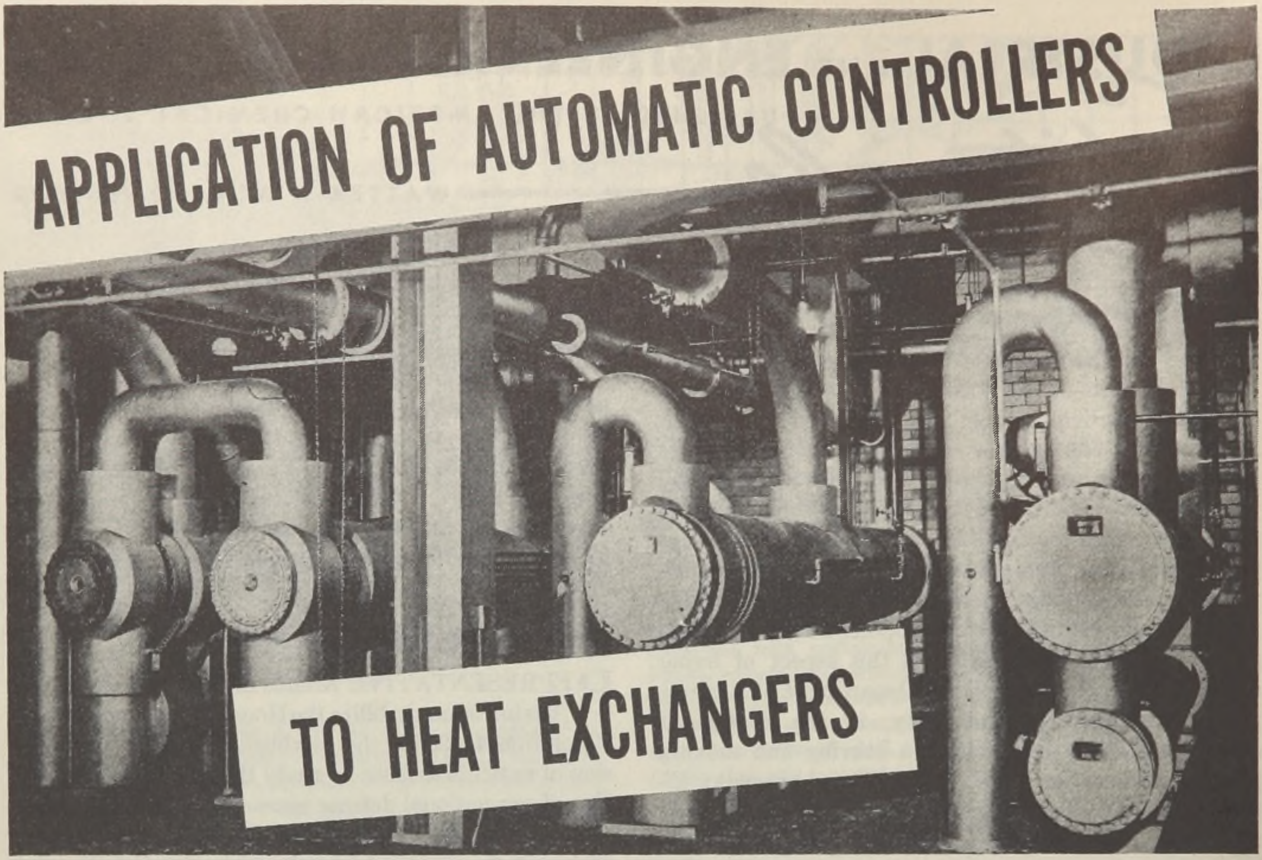
Winston Churchill expressed it early in the war when he said, in speaking of the yearning need for victory, "if we fail, then the whole world *** and all that we have known and cared for will sink into the abyss of a new dark age made more sinister, and perhaps more prolonged by the *lights of a perverted science*". Vision is the need, for without it the people will surely perish.

Revising National Defense

REPRESENTATIVE Arends of the State of Illinois has introduced a bill in the House of Representatives, Resolution 4152, for the establishment of a "commission of national defense to study the technological revision of our national defense necessitated by atomic and other weapons". To us, an appealing and admirable feature of the proposed act is that it makes provision for the commission to be staffed by "representatives of scientific and industrial research and other leading citizens who are conversant with the problems of the national defense". This group will be advised by military representatives who will give the commission full access to the facts relating to technological revolution in warfare. The commission, in turn, will make interim quarterly reports to Congress so that an adequate national defense program may be formulated. A fund of a half-million dollars is also recommended to enable the study to be carried out properly.

This proposal constitutes a step in the right direction. Our Nation has had a long-unfilled need for the services of scientific men in the executive direction of national defense and other problems of government. At long last this may come about, provided the bill is passed; but only because science has, with a new weapon of unsurpassed magnitude, contrived to impress upon the minds of the legislators the necessity of expert and adequate advice in this field. We hope not only for the passage of the Arends bill but also that many more proposals such as this one, providing for the cooperation of science, are introduced into the Congress of the United States. Science with its varied talents for research and investigation into the basic facts and laws underlying our civilization has much to offer, and we sincerely hope that the time has come for the complete recognition of this fact—and for its application, in a practical way, to this age and to its problems.

APPLICATION OF AUTOMATIC CONTROLLERS TO HEAT EXCHANGERS



COURTESY, THE LUMMUS COMPANY

An outline is presented of the methods used by Ziegler and Nichols for finding the optimum settings for temperature controllers. Applied to a heat exchanger, coefficient u to be used in the sensitivity equation, $S = u/R_1L$, was determined by the reaction or response curve method. The work was carried further by calculating the value of the capacitances of the exchanger which contribute to the form of the response curve and by graphically reconstructing this curve. Coefficient u found by this method compares favorably with the value determined experimentally.

THE refinements introduced into the design of industrial automatic control instruments in recent years, and the consequent rationalization of the knowledge of their characteristics, have resulted in a more systematic study of practical applications. The object of this study was to devise means of determining optimum controller settings for the various conditions of lag and capacitance which make up an industrial process.

The work of Ziegler and Nichols (*4*) resulted in the development of three means of determining optimum controller settings: ultimate sensitivity, response curve, and analytical response curve methods. The work described here was performed (*a*) to determine constants applicable to the response curve method when used to determine optimum settings for industrial heat exchangers, and (*b*) to evaluate effects of the various design factors of heat exchangers on the controllability of the process and thus make possible the application of the analytical response curve method to problems of industrial heat exchanger control.

The ultimate sensitivity and response curve methods for determining automatic controller settings and their application to a distillation process were reported by Allen (*1*). They will, therefore, be described only briefly in this paper. Generally, the most desirable controller setting for a given process is that at which the recovery curve obtained after any disturbance of the equilibrium of the process shows an amplitude ratio (ratio of magnitude of each oscillation to that of the oscillation preceding it) of 25%. Therefore, the three methods described below are intended to indicate the proper controller setting to give this 25% amplitude ratio.

ULTIMATE SENSITIVITY AND RESPONSE CURVE

In most processes a controller sensitivity (output change per unit of pen movement) of one half that at which an amplitude ratio of 100% is obtained (ultimate sensitivity) gives a recovery curve having an amplitude ratio of approximately 25%. Therefore, to determine the optimum setting by this method, it is necessary only to find a sensitivity at which sustained oscillation results from a process disturbance and set the instrument at half of that sensitivity. This method is applicable only to multiple-capacity processes, but as most industrial processes come under this classification, no great disadvantage is presented. The only drawback to the use of the ultimate sensitivity method lies in the time required to make the necessary tests. In large-scale processes having large capacities, the period of oscillation becomes very long, and determinations are time consuming.

The response curve for a process is obtained by suddenly changing the flow of the control agent and plotting the resulting changes in the controlled variable on a time base, in the absence of any controlling action. In practically all industrial processes the response curve is S-shaped (Figure 1). A tangent drawn through the point of inflection gives an indication of the characteristics of the process and serves as a means for determining optimum settings for its control.

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When a unit change in the control agent is made—e.g., that caused by a change of 1 pound per square inch in air pressure on a diaphragm valve—the product of the slope of the tangent to the point of inflection of the response curve, R_1, and its intercept on the horizontal axis, L, gives a direct reciprocal relation for the determination of optimum sensitivity of a controller applied to the process. L, the lag, is approximately constant for the process, regardless of the change made in the flow of the control agent; the reaction rate varies directly as the change made in the flow of the control agent and must be converted to a unit reaction rate in optimum setting determinations. The product, R_1L, for a process is represented by the intercept of the tangent through the point of inflection with the vertical axis.

Although the response curve method gives a direct reciprocal relation for determining optimum controller settings, many industrial processes require a factor to be applied to the R_1L values. The general formula for obtaining optimum settings from response curve is:

$$S = u/R_1L$$

where u is a constant which must be found experimentally for the various types of processes. Values for u have been reported as high as 5.4 on pure two-capacity processes, although most industrial processes show a value nearer unity.

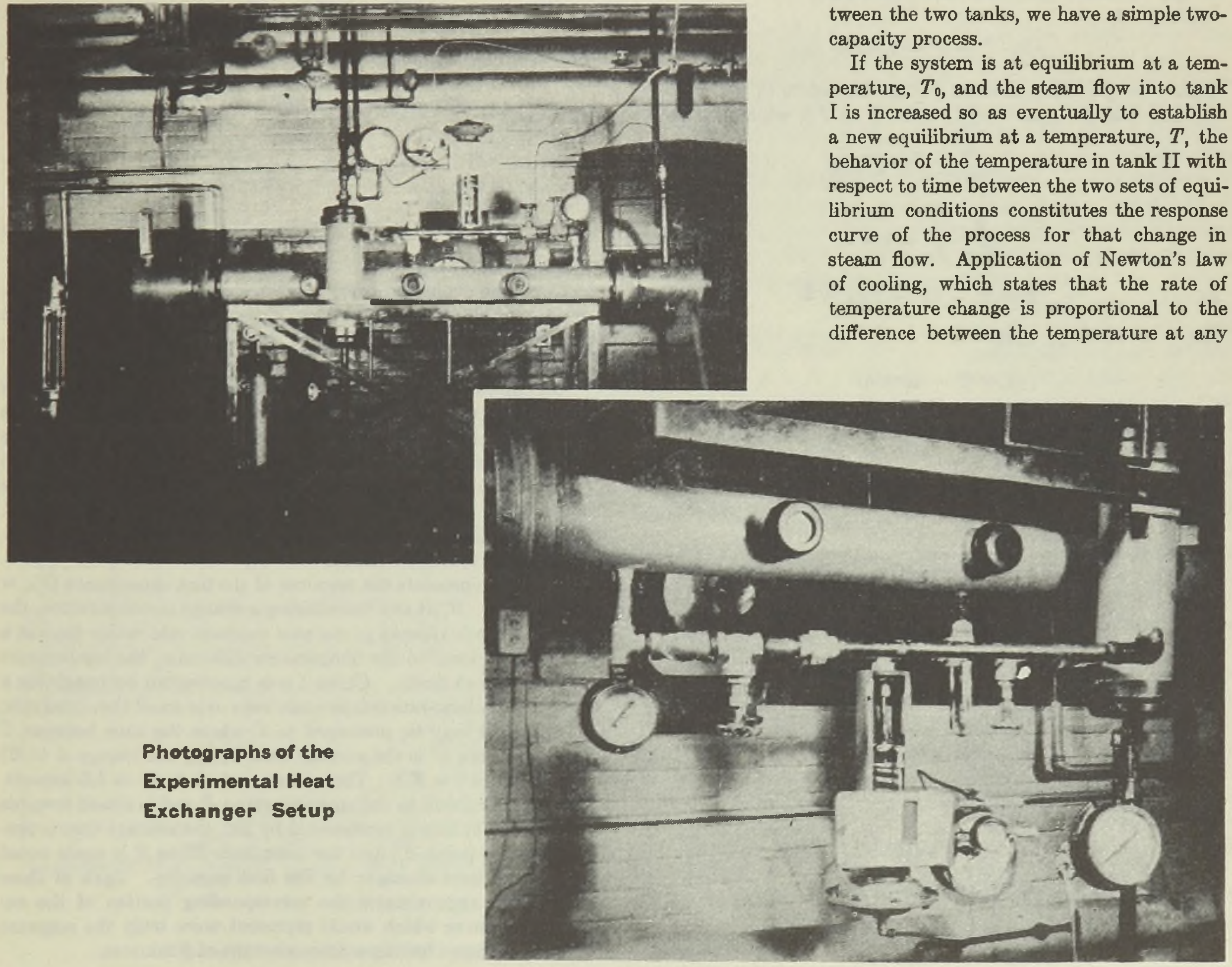
The response curve method has one disadvantage in practice: It frequently requires a relatively large disturbance in the process, and such disturbances cannot be made in many processes for practical and economic reasons.

ANALYTICAL RESPONSE CURVE

Mathematical Analysis. This method involves calculation of the response curve from calculated values of capacitance, resistance, and transport lag which make up the process. This determination may be either by purely analytical means or by graphical methods.

Calculation of analytical response curves may be illustrated by considering a pure two-capacity process. Figure 2 shows a process in which the water in tank I is heated directly by a steam jet, and that in tank II is heated by the overflow from tank I. Assuming perfect mixing in both tanks and neglecting the small resistance of the thermometer bulb and the transport lag between the two tanks, we have a simple two-capacity process.

If the system is at equilibrium at a temperature, T_0, and the steam flow into tank I is increased so as eventually to establish a new equilibrium at a temperature, T, the behavior of the temperature in tank II with respect to time between the two sets of equilibrium conditions constitutes the response curve of the process for that change in steam flow. Application of Newton's law of cooling, which states that the rate of temperature change is proportional to the difference between the temperature at any



Photographs of the Experimental Heat Exchanger Setup

instant and the ultimate temperature, makes it possible to calculate this curve.

Let t = temperature at any instant in tank I
T = ultimate temperature
T_0 = initial or datum temperature
K_1 = time constant for tank I, min.
K_2 = time constant for tank II, min.
θ = time

Then for tank I, Newton's law may be expressed as follows:

$$dt/d\theta = (T - t)/K_1$$

$$\frac{-d(T - t)}{T - t} = d\theta/K_1$$

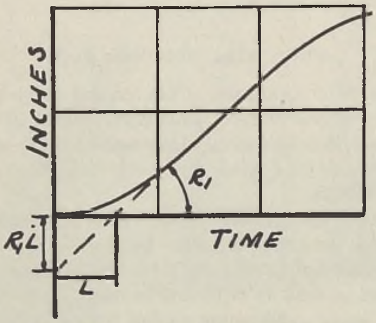


Figure 1. Unit Response Curve

Integrating,

$$-\ln (T - t) = \theta/K_1 + C_1$$

when $\theta = 0$, $\theta/K_1 = 0$, and $t = T_0$. Therefore $C_1 = -\ln(T - T_0)$ and $-\ln (T - t) = \theta/K_1 - \ln(T - T_0)$, which becomes

$$\frac{\ln (T - T_0)}{(T - t)} = \theta/K_1$$

$$\frac{T - t}{T - T_0} = e^{-\theta/K_1}$$

or

$$t = T - (T - T_0)e^{-\theta/K_1}$$

Let $T - T_0 = a$; then

$$t = T - ae^{-\theta/K_1} \tag{1}$$

which is the equation for the temperature of tank I at any instant.

Considering tank II,

$$\frac{dt'}{d\theta} = \frac{t - t'}{K_2}$$

where t = temperature of tank I
t' = temperature of tank II
K_2 = constant for tank II

$$\therefore K_2dt' = td\theta - t'd\theta$$

but

$$t = T - ae^{-\theta/K_1} \text{ (from Equation 1)}$$

$$\therefore K_2dt' = Td\theta - ae^{-\theta/K_1}d\theta - t'd\theta$$

$$K_2dt' = (T - t')d\theta - ae^{-\theta/K_1}d\theta \tag{2}$$

where t' and θ are variable. Let $t' - T = x$, and $e^{-\theta/K_1} = y$. Then,

$$dt' = dx$$

$$e^{-\theta/K_1}d\theta = -K_1dy$$

and

$$d\theta = -K_1\frac{dy}{y}$$

then

$$K_2dx = xK_1\frac{dy}{y} + aK_1dy \text{ (from Equation 2)}$$

$$\frac{K_2}{K_1}ydx - xdy - aydy = 0$$

Let $K_2/K_1 = b$ and multiply by ny^{n-1}; then,

$$bny^ndx - nxy^{n-1}dy - nay^ndy = 0$$

Let $bn = -1$,

$$\therefore n = -1/b$$

and

$$-d(y^nx) - \frac{na}{n + 1}dy^{n+1} = 0$$

Integrating,

$$xy^n + \frac{na}{n + 1}y^{n+1} = C_2$$

$$\therefore x = C_2y^{-n} - \frac{na}{n + 1}y \tag{3}$$

but

$$x = t' - T$$

$$y = e^{-\theta/K_1}$$

$$n = -\frac{1}{b} = -\frac{K_1}{K_2}$$

$$\therefore -n = \frac{K_1}{K_2}$$

$$\therefore \frac{n}{n + 1} = -\frac{K_1}{K_2 - K_1}$$

Substituting in Equation 3,

$$t' - T = C_2 (e^{-\theta/K_1})^{K_1/K_2} + \frac{K_1a}{K_2 - K_1}e^{-\theta/K_1}$$

$$= C_2(e^{-\theta/K_2}) + \frac{K_1a}{K_2 - K_1}e^{-\theta/K_1}$$

and

$$t' = T + C_2e^{-\theta/K_2} + \frac{K_1a}{K_2 - K_1}e^{-\theta/K_1} \tag{4}$$

C_2 can be evaluated from the fact that, when $\theta = 0$, $t' = T_0$. R and L can be calculated from Equation 4, but the method is cumbersome. The addition of a third capacity further complicates the final equation, and its usefulness disappears.

GRAPHICAL ANALYSIS. The substitution of values in complex equations can be avoided by graphically constructing response curves of processes whose time constants are known. Such curves (Figure 3) are close enough approximations to the true response curves for optimum setting determinations and are much more convenient than the purely mathematical analysis. Figure 3 was drawn for a three-capacity process with time constants of 4, 4, and 8 minutes.

Curve I represents the response of the first capacitance (K_1 = 8 minutes). If, at any time during a change in temperature, the temperature is allowed to rise at a constant rate rather than at a rate proportional to the temperature difference, the temperature curve becomes linear. Curve I was constructed by imagining a series of constant-rate temperature rises over small time intervals; i.e., A to B may be prolonged to C where the time between C and C' (where C' is the average time during the change A to B) is 8 minutes (= K_1). Time increment A to B is 1.0 minute. The next addition to the curve starts at B and is aimed towards E. This addition is represented by BC, the average time is represented by point E', and the time from E' to E is again equal to K_1, the time constant for the first capacity. Each of these short lines approximates the corresponding portion of the exponential curve which would represent more truly the response of a capacitance having a time constant of 8 minutes.

Curve II represents the response of the second capacitance (K_2 = 4 minutes) and is similar to curve I except that each of the short straight lines is directed toward the point on curve I with an abscissa 4 minutes removed from the mid-point of the line. This is because the potential temperature of the second capacitance at any instant is the temperature of the first capacitance at that same instant; e.g., F is 4 minutes removed from A, FG is drawn toward point C', the mid-point between F and G being 4 minutes from C', etc. Once again each time increment is 1.0 minute.

Curve III represents the response of the third capacitance (K_3 = 4 minutes) and is similar to the other two, except that the lines are directed towards corresponding points on curve II. This represents the response curve which would be obtained from a process having the characteristics described; from it the value of R_1L can be found in the manner described for experimental response curves.

When transport lags are present, they are included by adding a horizontal portion to the curve along the line of T_0. The final curve is drawn only as far as the point of inflection, which is easily found by noting the changes in inclination of the straightedge used to construct it. In the application of this method, the time constants can be used in any order without changing the final result, but it is generally more convenient to plot the curves in the order of descending magnitude of time constant.

Either of the modifications of the analytical response curve method for determining optimum settings can be used without experimental work, if constant u and the governing capacitances of the particular type of process are known. The following work is concerned with the evaluation of these factors for tubular heat exchangers.

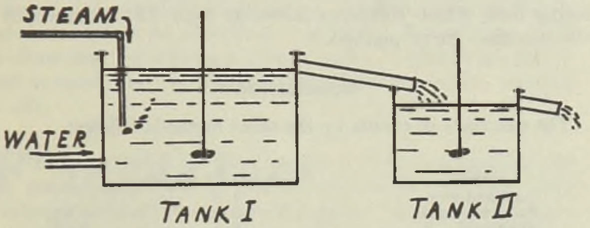


Figure 2. Example of Simple Two-Capacity Process

DESCRIPTION OF HEAT EXCHANGER

The heat exchanger used for this investigation is shown in Figure 4 and in the photographs on page 915. The outer chest is made of cast steel; it is 5 inches in diameter and has an over-all length of about 6 feet. Cold water enters from the left into the left-hand reservoir of the exchanger, and passes through four inner 1-inch steel tubes, where it is heated by the surrounding steam, to the right-hand reservoir or mixing chamber and then out through the outlet pipe past the temperature controller bulb. The steam is passed first through a dryer and then through the circuit containing the control valve to the steam chest where it heats the water in the inner tubes. The resulting condensate collects in the chamber at the bottom (Figure 4).

Constant water flow is attained by a large constant-head tank (not shown in Figure 4). The rate of water flow was measured by a calibrated rotameter. The upstream steam pressure was adjusted manually and was held constant throughout all the experimental work.

The control valve was of the air-to-close beveled disk type with a diaphragm motor. A Precisor was attached to ensure adequate response to changes in air pressure. Temperature was recorded and controlled by a Taylor Fulscope recording controller, equipped with proportional response.

DETERMINATION OF SENSITIVITY

TRIAL-AND-ERROR METHOD. The actual sensitivity setting required for satisfactory control was determined by making a series of settings of the sensitivity dial; for each value of the sensitivity selected, the system was upset by causing a sudden change in the heat supply. To do this, the control point was changed abruptly and then readjusted to its former value. The result of this operation gave the familiar wavelike tracing of temperature change about the control point. Sensitivity S, which gave a die-away curve having a 25% amplitude ratio, was found to be 7.8 lb. per sq. in./in. This value was taken as the most desirable sensitivity setting for the process.

RESPONSE CURVE METHOD. Under conditions of constant outlet water temperature, and with the controller acting as a temperature recorder only and not as a controller, the air pressure to the diaphragm of the control valve was suddenly changed. This resulted in a corresponding alteration in the steam supply and, hence, a change in the temperature of the outgoing water. To facilitate the plotting of the temperature response curve on rectilinear coordinates, the clock in the recorder was stopped, and the temperature chart of the instrument rotated by hand every 5 seconds. This resulted in a stepwise tracing of temperature *vs.* 5-second intervals.

A plot of the data obtained in this way gave the characteristic S-shaped curve.

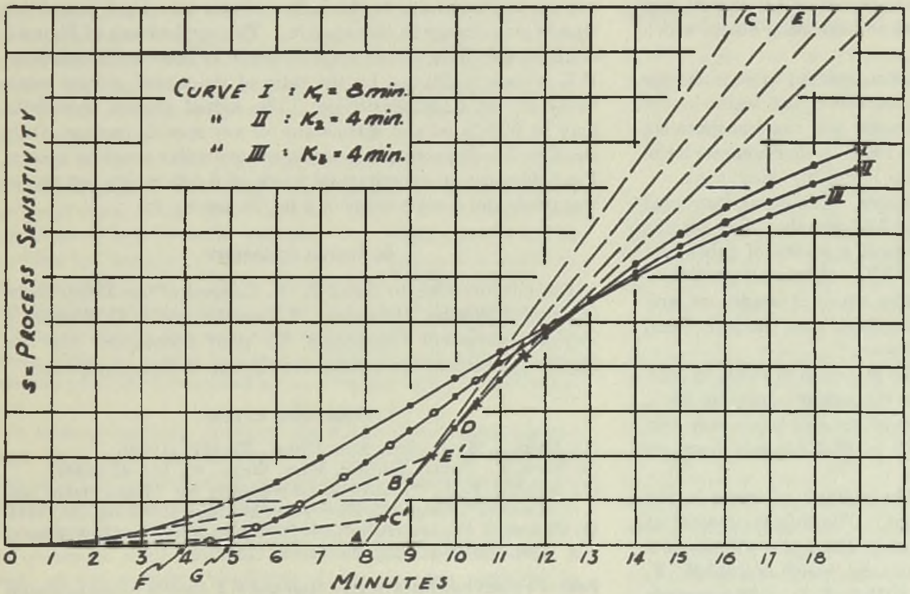


Figure 3. Graphical Construction of a Unit Response Curve

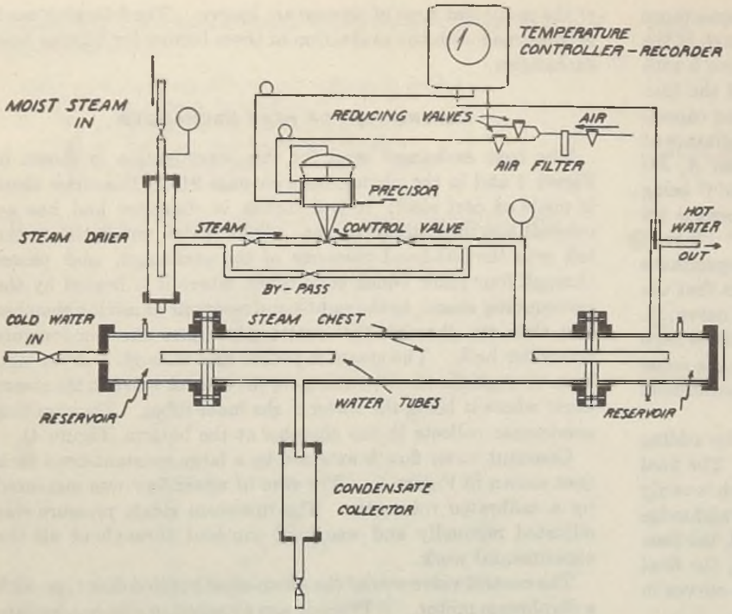


Figure 4. Diagram of Heat Exchange Setup

R_1L was found to be 5.3° F./lb. per sq. in., and hence the sensitivity is:

$$S = 45.6/5.3 = 8.6 \text{ lb. per sq. in./in.}$$

where 45.6° F./in. converts from degrees Fahrenheit to inches for this particular type of chart.

Comparing this value with S found by the trial-and-error method gives 0.91 for u, and the sensitivity equation becomes $S = 0.91/R_1L$ lb. per sq. in./in.

Analytical Method. Tubular heat exchangers consist of a complex system of lags. Besides the heat capacities of the various elements, there is the transfer lag governed by the heat conductivity of the tubes, and the transport lag due to locations of control valves and thermometer bulbs (*3*). To represent such a process by a small number of capacitances and transport lags involves lumping some capacitances and neglecting others which have little effect on controllability.

In the present case the system was considered to contain four major lags: the exchanger jacket and tubes, the water in the tubes, the recorder bulb and mechanism, and the transport lag due to the time for water to flow from tubes to thermometer bulb. Of these four lags, only the third was found by experiment.

Time Lag of Steam Jacket and Tubes. The total combined weight of steam chest and tubes was 120 pounds. The specific heat was 0.12 B.t.u./lb./° F. The heat capacity of tubes and chest was 120 × 0.12 = 14.5 B.t.u./° F. If it is assumed that the exchanger has been operating under constant conditions, and the heat supply is changed by y B.t.u./sec., then the jacket and tubes will rise at a rate of $y/14.5$° F./sec.

Water is flowing through the tubes at a rate of 0.305 lb./sec. and will rise a total of $y/0.305$° F. to the new temperature level. The capacity lag (or time lag) of the jacket and tubes may now be calculated as $(y/0.305)/(y/14.5) = 48.3$ seconds (say, 45 seconds).

Time Lag of Water in Tubes. The volume of water in the tubes at any instant is 0.12 cubic foot. The weight of water at any instant is 0.12 × 62 = 7.5 pounds. The water will rise at a rate of $y/7.5$° F./sec. to the new potential, which is $y/0.305$° F. From this, the time constant is $(y/0.305)/(y/7.5) = 24.6$ seconds (say, 25 seconds).

Recorder Bulb and Mechanism. During the early stages of the experimental work it was found necessary to reduce the sensitiveness of the bulb to small temperature fluctuations by wrapping the bare bulb with friction tape. Under normal conditions the time lag of the recorder and bulb is about 2 or 3 seconds. The time lag of the wrapped bulb was found by immersing it in hot water and then quickly placing it in position at the outlet of the exchanger, with cold water running through the tubes. The time-temperature curve was plotted on rectilinear coordinates, and the bulb constant determined by noting the time corresponding to 63.2% of the temperature change (*2*). This value was found to be 20 seconds.

Distance-Velocity or Transport Lag. The transport lag is made up of the time for the water to flow through the right-hand reservoir to the pipe leading up to the recorder bulb and the time for the water to flow up this pipe to the bulb. The total transport lag was found to be 10 seconds.

The three capacity lags were 45, 25, and 20 seconds, and the transport lag was 10 seconds. A response curve was constructed as indicated by Figure 3, and sensitivity S was found to be 8.1 lb. per sq. in./in. If the trial-and-error value of 7.8 lb. per sq. in./in. is assumed to be the true sensitivity setting, then u in the sensitivity equation becomes 0.96, which compares favorably with 0.91 obtained by the response curve method.

CONCLUSION

The summary of results by the three methods follows:

Method	S, Lb. per Sq. In./In.	u
Trial and error	7.8	..
Response curve	8.6	0.91
Analytical	8.1	0.96

The term "process sensitivity" (s) was suggested by J. G. Ziegler. Its units are inches per pound per square inch (in./lb. per sq. in.) and refer to the inches of pen travel per pound per square inch change in air pressure. The vertical axis of Figure 3 employs this unit, which may be made as large as is desirable. R_1L is then multiplied by the ratio of the actual process sensitivity to the scale sensitivity. The actual process sensitivity may be calculated and is constant for any specific process. Only the flow-lift characteristics of the control valve must be known. For this work an experimental value of 0.402 in./lb. per sq. in. was used, and a scale value of 6 in./lb. per sq. in.

ACKNOWLEDGMENT

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Part of a thesis submitted by J. L. More and F. J. Quail in partial fulfillment of the requirements for the degree of B.A.Sc. in Chemical Engineering, University of Toronto, 1944.

Corrosion of Lead by Oxidizing Agents and Lauric Acid in Hydrocarbon Solvents

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Rates of corrosion of pure lead by representative organic peroxides in hydrocarbon media containing organic acids are compared. Organic oxidizing agents other than peroxides or oxygen may be effective in causing corrosion of lead in these media; oxynitrogen compounds, quinones, and diacetyl are agents of this type. For hydroperoxides and oxygen it is likely that lead hydroxide or lead oxide is intermediate in the corrosion process. For other types of peroxides and nonperoxidic oxidizing agents the evidence indicates that there is no metal oxide or hydroxide intermediate in the process. Reactivity of oxidizing agents toward lead are compared at a constant acid concentration. To evaluate the effective corrosivity of an oil, it is necessary to consider the thermal stability of the oxidizing agent as well as its chemical reactivity. Evidence is cited to show that oxynitrogen compounds, as well as peroxides and oxygen, may be among the oxidizing agents present in oils.

FOR some time it has been known (*3, 7*) that oxygen must be present before metals will be attacked by pure fatty acid. The importance of the presence of oxygen or of peroxides formed from oxygen in the corrosion of bearing metals by acid lubricating oils was not emphasized until recently (*2, 10*). Denison postulated (*2*) that the corrosion of metal bearings takes place in the following steps: (*a*) formation of peroxides by reaction of oxygen with the oil, (*b*) reaction of peroxide with metal to form a metal oxide, and (*c*) dissolution of metal oxide in organic acid to form soluble soap. His results also indicated that after sufficient acidity had developed to dissolve the oxide coating initially formed, the corrosion rate was principally determined by peroxide concentration.

Recent work (*10*) confirmed many of Denison's conclusions, but in addition showed that, with acids present in the oil, dissolved molecular oxygen may form the metal oxide in step *b* without the formation of any peroxide intermediate. Thus step *b* must be modified to "reaction of peroxide and/or oxygen with metal to form a metal oxide". It was further found that the corrosion rate was independent of acid concentration and was determined only by oxygen or peroxide concentration above 0.02 to 0.03 *N* acid. There was some indication, however, that the corrosion rate was partially determined by acid concentration below 0.02 *N* acid.

It seemed desirable to study the mechanism of the reaction more thoroughly to determine the dependence of corrosion rate upon the concentration of acid and oxidizing agent. Many different initial ratios of the acid and oxidizing agent were used. Since there were indications from previous work (*10*) that different peroxides exhibited very different corrosive reactivities, a study of the corrosive reactivity of various pure peroxides in lauric acid solutions was undertaken. It occurred to the authors that corrosion of metals by acid in hydrocarbon media might be promoted by oxidizing agents in the more general sense as well as by such specific oxidizing agents as oxygen and peroxides. Consequently the corrosive reactivity of various general oxidizing agents which might conceivably be present in oils, such as organic nitrogen compounds and quinones, was tested and compared. This paper reports the results of these investigations.

Experimental procedures were described in a previous paper (*10*). Wheeler's method (*11*) for determination of peroxides was used in modified form in this work. When the reaction mixture was permitted to stand for a half hour and then heated to boiling prior to titration, it was possible to determine accurately all of the peroxides employed.

CORROSION BY PEROXIDES

If the corrosion rate is determined by the concentration of oxidizing agent and is independent of acid concentration, the rate expression may be formulated as follows:

$$-d\,C_{ox}/dt = k\,A\,C_{ox} \tag{1}$$

where C_{ox} = concentration of oxidizing agent at time t
A = test piece area
k = reaction rate constant

Upon integration the rate expression becomes

$$k = \frac{2.303}{tA}\log_{10} C^0_{ox}/C_{ox} \tag{2}$$

where $C^0_{ox} = C_{ox}$ when $t = 0$

It was often more convenient to express the ratio C^0_{ox}/C_{ox} in terms of the actual metal weight loss. Then if W_o is the metal weight loss after the reaction has gone to completion and W is the weight loss in time t, Equation 2 may be rewritten

$$k = (2.303/t\,A)\log_{10} W_o/(W_o - W) \tag{3}$$

Thus if the corrosion rate is proportional to the concentration of oxidizing agent, the values of k calculated from Equation 3 should be constant, and a straight line should be obtained when $(1/A)\log_{10} W_o/(W_o - W)$ is plotted against t.

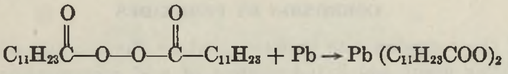
ACYL PEROXIDE. To test thoroughly the dependence of corrosion rate upon peroxide concentration, various concentrations of lauroyl peroxide were made up in benzene 0.1 *N* with respect to lauric acid. The rate of corrosion in these solutions of lead test pieces, whose total area averaged about 21.5 sq. cm., was measured at 70° C. One atmosphere of nitrogen was always maintained above the test solution in order to prevent refluxing of the solvent. Initial concentrations of peroxide ranging from 0.04 to 0.09 *N* were employed. Values of $(1/A)\log_{10} W_o/(W_o - W)$ calculated from the results are plotted against time in Figure 1. Within experimental error the points from the different initial concentrations fall on the same curve, which is linear in the early and middle stages of the reaction, and which passes through the origin as required by Equation 3.

To test the dependence of corrosion rate upon acid concentration, rate measurements were made on lauroyl peroxide solutions in which the acid concentration ranged from 0.001 to 0.106. Rate constants were calculated from Equation 3 at each acid concentration. Table I summarizes the average values of these constants and the mean deviations from them, and lists the number of determinations used in evaluating the constant at each concentration.

Table I. Corrosion Rate Constants of Lead by Lauroyl Peroxide and Lauric Acid in Benzene at 70° C.

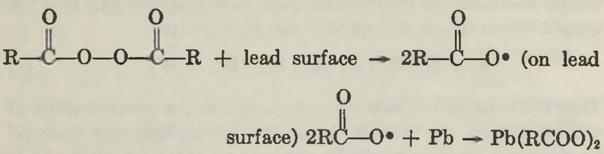
Initial Concn., Equiv./L.			
Lauroyl peroxide	Lauric acid	k (Min.$^{-1}$ Cm.$^{-2}$) × 10^3	No. of Determinations
0.20	0.106	2.42 ± 0.07	4
0.10	0.031	2.33 ± 0.21	3
0.06	0.106	2.33 ± 0.14	4
0.06	0.056	2.33 ± 0.32	5
0.06	0.031	2.38 ± 0.14	5
0.06	0.0185	2.58 ± 0.18	5
0.06	0.006	2.46 ± 0.16	4
0.06	0.001	2.44 ± 0.02	2

Since all k values summarized in Table I are essentially constant, it is apparent that the corrosion rate is independent of acid concentration in this case down to at least 0.001 N acid. When the lauroyl peroxide was in large excess, the equivalents of lead loss at infinite time exceeded the equivalents of acid present but was in all cases equivalent to peroxide added. This indicates that the over-all reaction is



$$C_{11}H_{23}\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_{11}H_{23} + Pb \rightarrow Pb\,(C_{11}H_{23}COO)_2$$

and raises the question of whether any acid is necessary in the corrosion of lead by acyl peroxides. To test this possibility corrosion measurements were made using recrystallized lauroyl peroxide in solutions of less than 0.0002 N acid concentration. Following an induction period of about 5 minutes in which no corrosion took place, the corrosion rate was the same as in the more concentrated acid solutions. This result suggests that the role of the small amount of residual acid in these solutions is to remove an invisible oxide coating and that the rate of attack of lauroyl peroxide upon a clean lead surface is not subject to acid catalysis. It would thus appear that the mechanism of corrosion of lead by acyl peroxides does not involve the formation of a lead oxide intermediate but proceeds in the following steps:



$$R-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-R + \text{lead surface} \rightarrow 2R-\overset{\overset{O}{\|}}{C}-O^{\bullet} \text{ (on lead surface)}$$

$$2R\overset{\overset{O}{\|}}{C}-O^{\bullet} + Pb \rightarrow Pb(RCOO)_2$$

Further evidence in favor of this mechanism for acyl peroxides is that no detectable coating is formed when lead is heated to 70° C. in a solution of recrystallized lauroyl peroxide in benzene, either during the induction period or afterward.

Hydroperoxides. Extended rate measurements were made using solutions of *tert*-butyl hydroperoxide and lauric acid in benzene at 70° C. to find the mechanism of corrosion by hydroperoxides (the type most likely to be present in an oil). Figure 2 shows a plot of $(1/A)\ \log_{10} W_o/(W_o - W)$ against time for initial peroxide concentrations ranging from 0.022 to 0.066. This curve is linear and through the origin as required by Equation 3. Table II summarizes the rate constants calculated from Equation 3 for varying initial ratios of peroxide and acid.

Table II shows that there is considerable dependence of the rate of hydroperoxide corrosion upon acid concentration. It appears that the rate of corrosion by hydroperoxides is independent of acid concentration only when the acid concentration at least equals or exceeds that of the peroxide. No draft with time was observed in the constants recorded in Table II down to acid concentrations as low as 0.01 N; thus for any given initial ratio of peroxide to acid concentration, a steady state must be established in which the corrosion rate is dependent upon peroxide concentration and independent of acid concentration for that ratio. A detectable black film was observed in all cases when the rate constant was considerably below the upper value of 4 × 10^{-3} in Table II. Therefore the variation of constants with ratio of acid to peroxide shown in Table II may be due to film formation. When the ratio of acid to peroxide is low, the acid concentration may be insufficient to prevent accumulation of an intermediate film and the lead surface will thus be partially blocked to further oxidation by peroxide. When the ratio of acid to peroxide is high, no film accumulates and the corrosion rate will be independent of acid concentration and determined by the oxidation rate alone. In contrast to the behavior of acyl peroxides, it may be remarked that, when lead is heated up in any solution of hydroperoxide containing no acid, a rather heavy oxide film is formed.

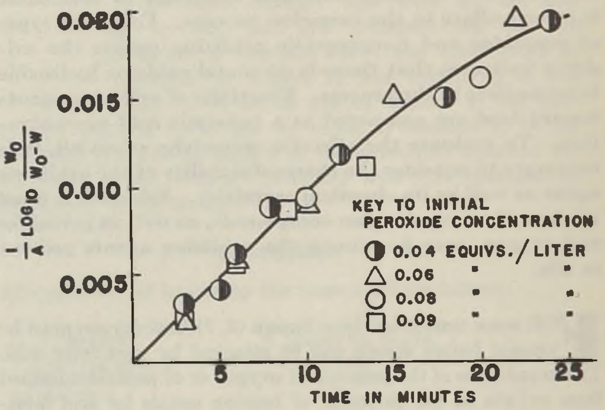


Figure 1. Test of First-Order Mechanism for Corrosion of Lead by Lauroyl Peroxide in Benzene Containing 0.1 N Lauric Acid at 70° C.

The evidence cited suggests a possible mechanism for the oxidation of lead by hydroperoxides whereby the hydroperoxides split into the fragments $R_3CO^{\bullet}$ and $^{\bullet}OH$ on the lead surface. These fragments may then react with the lead to form either hydrated or alcoholated lead oxide on the lead surface; they will react further with the acid to give the lead soap plus water and the alcohol derived from the peroxide. By this mechanism, which is similar to Denison's general mechanism, it is obvious that in the absence of acid a film of hydrated or alcoholated lead oxide will accumulate and hinder further oxidation.

Table II. Corrosion Rate Constants of Lead by *tert*-Butyl Hydroperoxide and Lauric Acid in Benzene at 70° C.

Initial Concn., Equiv./L.			
tert-Butyl hydroperoxide	Lauric acid	k (Min.$^{-1}$ Cm.$^{-2}$) × 10^3	No. of Determinations
0.01	0.025	4.05 ± 0.48	4
0.05	0.10	4.03 ± 0.48	5
0.05	0.05	3.96 ± 0.05	5
0.025	0.032	3.34 ± 0.21	5
0.020	0.025	3.15 ± 0.51	5
0.025	0.025	2.76 ± 0.21	4
0.10	0.05	1.45 ± 0.05	4
0.05	0.025	1.47 ± 0.14	

CORROSION REACTIVITY OF VARIOUS PEROXIDES

From these results it appeared that reactivities of various peroxides could be compared, provided the acid concentration was kept in sufficient excess. Corrosion rates were measured for a number of peroxides in benzene at 70° C. using a lauric acid concentration of 0.1 *N* and a peroxide concentration of 0.05 *N*. Rate constants were determined either from the slope of $(1/A) \log_{10} W_o/(W_o - W)$ *vs.* *t* plots, or by calculation from Equation 3. Values calculated from Equation 3 were essentially constant with time, as shown for cyclohexene hydroperoxide in benzene containing 0.1 *N* lauric acid at 70° C.:

Time, Min.	k (Min.$^{-1}$ Cm.$^{-2}$) × 10^3
3	2.92
5	2.85
7	3.06
9	3.04

Table III summarizes rate constants found for various peroxides; for comparison, the rate constant of oxygen was estimated from data in the previous paper (*10*), using the solubility of oxygen in benzene reported by Fischer and Pfleiderer (*6*), 0.03 equivalent per liter at 19° C. Since there is little change in oxygen solubility with temperature for hydrocarbon solvents, this figure was used at 70° C.

Table III. Corrosion Rate Constants for Peroxides on Lead in 0.1 *N* Lauric Acid Solutions in Benzene at 70° C.

Oxidizing Agent	k (Min.$^{-1}$ Cm.$^{-2}$) × 10^3	No. of Determinations
Oxygen	3.2[a]	..
Perbenzoic acid	5.3	..
1,1-Dihydroxy dicyclohexyl peroxide	7.6	..
Lauroyl peroxide	2.33 ± 0.14	4
tert-Butyl hydroperoxide	4.03 ± 0.48	5
Cyclohexene hydroperoxide	2.97 ± 0.08	4
1-Hydroxy cyclohexyl hydroperoxide	2.67 ± 0.25	5

[a] Estimated from data in a previous paper (*10*).

Perbenzoic acid and 1,1-dihydroxy dicyclohexyl peroxide decomposed rapidly by a side reaction concurrently with the oxidation of lead, and the constants for these substances were estimated from data taken for the first 3 minutes of reaction with a correction applied for the change in W_o due to the side reaction. Corrections were applied as follows:

$$W_o = \frac{W_o' + W_o'' + W}{2}$$

where W_o' = weight of lead equivalent to initial peroxide content
W_o'' = weight of lead equivalent to peroxide content at end of test
W = loss in weight of test piece
W_o = value used in equation

Considerable uncertainty exists in the values of these two constants, but the values given probably represent the lower limits of the actual constants.

The previous paper (*10*) pointed out that a rate equation of the same type as Equation 1 will result when the corrosion rate is determined either by diffusion of the oxidizing agent into the surface of the test piece or by the chemical rate of oxidation of the metal, or by both processes. In the general case where both diffusion and chemical reaction control the corrosion rate, it was shown that

$$-d\,C_{ox}/dt = \frac{k_1 D_1}{k_1 y_1 + D_1} C_{ox} \qquad (4)$$

where k_1 = chemical rate constant
y_1 = depth of diffusion layer
D_1 = diffusion coefficient of oxidizing agent in solvent

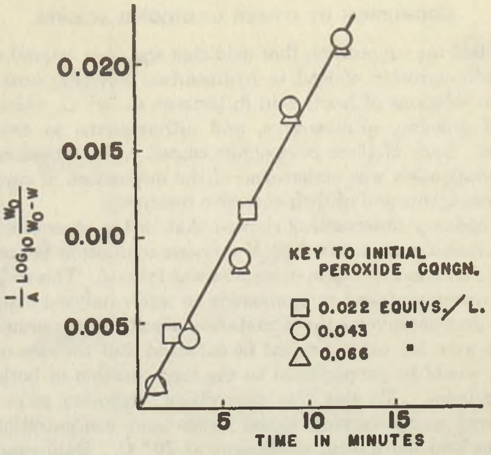


Figure 2. Test of First-Order Mechanism for Corrosion of Lead by *tert*-Butyl Hydroperoxide in Benzene Containing 0.1 *N* Lauric Acid at 70° C.

When oxygen was used as the oxidizing agent, indirect evidence seemed to indicate that the corrosion rates in xylene and benzene were controlled to an important extent by the chemical rate of oxidation of the metal; in the case of white oil it appeared that the rate of diffusion of oxygen into the surface may have been the rate determining factor.

In considering the rate constants found in this investigation, it would be of interest to separate the chemical rate constants (k_1 values) from the measured rate constants and thus compare the chemical reactivity of the oxidizing agents toward the metals. Although the data are insufficient to permit the evaluation of k_1 values, certain conclusions may be drawn concerning the chemical reactivity of the oxidizing agents used. Thus, comparing the rate constants for the various peroxides in benzene (Table III), it seems obvious that the relatively large constant for 1,1-dihydroxy dicyclohexyl peroxide indicates it to be chemically much more reactive toward lead than any other of the peroxides studied; its diffusion coefficient is probably relatively smaller than those of the others, with the exception of lauroyl peroxide. Likewise, since the molecular weight of perbenzoic acid is of the same order of magnitude as that of the hydroperoxides studied, it appears that perbenzoic acid is more reactive toward lead than the hydroperoxides. It is difficult to compare the chemical reactivity of lauroyl peroxide with that of the hydroperoxides because the smaller magnitude of the rate constant for lauroyl peroxide might be accounted for by a smaller diffusion coefficient. It thus appears possible to arrange the peroxides studied in the order of their chemical reactivity toward lead in benzene as follows:

$$\text{1,1-dihydroxy dicyclohexyl peroxide} > \text{perbenzoic acid} > \begin{cases} \text{hydroperoxides} \\ \text{lauroyl peroxide} \end{cases}$$

Whether it is generally true that dihydroxy dialkyl peroxides and peracids are more reactive in this respect than hydroperoxides and acyl peroxides cannot be ascertained without measuring the corrosion rate using other members of the dihydroxyl dialkyl peroxide and peracid series.

When lead was heated in a benzene solution of 1,1-dihydroxy dicyclohexyl peroxide containing no acid, there was no corrosion loss and no visible film formed on the test piece. Therefore, it seems that this oxidation is an acid-catalyzed reaction involving no intermediate formation of lead oxide. Corrosion by dihydroxy dialkyl peroxides and peracids probably takes place by mechanisms analogous to that proposed for acyl peroxides, in which the peroxide splits initially on the metal surface at the —O—O— linkage.

CORROSION BY OTHER OXIDIZING AGENTS

To test the supposition that oxidizing agents in general would promote corrosion of lead in hydrocarbon solvents, tests were run on solutions of lauric acid in benzene at 70° C. which contained quinone, nitrobenzene, and nitromethane as oxidizing agents. Each of these compounds caused rapid corrosion, and an investigation was undertaken of the mechanism of corrosion by these agents and of their corrosive reactivity.

Preliminary observations showed that in the absence of acid no corrosion occurred in 0.05 N quinone solution in benzene at 70° C., and no detectable oxide film was formed. This indicates that corrosion of lead by quinone is an acid-catalyzed oxidation which does not involve the formation of a lead oxide intermediate. If this were the case, it might be expected that the rate of corrosion would be proportional to the concentration of both acid and quinone. To test this supposition, corrosion rates were measured using varying initial ratios and concentrations of quinone and lauric acid in benzene at 70° C. Rate constants were then calculated from the following equations based on the assumption of a second-order mechanism:

$$k = \frac{2.303}{(a-b)t} \log_{10} \frac{b\,(a-x)}{a\,(b-x)} \tag{5A}$$

$$k = \frac{x}{t\,a\,(a-x)} \tag{5B}$$

where a = initial concentration of lauric acid
b = initial concentration of quinone
x = concentration of reactant decomposed in time, t, by reaction

Equation 5B is used when $a = b$. Second-order rate values calculated in the early stages of reaction were nearly constant for varying ratios, and initial concentrations of acid and base at concentrations of 0.10 N and lower. However, there was a decided drift upward of constants with time (Figure 3). This upward drift in rate constants suggested an autocatalytic action by lead laurate formed during the reaction. To obtain a measure of the rate constant for the reaction of quinone and lauric acid with lead, second-order rate constants calculated from Equation 5A or 5B were plotted against time for the various initial concentrations of the two reactants, and the curves were extrapolated to zero time to find the constant. Table IV summarizes the rate constants obtained in this manner and also gives rate constants with lead laurate present initially.

The results in Table IV reveal that the rate constants are essentially constant when no lead laurate is present initially for acid concentrations 0.10 N or below and for quinone concentrations 0.05 M or below. Thus when [quinone] < 0.05 M and [lauric acid] < 0.10 M the rate of corrosion of lead, dx/dt (for zero lead laurate concentration) is given by:

$$dx/dt = k\,[\text{lauric acid}]\,[\text{quinone}] \tag{6}$$

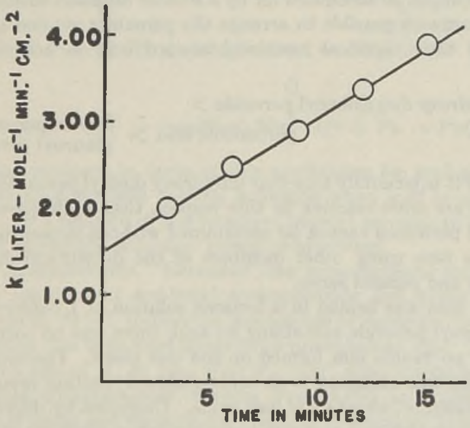


Figure 3. Second-Order Rate Constants for Corrosion of Lead by 0.10 N Lauric Acid and 0.05 N Quinone (Initial Concentrations) in Benzene at 70° C. as a Function of Time

When the lauric acid concentration is 0.25 M, the rate constant is abnormally small; the same is observed for a 0.10 M quinone concentration. Actually when the acid concentration exceeds 0.10 M and the quinone concentration exceeds 0.05 M, a constant rate of corrosion is obtained which is independent of the concentration of either reactant and which leads to the marked dropping off in rate constants observed at these high reactant concentrations. Under these conditions Equation 6 becomes:

$$dx/dt = k' \tag{7}$$

To ascertain the catalytic effect of lead laurate, a reaction product from a solution of the two reactants was made 0.03 M with respect to recrystallized lead laurate, and the rate constant was measured as before. Table IV shows that this constant is 3.6 times as large as the constant found in the absence of any initial lead laurate. This seems to confirm the supposition that lead laurate is responsible for the autocatalysis observed during the course of the reaction; in this connection, a saturated solution of hydroquinone in the presence of quinone causes no corrosion.

Table IV. Second-Order Rate Constants for Corrosion of Lead by Quinone and Lauric Acid in Benzene at 70° C.

Initial Concn., Mole/L.			
Quinone	Lauric acid	Lead laurate	k, Liter-Mole^{-1} Min.$^{-1}$ Cm.$^{-2}$
0.10	0.10	0	0.40
0.05	0.05	0	1.42
0.05	0.025	0	1.46
0.025	0.25	0	0.52
0.025	0.10	0	1.46
0.025	0.05	0	1.44
0.025	0.05	0.03	5.4
0.025	0.025	0	1.50
0.025	0.0125	0	1.36

These results seem to indicate that in the range of concentrations in which the reaction is second order with respect to acid and quinone, a transitory addition complex may be formed on the metal surface in which the quinone oxygen accepts a proton from the acid. This complex then reacts with lead to form a lead soap and hydroquinone. More work is necessary to establish the mechanism of the catalytic effect of lead laurate upon the course of the reaction. No autocatalytic effect of lead salts upon corrosion rate was observed in the case of peroxides and oxygen.

Although independence of corrosion rate on acid concentration above certain normalities had been encountered with other oxidizing agents, independence of corrosion rate on concentration of both acid and oxidizing agents above certain concentrations had not previously been encountered. Of several possible explanations of this phenomenon may be mentioned surface saturation of the lead with respect to reactants or diffusion of the lead soap away from the surface as the rate-determining step in the reaction.

Detailed kinetic studies were not made on oxidizing agents other than quinone. However, since it was desirable to compare reactivities of various oxidizing agents, corrosion rates were measured in 0.1 N lauric acid solutions in benzene at 70° C. which contained about 0.05 equivalent per liter of oxidizing agent in most instances. In all cases values calculated according to Equation 3 were sufficiently constant to justify the assumption that the corrosion rate is independent of acid concentration and is determined by the concentration of oxidizing agent for these concentrations. This is in accord with the results for

TABLE V. CORROSION RATE CONSTANTS FOR OXIDIZING AGENTS ON LEAD IN 0.1 *N* LAURIC ACID SOLUTIONS IN BENZENE AT 70° C.

Oxidizing Agent	Equivalents of Lead/ Mole Oxidizing Agent	k (Min.$^{-1}$ Cm.$^{-2}$) × 10^3	No. of Determinations
Oxygen	4	3.2	
Azoxybenzene	2	1.75 ± 0.09	5
Nitrosobenzene	2	2.23 ± 0.16	4
Nitrobenzene	5.6	2.30 ± 0.11	7
o-Nitrophenol	5.6	2.21 ± 0.18	4
m-Dinitrobenzene	2	0.73 ± 0.07	4
Nitromethane	2	0.444 ± 0.011	4
1-Nitropropane	2	0.073 ± 0.001	3
Isoamyl nitrite	2	0.012 ± 0.001	3
Quinone	2	3.80 ± 0.23	5
1,4-Naphthoquinone	2	2.33 ± 0.16	5

peroxides, oxygen, and quinone, for which it was shown that corrosion rates were independent of acid concentration at 0.10 *N* and above. Table V shows the average values of rate constants determined in this manner for various oxidizing agents and also the number of equivalents of lead which react at infinite time per mole of oxidizing agent added.

Several other possible oxidizing agents were tested but gave corrosion rates too small to be measured. Among them were picric acid, diphenyl sulfone, nitrogen dioxide, diacetyl, azobenzene, and heptaldehyde. However, some of these were later shown to be effective in causing corrosion in oil at 140° C. Failure of picric acid to corrode may be ascribed to formation of an insoluble film of lead picrate rather than to lack of oxidation reactivity on the part of picric acid.

Considerable interest attaches to the corrosion of lead by nitrobenzene in that almost complete reduction to aniline occurs with no apparent break in reaction mechanism corresponding to various stages of reduction of the nitro group. Figure 4, a plot of $(1/A)\ \log_{10} W_o/(W_o - W)$ against t, is linear up to at least 4 equivalents of lead reacted per mole of nitrobenzene originally present. Qualitative tests showed aniline to be present in the mixture at the end of the reaction. Table V indicates that *o*-nitrophenol is also reduced almost completely to the corresponding amino compound. No visible film and no weight loss is observed when lead is heated at 70° C. in a 0.01 *M* solution of nitrobenzene in benzene. This would indicate that no metal oxide intermediate is involved in the corrosion of lead by nitrobenzene and lauric acid, but that the mechanism of corrosion in this case is somewhat similar to that proposed for quinone.

It is fairly certain that the comparatively low values of the rate constants for such relatively small molecules as 1-nitropropane, nitromethane, and isoamyl nitrite are caused by a slow rate of chemical oxidation of the lead, and that this step must almost alone determine the reaction rate. As with the peroxides, these oxidizing agents may be roughly classified in the order of their chemical reactivity toward lead as follows:

$$\left.\begin{matrix}\text{quinones}\\ \text{hydroperoxides}\end{matrix}\right\} > \left\{\begin{matrix}\text{nitrobenzene}\\ \text{nitrosobenzene}\\ o\text{-nitrophenol}\\ \text{azoxybenzene}\end{matrix}\right\} > m\text{-dinitrobenzene}$$

nitromethane > 1-nitropropane > isoamyl nitrite

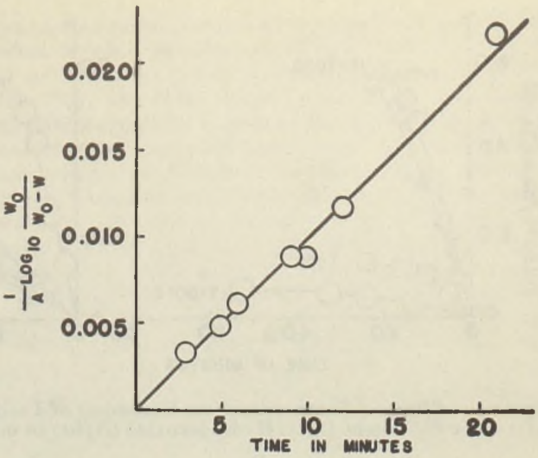


Figure 4. Test of First-Order Mechanism for Corrosion of Lead by Nitrobenzene in Benzene Containing 0.1 *N* Lauric Acid at 70° C.

EFFECT OF TEMPERATURE

An attempt was made to determine oxidation rate constants for lauroyl peroxide and *tert*-butyl hydroperoxide in benzene as a function of temperature. Corrosion rates were measured from 40° to 75° C., and the results are plotted in Figure 5. Since lead laurate films formed on the test pieces at temperatures below 70° C., rate constants could not be measured with accuracy at these temperatures. This accounts for the striking difference between the corrosion rates at 70° and higher with those below 70° C. It is noteworthy that the film formed below 70° C. when lauroyl peroxide was used as the oxidizing agent almost completely stops further corrosion, but that formed when *tert*-butyl peroxide was used permits further corrosion at a comparatively rapid rate. The latter film was much looser than the former; it is probable that a film, formed rapidly in the initial stages, will be more porous than a film of the same material formed more slowly. *tert*-Butyl hydroperoxide oxidizes lead at a more rapid rate than does lauroyl peroxide.

CORROSION RATES IN WHITE OIL

Measurements of corrosion were extended to white oil at 100° and 140° C. A number of oxidizing agents were found to be reactive in white oil at these temperatures although they showed no appreciable reactivity in benzene at 70° C. Among them was nitrogen dioxide. Figure 6 compares the corrosion of lead by nitrogen dioxide and oxygen in white oil containing 0.1 *N* lauric acid under gas pressures of 250 mm. at two temperatures. Initial corrosion rates are nearly identical for the two gases but nitrogen dioxide leads to much greater total corrosion at 140° C. As explained previously (*10*), the lower rate of corrosion by oxygen at 140° C. in the later stages is caused by a side reaction in which oil is oxidized in preference to lead.

Table VI summarizes the rate constants and the mean deviation from the average value calculated from Equation 3 for the other oxidizing agents tested in white oil and compares them with those found in benzene at 70° C.

In changing solvents from benzene at 70° C. to white oil at 100° C., the rate constants may increase or decrease, depending on the relative importance of chemical reaction and diffusion in determining the reaction rate. From 70° to 100° C., thermal activation should markedly increase the rate of chemical reaction since the two solvents are somewhat similar. On the other hand, since white oil is much more viscous at 100° than benzene

TABLE VI. COMPARISON OF CORROSION RATE CONSTANTS FOR OXIDIZING AGENTS IN 0.1 *N* LAURIC ACID SOLUTION IN WHITE OIL

Oxidizing Agent	k (Min.$^{-1}$ Cm.$^{-2}$) × 10^3		
		White Oil	
	Benzene at 70° C.	100° C.	140° C.
Oxygen	3.2	1.5[a]	......
tert-Butyl hydroperoxide	4.03 ± 0.48 (5)[b]	1.01 ± 0.06 (5)	2.23 ± 0.42 (7)
Quinone	3.80 ± 0.23 (5)	....	1.57 ± 0.08 (9)
Nitrobenzene	2.30 ± 0.11 (7)	0.69 ± 0.03 (4)	1.93 ± 0.18 (5)
1-Nitropropane	0.073 ± 0.001 (3)	0.196 ± 0.013 (5)	0.74[a]
Diacetyl	......	......	0.58 ± 0.02 (4)
Azobenzene	......	......	0.59 ± 0.07(5)

[a] Determined by graphical procedure.

[b] Numbers in parentheses represent number of determinations of each constant.

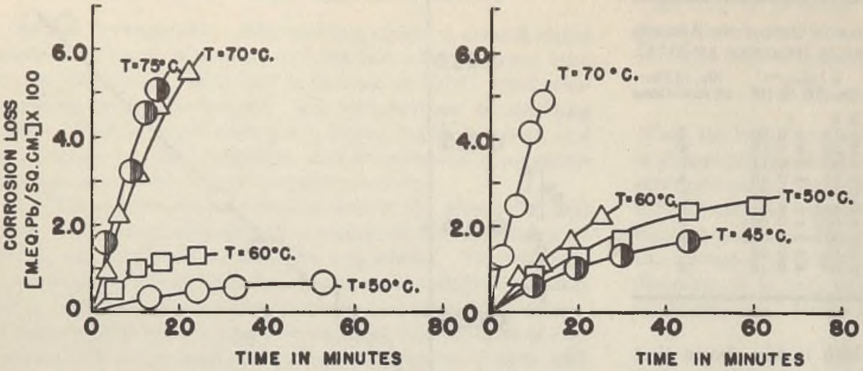


Figure 5. Effect of Temperature on Corrosion of Lead by 0.06 *N* Lauroyl Peroxide (*left*) and 0.043 *N tert*-Butyl Hydroperoxide (*right*) in 0.1 *N* Lauric Acid in Benzene

at 70° C., diffusion of reactants into the metal surface will be slower in white oil than in benzene. Thus, when the corrosion rate is controlled principally by chemical reaction in benzene or in both solvents, the rate constant in white oil at 100° may be expected to be greater than in benzene at 70° C.; if the corrosion rate is controlled principally by diffusion in both solvents, the reverse will be the case.

Table VI shows that the more active oxidizing agents in benzene—namely, *tert*-butyl hydroperoxide, quinone, and nitrobenzene—show smaller rate constants in white oil. This indicates that rates of corrosion by these substances are partially limited by diffusion in benzene solution and are almost wholly limited by diffusion in white oil solution under the conditions of the experiments. Oxidizing agents which are less active in benzene—namely, 1-nitropropane, diacetyl, and azobenzene—show larger rate constants in white oil than in benzene. This behavior indicates that the corrosion rate in benzene is limited principally by chemical reaction; and since the rates of these agents are still considerably smaller than those of the more reactive agents in white oil, chemical reaction probably also determines the corrosion rate in white oil. Of the oxidizing agents studied, all show the same order of reactivity in white oil as in benzene except that quinone and nitrobenzene are reversed. A rate constant for quinone at 100° C. could not be determined because of the formation of an insoluble film at this temperature, presumably composed of $Pb(O_2C_6H_5)_2$.

All the peroxides studied decomposed to a considerable extent in white oil containing the lead samples at 100° and 140° C. At 100° both lauroyl peroxide and 1,1-dihydroxy dicyclohexyl peroxide decomposed almost completely before lead had corroded to any appreciable extent. In this connection, lauroyl peroxide rapidly decomposes under these conditions in the absence of metal while 1,1-dihydroxy dicyclohexyl peroxide decomposes only if lead is present. Hydroperoxides were much more stable than the other types but only in the case of *tert*-butyl hydroperoxide was the stability sufficient to permit rate constants to be measured with reasonable accuracy at both 100° and 140° C.

This finding emphasizes the importance of stability in determining the effective corrosivity of various oxidizing agents. Thus, although 1,1-dihydroxy dicyclohexyl peroxide is much more reactive on lead than any of the hydroperoxides studied, its effectiveness in causing corrosion is almost negligible since it decomposes on a lead surface in a short time. Likewise such compounds as quinone and nitrobenzene, if present in oil, would prove much more damaging as corrosive reagents than any of the peroxides studied since they decompose only by reaction with lead and acid, whereas the peroxide may rapidly decompose without reaction with lead.

Diacetyl and azobenzene, although ineffective in causing corrosion in benzene at 70°, proved effective in oil at 140° C. because of thermal activation. Considerable interest attaches to the corrosion mechanism of lead by azobenzene since the molecule contains no oxygen and there is no possibility that a lead oxide intermediate may form. Therefore the mechanism of lead corrosion by azobenzene was studied in some detail. Corrosion rate constants were determined at different starting ratios of acid and azobenzene upon the assumption of a second-order mechanism. Table VII lists these constants.

These constants indicate that the reaction is second order up to an acid concentration of 0.10. Above this concentration however, the rate is independent of acid concentration. The reaction mechanism in this case is probably similar to that for quinone and lauric acid on lead. Two equivalents of lead reacted at infinite time with one mole of azobenzene, from which it may be inferred that the reduction product is hydrazobenzene.

From the rate constants at two temperatures in Table VI, activation energies were calculated for various oxidizing agents and lauric acid in white oil:

Oxidizing Agent	Activation Energy, Cal./Mole
tert-Butyl hydroperoxide	6,000
Nitrobenzene	7,900
1-Nitropropane	10,200

These activation energies are in the expected order if it is assumed that the activation energy for the chemical reaction involved is considerably greater than that for diffusion of reactant into the test piece, which is probably the case. If this is true, the activation energy should be highest for the least active oxidizing agent. Comparison of the activation energies with rate constants in Table VI shows that, as the rate constant decreases, the activation energy increases for the compounds studied.

Table VII. Second-Order Rate Constants for Corrosion of Lead by Lauric Acid and Azobenzene in White Oil at 140° C.

Initial Concn. Moles/L.			
Lauric acid	Azobenzene	k, Min.$^{-1}$ Mole^{-1} Liter-Cm.$^{-2}$	No. of Determinations
0.025	0.05	0.0156 ± 0.0024	4
0.05	0.05	0.0160 ± 0.0023	4
0.10	0.05	0.0146 ± 0.0023	5
0.25	0.05	0.0070 ± 0.0009	5

DISCUSSION

From the work of Denison, the authors, and others there can be no doubt of the role of peroxides and molecular oxygen in causing corrosion of bearing metals. Proof that many of the other oxidizing agents studied are present or are formed in oil would be difficult; but from a corrosion standpoint these compounds would prove far more damaging in a lubricant than peroxides and oxygen because they tend to oxidize the metal in preference to the oil at all temperatures studied. For oxygen and peroxides the reverse is likely to be true at high temperatures.

Nitrogen compounds which are oxidizing agents or which may readily oxidize to give oxidizing agents may arise in a lubricant in a number of ways. Ordinary lubricating oils may contain appreciable amounts of nitrogen compounds present naturally. If inhibitors containing nitrogen are added to lubricants, they may oxidize to oxynitrogen compounds and, in the long run, prove damaging from a corrosion standpoint. Any nitrobenzene remaining in oil after extraction procedures, even if present to the extent of only 0.01%, would cause rapid corrosion after acids were formed.

There is considerable evidence in the literature to indicate that nitrogen compounds may also arise in the oil from the interaction of nitric oxide produced in the combustion of engine gases with heated oil. Pomeroy (*9*) lists nitrogen oxides among the contaminants of lubricants. Graefe (*8*) and Ehlers (*4*) were able to establish the existence of nitro compounds in used motor oils, and attributed their presence to reaction between the hydrocarbons and nitrogen oxides formed in the combustion of engine gases. Later Ehlers (*5*) analyzed quantitatively for nitric acid in used oils and engine sludges. He found as much as 0.04% nitric acid in used oils, but states that most of the nitrogen present in such oils was probably as nitrohydrocarbons rather than as nitric acid. Crankcase sludges were found to contain up to 0.5% nitric acid. Work is in progress in this laboratory on the determination of nitrogen compounds in crankcase oils.

Since diacetyl proved effective in causing corrosion at high temperatures, other diketo compounds were tested. In the aliphatic series only diketo compounds with adjacent carbonyl groups caused corrosion with any appreciable speed. It is possible that compounds with this structure will be formed in the oxidation of oils.

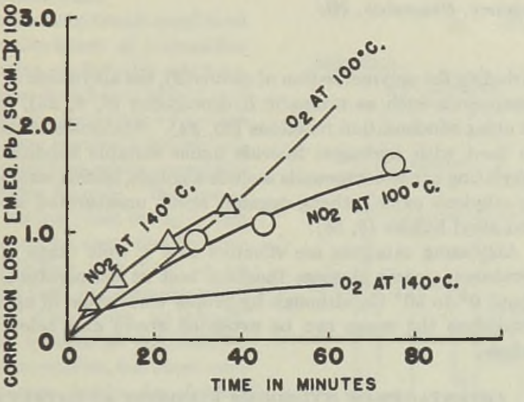


Figure 6. Comparison of Corrosion Loss of Lead Due to Oxygen and Nitrogen Peroxide at 250 Mm. Pressure over Lauric Acid in White Oil

Attempts were made to correlate the reactivity of various oxidizing agents toward lead with some of their other properties. It became apparent that no simple correlation existed. For example, a connection was sought between the oxidation potential and oxidation reactivity; it was found that, while quinone having the higher oxidation potential was more reactive than 1,4-naphthoquinone, *m*-dinitrobenzene was less reactive than nitrobenzene or *o*-nitrophenol even though its oxidation potential (measured in alcoholic solution) is higher than either. Further, it was found by the method of Conant and Lutz (*1*) that all the peroxides used had higher oxidation potentials in alcohol solution than quinone, although quinone was more reactive than many of them.

From these results it is clear that no completely general mechanism for bearing corrosion can be formulated, although an oxidizing agent and an acid are generally involved in the process. It appears that for oxygen the type of mechanism proposed by Denison for peroxides involving the formation of an oxide intermediate is valid. Solution rates of PbO, Pb_3O_4, and PbO_2 powders were studied in 0.1 *N* lauric acid solution in benzene at 70° C.; while Pb_3O_4 and PbO_2 dissolved very slowly, PbO dissolved with sufficient rapidity to account for the observed rate of corrosion of lead by lauric acid plus oxygen. Also the formation of lead hydroxide or alkoxide as an intermediate in corrosion by hydroperoxides plus acid is essentially in accord with Denison's mechanism. In view of the observations on the stability of various types of peroxides, it appears that hydroperoxides are likely to be the most stable in an oil with metal surfaces present.

In the case of oxidizing agents other than hydroperoxides and oxygen, no oxide or hydrated oxide intermediate seems to be involved in the corrosion step. This seems to be true for dihydroxy dialkyl and acyl peroxides and for all the nonperoxidic oxidizing agents studied. In the latter case the oxidizing agents appear to serve as electron pair donors for the hydrogen from the acid; electrons are then accepted from the lead by the resulting complex.

It appears also that the dependence of corrosion rate upon acid concentration is not so simple as it seemed at first. For oxygen and hydroperoxides the corrosion rate was found to be independent of acid concentration only when the acid was present in some excess over the oxidizing agents. Only for acyl peroxides was the corrosion rate completely independent of acid concentration down to the practical limit of its determination. For nonperoxidic oxidizing agents exclusive of oxygen, the corrosion rate is proportional to the concentration of both acid and oxidizing agent for solutions less than 0.1 *M* in acid.

SUMMARY

Corrosion of lead by an acyl peroxide is independent of acid concentration down to concentrations as low as 10^{-3} mole of acid per liter and is determined only by peroxide concentration. Corrosion of lead by hydroperoxides is independent of acid concentration when the ratio of acid concentration to hydroperoxide concentration is greater than unity. At lower ratios there is a marked dependence of corrosion rate upon acid concentration as well as upon hydroperoxide concentration. A dihydroxy dialkyl peroxide and a peracid showed much greater corrosive reactivity toward lead than hydroperoxides.

Organic oxidizing agents other than peroxides may be very effective in causing corrosion of lead in hydrocarbon solvents containing fatty acids. Oxynitrogen compounds, quinones, and diacetyl are oxidizing agents in this class which cause rapid corrosion of lead in benzene and white oil. Detailed studies of the mechanism of reaction of quinone and lauric acid with lead in benzene at 70° C. showed that at reactant concentrations below 0.05 mole per liter the reaction is second order, and the rate is proportional to the concentration of both quinone and lauric acid. Further, lead laurate had a pronounced catalytic effect upon the rate of this reaction. For hydroperoxides and oxygen it is probable that $Pb(OH)_2$ or PbO is intermediate in the corrosion process. For dihydroxy dialkyl peroxides, acyl peroxides, and nonperoxidic oxidizing agents, however, the evidence indicates that no metal oxide or hydroxide is intermediate in the process. Reactivity of the various oxidizing agents toward lead have been compared at a constant acid concentration.

In white oil solution at 100° C. and above, the oxidizing agents which were relatively inactive toward lead in benzene at 70° C. proved to be more active in white oil as a result of thermal activation of the chemical reaction. Oxidizing agents which were relatively reactive toward lead in benzene at 70° were less reactive in white oil at 100° C. because of the high viscosity of white oil relative to benzene.

To evaluate the effective corrosivity of oxidizing agents in oils toward metals it is necessary to consider the thermal stability of the oxidizing agent as well as its chemical reactivity. Hydroperoxides, although less reactive toward lead than either dihydroxy dialkyl or acyl peroxides, are likely to be much more damaging from a corrosion standpoint since they possess greater stability toward heated oil. If nonperoxidic oxidizing agents other than oxygen were present in oils, they would prove to be much more damaging than peroxides because of their high stability with respect to heated oil.

Although hydroperoxides and oxygen are the oxidizing agents most likely to be present in oils, there is a possibility that nonperoxidic oxidizing agents may form from (*a*) oxidation of nitrogen containing inhibitors and natural nitrogen compounds in the oil, (*b*) oxidation of oil, (*c*) reaction of nitrogen oxides produced in the combustion of engine gases with the heated oil, or (*d*) nitrobenzene not completely removed following solvent extraction of the oil.

At low temperatures insoluble soap films formed on the lead surface are very effective in slowing the corrosion rate. A film formed slowly appears to be more protective than one formed rapidly.

ACKNOWLEDGMENT

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Alkylation of Isoparaffins by Olefins in Presence of Hydrogen Fluoride

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HYDROGEN fluoride is widely used as a catalyst for the interaction of olefins and isobutane to produce highly branched liquid paraffins (*1, 7, 10*), a process which has an important place in the aviation gasoline program. The liquid product of the alkylation process, known as alkylate, consists of highly branched-chain paraffins and has superior antiknock properties both with and without added tetraethyllead. The amount of alkylate being regularly incorporated in aviation gasoline blends runs from about 25 to 40%.

The discovery that isoparaffins would react with olefins in the presence of a catalyst (*14, 15, 16*) overthrew the classical concept of the chemical inertness of the paraffins and opened extensive new fields for research. It has been found that alkylation of isoparaffin hydrocarbons can be catalyzed by numerous compounds including metal halides such as aluminum chloride (*14, 16, 17, 21*), zirconium chloride, etc. (*8*), sulfuric acid (*3, 4, 19, 20*), boron fluoride (*15*), hydrogen fluoride (*10*), and others. Of these, hydrogen fluoride, sulfuric acid, and aluminum halides are being used commercially. The alkylation processes are of great commercial importance and our HF alkylation process is of particular interest as a chemical and engineering development (*7*).

Anhydrous hydrogen fluoride catalyzes various reactions, including the polymerization of olefins (*9*), the alkylation of cyclic compounds such as aromatic hydrocarbons (*6, 9, 24*), as well as other condensation reactions (*23, 24*). Materials which may be used with hydrogen fluoride under suitable conditions for alkylating cyclic compounds include alcohols, olefins, oxides such as ethylene oxide, ethers, organic acids, unsaturated alcohols, and alkyl halides (*6, 25*).

Alkylating catalysts are effective over a wide range of temperatures; many of them function best at temperatures from about 0° to 50° C., although by proper correlation of operating conditions the range can be extended above and below these values.

ADVANTAGES OF HYDROGEN FLUORIDE AS CATALYST

Hydrogen fluoride has a number of advantages which recommend its use as a catalyst, particularly in the process for alkylating isoparaffins with olefins. Among these are the following physical properties: molecular weight, 20.01; specific gravity, 0.988; melting point, −83° C.; boiling point, 19.4° C.

Hydrogen fluoride is one of the most stable compounds; it can be subjected to high temperatures and pressures and to the action of other catalytic agents without being broken down. Many of its organic compounds decompose either by heat alone or in the presence of catalysts to regenerate hydrogen fluoride,

Hydrogen fluoride catalyzes the interaction of olefins and isoparaffins to form saturated products consisting of highly branched paraffinic hydrocarbons. The alkylation was carried out in the laboratory, both by continuous and batch operation, in apparatus of simple design. The effects of temperature, contact time, ratio of isoparaffin to olefin, and catalyst concentration in water are described. Runs involving the paraffins isobutane and isopentane, and the olefins, propene, isobutylene, 1-butene, and 2-butene, are reported, as well as the production of alkylate from a butane-butene mixture. Normally the fluorine content of the alkylate is low and can be reduced further by treatment with certain materials such as calcium fluoride and aluminum fluorides at elevated temperatures.

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an important factor from a commercial standpoint since it makes possible low catalyst consumption. Substantially all of the combined fluorine in the alkylation reaction products is recoverable as hydrogen fluoride. In this respect it is unlike many other catalysts which are less chemically stable and undergo reaction with one or more of the materials in the system being catalyzed.

Hydrogen fluoride is stable toward both oxidizing and reducing conditions; this makes for low catalyst consumption and prevents loss of reactants occasioned by oxidation reactions.

Hydrogen fluoride may, under alkylation conditions, form alkyl fluorides with olefins (*9*). As long as sufficient hydrogen fluoride is present, the alkyl fluoride formed reacts with isoparaffin to form alkylate (*18*). Under optimum conditions of operation, the organically bound fluorine in the paraffinic reaction product is usually less than 0.01%.

Even such small amounts of fluorine may be objectionable, both because of increased catalyst consumption and contamination of the finished product with fluorine. The bound fluorine may be readily decomposed by passing the alkylate over a catalyst such as calcium fluoride or aluminum fluoride at an elevated temperature, usually about 100° C. The hydrogen fluoride resulting from this decomposition can be subsequently separated and recovered. If the amount of fluorine present is so low that its recovery is not essential to the economical operation of the process, it can be removed by treatment with lime, bauxite, or alkaline materials such as sodium hydroxide, usually at a slightly elevated temperature or with a sulfuric acid wash.

Even under optimum conditions for the alkylation of isoparaffins with olefins, undesirable side reactions occur to a minor extent and result in the formation of certain high-boiling materials not utilizable as motor fuel, which are soluble in hydrogen fluoride. Because of its low boiling point the hydrogen fluoride can be recovered by simple distillation with little or no loss other than that occasioned by handling. The sludge, as formed, contains fluorine in combination with hydrocarbons, but these compounds can easily be broken down by heating to drive off and recover hydrogen fluoride. This is the basis for the catalyst regeneration in the hydrogen fluoride alkylation process (*7*).

An important advantage for hydrogen fluoride is that, by virtue of its chemical stability and low freezing point, it may be employed over a wide range of operating conditions. Conditions can be employed which are most satisfactory thermodynamically or economically, without limitations due to catalyst properties. For example, in the alkylation reaction, atmospheric or slightly superatmospheric temperatures may be used with hydrogen fluoride; hence it is unnecessary to utilize refrigeration as is the case when certain other isoparaffins are the alkylation catalysts. The vapor pressure of hydrogen fluoride makes it unnecessary to resort to extreme pressures to maintain the catalyst in liquid phase. Its freezing point permits its use at temperatures much lower than is possible with most catalysts, which either freeze or become highly viscous at low temperatures. Although, in the alkylation of isobutane with olefins to produce aviation blending fuel, the usual operating conditions are of the order of 30° C., there are catalytic reactions which are favored by low temperatures. Since hydrogen fluoride catalyzes such reactions, it has a distinct advantage because of its physical properties. Conversely, since hydrogen fluoride is thermally stable, it can be employed at much higher temperatures than those of alkylations with other catalysts. This is a unique property of hydrogen fluoride.

Anhydrous hydrogen fluoride does not corrode ordinary iron equipment under most conditions. It is undesirable to have large percentages of water present, both because of the corrosion rate and the alkylation reaction; hence in the hydrogen fluoride alkylation process, steps are taken to maintain it practically anhydrous. Hydrogen fluoride cannot be separated by simple distillation because it forms a constant-boiling mixture with water.

In the isoparaffin alkylation process the alkylate is substantially insoluble in hydrogen fluoride. The hydrogen fluoride has a relatively low solubility in the hydrocarbon product, of the order of 1% or less. This is an important property of an alkylation catalyst, since it simplifies the separation and recovery of the catalyst and the product.

Hydrogen fluoride may be readily dissolved from the reaction products by distillation which is similar to the separation of dissolved water from hydrocarbons, described by Hachmuth (*12*) and commercially practiced for many years. Figure 1 is a flow sheet of a commercial plant in which the hydrogen fluoride and part of the hydrocarbon are taken overhead from the hydrogen fluoride stripper column and HF-free hydrocarbon is taken as bottoms. The overhead vapor from the column contains a concentration of hydrogen fluoride in excess of the amount which can be held dissolved in the hydrocarbon and hence separates into a two-phase system on condensation. The hydrocarbon phase is returned to the fractionation system, and the hydrogen fluoride is recovered for re-use. The workability of this system can be established by calculations based on the vapor pressures of pure hydrogen fluoride and the pure hydrocarbon, and on the solubility of the hydrogen fluoride in the hydrocarbon (*7*).

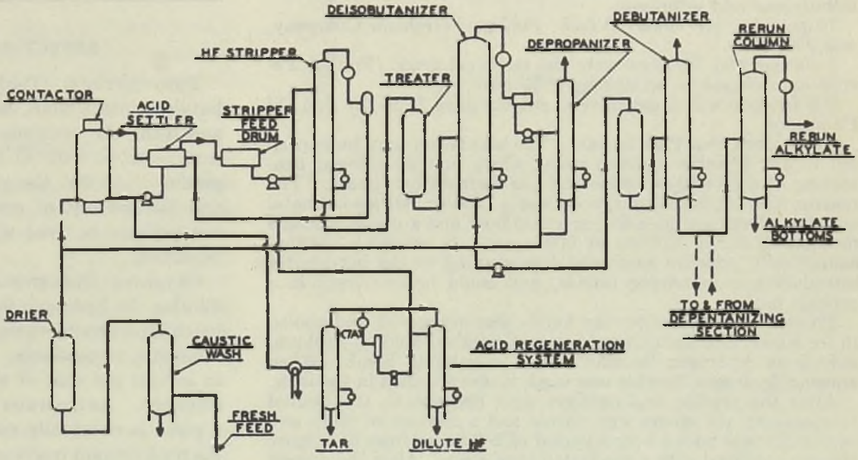


Figure 1. Flow Sheet of Commercial Alkylation Plant Utilizing Hydrogen Fluoride as Catalyst

EXPERIMENTAL PROCEDURE

Source of Reagents. Hydrogen fluoride (Harshaw Chemical Company) was water-white and contained less than 1% water, and the residue left upon evaporation was less than 0.04%.

Isobutane, obtained from Phillips Petroleum Company, was more than 99% pure.

Propylene, from the Matheson Company, Inc., was 99% pure.

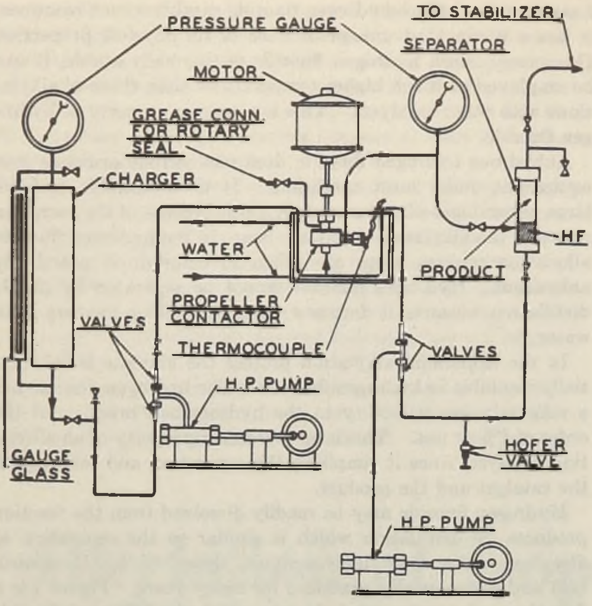


Figure 2. Setup for Continuous Alkylations

Isobutylene and *n*-butenes were prepared by dehydration of *tert*-butanol and *sec*-butanol, respectively, over alumina (*13*). These olefins were fractionated and finally analyzed as 98% pure isobutylene and *n*-butene.

Isopentane, c.p. material from Phillips Petroleum Company, was 99% pure.

1-Butene and 2-butene were the technical grade (Phillips Petroleum Company), analyzing 95% pure.

BB fraction was a commercial cut obtained from the Sun Oil Company.

Apparatus and Procedure. The alkylation may be carried out in any suitable reaction vessel which permits efficient contacting of the catalyst phase and the hydrocarbon phase. The reactor used for batch operations was a 1200-cc. Allegheny metal autoclave having a close-fitting nickel liner and a pressure-sealed mechanical stirrer turning at 600 r.p.m. It carried a thermocouple well, pressure gage, and line running to the bottom for introducing or removing liquids, and could be immersed in a cooling bath.

To start the operation the bomb was evacuated and cooled in ice water, and then charged with a weighed amount of liquid anhydrous hydrogen fluoride from a duralumin bomb. When aqueous hydrogen fluoride was used, it was weighed in the liner.

After the reactor and catalyst were brought to the desired temperature, the stirrer was started and a mixture of olefin and isoparaffin was added over a period of 2–3 hours from a pressure charger equipped with a graduated gage glass. After the desired time the autoclave contents were slowly purged through a copper line into a 1500-cc. copper flask containing 100 grams of water and immersed in a bath of solid carbon dioxide and acetone. (At room temperature anhydrous hydrogen fluoride reacts violently with water, but at low temperatures the reaction is moderate.) The material in the copper receiver, consisting of dilute hydrogen fluoride, alkylate, and unreacted isoparaffin, was allowed to come to room temperature. The alkylate was rapidly separated from the hydrofluoric acid in a glass separatory funnel, washed several times with ice water, and dried with potassium carbonate. The liquid product was distilled through a high-temperature Podbielniak column, and the condensable gas fraction was analyzed in a low-temperature Podbielniak apparatus.

Figure 2 shows an apparatus for continuous experiments. The reactor had a capacity of 25 cc. and was agitated by a mixer turning at 1700 r.p.m. Hydrogen fluoride was added to the reactor before the run began. After the run started, a mixture of olefin and isoparaffin was continuously pumped into the reactor. The reaction mixture passed from the reactor into a settling chamber from which the catalyst layer was recycled. The hydrocarbon layer was forced into a receiver, and the pressure released to atmospheric; the alkylate was then debutanized and water-washed. A small amount of hydrogen fluoride was continuously lost from the system due to its solubility in hydrocarbons; this could be readily determined by titration. This apparatus was well adapted to the preparation of considerable amounts of product. Moreover, it could be used to determine that the catalyst had a long life although the values obtained were necessarily not the best since there was no provision for recovering and recycling the hydrogen fluoride dissolved in the effluent from the settler.

Determination of Organic Fluorine. The procedure used to analyze for fluorine in the liquid alkylate was a modification of that employed to determine sulfur in gasoline (*2*). The techniques used in the combustion of the sample and the absorption of the combustion products were identical with the sulfur method; the same solution, 0.06 *N* sodium carbonate, was used in the scrubber. The fluoride present was determined by titration with standard thorium nitrate in the presence of alizarin sulfonate as indicator (*22*).

The data are largely taken from early experiments on the investigation of hydrogen fluoride as a catalyst. Recent data, which cannot be reported because of censorship restrictions, have extended the knowledge of the reaction and of the operating variables.

Table I. Isobutane-Isobutylene Alkylation

Temperature, ° C.	−24	32	60
Ratio, hydrocarbon/HF, by vol.	0.8	0.2	0.8
Charge, grams			
Iso-C_4H_8	177	344	168
Iso-C_4H_{10}	420	561	397
Butane-free product, grams	351	670	298
Properties of product			
Bromine number	0	0	0
Fluorine, %	0.4	<0.1	0.6
Engler distillation			
50% point, ° C.	127	115	130
% over at 205° C. (end point)	85	94	83
Octane No., A.S.T.M. motor method	91.5	92.0	89.0

EFFECT OF OPERATING VARIABLES

Temperature. Table I lists data from three isobutane-iso. butylene interactions, carried out at −24°, +32°, and +60° C. and using the continuous contactor. Changes in temperature from −24° to +32° C. had little effect on the yield or quality of product. At 60° the yield was reduced; the fluorine content and the amount of cracking increased. Higher temperatures can perhaps be used with the proper correlation of operating variables.

Catalyst Concentration. Table II shows the effect of diluting the hydrogen fluoride with water; the results are from batch experiments where isobutane was reacted with propene and *n*-butenes, respectively. In general, the catalyst will tolerate up to several per cent of water without serious impairment of its efficiency. As the water content is increased, activity falls off and a point is eventually reached where hydrofluorination becomes the predominant reaction. Thus, the presence of 10% by weight of water in the catalyst did not seriously affect the isobutane-butylene interaction; however, when 26% water was used, the formation of sec-butyl fluoride became the main reaction. Propene failed to react with isobutane in the presence of 10% water but was converted into isopropyl fluoride.

In this connection, it must be stated that the dilution effect of water is not necessarily the same as that of other substances. The actual concentration of hydrogen fluoride in an alkylation catalyst may be considerably less than 90% by weight, provided the diluent is not water but is, for example, that formed during the alkylation process. Hydrogen fluoride concentrations of 75% or lower, in such conditions will function as catalyst.

Contact Time. Periods of contact as short as a minute and as long as several hours have been successfully used. For example, the continuous experiments of Table I were satisfactorily carried out with contact times of less than 2 minutes; the batch runs reported in Tables II and III lasted several hours. The optimum contact time is dependent upon the degree of mixing, and at the time of these experiments all factors had not been entirely investigated. Restrictions prevent full discussion of this variable at this time.

Table II. Effect of Water on Hydrogen Fluoride as an Alkylation Catalyst

Olefin used	Propene		*n*-Butenes		
Water in catalyst, % by wt.	1	10	1	10	26
Temp., ° C.	25	25	28	25	25
Pressure, av. lb./sq. in. gage	75	80	80	50	75
Reaction time, hr.	2.5	3.0	3.3	4.0	3.5
Vol. ratio, catalyst/hydrocarbon	0.68	0.52	0.23	0.56	0.56
Reactants, grams charged					
Isobutane	153	192	270	140	140
Propene	63	88	0	0	0
n-Butenes	0	0	162	95	95
Hydrocarbon recovery, grams					
Propane	10	0	0	0	0
Butanes	61	180	95	44	130
Pentanes and higher	135	[a]	323	182	[b]
Loss	10	..	14	9	..
Wt. % fluorine liquid	0.02	..	0.01	0.06	..
Yield liquid alkylate as wt. % of olefin reacting	214	Near 0	199	192	Near 0

[a] Propene largely converted to isopropyl fluoride. Only 8 grams of material boiling above 0° C.

[b] Butenes largely converted to *sec*-butyl fluoride. Only 10 grams of material boiling above 30° C.

Ratio of Olefin to Paraffin. The ratio of isobutane to butylene was studied over a range of 1.5 and higher. In each case the products were completely saturated. The yield of alkylate obtained would indicate that higher ratios of isobutane to butylene would improve the operation by making it more selective. The octane content of the product should be increased by the higher ratio of isobutane to olefin. This should also result in a product of improved quality for utilization in aviation blending fuel.

Ratio of Acid to Hydrocarbon. Ratios of hydrogen fluoride to hydrocarbon of 0.15 to about 5.0 by volume were investigated. Satisfactory results were obtained at a ratio of about one part of acid to one of hydrocarbon.

ISOPARAFFIN-OLEFIN INTERACTION

Table III gives data from batch experiments at 10° C. with pure reactants and one continuous run at 38°. The respective products were distilled on a Podbielniak Hyper-Cal Heligrid-packed column of greater than fifty-plate efficiency; and distillation curves are shown by Figures 3 to 9. In the discussion, "selective alkylation" refers to a reaction giving a relatively high product content of the paraffin species, corresponding to the sum of the molecular weights of the olefins and isoparaffin involved (Equation 1).

Table III. Data from Seven Batch and One Continuous Experiment

Temperature, ° C.	10	10	10	10	10	10	10	38[a]
Reaction time, hours[b]	5.0	5.0	5.0	5.0	5.0	5.0	5.0	...
Catalyst/hydrocarbon ratio	0.13	0.16	0.16	0.16	0.16	0.15	0.15	1.1
Isoparaffin/olefin mole ratio	3.5	3.0	3.3	3.2	3.5	3.3	1.5	6
Charging stock, mole %								
Propene	22	25	0	0	0	0	0	4[c]
Isobutylene	0	0	0	0	22	19	20	..
1-Butene	0	0	22	4	0	0	0	2
2-Butene	0	0	1	10	0	0	0	9.5
Isobutane	0	75	77	76	78	62	30	72.5
n-Butane	0	0	0	0	0	19	50	11.5
Isopentane	78	0	0	0	0	0	0	0.5
Liquid alkylate yield								
Wt. % olefin reacted	272[d]	230	194	203	197	210	168	227
Fluorine in alkylate[e], %	0.08	0.01	0.01	0.01	0.01	0.01	0.01	0.026
150° end-point gasoline as wt. % of product	73	81	85	91	91	89	69	95
Octane No. of 300° end-point product	..	90.5	92.7	95.3	96.7	95.6	92	94.9
Figure No. of distn. curve	3	4	5	6	7	8	9	..

[a] Commercial BB fraction as source of olefin.

[b] Time from beginning of addition of hydrocarbon charge until product was removed from autoclave.

[c] Propane and propene.

[d] Exclusive of pentanes. Counting isobutane formed as product, the yield was 291%.

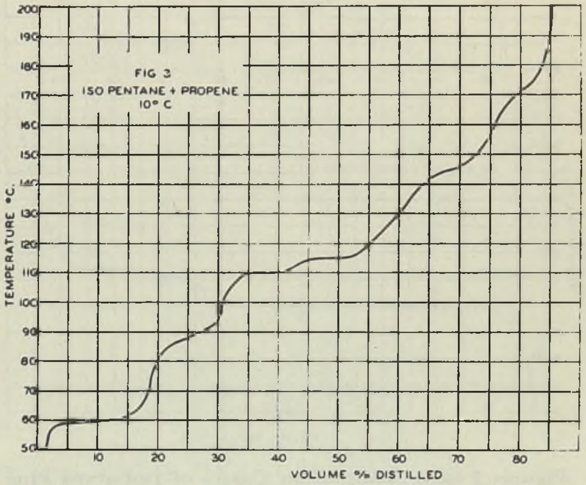
[e] Not treated to remove fluorine. In commercial operations this is always done. After treatment the fluorine content was 0.0056%.

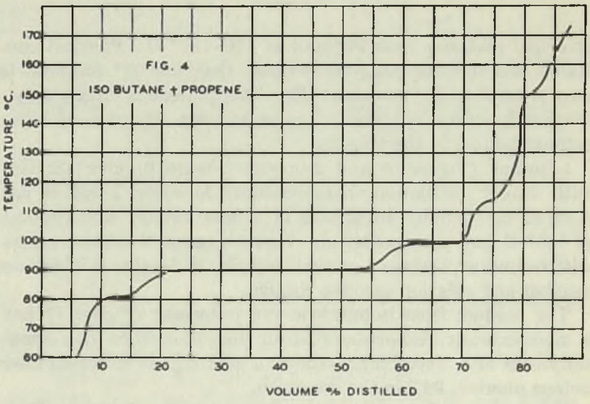
Isopentane + Propene. Only 26% of the reaction product boiled in the octane range, and the distillation curve (Figure 3) shows many plateaus. This indicates a nonselective reaction with extensive autodestructive alkylation. The yield of alkylate boiling higher than pentanes was 272% of the olefin reacted; however, isobutane was also found and if this is included in the calculation as product, the yield becomes 291%. The octane number of this material was not determined; from other runs involving these reactants, the octane number found has been in the high eighties.

In general, these results are characteristic for alkylation with isopentane, the reacting paraffin. Usually the reaction is nonselective, isobutane is a reaction product, and the yield based on the olefin is greater than corresponds to equimolecular combination with isopentane.

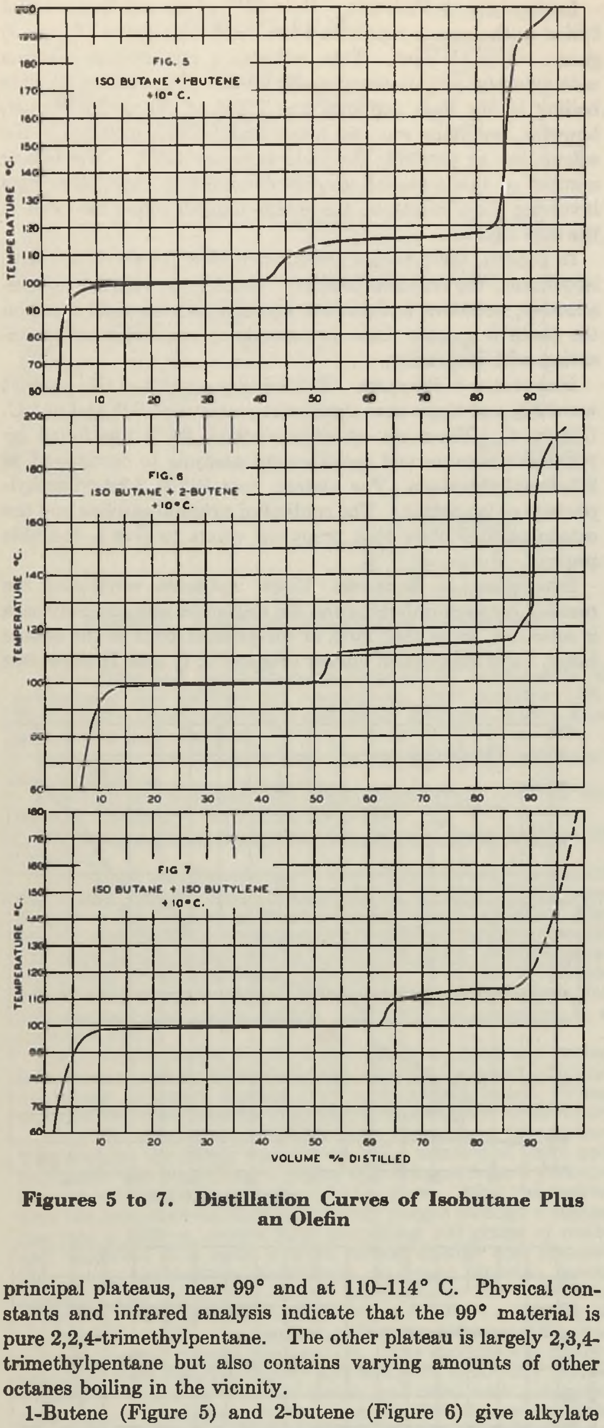
Isobutane + Propene. The heptane content of this product was 50% and there were significant plateaus at 80° and 89° C. (Figure 4). The more extensive of these (89°) was found by physical constants and spectroscopic analysis to correspond to 2,3-dimethylpentane. The plateau near 99° is 2,2,4-trimethylpentane or iso-octane. The content of aviation gasoline and the octane number show that propylene reacts to give a desirable product.

Isobutane + Butenes. Under optimum conditions the reaction between isobutane and the respective isomeric butylenes is selective; more than 80% of the product boils in the octane range. The distillation curves (Figures 5, 6, and 7) show two





Figures 3 and 4. Distillation Curves for an Isoparaffin Plus Propene



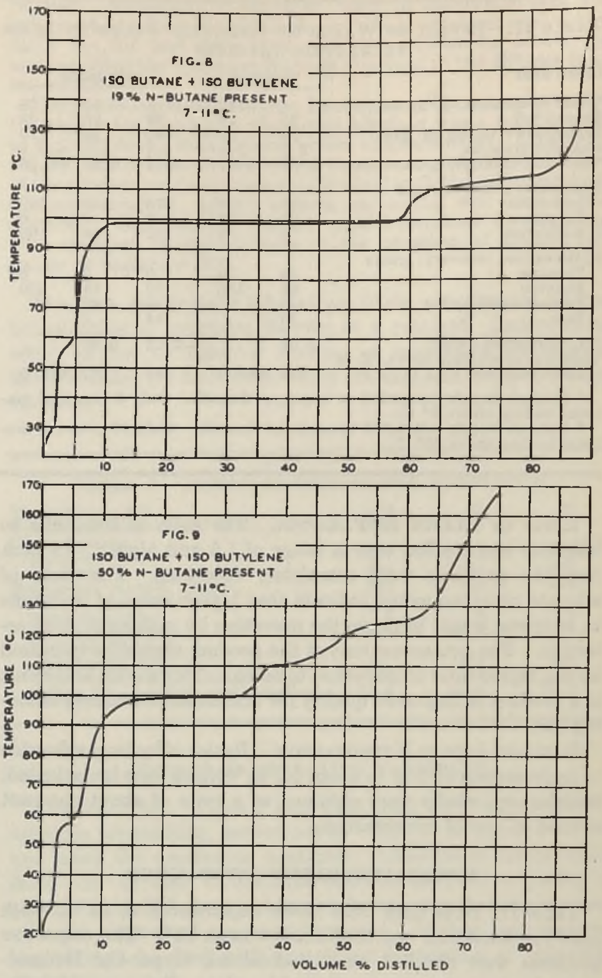
Figures 5 to 7. Distillation Curves of Isobutane Plus an Olefin

principal plateaus, near 99° and at 110–114° C. Physical constants and infrared analysis indicate that the 99° material is pure 2,2,4-trimethylpentane. The other plateau is largely 2,3,4-trimethylpentane but also contains varying amounts of other octanes boiling in the vicinity.

1-Butene (Figure 5) and 2-butene (Figure 6) give alkylate with similar distillation characteristics; however, 2-butene has a small but definite advantage in octane number and content of 150° C. end-point material. Likewise, since 2-pentene reacts with isobutane, it gives a product superior to 1-pentene in octane number and aviation gasoline content.

The product from isobutylene and isobutane (Figure 7) has a more extensive iso-octane plateau than that from the normal butylenes and, accordingly, shows a still higher motor-method octane number, 96.7 in the run given.

Isobutane + Isobutylene in Presence of *n*-Butane. Two runs in Table III show the effect of adding *n*-butane to the isobutane-isobutylene interaction. The run with 19% *n*-butane gave results comparable to those obtained in its absence. The octane number and yield of 150° C. end-point material were slightly reduced but the distillation curves are similar (Figures 8 and 9). When *n*-butane was present to the extent of 50% of the charge, there was a marked reduction in the yield and quality of alkylate (Figure 9). The effect observed was probably due to the reduction in the ratio of isobutane to olefin rather than to any effect of the *n*-butane.



Figures 8 and 9. Distillation Curves for Isobutane and Isobutylene in the Presence of *n*-Butane

Butane-Butene Fraction. The run on the commercial butane-butene fraction (BB) was made on a continuous pilot plant. It shows that mixtures of butenes can be used in the process to produce high-quality product.

Properties of Reaction Product. All the laboratory work and later the results from larger installations point to the fact that the reaction is usually not simple. With any pair of reactants the most desirable product appears to be the type of paraffin resulting from the direct stoichiometric reaction of the olefins and isoparaffin which, for convenience, is referred to as primary alkylation:

$$C_mH_{2m+2} + C_nH_{2n} \longrightarrow C_{m+n}H_{2(m+n)+2} \qquad (1)$$

This result can be achieved to the extent of 80% or better, depending upon operating conditions. Other reactions occur to a greater or lesser extent, among which are: overalkylation (i.e., the reaction of the product of Equation 1 with additional olefin),

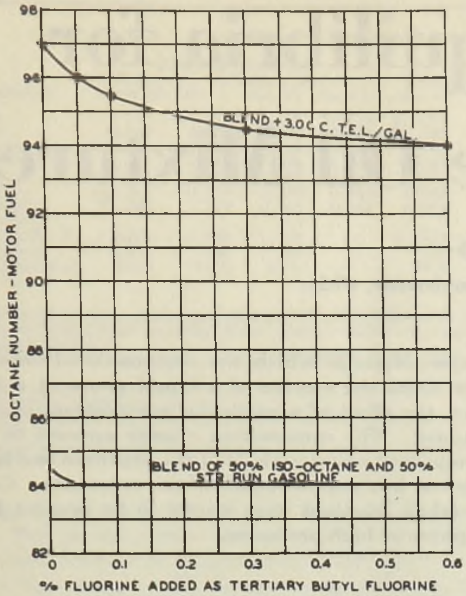


Figure 10. Effect of Organic Fluorine on Octane Number and Tetraethyllead Susceptibility of a Blend of 50% Iso-octane and 50% Straight-Run Gasoline

autodestructive alkylation or cracking, polymerization of the olefin, isomerization, and hydrogen transfer reactions. The desired reaction of primary alkylation may be favored by using a moderate reaction temperature, by increasing the ratio of isoparaffin to olefin.

Normally the alkylate is completely saturated, contains only traces of combined fluorine, boils in the gasoline range, and has excellent antiknock properties when used with or without tetraethyllead.

FLUORINE IN THE ALKYLATE

Figure 10 shows the effect of fluorine on the properties of the alkylate, for a blend of iso-octane and straight-run gasoline, both clear and containing 3 cc. of tetraethyllead per gallon; the major effect is on the latter. Up to about 0.1% there is a loss of about 1 octane number per 0.05% of fluorine added to the mixture containing tetraethyllead. The fluorine was added in the form of *tert*-butyl fluoride.

Table IV. Removal of Fluorine from a Solution of *tert*-Butyl Fluoride in Iso-octane

Material	Temp., ° C.	Pressure, Atm.	Contact Time, Hr.	F Content, %		F Removed, %
				Charge	Product	
Burrell charcoal	20	1	1.5–2	1.63	1.90	0
	100	1	1.5–2	1.63	1.55	5
	100	10	1–2	0.58	0.43	26
	60–100	2–10	3	0.58	0.62	0
	200	10	2	0.77	..	..
	200	10	2	0.77	0.32	58
	200	10	2	0.77	0.24	69
	100	10	1	0.77	0.36	53
Charcoal + 10 grams of HF	100	10	2	0.58	0.09	85
	60–100	2–10	3	0.58	0.09	85
	100	10–1	1.5–2	0.62	0.26	58
	100	1	1.5–2	0.62	0.48	23
CaF on charcoal	100	10	2	0.62	..	..
	100	10	1	0.62	0.64	0
	200	10	2	0.62	0.32	50
	200	2–4	2	0.62	0.18	71
	200	6–10	2	0.59	0.22	60
	200	10	2	0.59	0.33	44
	100	10	2	0.59	0.46	22
	100	10	2	0.59	0.30	49
Same + 7 g. HF	100	2–10	1	0.62	0.11	82

Table V. Paraffins Identified in Reaction Product

Paraffins Used	Olefins Used	Boiling Range of Sample at 750 Mm., ° C.	Paraffins Identified
Iso-C_4H_{10}	C_3H_6	75.7–79.0	2,4-Dimethylpentane
Iso-C_4H_{10}	C_3H_6	83.5–85.5	2,4-Dimethylpentane, 2,3-dimethylpentane
Iso-C_4H_{10}	*n*-C_4H_8	98.0–99.0	2,2,4-Trimethylpentane
Iso-C_4H_{10}	Iso-C_4H_8	98.0–99.0	2,2,4-Trimethylpentane
Iso-C_5H_{12}	C_3H_6	79.5–81.0	2,4-Dimethylpentane
Iso-C_5H_{12}	C_3H_6	89.0–90.0	2,3-Dimethylpentane
Iso-C_5H_{12}	C_3H_6	108.0–110	2,5-Dimethylhexane
Iso-C_5H_{12}	C_3H_6	115.0–116.0	2,3-Dimethylhexane

Removal of Fluorine. Table IV shows the effect of various materials upon fluorine removal. Activated charcoal, calcium fluoride, and aluminum fluoride have substantial defluorinating properties. Commercial and semicommercial runs have borne out the desirability of removing fluorine from the alkylate, although complete defluorination is not necessary.

PARAFFINS IDENTIFIED IN PRODUCT

Table V presents an analysis of a number of fractions from representative hydrogen fluoride alkylates using Raman spectra (*11*, compare *5*).

ACKNOWLEDGMENT

The authors wish to thank Willard F. Mann, now an officer in the Navy, for assistance with the laboratory work.

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Vapor-Liquid Equilibria for Natural Gas–Crude Oil Mixtures

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A consistent set of equilibrium constants and related phase data were obtained for a mixture of League City natural gas and Billings crude oil for pressures from 1000 to 10,000 pounds per square inch and at temperatures of 120° and 200° F. Data were also obtained for miscellaneous mixtures of the oil and gas, and were compared to the data for the fixed-composition mixture. The effect of composition upon the equilibria is noted, and through two experiments in which the composition is varied by removal from the system of a liquid phase at a higher pressure the effect of a particular composition change is determined. The composition change appears to affect the component characteristic of the heptanes and heavier component but not the equilibrium constants. Colored hydrocarbon fractions were shown to be present in the vapor phase at high pressures.

VAPOR-liquid equilibrium constants and related data have been determined for mixtures of a natural gas and crude oil at 120° and 200° F. for pressures from 1000–10,000 pounds per square inch. These data are useful to those engaged in process design and reservoir engineering for predicting phase relations. The range of temperatures and pressures studied include those which represent the initial conditions existing in most of the known oil and gas producing reservoirs.

Several investigators have reported vapor-liquid equilibrium constants for multicomponent hydrocarbon mixtures with a wide range of volatility such as occur in natural gas and crude oil separations. Katz and Hachmuth (*2*) presented data for pressures to 3000 pounds per square inch at 40°, 120°, and 200° F., determined with natural gas and Oklahoma City Wilcox crude oil mixtures. These data were extrapolated in the published article to a convergence pressure of 5000 pounds per square inch. Webber (*5*) published equilibrium constant data for hydrocarbons in absorption oil at 33°, 100°, and 180° F. and pressures from 100 to 5000 pounds per square inch. These mixtures were made up synthetically by adding the pure hydrocarbons to the absorption oil. The varying amounts of hydrocarbons used affected the equilibrium constants and thus indicated how important were the relative amounts of hydrocarbons present at pressures above 1000 pounds. Roland, Smith, and Kaveler (*3*) published equilibrium constant data for Gulf Coast distillate–natural gas mixtures at 40°, 120°, and 200° F. for pressures from 200 to 4000 pounds per square inch. Measurements were made at pressures both above and below the limit for existence of a two-phase condition, and the determinations established with a reasonable degree of certainty the existence of a convergence pressure (pressure at which the equilibrium constants appear to converge to unity for certain mixtures). Eilerts and Smith (*1*) included some equilibrium constant data obtained in a study of separator gas–liquid hydrocarbon mixtures from a distillate well. These data were obtained at 3192 pounds per square inch pressure and 228° F. for various mixtures of separator gas and liquid. They show a considerable variation of the equilibrium constant with the ratio of gas to liquid in the mixture. Standing and Katz (*4*) published equilibrium constant data for four different mixtures of natural gas and crude oils at 35° to 250° F. from 100 to 8220 pounds per square inch. Their measurements included the phase densities under the equilibrium conditions; these data assist in determining whether the increase in pressure on the system produces a bubble point or a dew point. At high pressures their equilibrium constant data as plotted against pressure on logarithmic paper indicated a reversal in the curvature of the equilibrium constant lines similar to that shown in the plots of Webber. That such reversal of curvature was not present in the distillate systems may be attributed to the fact that, for the distillate mixtures, the temperature of the determinations was much nearer the critical temperatures of the mixtures.

The data obtained in the experimental work of this paper may be divided into three groups. In the first, gas and crude oil were combined in various proportions to produce miscellaneous mixtures. The equilibrium data were then determined for these mixtures. In the second group the gas and oil were combined in a fixed ratio, and the equilibrium data were determined for various pressures from 1000 to 10,000 pounds per square inch. In the third group a vapor phase was removed from one of the equilibria of the second group and used as a system at a lower pressure for which the equilibrium constants and related phase data were determined.

In addition to the equilibrium constant data, particular attention was given to the specific gravity and molecular weight of the heptanes and heavier fractions. In the phase equilibria at high pressures such as are encountered in reservoir studies, the equilibrium constant of the heptanes and heavier fraction is of prime importance and in many cases is the determining factor in a calculation. The significant variations of the molecular weight and specific gravities are important in helping to select the correct value for the heptanes and heavier constant.

EXPERIMENTAL DETAILS

The apparatus included an equilibrium cell, constant-temperature bath, gages, hand-operated mercury pump, volumetric mercury-displacement pump, and analytical apparatus. The equilibrium cell was of the rocking-bomb type. The analytical equipment included two sets of low-temperature fractionating columns; a balance, pycnometers, and cryoscopic molecular weight apparatus were used to study the heptanes and heavier fractions.

CRUDE OIL AND NATURAL GAS. The crude oil used in making up the equilibrium samples was a pipe line oil from the Wilcox formation near Billings, Okla., in Noble county. A commercial preparation (Tretolite) was added to the oil to assist in removing the water. The percentage of Tretolite was very small and was assumed to have no effect on the equilibria. Thirty gallons of this oil were thoroughly agitated in a drum. From this drum 23 quart cans were filled and sealed so that a fresh can of oil would be available for each charge of the equilibrium cell. Table I gives a fractional analysis of the oil and Figure 1 shows a distillation chart.

Table I. Analysis of Oil and Gas

Hydrocarbon	Charging Materials: Billings crude oil	Natural Gas No. 7	No. 8[a]	No. 8a[b]	Composite Compositions No. 1[c]	No. 2[d]	No. 3[e]
Methane	...	91.150	91.136	91.419	81.113	81.107	81.358
Ethane	0.052	4.368	4.392	4.386	3.896	3.914	3.909
Propane	1.142	2.047	2.059	1.990	1.948	1.958	1.897
Butanes	4.423	1.288	1.283	1.251	1.629	1.628	1.600
Pentanes	6.054	0.513	0.493	0.459	1.123	1.105	1.075
Hexanes	8.535	0.317	0.290	0.270	1.222	1.197	1.179
Heptanes and heavier	79.794	0.317	0.347	0.225	9.069	9.091	8.982
Sp. gr. at 60° F.	0.8285	0.735	0.753	...	0.8268	0.8268	0.8268
Mol. weight	200.8	105	107	...	198	198	198
A.P.I. gravity at 60° F.	39.3	61.0	56.4	...	39.6	39.6	39.6

[a] Cylinder H9017 after removing liquid at 32° F. and 1900 lb./sq. in. gage.
[b] Cylinder H9017 after removing more liquid resulting from pressure drop to 1050 lb./sq. in. gage at 75° F.
[c] Applies to 120° F. samples at pressures of 3566, 5581, 5831, 6580, 7940, 9374 lb./sq. in. abs.
[d] Applies to 200° F. samples at pressures of 1600, 1907, 2500, 3560, 3792, 4957, 5737, 6740, 7470, 7965, 8078 lb./sq. in. abs.
[e] Applies to 200° F. samples at pressures of 1047, 5402, 7905 lb./sq. in. abs.

The gas was obtained from the Lobit No. 2 well, League City, Texas. This gas was chosen because it was accessible, similar in composition to other natural gases, and available at a well head pressure high enough to fill the gas storage cylinders to 2000 pounds per square inch gage pressure. The casing-head gas from this well was passed through charcoal into the cylinders to remove the heavier constituents. The gas was further denuded of its heavier constituents by cooling the cylinders in a crushed ice bath, inverting, and draining the condensed liquid from each cylinder. This procedure was assumed to give a supply of gas which would not undergo retrograde condensation upon further pressure reduction and hence be of constant composition during use. Frequent checks of the gas cylinders during and following the run at 120° F. showed the cylinder to be free of liquid hydrocarbons. During the 200° F. run a small amount of liquid was found in one cylinder after three determinations had been made; the gas was reanalyzed and the analyses were only slightly different. Both analyses are recorded in Table I.

Procedure. Previous experience in the determination of equilibrium constants for the gas distillate and other crude oil systems indicated that the equilibrium cell might be charged with liquid and gas to some high pressure and samples be removed at several pressures until one or another of the phases was depleted. At this point more liquid or gas could be added to restore the depleted phase and additional samples be taken. The composite composition could be calculated, and any change in the value of the equilibrium as a result of change in cell composition could be correlated with the change in one of the other variables. A group of equilibrium points were determined in this way. Although this method accelerated the experimental work, the data showed more variation than was anticipated, and correlation was made impossible. It was therefore decided to determine the equilibrium constants for a constant-composition system. This system would be made up each time by adding gas and crude oil in the mole ratio of 8.086 to 1. A typical experimental run involved the following procedure:

The temperature and pressure of the desired equilibrium were selected. The approximate volume of the liquid phase which would be present in the cell at the selected conditions was computed from previous data for the phase density or, if necessary, by the use of generalized correlations available in the literature. With this information the mercury level in the cell was adjusted so that a sufficient volume of the liquid phase equal to the desired volume of sample would be available below the intake to the liquid-phase eduction tube. This would ensure an adequate amount of liquid sample being taken since, during the sampling, the mercury level would rise and finally cover the entrance to the eduction tube.

The cell was evacuated with a Hyvac pump. The desired quantity of gas to be added to the equilibrium cell was measured in an auxiliary cell. The compressibility of this gas was previously determined so that the volume at a desired temperature and pressure would be known. The gas was then displaced with mercury into the equilibrium cell.

The crude oil was measured in a graduate at 60° F. and added to the smaller auxiliary cell from which it was displaced with mercury into the equilibrium cell, care being taken to use a fresh quart can of crude oil each time the equilibrium cell was charged.

After charging the equilibrium cell with the requisite quantities[1] of gas and liquid, the cell was rocked for 10 or 15 minutes to bring the contents to equilibrium. The cell was then fixed in an upright position, and the sample valves were connected to the sampling lines.

The volumetric mercury pump was connected to the bottom of the cell and used to maintain the pressure constant during the withdrawal of vapor or liquid from the cell. Each valve was opened slightly, and material was removed from the cell until it was assured that only the desired phase was being obtained. Samples were then displaced into the analytical columns. Records were made of the volumes displaced by the volumetric mercury pump.

The first part of the analytical column setup contained a small detachable glass trap through which the equilibrium sample was passed to remove the heavier components before condensing the lighter components in the kettles cooled with liquid nitrogen. This procedure prevented the heavier materials from plugging

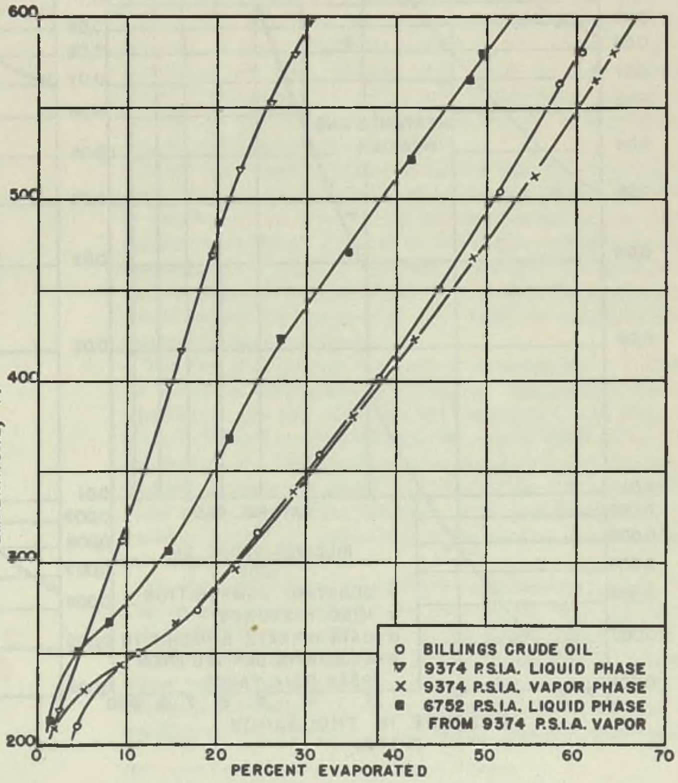

Figure 1. Distillations of Heptanes and Heavier Fractions

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[1] In some cases, particularly the equilibria at higher pressures, it was necessary to rock the cell when adding the liquid so that the pressure during solution of the gases could be kept below the upper pressure limit of the gages.

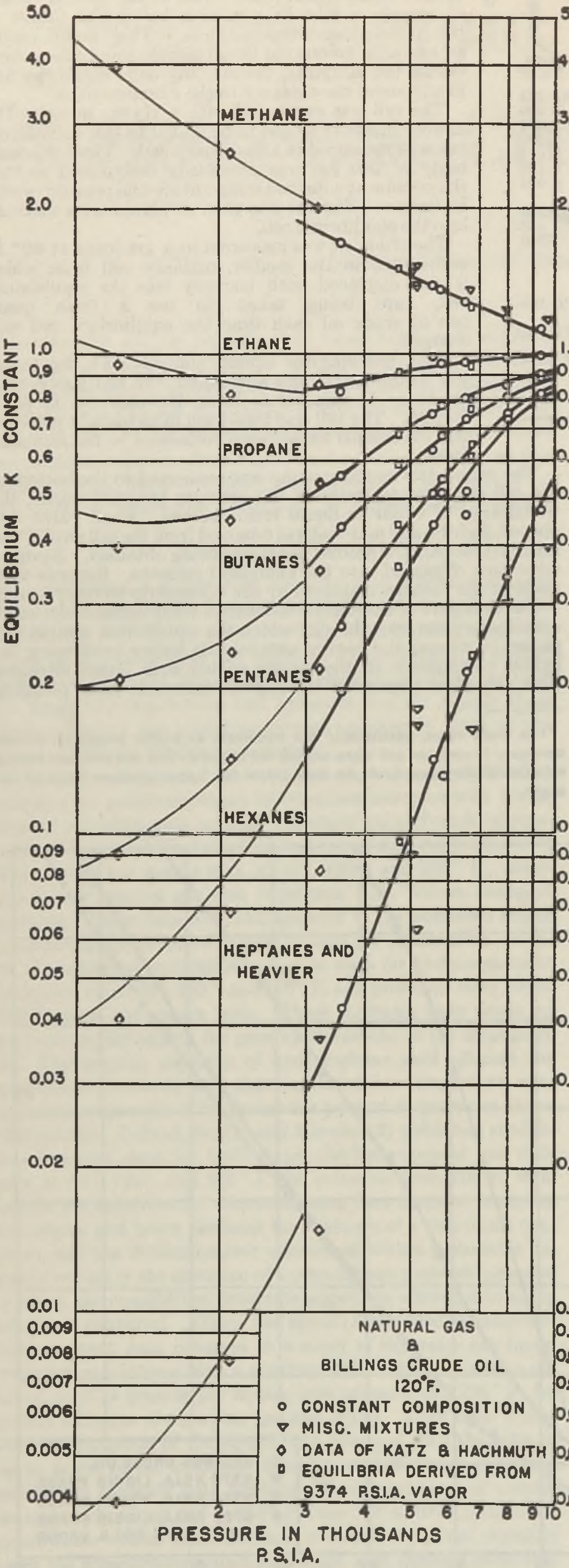

Figure 2. Vapor-Liquid Equilibrium Constants for Natural Gas and Billings Crude Oil at 120° F.

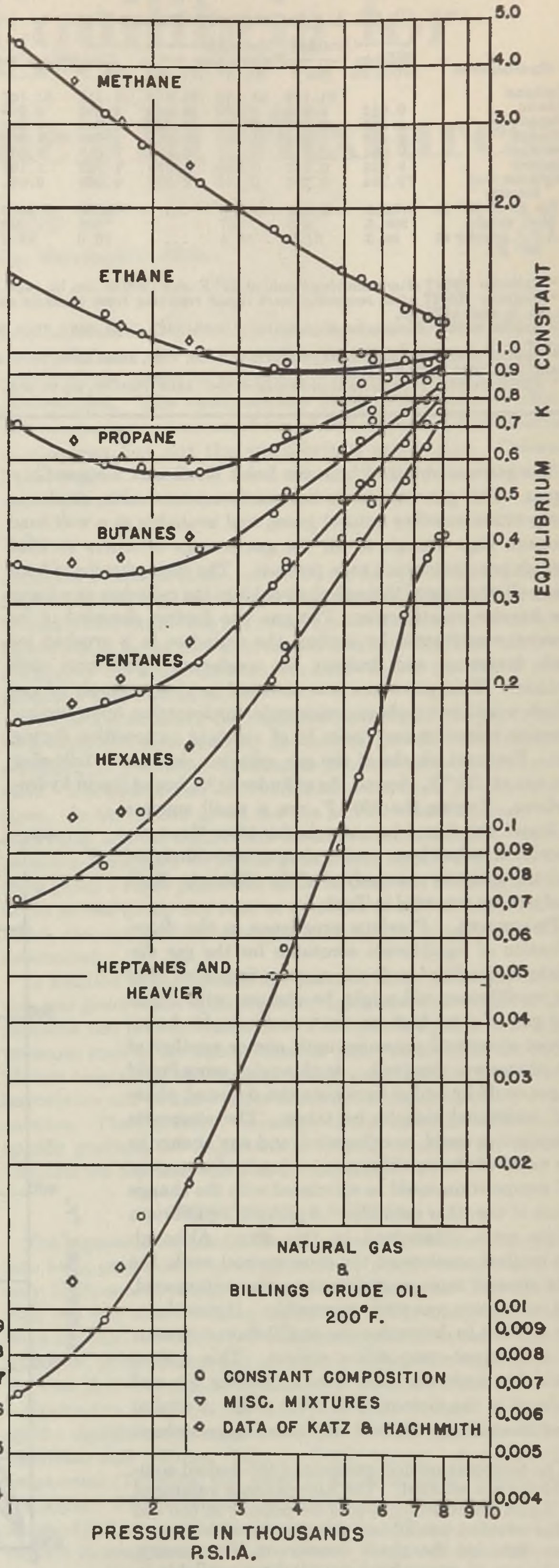

Figure 3. Vapor-Liquid Equilibrium Constants for Natural Gas and Billings Crude Oil at 200° F.

Table II. Phase Analyses and Equilibrium Constants for Miscellaneous Mixtures of Natural Gas and Billings Crude Oil

	3201 Lb.[a], 120° F.			5040 Lb., 120° F.			5153 Lb., 120° F.			5153 Lb., 120° F.		
	Vapor	Liquid	K	Vapor	Liquid	K	Vapor	Liquid	K	Vapor	Liquid	K
Methane	91.256	50.454	1.809	88.766	59.365	1.480	87.442	62.971	1.388	86.745	62.298	1.392
Ethane	3.500	4.034	0.867	3.969	4.314	0.922	3.080	3.192	0.965	3.294	3.468	0.950
Propane	1.484	2.682	0.553	1.914	2.621	0.730	1.561	2.340	0.667	1.713	2.228	0.769
Butanes	1.221	3.463	0.352	1.380	2.428	0.568	1.536	2.482	0.618	1.526	2.505	0.609
Pentanes	0.750	3.083	0.244	0.786	1.797	0.438	1.170	2.090	0.560	1.172	2.181	0.537
Hexanes	0.567	3.596	0.158	0.692	2.025	0.342	1.020	2.170	0.470	1.041	2.645	0.394
Heptanes and heavier	1.222	32.688	0.0374	2.492	27.451	0.0908	4.191	24.760	0.169	4.510	24.676	0.183
Mol. weight	115	207	...	136	227	...	132	196.5	...	130	196.5	...
Sp. gr. at 60° F.	0.7533	0.8326	...	0.7749	0.8459	...	0.7722	0.8293	...	0.7787	0.8310	...
Moles sampled	1.1181	0.1492	...	0.8495	0.4140	...	0.5981	0.3921	...	0.3044	0.2443	...
Cc. sampled	107.8	21.3	...	62.8	47.800	...	43.97	40.91	...	21.32	26.03	...
$Z = PV/NRT$	0.795	1.174	...	0.958	1.495	...	0.974	1.383	...	0.927	1.413	...

	5173 Lb., 120° F.			6678 Lb., 120° F.			7968 Lb., 120° F.			9695 Lb., 120° F.		
Methane	89.532	58.807	1.522	87.332	64.072	1.363	84.595	68.642	1.230	82.112	69.451	1.182
Ethane	4.185	4.616	0.907	3.486	4.327	0.806	3.918	4.010	0.976	4.208	3.972	0.944
Propane	1.942	2.748	0.707	1.980	2.486	0.796	1.933	2.220	0.868	2.034	2.059	0.988
Butanes	1.367	2.448	0.559	1.605	2.337	0.688	1.629	1.989	0.818	1.734	2.061	0.841
Pentanes	0.687	1.574	0.437	0.958	1.772	0.541	1.037	1.416	0.732	1.220	1.621	0.753
Hexanes	0.508	1.843	0.276	0.850	2.018	0.421	1.037	1.665	0.662	1.111	1.879	0.592
Heptanes and heavier	1.778	27.964	0.0636	3.790	22.988	0.165	5.851	20.053	0.302	7.582	18.958	0.400
Mol. wt.	143	254	...	154	254	...	171	229	...	186.5	280	...
Sp. gr. at 60° F.	0.7805	0.8587	...	0.7918	0.8602	...	0.8041	0.8566	...	0.8205	0.8807	...
Moles sampled	0.758	0.1339	...	0.9104	0.3017	...	0.6895	0.3171	...	0.7012	0.2475	...
Cc. sampled	55.770	17.94	...	62.38	33.7	...	46.20	30.9	...	52.41	23.06	...
$Z = PV/NRT$	0.979	1.785	...	1.178	1.919	...	1.372	1.998	...	1.862	2.322	...

[a] Pressure in pounds per square inch.

the small neck leading to the kettle of the column. At the end of sampling, the trap was heated to drive all components more volatile than heptane into the kettle of the analytical column.

Analysis of the sample was carried through the hexanes, and the residue of heptanes and heavier was condensed and weighed.

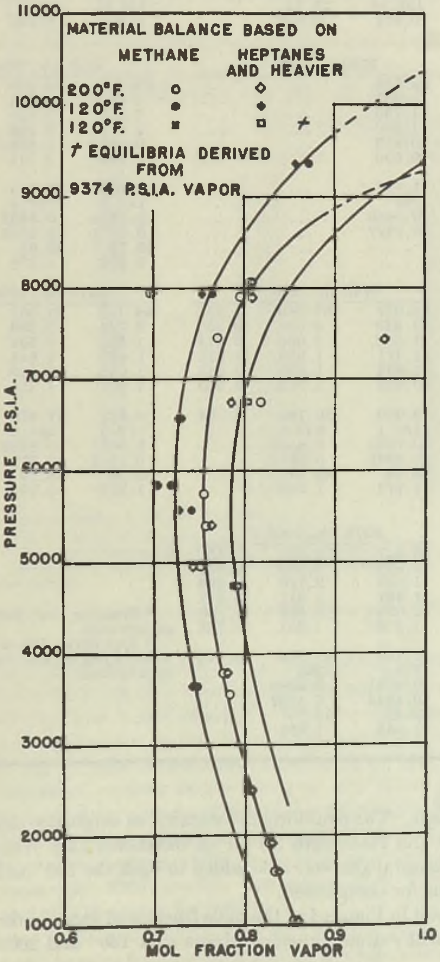

Figure 4. Phase Distribution at Equilibrium Pressure and Temperature

The molecular weight was determined by the cryoscopic method, using benzene saturated with water. Standardization of molecular weight determinations was carried out against pure iso-octane. The density of the residue was determined in calibrated pycnometers, and the remaining residue was sealed in bottles and retained for further examination.

EQUILIBRIUM CONSTANT DATA

The data determined at 120° F. for miscellaneous mixtures of natural gas and Billings crude oil are recorded in Table II. These constants and the other recorded phase data show that variables other than temperature, pressure, and general type of system—i.e., distillate or crude oil systems—are important in determining the value of the constant. These variables are the relative amounts of each component present in the mixture. In this connection the term "component" refers to each individual chemical component and, when used in this sense, the effect of the mixture of components commonly reported as heptanes and heavier may be properly understood.

Many investigators have pointed out that by the phase rule there are $(n - 2)$ variables besides temperature and pressure to be satisfied before a two-phase multicomponent system with n components is fixed. To fix all these variables would be virtually impossible in a practical problem; therefore it is desirable to find the minimum number of general properties that may be determined and readily measured in order to fix the equilibria with a reasonable degree of accuracy.

The first problem was to obtain a consistent set of equilibria for a system with a fixed composition. Accordingly, for each equilibrium, gas and oil having the compositions and properties given in Table I were combined in the ratio of 8.086 moles of gas per mole of oil. The equilibria determined for this constant composition system are recorded in Table III for 120° and 200° F. Plots of the equilibrium constants and related data were prepared to inspect the consistency of the data so that possible errors might be eliminated.

Figures 2 and 3 were prepared from equilibrium constant data. Curves were drawn through the data for the fixed composition system beginning at 3000 pounds per square inch absolute for the 120° F. isotherm and 1000 pounds for the 200° F. isotherm. Those values found to be inconsistent were considered from the standpoint of whether the errors were introduced in charging the equilibrium cell, sampling, or analyzing. The related phase data

Table III. Phase Analyses and Equilibrium Constants for a Constant-Composition Mixture of Natural Gas and Billings Crude Oil

	3566 Lb.[a], 120° F.			5581 Lb., 120° F.			5831 Lb., 120° F.			6580 Lb., 120° F.		
	Vapor	Liquid	*K*	Vapor	Liquid	*K*	Vapor	Liquid	*K*	Vapor	Liquid	*K*
Methane	90.658	52.792	1.717	87.393	63.119	1.383	87.684	64.370	1.362	86.443	66.903	1.289
Ethane	3.790	4.521	0.838	4.129	4.127	0.990	3.971	4.131	0.961	3.938	4.077	0.960
Propane	1.584	2.846	0.557	1.727	2.300	0.750	1.770	2.267	0.781	1.818	2.244	0.805
Butanes	1.281	2.924	0.438	1.417	2.224	0.637	1.446	2.130	0.679	1.494	2.027	0.735
Pentanes	0.697	2.565	0.272	0.929	1.812	0.512	0.948	1.727	0.549	0.815	1.568	0.518
Hexanes	0.630	3.186	0.198	0.981	2.226	0.440	1.105	2.141	0.516	0.902	1.949	0.462
Heptanes and heavier	1.360	31.166	0.0436	3.424	24.190	0.142	3.076	23.234	0.132	4.590	21.233	0.218
Mol. weight	124	222.8	...	148	228.5	...	146	228	...	159	243	...
Sp. gr. at 60° F.	0.7588	0.8361	...	0.7821	0.8451	...	0.7844	0.8464	...	0.7698	0.8499	...
Moles sampled	1.0561	0.2813	...	0.8987	0.3462	...	0.8970	0.3826	...	0.6947	0.3694	...
Cc. sampled	99.95	36.28	...	64.41	38.45	...	...	...	...	47.59	37.94	...
$Z = PV/NRT$	0.868	1.183	...	1.027	1.592	...	...	...	...	1.158	1.737	...
	7940 Lb., 120° F.			9374 Lb., 120° F.			4725 Lb.[b], 120° F.			6752 Lb.[b], 120° F.		
Methane	84.253	70.913	1.190	82.358	72.723	1.132	88.681	59.116	1.500	85.833	68.529	1.263
Ethane	3.931	4.013	0.980	3.952	3.979	0.993	3.826	4.164	0.919	3.835	4.101	0.942
Propane	1.820	2.115	0.860	1.854	2.044	0.905	1.680	2.455	0.684	1.780	2.226	0.806
Butanes	1.548	1.912	0.810	1.616	1.806	0.892	1.408	2.384	0.591	1.509	1.967	0.773
Pentanes	1.076	1.423	0.756	1.119	1.350	0.828	0.873	1.969	0.443	1.011	1.566	0.652
Hexanes	1.226	1.666	0.736	1.274	1.560	0.818	0.883	2.447	0.361	1.145	1.867	0.617
Heptanes and heavier	6.147	17.959	0.342	7.827	16.538	0.473	2.649	27.465	0.0965	4.887	19.745	0.236
Mol. weight	173	240.8	...	193	270	...	133.5	203	...	156	228	...
Sp. gr. at 60° F.	0.8077	0.8547	...	0.8238	0.8710	...	0.7714	0.8359	...	0.7933	0.8452	...
Moles sampled	0.9547	0.3682	...	0.9535	0.3838	...	0.9459	0.3438	...	0,7933	0.4726	...
Cc. sampled	64.8	35.21	...	66.12	36.39	...	71.80	37.95	...	53.53	46.74	...
$Z = PV/NRT$	1.385	1.950	...	1.668	2.282	...	0.921	1.340	...	1.172	1.720	...
	1047 Lb., 200° F.			1600 Lb., 200° F.			1907 Lb., 200° F.			2500 Lb., 200° F.		
Methane	91.570	20.640	4.437	91.560	28.879	3.170	91.307	33.335	2.740	91.108	39.956	2.280
Ethane	4.088	2.906	1.407	4.013	3.336	1.203	3.992	3.634	1.098	3.977	3.933	1.011
Propane	1.755	2.456	0.715	1.714	2.914	0.588	1.687	2.918	0,578	1.693	3.010	0.563
Butanes	1.186	3.274	0.362	1.165	3.378	0.345	1.152	3.289	0.350	1.199	3.071	0.390
Pentanes	0.607	3.545	0.171	0.594	3.163	0.188	0.629	3.203	0.196	0.635	2.787	0.228
Hexanes	0.386	5.352	0.0721	0.450	5.281	0.085	0.461	4.184	0.110	0.501	3.907	0.128
Heptanes and heavier	0.409	61.828	0.00662	0.504	53.050	0.0095	0.773	49.437	0.0156	0.886	43.337	0.0204
Mol. weight	...	208.7	...	110	208	...	114	210	...	116	211.5	...
Sp. gr. at 60° F.	...	0.8346	...	0.7447	0.8354	...	...	0.8340	...	0.7501	0.8383	...
Moles sampled	0.4846	0.1560	...	0.7579	0.1702	...	0.7152	0.1490	...	0.844	0.3507	...
Cc. sampled	220.63	37.63	...	192.07	31.58	...	151.84	28.71	...	133.01	55.65	...
$Z = PV/NRT$	1.077	0.572	...	0.917	0.672	...	0.913	0.830	...	0.890	0.898	...
	3560 Lb., 200° F.			3792 Lb., 200° F.			3792 Lb., 200° F.			4957 Lb., 200° F.		
Methane	89.919	49.043	1.833	89.703	51.425	1.744	89.878	...	...	88.333	59.384	1.487
Ethane	3.846	4.163	0.924	3.853	4.047	0.952	3.846	...	...	3.961	4.104	0.965
Propane	1.721	2.708	0.636	1.741	2.583	0.674	1.730	...	...	1.912	2.426	0.788
Butanes	1.300	2.806	0.463	1.303	2.538	0.513	1.293	...	...	1.417	2.248	0.630
Pentanes	0.791	2.407	0.329	0.790	2.210	0.357	0.813	...	...	0.903	1.838	0.491
Hexanes	0.654	3.155	0.207	0.652	2.836	0.230	0.696	...	...	0.922	2.241	0.411
Heptanes and heavier	1.768	35.719	0.050	1.957	34.362	0.057	1.744	...	...	2.555	27.758	0.0921
Mol. weight	121	217	...	128	214	...	128	...	...	142.5	227.5	...
Sp. gr. at 60° F.	0.7568	0.8394	...	0.7638	0.8379	...	0.7640	...	...	0.7764	0.8452	...
Moles sampled	0.7409	0.2258	...	0.9449	0.2911	...	0.7327	...	...	0.5571	0.2509	...
Cc. sampled	83.41	32.92	...	101.24	40.35	...	...	...	...	48.73	30.85	...
$Z = PV/NRT$	0.906	1.172	...	0.919	1.188	...	...	...	...	0.978	1.378	...
	5402 Lb., 200° F.			5737 Lb., 200° F.			6740 Lb., 200° F.			7470 Lb., 200° F.		
Methane	87.750	61.270	1.432	86.970	63.185	1.376	84.037	67.940	1.237	84.119	71.051	1.184
Ethane	3.880	3.898	0.996	3.861	4.012	0,962	3.843	4.007	0.959	3.774	3.968	0.951
Propane	1.781	2.072	0.860	1.730	2.289	0.756	1.806	2.066	0.874	1.831	2.104	0.869
Butanes	1.372	2.092	0.656	1.533	2.127	0.721	1.471	1.959	0.751	1.465	1.845	0,794
Pentanes	0.876	1.645	0.532	0.912	1.707	0.534	1.988	1.502	0.648	1.032	1.440	0.717
Hexanes	0.841	2.078	0.405	0.969	1.998	0.485	0.953	1.763	0.540	1.091	1.654	0.640
Heptanes and heavier	3.500	26.946	0.130	4.025	24.685	0.163	5.902	20.762	0.284	6.688	17.938	0.373
Mol. weight	143.7	225	...	149.3	230	...	159.1	233.5	...	172.5	241.5	...
Sp. gr. at 60° F.	0.7807	0.8436	...	0.7859	0.8471	...	0.7943	0.8458	...	0.8035	0.8498	...
Moles sampled	0.6876	0.4663	...	0.6934	0.5052	...	0.5595	0.3962	...	0.8507	0.3774	...
Cc. sampled	65.80	55.50	...	57.64	61.19	...	43.04	43.67	...	65.29	38.79	...
$Z = PV/NRT$	1.170	1.453	...	1.079	1.570	...	1.172	1.680	...	1.297	1.736	...
	7905 Lb., 200° F.			7965 Lb., 200° F.			8078 Lb., 200° F.					
Methane	83.465	71.990	1.159	83.180	76.346	1.090	83.317	71.871	1.159			
Ethane	3.879	3.996	0.971	3.907	3.987	0.978	3.898	3.965	0.983			
Propane	1,852	2.139	0.866	1.874	2.061	0.909	1.833	2.110	0.868			
Butanes	1.496	1.726	0.867	1.551	1.704	0.910	1.482	1.811	0.818			
Pentanes	1.059	1.330	0.797	1.057	1.255	0.842	1.099	1.494	0.736			
Hexanes	1.080	1.532	0.705	1.095	1.450	0.755	1.176	1.551	0.758			
Heptanes and heavier	7.169	17.286	0.415	7.337	13.197	0.556	7.195	17.200	0.418			
Mol. weight	181	247	...	180	239.7	...	179	253	...			
Sp. gr. at 60° F.	0.8138	0.8608	...	0.8123	0.8504	...	0.8081	0.8586	...			
Moles sampled	0.8616	0.2524	...	0.6792	0.5235	...	0.4844	0.1797	...			
Cc. sampled	66.60	27.28	...	52.23	49.70	...	39.45	19.23	...			
$Z = PV/NRT$	1.382	1.932	...	1.385	1.712	...	1.488	1.955	...			

[a] Pressure in pounds per square inch.

[b] Equilibria determined with 9374 lb./sq. in. abs. vapor phase as a system.

served to assist in this consideration and in constructing the equilibrium constant lines as drawn. The equilibrium constants of methane and of heptanes and heavier for the miscellaneous mixtures of League City natural gas and Billings crude oil were added to the 120° F. isotherm. The variations of the constants for the miscellaneous mixtures show a definite effect of composition on the system. The equilibrium constants as originally determined by Katz and Hachmuth (*2*) for an Oklahoma City Wilcox crude oil and natural gas were also added to both the 120° and 200° F. isotherms for comparison.

The plot in Figure 4 of the mole fraction of vapor in the equilibrium cell at various pressures shows that 120° and 200° F. were

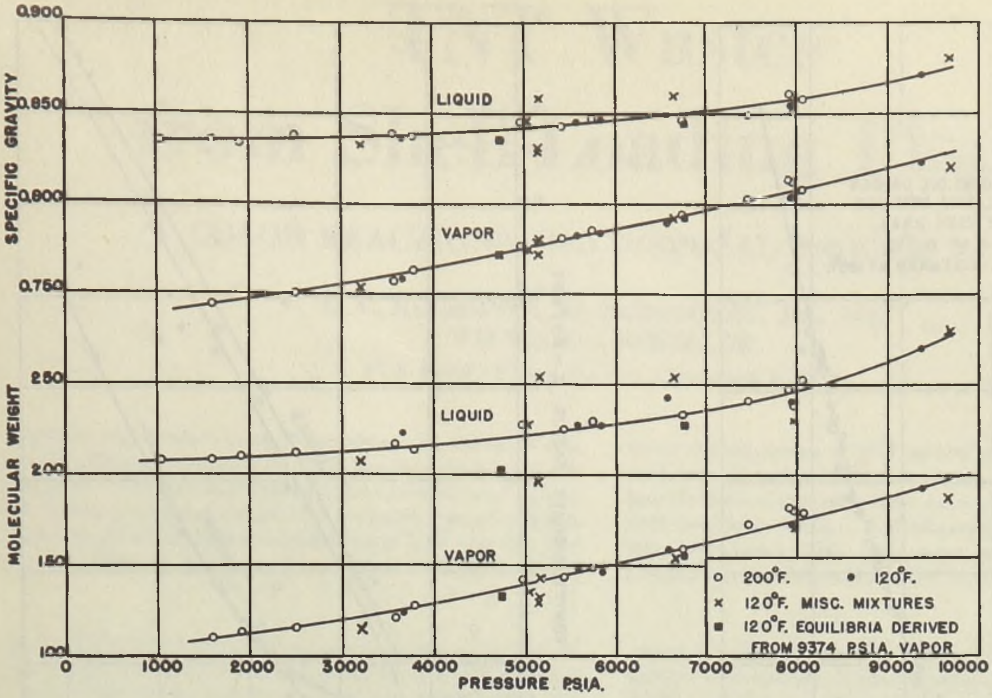

Figure 5. Molecular Weights and Specific Gravities of Heptanes and Heavier Fractions

Table IV. Proportion of Cell Contents in Vapor Phase at Various Pressures and Temperatures

Pressure, Lb./Sq. In. Abs.	Temp., ° F.	Mole Fraction Vapor[a] by: Methane balance	Mole Fraction Vapor[a] by: Heptanes and heavier balance
3566	120	0.748	0.741
5581	120	0.741	0.728
5831	120	0.718	0.703
6580	120	0.727	0.731
7940	120	0.765	0.753
9374	120	0.871	0.857
1047	200	0.853	0.859
1600	200	0.832	0.838
1907	200	0.825	0.828
2500	200	0.804	0.807
3560	200	0.784	0.785
3792	200	0.776	0.781
4957	200	0.751	0.742
5402	200	0.758	0.764
5737	200	0.754	0.754
6740	200	0.818	0.786
7470	200	0.770	0.957
7905	200	0.795	0.810
7965	200	0.697	0.700
8078	200	0.807	0.808
4725[b]	120	0.788	0.792
6752[b]	120	0.800	0.803

[a] Mole fraction vapor = $(Z_n - X_n)/(Y_n - X_n)$
where Z_n = mole fraction component in composite
Y_n = mole fraction component in vapor phase
X_n = mole fraction component in liquid phase

[b] Derived system.

above the critical temperature of the constant composition mixture. As the mole fraction vaporized for this plot was computed (Table IV) by both a methane and a heptanes and heavier balance, the few points not on the curve indicate an error in some of the mole percentages of methane or of heptanes and heavier. The extrapolated portions of the curves at the higher pressures are based in part on a study of both the variation in the phase compositions and the equilibrium constants with pressure. From this extrapolation it appears that the cell contents were all vapor at approximately 9200 pounds per square inch absolute for 200° F. and 10,500 pounds for 120° F.

In Figure 5 the molecular weight and specific gravity of the heptanes and heavier fraction are shown as a function of pressure, and in Figure 6, as a function of each other. Within the accuracy of the data it does not appear that temperature effect on these two properties may be established. These data are particularly useful in defining the accuracy of the heptanes and heavier equilibrium constant and for the implication they may extend to reservoir studies showing, for example, that very heavy crude oil may have been in the vapor phase at one time or another. This is illustrated by the vapor phase analysis in Table III for the sample at 8078 pounds and 200° F. The vapor phase contains 7.195 mole per cent of heptanes and heavier, which is 43% by weight, and has a molecular weight of 181 and specific gravity of 0.8138. This vapor phase could, upon pressure reduction, form a liquid phase similar in composition to the composite analyses of many producing crude-oil reservoirs during the period of initial discovery and development.

In Figure 7 the compressibility of each phase is shown as computed from the displaced volumes, a direct measurement. The mole quantity of each sample is an indirect measurement partly dependent upon the molecular weights of the heptanes and heavier fractions which were determined by the cryoscopic method. These data aid in deciding whether a liquid phase sample may have been contaminated with some gas phase during displacement of the sample. The ratio of vapor to liquid compressibility, multiplied by the ratio of mole fraction of vapor to mole fraction of liquid from Figure 4 gives the ratio of vapor volume to liquid volume in the system at a given pressure and temperature.

Table V. Examination of Heptanes and Heavier Fractions

	Vapor Phase at 9374 Lb.[a] and 120° F.	Liquid Phase[b] at 6752 Lb. and 120° F.	Liquid Phase at 9374 Lb. and 120° F.	Billings Crude Oil
Mol. weight	193	22	270	200.8
Sp. gr. at 60° F.	0.8238	845	0.8710	0.8285
% evapd. at 580° F.	62.0	49.3	39.0	55.0
Sp. gr. at 60° F.	0.789	0.801	0.804	0.791
Sp. gr. of residue at 60° F.	0.879	0.886	0.916	0.886
Viscosity, centistokes				
100° F.	0.29	0.76[c]	1.80	0.454
130° F.	0.148	0.197	0.65	0.203
Viscosity, Saybolt sec.				
100° F.	139	351[c]	832	210
130° F.	78	98	299	101
Conradson carbon of 580° F. residue		0.64 (mixture)		
Appearance at room temp.	Light red brown & yellowish crystals, wax	Chunks of wax, dark yellowish brown	Black, viscous	Dark

[a] Pressure in pounds per square inch absolute.

[b] Liquid phase obtained by reducing pressure on 9374 psia vapor phase.

[c] Difficult to obtain duplicate results—wax may not have melted.

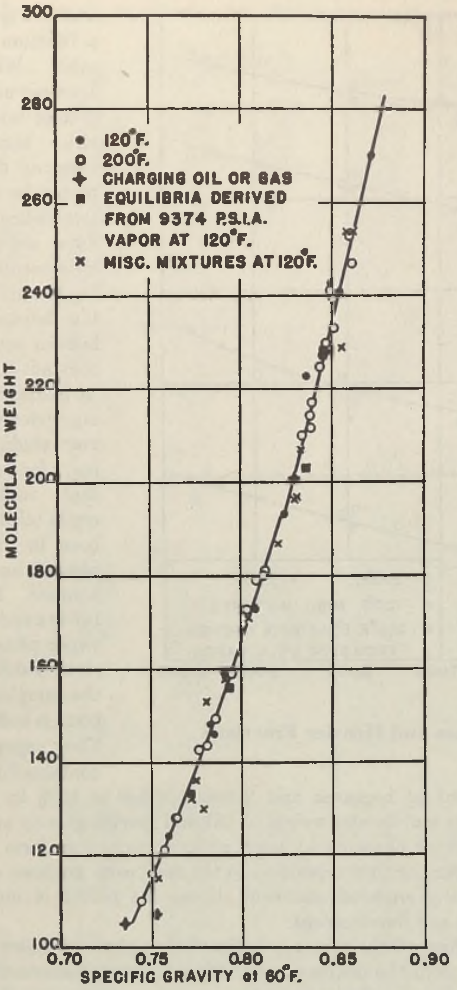

Figure 6. Relation of Specific Gravity to Molecular Weight for Heptanes and Heavier Fractions

The determinations for the fixed composition mixture were considered to be a consistent set of equilibria. It was therefore decided to alter the constant composition system by removing at some high pressure the liquid phase from the system and then, by lowering the pressure of the remaining vapor phase and taking advantage of the retrograde condensation, to form a new vapor-liquid equilibrium. Accordingly, two sets of equilibria were measured in which the 9374 pound–120° F. equilibrium liquid phase was removed. The pressure was lowered to 6752 and 4725 pounds per square inch absolute, respectively, and the equilibrium data were measured.

Significant changes were noted in the molecular weights, specific gravities, and other properties of the heptanes and heavier fractions as listed in Table V. At 4725 pounds pressure the liquid phase of the derived system had a molecular weight about 18 points lower than the smoothed value of 220 for the parent system at the same pressure. The equilibrium constants were, however, not significantly different from those of the parent system at a corresponding pressure. This suggested that the characteristic of the heptanes and heavier fraction was not so important at these equilibrium conditions. A study of the phase compositions showed that the distribution of the components was not materially changed by removing the liquid phase at 9374 pounds per square inch absolute, although the molecular weight of the heptanes and heavier fraction was changed.

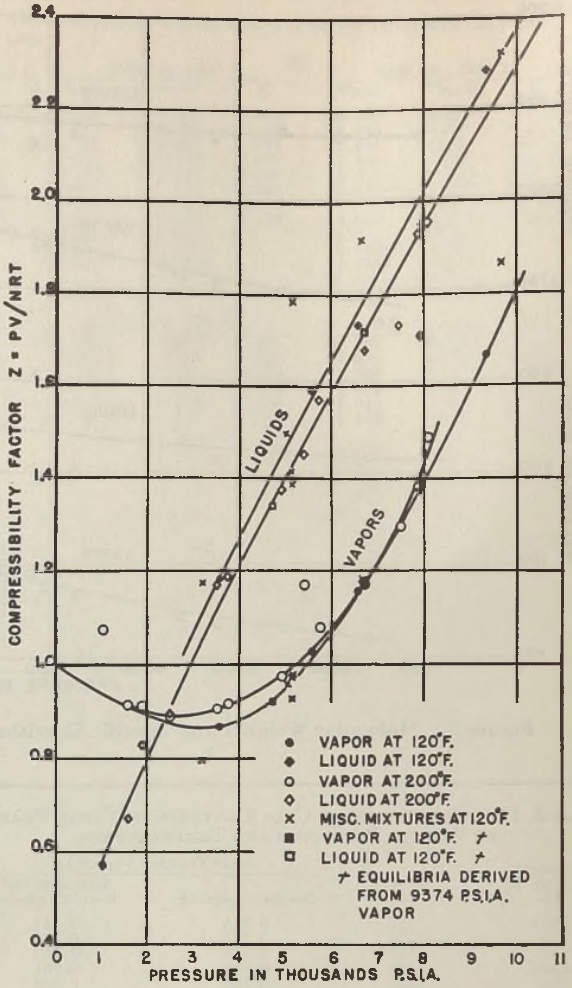

Figure 7. Compressibility, $Z = PV/NRT$, of Equilibrium Phases

A phenomenon encountered in all high-pressure vapor phase samples was the appearance of colored hydrocarbons. At very high pressures the condensed liquid in the analytical fractionating column kettles was like a light lube oil in color. The material was colored as it came from the equilibrium cell, and the degree of color which it showed was roughly an indication of the pressure of the equilibrium—the higher the pressure the darker the liquid.

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TNT Wastes from Shell-Loading Plants

COLOR REACTIONS AND DISPOSAL PROCEDURES

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This study was made to assist in solving the problem of the disposal of liquid wastes from TNT bomb- and shell-loading plants. The factors affecting the conversion of alpha-TNT in these wastes to a colored derivative were studied; it was found that natural degradation of TNT was too slow for application to the treatment of wastes. Small quantities of both forms of TNT reduce the rate of biochemical oxidation in polluted waters without reduction of TNT. Interference with biological treatment prevents treatment with domestic sewage. Soil absorption and activated carbon treatment were the most promising procedures studied for the removal of TNT from these wastes.

AT SEVERAL shell- and bomb-loading plants in the United States, the problem of disposing of alpha TNT[1] (2,4,6-trinitrotoluene) waste waters arose. These waste waters are produced when the kettles for melting TNT are washed out and thoroughly cleaned with steam and water. The water solution of the TNT is collected in a concrete tank where most of the TNT crystallizes out and can be removed. However, the overflow from these tanks, in most cases, is allowed to flow through open drainage ditches to the nearest creek or stream. The pollution from TNT in the ditches and very small streams is evidenced by the dark red color of the water.

During an inspection at several of these plants, the opinion was expressed by those in authority that the TNT in aqueous solution was decomposed and destroyed by two reactions in the water. The first method of destruction suggested was photochemical and chemical reaction induced by the sun; the second was biochemical. No evidence was submitted, however, that either of these reactions was effective. It was also suggested that infiltration into soil would effectively remove and destroy the TNT, but again no evidence was available to indicate to what extent this could be depended upon.

These wastes are neutral, contain TNT in concentrations up to about 100 p.p.m., and may have up to 1.0 or 2.0 p.p.m. of nitrotoluene sulfonates. Water containing 5 p.p.m. of TNT will kill fish, and is considered unfit for human consumption. These wastes are different from those from TNT manufacture. Nevertheless, the previous paper on TNT wastes (*3*) from manufacture indicated the stability of the nitrotoluenes and some of the difficulties of treatment. The present study was made to assist in the safe and economical disposal of TNT wastes from loading plants.

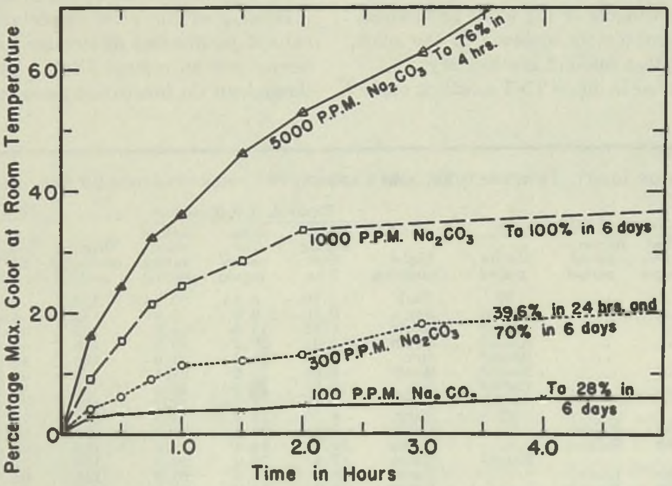

Figure 1. Effect of Carbonate Concentration on Carbonate TNT Color Development in a Solution Containing 126 P.P.M. of TNT

The fact that TNT waste in the drainage ditches at shell-loading plants was red while fresh TNT solutions are uncolored suggested that the waste was reacting or decomposing. An experiment with uncolored TNT was therefore started. Duplicate portions of tap water (*A*), polluted water (75% tap, 25% sewage plant effluent) (*B*), and activated sludge plant effluent (*C*) were dosed so that they all contained 26 p.p.m. of TNT. One set of samples was held in the dark, and the other in direct sunlight as long as possible each day.

Samples *A*, *B*, and *C*, held in the dark at 20° C., showed no perceptible change in TNT concentration during an 80-day period by the spectrophotometric method for α-TNT and colored TNT (*2*). The maximum extinction values observed on direct examination during the 80-day period were 0.14 for *A* and *B* and 0.35 for *C*. In other words, the slight trace of color formed in the dark gave practically no indication that TNT was present. It was concluded that, in the dark, TNT in polluted water solutions was not altered materially in 80 days at ordinary temperatures.

The samples exposed to intermittent sunlight progressively increased in color, and at the end of 80 days had extinctions at 460μ of 1.84, 2.00, and 1.88 for *A*, *B*, and *C*, respectively. This color is due to the conversion of α-TNT to the colored complex (Table I). These data indicate the course of the reaction in terms of alpha and the combined or colored TNT derivative, and show that α-TNT decreased from 26 to 5–9 p.p.m. and the colored form increased from 0 to 10–11 p.p.m. The total TNT (sum of both forms) decreased slowly; 65 to 75% of the original TNT remained after 80 days.

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[1] Wherever TNT is mentioned in this paper, alpha TNT is meant.

Table I. Estimates of Alpha and Colored TNT in Solutions Exposed to Sunlight at Room Temperature

Sunlight Exposure, Days	Colored TNT[a], P.P.M.			Alpha TNT[b], P.P.M.			Total TNT Remaining, P.P.M.		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
0	0	0	0	26.1	25.5	26.5	26.1	25.5	26.5
2	1.7	1.7	2.3	25.2	24.5	25.4	26.9	26.2	27.7
7	2.3	2.2	3.7	25.0	21.1	19.4	27.3	23.3	23.1
13	3.5	3.7	4.4	19.4	18.8	18.3	22.9	22.5	22.7
20	4.4	4.5	5.2	20.9	18.8	16.8	25.3	23.3	22.0
28	4.1	4.8	5.9	20.0	17.2	14.2	24.1	22.0	20.1
35	6.5	5.9	6.0	17.2	16.0	14.2	23.7	21.9	20.2
49	7.1	9.1	9.4	14.9	11.8	12.0	22.0	20.8	21.4
80	10.0	11.0	10.7	9.4	5.6	6.7	19.4	16.6	17.4

[a] Based on the color produced on standing and the carbonate TNT complex extinction correlation at 460μ.

[b] Based on the net extinction due to sulfite-hydroxide treatment at 505μ.

COLORED TNT COMPLEX IN WATER CONTAINING NORMAL CARBONATE

Data on the effect of carbonate concentration, temperature, and light upon the formation of colored TNT derivative are given in Table II. The term "equivalent extinction" is used for the extinction observed at a dilution multiplied by the dilution factor.

Using the maximum extinction values obtained at room temperatures throughout the period of observation as 100%, the percentage color intensities were calculated. These percentages are plotted to show the effects of various factors in Figures 1, 2, and 3. Figure 1 illustrates the maximum color developed at room temperature in the presence of ordinary daylight (but no direct sunlight) for 5 hours with variations in carbonate concentration; it demonstrates the great importance of carbonate or a similar constituent in the solution for rapid color formation.

The four lower curves of Figure 2 show the effect of temperature on color formation in the TNT solution containing 300 p.p.m. of sodium carbonate. Unfortunately the light conditions were not similar for all of these samples. *H* and *I* were held in the dark; *D*, *J*, *K*, and *M* were held in daylight in the laboratory. Even so, the temperature was the most important factor and gave color results increasing with temperature for the first two hours.

The lower curve of Figure 3 demonstrates that in the absence of sodium carbonate the effect of sunlight was negligible. With solutions containing 300 and 1000 p.p.m. of sodium carbonate, the curves showing the rate of color formation in sunlight are more erratic and have minor fluctuations due apparently to changes in intensity of sunlight. On the whole, however, these curves follow fairly closely the trend noted in the absence of direct sunlight. The data in Figures 1, 2, and 3 indicate that temperature and chemical constituents of the water and stream bottom are the most important factors involved in the color reaction in TNT solutions and that sunlight is secondary.

To follow the progressive change in dilute TNT solutions under some of the pertinent conditions of the last experiment, another experiment was set up. The data (Table III) indicate again that pH and chemical constituents in the water and light conditions influence the progressive change in dilute TNT solutions. The alpha TNT was converted to the colored addition product in all cases, and the rate of this reaction increased with the carbonate concentration and with sunlight. The maximum concentration of the colored form was produced after one day in the presence of 1000 p.p.m. of carbonate in this experiment. The rate of reduction in total TNT in this experiment was not so great as the change from one form to the other. When the experiment was terminated after 36 days, from 53.1 to 73.0% of the original TNT remained in the various portions, largely as the colored addition product. This demonstrates again that these slow decomposition reactions produced by the concentration of sodium carbonate used here cannot be depended upon as a satisfactory method of destroying TNT.

EFFECT OF TNT ON NATURAL BIOCHEMICAL PURIFICATION IN STREAMS

An earlier study (*3*) showed that wastes from TNT manufacture in considerable concentration had no B.O.D. and adversely affected the B.O.D. reaction. These earlier data were obtained by crude methods before the method for determining TNT concentration and B.O.D. reaction separately had been devised Consequently, a number of experiments were performed on sewage dilutions to determine the extent of the interference of small quantities of TNT on the natural biochemical oxidation of organic matter. Table IV lists the data obtained in one experiment with concentrations of 1.17 to 80 p.p.m. of TNT in 1% sewage in a mineralized dilution water (*1*). The B.O.D. data indicate that all concentrations of TNT down to 1.17 p.p.m. had a decided retarding effect on the observed B.O.D. throughout the 6-day observation period. The mean percentage of the normal B.O.D. that can be expected with short incubation periods (up to 6 days) in the presence of TNT has been calculated from the data. In dilutions having oxygen depletions up to about 4 p.p.m., 1 to 2 p.p.m. of TNT reduce the B.O.D. values 15 to 30% below normal. As the TNT concentration increases, a smaller percentage of the normal B.O.D. can be expected. With 80 p.p.m. of TNT, only 44% of the normal B.O.D. was obtained.

Although some fluctuations in TNT concentration are shown during the incubation period, 60 to 90% of the initial concentration remained in these samples after 25 days. These data suggest that TNT is not attacked biochemically to any appreciable extent, regardless of the initial concentration.

Because of the great importance of the B.O.D. reaction in natural purification in streams, the above experiment was also carried out on colored TNT. The oxygen depletions obtained throughout the incubation period in this experiment decreased as

Table II. Effect of Light, Temperature, and Carbonate Concentration on Colored TNT Formation

Sample	Observation Period, Days	Na Carbonate Added, P.P.M.	Temp. of Sample, ° C.			Light Condition	Equivalent Extinction[a]			TNT Concn., P.P.M.				Original TNT Accounted for, %
			First 2–3½ hours	Remainder of period	Entire period		Max. during first 3 hr.	Max. for entire period	End of observation period	Original uncolored α-TNT	Final			
											Colored TNT complex	Uncolored α-TNT	Total TNT in soln.	
A	37	None	..	....	20	Dark	0.10	0.15	0.15	126	0.5	125.5	126	100
B	37	None	..	....	Room[b]	Sun	0.10	9.0	9.0	192	4.3	147.0	151.3	78.4
C	37	100	..	....	Room[b]	Room	1.32	13.6	13.6	192	95.5	61.0	156.5	81.1
D	32	300	..	....	Room[b]	Room	5.05	20.2	20.2	126	80.8	24.8	105.6	83.8
E	32	300	..	....	Room[b]	Sun	5.45	21.6	21.6	126	86.0	18.9	104.9	83.3
F	32	1000	..	....	Room[b]	Room	9.25	27.5	21.8	126	88.0	4.6	92.6	73.5
G	32	1000	..	....	Room[b]	Sun	10.75	26.0	21.4	126	80.2	10.0	90.2	71.6
H	31	300	..	....	10–12	Dark	2.80	17.7	17.7	126	72.9	50.1	123.0	97.6
I	31	300	..	....	37	Dark	4.70	19.2	19.2	126	73.7	17.8	91.5	72.6
J	29	300	50	Room[b]	....	Room	9.1	20.8	20.8	126	78.9	16.8	95.7	75.9
K	29	300	80	Room[b]	....	Room	24.0	23.4	23.4	126	88.5	18.1	106.6	84.6
L	26	5000	..	....	Room[b]	Room	17.4	20.0	20.0	126	77.5	8.5	86.0	68.2
M	27	1000	80	Room[b]	....	Room	33.5	33.5	25.0	126	95.7	11.6	107.6	85.1
N	27	2000	80	Room[b]	....	Room	31.0	31.0	26.0	126	97.5	11.6	109.1	86.6

[a] *E* × dilution factor (for sample as result of treatment described and without sulfite-hydroxide treatment).

[b] Varied from about 15° to 26° C.

TABLE III. PROGRESSIVE CHANGE IN DILUTE TNT SOLUTIONS UNDER VARIOUS CONDITIONS

Time of Reaction	% of Initial TNT (42.6 P.P.M.) Remaining														
	As Colored TNT					As Alpha-TNT					Colored + Alpha				
	Room			Sunlight		Room			Sunlight		Room			Sunlight	
	300[a]	1000[a]	5000[a]	300	1000	300	1000	5000	300	1000	300	1000	5000	300	1000
Initial	0	0	0	0	0	100	100	100	100	100	100	100	100	100	100
4 hr.	6.1	25.6	67.6	..	..	93.2	76.3	31.0	...	...	99.3	101.9	100	...	...
1 day	20.4	61.3	77.9	44.1	84.5	71.4	35.0	9.6	52.8	9.9	91.8	96.2	87.6	96.9	94.0
3 days	33.8	70.7	70.0	52.1	65.0	53.0	18.3	8.2	33.8	8.0	91.5	89.0	78.2	86.8	72.8
4 days	..	74.4	62.2	..	67.6	...	16.0	6.6	...	7.0	...	90.4	68.8	...	74.6
5 days	50.7	..	..	55.6	..	41.1	...	...	20.4	...	91.5	...	...	76.5	...
7 days	62.7	70.4	59.6	..	..	30.8	7.5	4.9	...	...	93.4	77.9	64.4	...	...
14 days	60.1	63.6	50.9	55.6	48.4	21.1	6.8	4.0	10.1	6.1	81.2	70.4	54.9	65.7	54.5
26 days	66.0	58.7	52.1	56.6	50.0	12.4	6.3	4.7	5.4	3.8	78.4	65.0	56.8	61.9	53.8
36 days	66.0	58.7	50.7	49.8	47.4	7.0	6.3	4.9	5.4	5.6	73.0	65.0	55.6	55.2	53.1

[a] Sodium carbonate concentration, in p.p.m.

TABLE IV. BIOCHEMICAL OXYGEN DEPLETIONS AND (UNCOMBINED) α-TNT CONCENTRATIONS IN A SEWAGE DILUTION AFTER VARIOUS PERIODS OF INCUBATION

Days Incubated at 20° C.	A, 1% Sewage	B, 1% Sewage + 80 P.P.M. TNT				C, 1% Sewage + 35 P.P.M. TNT				D, 1% Sewage + 22.5 P.P.M. TNT				E, 1% Sewage + 10.9 P.P.M. TNT			
	Oxygen depletion, p.p.m.	Oxygen depletion, p.p.m.	TNT concn., p.p.m.	% of normal oxygen depletion	% of TNT remaining	Oxygen depletion, p.p.m.	TNT concn., p.p.m.	% of normal oxygen depletion	% of TNT remaining	Oxygen depletion, p.p.m.	TNT concn., p.p.m.	% of normal oxygen depletion	% of TNT remaining	Oxygen depletion, p.p.m.	TNT concn., p.p.m.	% of normal oxygen depletion	% of TNT remaining
1	1.69	0	70	0	87.5	0.81	30.8	47.9	88.0	0.93	18.8	55.0	83.6	1.12	8.5	66.3	78.0
2	2.38	1.23	73	51.7	91.2	1.36	29.8	57.1	85.1	1.28	21.2	53.8	94.2	1.38	9.6	58.0	88.1
3	3.14	1.33	78.2	42.3	97.7	1.65	33.4	52.5	95.3	1.64	19.7	52.2	87.6	1.87	9.2	59.6	84.4
4	3.49	1.47	81.8	42.3	102.2	1.66	33.7	47.8	96.3	1.78	21.8	51.3	96.9	2.18	10.4	62.8	95.4
6	3.83	1.57	71	41.0	88.7	2.28	29.6	59.5	84.6	2.12	21.2	55.4	94.2	2.51	9.4	65.5	86.2
10	...	..	75.3	..	94.1	..	31.7	..	90.6	..	19.8	..	88.1	..	9.6	..	88.1
25	...	..	73.3	..	91.6	..	30.6	..	87.4	..	18.9	..	84.1	..	9.1	..	83.5
Mean[a]				44.3				53.0				53.5				62.4	

	1% Sewage	F, 1% Sewage + 3.5 P.P.M. TNT				G, 1% Sewage + 1.8 P.P.M. TNT				H, 1% Sewage + 1.17 P.P.M. TNT			
	TNT based on E observation, p.p.m.												
1	0.228	1.04	1.70	61.5	48.6	1.16	1.01	68.6	56.1	1.51	0.537	89.3	45.9
2	0.205	1.59	1.95	66.8	55.7	1.53	0.91	64.3	50.6	2.03	0.594	85.3	50.8
3	0.274	2.14	2.06	68.2	58.9	2.28	1.08	72.6	60.0	2.74	0.685	87.3	58.5
4	0.183	2.60	2.55	74.9	72.9	2.67	1.54	76.9	85.6	2.76	0.742	79.5	63.4
6	0.217	2.77	2.41	72.3	68.9	2.84	1.13	74.2	62.8	3.48	0.615	86.2	52.6
10	0.125	..	2.82	..	80.6	..	1.16	..	64.4	..	0.696	..	59.5
25	[b]	..	2.59	..	74.0	..	1.11	..	61.7	..	[b]	..	..
Mean[a]				68.7				71.3				85.5	

[a] First 6 days.
[b] Insufficient sample for the determination.

TABLE V. BIOCHEMICAL OXYGEN DEPLETIONS AND TNT CONCENTRATIONS (COLORED AND UNCOMBINED) IN A SEWAGE DILUTION AFTER VARIOUS PERIODS OF INCUBATION

Days Incubated at 20° C.	B, 1% Sewage + 60.6 P.P.M. TNT				C, 1% Sewage + 30.4 P.P.M. TNT				D, 1% Sewage + 15.2 P.P.M. TNT				E, 1% Sewage + 7.56 P.P.M. TNT			
	Oxygen depletion, p.p.m.	TNT Concn., P.P.M.			Oxygen depletion, p.p.m.	TNT Concn., P.P.M.			Oxygen depletion, p.p.m.	TNT Concn., P.P.M.			Oxygen depletion, p.p.m.	TNT Concn., P.P.M.		
		Colored	Alpha	Total		Colored	Alpha	Total		Colored	Alpha	Total		Colored	Alpha	Total
Initial[a]	..	45.5	15.1	60.6	..	22.8	7.6	30.4	..	11.4	3.8	15.2	..	5.68	1.88	7.56
Initial[b]	..	51.5	4.6	56.1	..	22.6	5.7	28.3	..	11.6	1.9	13.5	..	5.80	0.89	6.69
3	0.18	43.0	8.7	51.7	0.68	21.0	6.3	27.3	..	11.2	1.8	13.0	1.08	5.40	0.63	6.03
5	0.40	43.8	8.7	52.5	0.84	22.6	7.2	29.8	1.47	11.4	3.4	14.8	1.50	5.60	1.45	7.05
7	0.43	...	...	..	1.05	...	..	..	1.14	..	..	..	1.45	..	..	..
10	1.70	43.0	11.0	54.0	1.86	23.0	5.5	28.5	1.99	10.8	2.9	13.9	1.83	5.75	1.48	7.23
25	1.98				2.52				2.28				2.20			

	F, 1% Sewage + 3.78 P.P.M. TNT				G, 1% Sewage + 1.89 P.P.M. TNT				H, 1% Sewage + 0.95 P.P.M. TNT				A, 1% Sewage
Initial[a]	..	2.84	0.94	3.78	..	1.42	0.47	1.89	..	0.71	0.24	0.95	...
Initial[b]	..	3.08	0.60	3.68	..	2.18	0.29	2.47	..	0.93	0.15	1.08	...
3	1.14	2.70	0.16	2.86	1.43	1.45	0.00	1.45	2.01	0.98	0.00	0.98	2.00
5	1.55	2.65	0.65	3.30	1.78	1.56	0.25	1.81	2.38	1.00	0.14	1.14	2.52
7	1.55	...	...	..	2.27	...	..	..	2.41	..	..	..	2.79
10	1.97	2.59	0.62	3.21	2.32	1.48	0.37	1.85	2.85	0.96	0.31	1.27	3.15
25	2.32				..				5.40				>8.21

[a] Calculated on basis of mixture prepared.
[b] Observed on basis of analytical procedure described.

the concentration of TNT was increased. The percentages of normal oxygen depletion for sewage obtained in the presence of colored TNT were calculated from these data and are shown in Table V. The mean percentages of normal depletions for the 3-, 5-, and 7-day periods were calculated and are also shown in Table V. These mean values may be considered as representing the expected biochemical oxidation performance during the period of carbonaceous oxidation. Comparison of these mean percentages with similar values from Table IV for α-TNT indicate that colored TNT is equally as inhibitive of normal biochemical oxidation as the uncolored alpha form. On the basis of these data it must be concluded that rates of natural biochemical purification of organic matter in streams are reduced in the presence of TNT. The retardation to be expected will increase

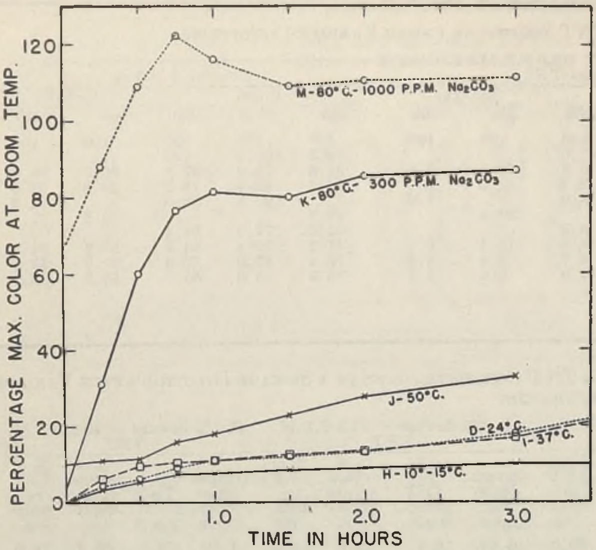

Figure 2. Effect of Temperature on Carbonate TNT Color Development in a Solution Containing 126 P.P.M. of TNT

TABLE VI. RECORD OF α-TNT IN SEWAGE SUPERNATANT

	E (Control)	A	B	C	D
Initial suspended solids, p.p.m.	200	182	161	134	100
Initial TNT, p.p.m.	0	9.75	21.4	35.8	53.7
TNT remaining after:					
4 hr.	0.58[a]	8.1	21.4	35.5	52.0
1 day	0.73[a]	0.8	2.40	4.65	31.0
2 days	0.55[a]	0.55	1.70	3.40	21.0
3 days	0.66[a]	0.16	0.58	2.22	17.6
7 days	0.71[a]	0.05	0.43	1.92	10.1
31 days	1.40[a]	0.46	1.20	0.27	4.0

[a] Color after sulfite-hydroxide treatment, in terms of TNT deducted from readings on all other samples to obtain the net TNT values shown.

with increasing concentrations of TNT, regardless of the form in which it is present. Roughly 0.6 to 0.8 p.p.m. may be considered the critical concentration below which no substantial retarding action is expected to occur on natural purification.

Data on colored TNT remaining through the first 10-day period (Table V) indicate that no reduction of colored TNT can be expected during the natural biochemical purification process. While there was a slight reduction in α-TNT (Table IV), particularly in the lower concentrations, there was no parallel reduction in the colored form. It must be concluded, therefore, that both alpha and colored TNT not only interfere with and reduce the rates of natural purification in streams, but are not attacked biologically and remain for long periods, even in low concentrations.

REMOVAL OF TNT IN SEWAGE

PRIMARY TREATMENT FOR α-TNT. An early experiment showed that the suspended organic matter in sewage removed TNT from solution. To study this phenomenon, increasing quantities of a TNT solution were added to domestic sewage, and the progress of anaerobic digestion was followed. The record of original TNT present and the quantity remaining in the supernatant of these sewage samples for a 31-day period is presented in Table VI.

These data show that almost no TNT was removed from solution during the first 4 hours of contact with sewage, but by the end of 24 hours the largest portion of TNT was removed from solution in samples *A*, *B*, and *C*. In sample *D* the dose of TNT per unit of suspended matter was much higher than in the other samples. Although 21 p.p.m. were removed in the first 24 hours, later removal was very slow and did not reach completion in 31 days. Odor tests on these samples from time to time also indicated that the reduction of the sulfur compounds in the various samples was delayed for longer periods in the samples containing the higher quantities of TNT. In fact, sample *D* had practically no odor for the first 15 days, but at the end of 36 days it had a foul odor that was different from that obtained in normal sludge digestion. After 36 days the pH values of all samples were determined; the solids were then separated from the liquor by centrifuging, and the moisture, volatile matter, and ash contents of the solids were determined:

	E	A	B	C	D
pH	7.27	7.47	7.05	7.05	7.37
Moisture, %	95.1	96.0	95.9	97.5	96.3
Volatile solids, %	61.2	75.5	81.9	68.6	84.7
Ash, %	38.8	24.5	18.1	31.4	15.3

These data indicate that digestion time is increased with TNT concentration. Apparently, little TNT is needed to slow down the digestion. Consequently, although sewage seems to lend itself well to the removal of TNT from solution, difficulties would be encountered later in the digestion of the sludge.

PRIMARY TREATMENT FOR COLORED TNT. Tests were made with colored TNT solution in domestic sewage similar to those described for α-TNT. Increasing quantities of the colored solution containing a total of 133.7 p.p.m. (103.4 p.p.m. colored and 30.3 p.p.m. alpha) TNT were added to portions of raw domestic sewage, and the following data were obtained:

	A, Control	B	C	D	E
Initial pH of mixt.	7.2	8.05	8.35	8.58	8.89
Initial concn. of suspended solids, p.p.m.	104	95	83	70	52
Initial 5-day B.O.D., p.p.m.	324	294	260	217	162
Initial TNT (total), p.p.m.	0	10.2	26.8	44.9	66.9
TNT remaining after:					
24 hours, p.p.m.	0	7.7	18.9	28.8	49.1
5 days, p.p.m.	0	4.7	19.6	33.8	41.3
24 hours, %	...	75.5	70.5	64.1	73.4
5 days, %	...	46.1	73.1	75.3	61.7

These data indicate poor removal of colored TNT with the domestic sewage solids, and are in contrast to the effectiveness of such treatment for removal of the alpha compound.

ACTIVATED SLUDGE TREATMENT. Experiments on the treatment of sewage containing TNT with activated sludge were made in the laboratory in bottles. When 30 to 40 p.p.m. of TNT in sewage was fed to activated sludge, a reduction in the rate of sewage purification was obtained. Biological observations indicated such a large reduction in the nonzoogloeal microflora and -fauna as a result of TNT that a complete breakdown in the performance of the sludge would be expected from biological observations only. The chemical data showed that the removal of TNT was very slow, that operation of a plant on a normal aeration cycle of 4 to 6 hours would result in a poorly clarified effluent,

TABLE VII. COMPARISON OF RESULTS OF FEEDING COLORED AND α-TNT WITH SEWAGE TO ACTIVATED SLUDGE

	Sewage + α-TNT	Sewage + Colored TNT
Mean sludge suspended solids, p.p.m.	4210	2599
Mean B.O.D. of sewage feed, p.p.m.	365	248
Mean B.O.D. of 24-hr. effluent, p.p.m.	20	10.5
Mean % reduction of B.O.D. after aeration for	57.9[a]	48.5[a]
4.5 hours	86.6	84.1
24 hours	94.4	91.2
Mean TNT fed, p.p.m.	38.0	36.7
Mean TNT in 24-hr. effluent, p.p.m.	0.72	15.5
Mean % reduction in TNT in 24-hr. aeration	98.0	59
Effect on biological counts	Over 90% reduction	No noticeable effect
Effect on settling qualities of sludge	None	None

[a] Immediately after mixing.

and that aeration periods of 24 hours or more would be required for removal of more than 90% of both TNT and sewage B.O.D. To permit easy comparison of the effects of colored and α-TNT in sewage on the activated sludge process, the results of the experiments with both forms are summarized in Table VII. Neither form of TNT had any detectable effect on the settling qualities of the sludge. The colored form had no appreciable effect on biological counts and was only partially removed in the process. In fact, an average of only 59.5% of colored TNT was removed in a 24-hour aeration period compared to 98% removal of α-TNT. The process is unsatisfactory for colored wastes. α-TNT can be satisfactorily removed but at the risk of breaking down the entire process if overdosed. The aeration time would also have to be increased considerably, which would increase the cost of treatment. Consequently, it may be concluded that activated sludge treatment would not be successful for treating TNT wastes in either form.

Percolation through Soil. As soil seepage is used at one plant for disposing of TNT waste, laboratory experiments were performed to determine the effectiveness of this procedure. Data on filtration of the uncolored TNT solution are summarized in Table VIII and indicate great difference in the performance of the different soils. The poorest removal performance was obtained with the sand which removed only 9.6 mg. or 10.5% of the TNT applied. The clay soils filtered slowly, as would be expected, and although they removed considerably more TNT than sand, they did not approach the performance of black garden top soil (sample 3); 234 mg. of TNT were applied to the latter, and it removed 148.1 mg. or 59.8%. Even in this case the percentage removal of TNT had fallen considerably when the experiment was terminated; and the total TNT absorbed represented only 0.10% of the weight of the soil.

To determine to what extent TNT could be washed out of the absorbing soil by fresh water, this experiment was carried further on samples 1 and 4. As it became evident that the absorbing capacity was about exhausted, distilled water was passed through the filter in 100-ml. portions. The quantities of TNT recovered in the wash water on these samples follow:

Mg. TNT Recovered from Distd. Water Washes	Mg. of TNT Recovered Sample 1	 Sample 4
1st 100 ml.	6.75	2.91
2nd 100 ml.	1.32	2.08
3rd 100 ml.	0.26	1.19
4th 100 ml.	0.12	0.91
5th 100 ml.	0.06	0.59
6th 100 ml.	...	0.34
7th 100 ml.	...	0.29
8th 100 ml.	...	0.20
9th 100 ml.	...	0.17
10th 100 ml.	...	0.16
11th 100 ml.	...	0.10
Total	8.51	8.94
Total TNT absorbed, mg.	9.60	61.4
% TNT recovered	88.7	14.6

These data indicate that the TNT is rather easily removed from the sand filter. However, in the case of soil sample 4, eleven washes were required to remove 14.6% of the absorbed TNT. An additional experiment showed that it is much more difficult to wash TNT out of black garden soil (sample 3), once it has been absorbed.

The experiment was repeated with similar soil samples and a solution containing most of its TNT in the colored form. The data are summarized in Table IX. The sand filter removed 66.3 mg. of colored and 38.17 mg. of α-TNT in the fourteen 100-ml. portions of solution filtered. As the previous experiment showed that sand is ineffective for removing α-TNT, it is assumed that most of the 44.87 mg. of α-TNT applied here was converted to the colored form during passage through the sand because of the higher alkalinity of the water (300 p.p.m. sodium carbonate). The various soils in these experiments removed about 47–84% of the TNT applied. The highest removals were again obtained with the black garden soil, which absorbed about 0.14% of its weight of TNT in removing 70.6% of the TNT from 2200 ml. of solution. Comparison between the percentage removals of α-TNT in Table VIII and colored TNT in Table IX indicates that all soils tested were more effective in removing the colored form. Experiments on the removal of colored TNT from the sand filter with distilled water gave variable results. In three experiments with 500 to 1400 ml. of wash water, from 18 to 65% of absorbed TNT was washed out of the sand. These results suggest that it is more difficult to remove colored TNT from soil after absorption than the uncolored α-TNT.

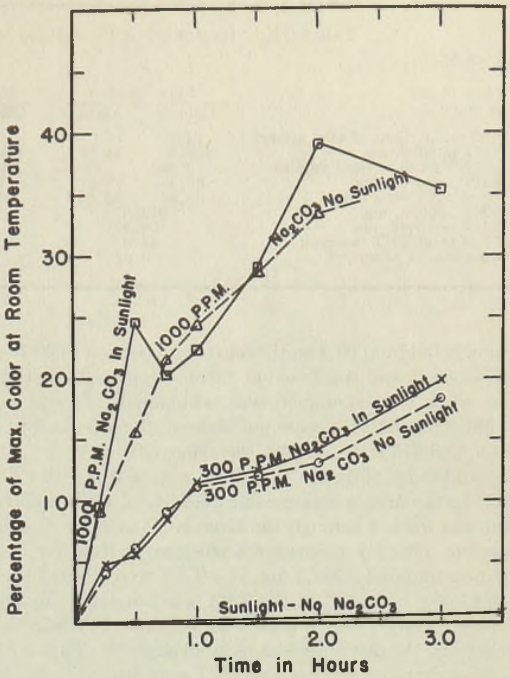

Figure 3. Effect of Sunlight on Carbonate TNT Color Development in a Solution Containing 126 P.P.M. of TNT

Table VIII. Removal of Alpha (Uncolored) TNT from Solution by Filtration through Soil

Soil sample No.	1	2	3	4	5
Description of soil	Filter sand	High-clay soil	Black garden soil	Like 3 but with some clay	Like 4 but with more clay
No. of 100-ml. portions of soln. filtered	5	9	15	9	6
Total TNT applied, mg.	91.5	149.1	234.0	148.2	85.2
Total TNT removed, mg.	9.60	37.6	148.1	61.4	54.4
Mean % TNT removed	10.5	22.9	59.8	45.8	63.8
TNT absorbed, % soil wt. (150 grams)	0.006	0.025	0.10	0.04	0.035

ACTIVATED CARBON TREATMENT

Removal of TNT from Water. Experiments on the treatment of wastes with activated carbon and on filtration through a filter of powdered activated carbon were carried out to determine which procedure would be most effective to remove alpha and colored TNT from waste waters. Using 10 grams of Cliffchar R coarse in such a filter, 100% removal was obtained from a solution containing 130.4 p.p.m. of α-TNT (uncolored) on the first thirteen of the 100-ml. portions filtered. The percentage removal

Table IX. Removal of Combined (Colored) TNT from Solution by Soil Filtration

Soil sample No.	1		2		3		4		5	
Description of soil	Filter Sand		High-Clay Soil		Black Garden Top Soil		Like 3 but with Some Clay		Like 4 but with More Clay	
Form of TNT	Colored	Alpha	Colored	Alpha	Colored	Alpha	Colored	Alpha	Colored	Alpha
No. of 100-ml. portions of soln. filtered	14	14	17	17	22	22	18	18	6	6
Total TNT applied, mg.	172.8	44.87	183.5	51.23	232.3	67.75	186.3	53.28	67.1	17.62
Colored TNT as % of total applied	79.38	...	78.17	...	77.42	...	77.76	...	79.20	...
Total TNT removed, mg.	66.3	38.17	63.3	43.64	148.9	62.95	133.1	51.45	54.7	16.98
Mean % of TNT removed	38.4	85.09	34.5	84.98	63.9	94.85	71.5	96.48	81.5	95.92
Total TNT applied, mg.	217.67		234.73		300.05		239.58		84.72	
Total TNT removed, mg.	104.47		109.94		211.85		184.55		71.68	
Mean % of total TNT removed	48.0		46.8		70.6		77.0		84.6	
TNT absorbed, % of soil wt.	0.07		0.07		0.14		0.12		...	

then slowly fell from 99.3 on the fourteenth portion to 36.7 on the twenty-seventh and continued at this level through the thirtieth portion when the experiment was terminated. In this experiment 391.2 mg. of TNT were put through the filter in 3 liters of solution, and 313.2 mg. or 80% was removed.

Two additional filtration experiments were run with Cliffchar R fine. In the first, a considerable quantity of the fine activated carbon was washed through the filter into the effluent, and this mechanical difficulty reduced the efficiency. However, 3 liters of solution containing 391.2 mg. of α-TNT were filtered through, and 374.1 mg. or 95.6% of the TNT was removed. In the last experiment a larger bed of glass wool was used to retain the fine Cliffchar and the filter rate was reduced slightly. Then 3.5 liters of solution containing 522 mg. of TNT were filtered through, and 482 mg. or 92.6% were removed. On the basis of the α-TNT removed in the last experiment, it may be concluded that the fine activated carbon is about forty-eight times more effective in removing TNT than the best soil sample. Trial experiments on filtration of colored TNT solutions through fine activated carbon filters indicated filter clogging, with such a great reduction in the rate of filtration that the experiments were abandoned. These trials indicated that filtration of the colored solution through carbon would be more difficult and less successful than filtration of α-TNT solutions.

Powdered Activated Carbon. The treatment of TNT solution with powdered activated carbon, as in water purification practice, was tried next. Doses of Cliffchar R fine of 0.3, 0.6, and 0.9 gram were added to liter portions of TNT solution, and the samples were aerated for one hour. The carbon was then separated by filtration through paper, and the TNT remaining in the filtrate was determined:

	121.8 P.P.M. α-TNT			115.4 P.P.M. Colored TNT		
Carbon dose, p.p.m.	300	600	900	300	600	900
TNT removed						
Mg.	82.4	118.3	120.7	46.1	55.4	56.1
Per cent	67.9	97.6	99.5	40.0	48.0	48.7
Mg./g. carbon	274.6	197.8	134.1	153.8	92.3	62.4

These results indicate that treatment with powdered activated carbon is definitely more effective than filtration through carbon. They show further that it is more difficult to treat colored than α-TNT by either method. The same dose of carbon removes only about half as much of the colored form as the alpha form. Mechanical stirring and bubble aeration were found equally effective in removing α-TNT with activated carbon. With vigorous mixing of the carbon in the solution, 5-minute contact is sufficient to remove 98% of α-TNT from ordinary waste solutions with an adequate carbon dose. With slow stirring or mixing, 15 to 30 minutes of contact may be required. When the carbon dose is insufficient, periods of mixing and contact up to 2 hours did not increase the percentage removal significantly over that accomplished in 15 minutes.

Although the doses of carbon required were large (equivalent to about 17–50 grains per gallon of waste), they would be practicable for the volumes of waste at loading plants. About 50,000 gallons of waste per day with the TNT largely in the alpha form might be effectively treated (80 to 90% removal of TNT) with 100 to 300 pounds of activated carbon per day. With carbon selling at about $90.00 per ton, the carbon costs of treatment might be estimated to run from $4.50 to $15.00 per day, depending on the kind of carbon used, the effectiveness of the mixing and holding system provided, and the quantity and form of TNT in solution.

DISCUSSION

In deciding on a corrective procedure for pollution problems at a TNT shell-loading plant, an important factor is the quantity of flow, which is normally on the order of 50,000 gallons per day. This flow is relatively minor compared with flows from TNT manufacturing plants. On the other hand, shell- and bomb-loading plants are frequently located on small streams and may require corrective measures despite the small magnitude of flow involved.

The disadvantage brought out by the study of disposal by seepage through soil is that, sooner or later, the ground will become saturated with TNT and lose its capacity for removal. In the case of treatment with activated carbon, a treatment plant may operate indefinitely with satisfactory results and with only a minor problem of disposal of carbon sludge. In practice, the carbon may easily be mixed with the waste by a 15–30 minute contact period in a diffused air aeration tank. The carbon-treated waste would not have to be filtered but could be passed through a plain settling tank with a 24-hour detention period, or into settling ponds of still larger capacity. Settling in this manner would remove 97% of the carbon from the waste. The small amount of carbon lost in the waste effluent would not be objectionable. The settled carbon sludge could periodically be removed from the settling tank or pond for disposal on burning grounds.

The shell- and bomb-loading plants now in operation are generally temporary and will be abandoned at the termination of the war. Therefore, disposal by seepage through soil offers a simple solution which should be effective for the short time plants are in operation. The practical installation consists of seepage and evaporation ponds of the size necessary to dispose of the wastes at seepage rates experienced in the particular locality. Seepage is supplemented to a varying degree, depending on locality, by evaporation which in some places may approach or even exceed the disposal by seepage.

To prevent a dangerous accumulation of TNT in the bottom of seepage ponds, it is desirable to take successive ponds from service, allow them to dry, and remove deposited TNT for disposal at burning grounds. Although no opinion is offered as to hazards connected with disposal of TNT wastes, reasonable precautions would involve placing the ponds or treatment plant at remote locations and handling all dry sludges with care commensurate to the nature of the sludge.

SUMMARY

The intensity of the color produced in dilute solutions of α-TNT in natural waters is dependent upon the following factors: concentration of TNT, concentration of normal carbonate or alkaline constituents of the water which raise the pH, temperature,

and light conditions. The colored complex seems more stable than the α-TNT, and it is difficult to reverse the reaction, once the colored complex is formed. All water samples containing colored TNT must be examined for TNT in both forms. α-TNT solutions in tap waters of low alkalinity or polluted waters will remain uncolored for 100 days and longer in the dark at 20° C. α-TNT solutions in distilled water can be exposed to sunlight for long periods with the formation of only a trace of colored complex and without other decomposition. With relatively pure or polluted surface waters, from 40 to 55% of α-TNT is converted to the colored form in 80 days at ordinary temperatures in intermittent sunlight. The percentage of colored TNT formed can be increased to 90% or more in one day or less by increasing the alkaline constituents of the water and/or the temperature.

The conversion of α-TNT to the colored form is considered the principal reaction during prolonged storage of TNT solutions. During this conversion, however, there is a slow reduction of total TNT which depends to a large extent upon carbonate concentration or pH and light conditions. In the surface and polluted water samples tested, 65 to 75% of the original TNT remained in one form or the other after 80 days in intermittent sunlight. In water containing 300 to 1000 p.p.m. of normal carbonate, 53 to 55% of the TNT remained (largely in the colored form) after 36 days in intermittent sunlight. This decomposition reaction is considered too slow for practical application.

Concentrations of α-TNT above 1.0 p.p.m. have a retarding effect on the biochemical oxidation of sewage. There is little biochemical removal of TNT as the result of biochemical oxidation in dilute sewage. Colored TNT was equally as inhibitive as α-TNT to normal biochemical oxidation of organic matter during the carbonaceous stage. The study of colored TNT wastes indicated that no reduction of the color can be expected by natural biochemical purification in streams.

Raw domestic sewage at pH values of 7.2 to 7.8 removed concentrations of α-TNT up to about 35 p.p.m. from solution in a 24-hour contact period. The quantity of TNT removed seems to depend upon the suspended organic matter in the sewage. The rate of anaerobic digestion of sewage solids is decreased considerably by the TNT absorbed. It was more difficult to remove colored TNT from solution during primary treatment of sewage than α-TNT.

Even with concentrations of α-TNT as low as 30 p.p.m. in sewage, activated sludge treatment requires aeration periods up to 24 hours for 90% removal of both TNT and B.O.D. Although colored TNT did not inhibit the process as much as alpha, it was not removed so readily.

Filtration experiments indicated that a black garden soil was best for removing TNT. Such soils might be expected to remove a total amount of TNT up to about 0.1% of their weight. Colored TNT is removed more effectively by all soils than α-TNT. Alkalinizing the waste slightly with soda ash to convert the TNT to the colored form is advantageous for soil percolation. As the absorption capacity of the soil becomes exhausted, fresh water removes some of the absorbed TNT.

Dosing and mixing activated carbon into the waste were more effective in removing TNT than filtration through carbon. α-TNT was removed from solution more readily than the colored derivative. A satisfactory chemical treatment of TNT wastes from shell-loading plants would involve holding the TNT in the alpha form, followed by treatment with activated carbon to remove it from solution. Such a procedure is considered practical for the volumes of waste discharged from shell-loading plants.

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CARBOXYMETHYLCELLULOSE . . . .

Uses and Applications

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THE newest member of the cellulose derivative family to be introduced commercially, carboxymethylcellulose, is finding wide acceptance in industry. It is the reaction product of monochloroacetic acid on alkali cellulose, and is generally supplied to the trade as the sodium salt which is a white, granular, odorless, and tasteless powder. This salt is readily soluble or dispersible in water or alkaline solutions to form highly viscous solutions useful for their thickening, suspending, and stabilizing properties; furthermore, these solutions can be evaporated to form tough films.

The sodium salt of carboxymethylcellulose is known in the trade by several different names including cellulose gum, sodium cellulose glycolate, Carboxymethocel, Collocel, and CMC. The first two are used as general trade designations; the last three are trade names for specific types sold by individual producers.

A reasonably complete summary of published literature (both patents and technical articles) on carboxymethylcellulose and its derivatives is assembled here. No effort has been made to evaluate the literature references, because commercial exploitation of carboxymethylcellulose is so recent and is expanding at such a rate that any critical evaluation could be out of date before publication. Research in this laboratory has been carried out on possible useful applications of the product. Conclusions not yet published are cited throughout this paper without literature references; they are for the reader's use in conjunction with his study of the references cited.

Since it was first developed by Jansen (*40*) in Germany toward the end of World War I, carboxymethylcellulose has been suggested as a substitute for such products as gelatin, glue, gum arabic, agar-agar, carragheen moss, tragacanth, cherry gum, wheat gluten, and locust bean gum (*33*, *40*). The original Jansen process was later improved upon by Chowdhury (*5*) and Höppler (*33*).

Carboxymethylcellulose is usually used in the form of its sodium salt (cellulose gum) which, so far, is its most important industrial derivative (*3*). Low-substituted types, soluble in alkali but not in water (*20*, *50*), are known. A highly substituted form (*10*), insoluble in alkali or water but soluble in organic solvents, has also been produced. The potassium salt resembles the sodium salt in many of its properties and gives a similar solution in water. The ammonium salt also is water soluble, and is particularly interesting because it is unstable and loses ammonia on heating to 50–60° C. The chief insoluble salts of carboxymethylcellulose so far investigated are those of lead, silver, mercury, and aluminum, all of which are colorless, the copper and nickel salts which are blue, and the ferric salt which is red.

Generally speaking, sodium carboxymethylcellulose is indicated wherever hydrophilic colloids possessing marked suspending, thickening, stabilizing, and film-forming properties are required. Some of the better-known applications cited are as thickening agents in textile print pastes and as textile finishing and sizing agents (*33*). Sodium carboxymethylcellulose can be used as an emulsifying agent. Also, it is applicable wherever a protective colloid is needed in oil-in-water emulsions (*3*). Its excellent film-forming properties should be valuable in paper sizing and coating. Höppler (*33*) disclosed the use of sodium carboxymethylcellulose in adhesives, color agglutinants, emulsifying agents, finishing and sizing agents, low-viscosity material to be used for textile finishes and sizes (the medium- and high-viscosity materials were disclosed for use as color agglutinants), paper-hanging paste, thickeners, and emulsifying agents. Feeding tests (*3*) on animals showed it to be harmless physiologically.

Commercial usage of carboxymethylcellulose, usually in the form of its sodium salt, has increased rapidly in recent years. This product is a cellulose derivative formed by the reaction of monochloroacetic acid on alkali cellulose. The sodium salt is readily soluble or dispersible in water to form highly viscous solutions. Such solutions are utilized for their thickening properties, to aid in the suspension of pigments and other finely divided solids in liquid media, and to stabilize emulsions of various types. This article discusses briefly and gives references to most of the published literature without effort to evaluate the many and varied suggestions. Most of the references in the appended bibliography show publication dates of recent years.

TEXTILE INDUSTRY

In the textile industry many uses based on the high-viscosity and film-forming properties of sodium carboxymethylcellulose have been proposed. This water-soluble product has been suggested for use in printing pastes, sizes, finishes, and lubricants. Allan and Wainwright (*1*) disclosed its application as an aqueous printing paste for use on cellulose-derivative fabrics such as those from cellulose acetate. The paste contained a high-boiling solvent for the fabric material, a coloring material, water, and, as a thickening agent, enough water-soluble carboxymethylcellulose to give a 5% aqueous solution having a specific viscosity of 20 centipoises (capillary tube method). Johnson (*41*) used less than 1% of the sodium salt of carboxymethylcellulose to stabilize dye suspensions, and to prevent settling and froth or foam formation upon storage. Sodium carboxymethylcellulose treated with epichlorohydrin to increase its viscosity was reported as being useful in printing pastes for textiles (*58*). Oxley and co-workers suggested the use of carboxymethylcellulose for printing pastes (*71*). In order to increase dye penetrations in fabric coloring, the wetting property of the sodium salt was utilized (*23*). Also, this wetting property was said to be useful for promoting bleeding or running in the dyeing of piece goods (*37*). Sodium carboxymethylcellulose has also been suggested (*7*) as a retardant in vat dyeing of textiles.

Sponsel (*82*) discussed the use of water-soluble carboxymethylcellulose in sizes and in water-soluble finishing agents; it was considered particularly valuable for wool sizing on account of its good film-forming properties. In finishing operations, the stability of carboxymethylcellulose toward the effects of light, temperature, and bacteria were said to be very good. This investigator reported that the water-soluble carboxymethylcellulose can be mixed and used together with not only the older known starches and usual fatty substances but also with such synthetic substances as acrylic acid esters and polyvinyl ethers. A gas-retaining fabric was prepared (*39*) by coating a base fabric with an aqueous solution of a soluble salt of carboxymethylcellulose and insolubilizing it with acetic acid.

Dreyfus and co-workers disclosed the warp sizing of yarns with aqueous solutions or dispersions of carboxymethylcellulose (*18*), as well as the use of these solutions in the sizing of filaments, threads, yarns, fabrics, and other textile material (*19*). Dreyfus (*15*) employed aqueous solutions of an ammonium salt of carboxymethylcellulose for sizing textile yarns, and Roberts described for the same purpose the use of the aluminum salt which is insoluble in water (*78*). A water-soluble carboxymethylcellulose powder prepared by drying an aqueous solution in thin films at above 100° C. has been proposed for use in various sizes and as a thickener for printing inks (*67*). A glazed finish for fabrics was reported as having been obtained by applying carboxymethylcellulose and a reactive decomposable quaternary ammonium salt, drying, calendering, and at some stage reacting the carboxymethylcellulose and the ammonium compound by heating to yield an insoluble coating (*36*). Films of water-soluble carboxymethylcellulose can be used for sizing dairy filter cloth.

Brown and Houghton (*3*) revealed that sodium carboxymethylcellulose acts as an effective stabilizer for oil emulsions; they used 0.5 to 1%, preferably, of the high-viscosity type with such oils as castor, linseed, rapeseed, and liquid paraffin in conjunction with sodium stearate and members of the olive oil series.

In the field of textile finishing, the water-insoluble alkali-soluble type of carboxymethylcellulose was said by Sponsel (*82*) to be important because of the permanence of the finish which could be obtained. He stated that twenty-five washings of fabrics treated with an alkali-soluble cellulose ether did not remove the ether from the fabric. Since the alkali-soluble cellulose derivative may be applicable to cotton goods, denims, and linenlike cotton white goods, the principal field for it was thought to be in cellulose wool, artificial silk, and mixed fabrics. This finishing agent also was said to allow production of a plastic effect on velvet, clothing, and furniture fabrics. Lilienfeld (*50*) advocated the use of the alkali-soluble carboxymethylcellulose in textile finishing and disclosed a process in which cotton or other woven fabrics were coated with one or several layers of carboxymethylcellulose, dried between coats, steamed after the last coat, passed through a precipitating bath, washed and dried, all under tension. The precipitating or coagulating medium for a permanent size of alkali-soluble carboxymethylcellulose was reported to be a 10% sulfuric acid solution (*20*). Brown and Cooper (*4*) utilized the material as a laminating layer for fabrics. Using the type of carboxymethylcellulose which is soluble in alkali at low temperatures only, Bolton (*2*) sized cotton fabrics with a caustic soda solution of the carboxymethylcellulose and coagulated the carboxymethylcellulose on the fabric with 8% sulfuric acid followed by 5% alum solution.

The alkali-soluble carboxymethylcellulose has been reported as being useful in printing pastes. According to Lilienfeld (*50*), 100 parts of carboxymethylcellulose, 6 to 10 parts of mica or 4 parts of lampblack or 8 to 10 parts of zinc oxide can be printed with suitable printing rollers on cotton materials; the printed fabric in the dry condition is then treated with a precipitating solution to set the layer. Houghton and Craik (*34*) treated a solution of carboxymethylcellulose in dilute aqueous alkali with a coagulating agent so as to produce gelatinous properties without complete gelation or precipitation, and used this dispersion with pigments on textiles. Clark (*6*) showed that alkali-soluble carboxymethylcellulose is a carrier for those dyestuffs which are developed after their application to textile material.

Alkali-soluble carboxymethylcellulose after heat treatment at 40° C. for 12 to 24 hours plus treatment at 250° C. for 5 minutes may be used, according to Lilienfeld (*57*), for fabric dressings, textile printing pastes, book cloth, tracing cloth, and yarn sizing. Lilienfeld (*49*) partially reacted cellulose in the form of fabrics with monochloroacetic acid in the presence of an alkali at 50° to 60° C. until the effect desired was obtained. It was claimed that patterns and differential printing effects could be produced in this way. Dreyfus elaborated on this textile treatment (*14*). Textile fabrics of carboxymethylcellulose were stabilized by treatment with 0.25 to 5.0% of a soluble thiocyanate (*35*).

PAPER INDUSTRY

Carboxymethylcellulose has been proposed for sizing and coating compositions, and for use in pulp impregnants. Thomas and Oxley (*85*) disclosed the use of boric-acid-treated carboxymethylcellulose as a size for paper. The grease-resistant properties of carboxymethylcellulose suggested that it might be especially valuable in greaseproofing paper. Merrill (*65*) disclosed it as both a beater size and a surface size for greaseproof paper, useful for packaging foodstuffs. He claimed that such sizes also could be used to control printing ink penetration. Wrapping paper for dynamite cartridges, sized with carboxymethylcellulose, was said to have a lower rate of vapor diffusion for volatile explosive constituents such as ethylene glycol dinitrate.

To a beater furnish, Larson (*48*) added a 1% solution of carboxymethylcellulose which was then precipitated with alum. This furnish was then sheeted and treated with an alkaline agent to render the size highly swollen to just short of a sol state. The action of the swelling agent was stopped at that point, and the sheet dried in the usual manner, to give a grease-resistant paper suitable for packaging foodstuffs and lubricating oil.

Paper coatings of carboxymethylcellulose and its sodium salt were described by Gloor (*27*) who combined 10 parts of carboxymethylcellulose with 2 to 30 parts of an alkali metal silicate, such as water glass, to coat or impregnate paper or fiberboard. Kallock (*42*) used carboxymethylcellulose in a blushing lacquer for paper to give a pressure-sensitive chart paper.

The alkali-soluble water-insoluble carboxymethylcellulose was first disclosed for use as a paper size and coating by Lilienfeld (*50*). An example of sizing with this type was given by Maxwell and Larson (*60*) in which a sodium carboxymethylcellulose was added to a clay coating composition. The binding effect given by one third as much carboxymethylcellulose as had been previously used of casein was said to be equivalent to that obtained with a good grade of casein. Dilute, aqueous, colloidal solutions of the salts of carboxymethylcellulose were claimed to be suitable for sizing colored paper (*30*). Krestinskiĭ (*46*) found alkali-soluble carboxymethylcellulose useful in the impregnation of pulp for waterproofing. Freeman, Peterson, and Greminger (*25*) disclosed a greaseproofed paper treated with an ammoniacal solution of aluminum carboxymethylcellulose. Roberts (*78*) reported aqueous aluminum carboxymethylcellulose solutions for sizing paper, and Sichel (*81*) also showed viscous solutions of the aluminum salt to be useful as size.

FOOD INDUSTRY

Tests were carried out by Brown and Houghton (*3*) in England and Werle (*91*) in Germany to establish the fact that sodium carboxymethylcellulose is physiologically inert. The chemical constitution suggested to them that it should be innocuous, and their feeding tests indicated that rats and dogs suffered no ill effects. Post mortem examination of the vital organs showed these to be normal in every way. An analysis (*3*) of the foodstuff quality of one variety of carboxymethylcellulose showed the lead content of the salt to be only 8 parts per million, and copper and zinc were each less than 1 p.p.m. It was concluded, therefore, that it could be used in preparations for internal consumption such as medicine and foodstuffs as well as in toilet preparations for external application (*3, 91*).

Maxwell (*58*) disclosed that carboxymethylcellulose treated with epichlorohydrin could serve as a thickener for food, and Wallach (*89*) claimed that the addition of 10 to 50% water-soluble carboxymethylcellulose based on the weight of pure carbohydrate or carbohydrate foodstuffs would reduce the absorbability of such foods. The alkali-soluble carboxymethylcellulose may be used, it is said (*9*), to stabilize salts of hydrosulfurous acid and related hydrosulfite compounds toward moist air, particularly where the hydrosulfite product is used in an alkaline bath. These stabilized hydrosulfite compounds were disclosed for bleaching fats and sugar (*9*).

The water-soluble salts of carboxymethylcellulose, particularly sodium carboxymethylcellulose, are being used to stabilize ice cream, sherberts, and ices, as well as chocolate milk and some types of cheese. They can be used in place of gums in icings, meringue powders, doughs, flours, jellies, pie fillings, puddings, and other bakery products. Their effective function as a protective colloid is used in oil-in-water emulsions such as flavor emulsions, salad dressing, and some types of mayonnaise.

Reichel (*76*) and co-workers suggested the preparation of sausage casings from carboxymethylcellulose followed by conversion of the carboxymethylcellulose to cellulose hydrate. Such casings also have been prepared by extruding a mixture of alkali-soluble carboxymethylcellulose and cellulose xanthate in alkaline solution and coagulating the mixture, followed by reconversion of the xanthate to cellulose hydrate (*74*).

A film of carboxymethylcellulose is reported as having found use as a flexible wrapper for frozen foodstuffs (*75*). Greasy or oily foods may be packaged in paper containers coated with water-soluble carboxymethylcellulose according to Collings, Peterson, and Kelly (*8*).

DRUGS AND COSMETICS

One investigator reported that sodium carboxymethylcellulose may be used to replace tragacanth, carob gum, and gum arabic in the manufacture of face creams, and may be used as a base or stabilizer in medicinal preparations (*43*). According to Wenck (*90*), it may be employed with agar-agar as a medium for cultivating bacteria. Hiatt (*32*) reported that medicaments, such as capsules, tablets, and powders surrounded by an enteric film or layer of carboxymethylcellulose, are insoluble in the stomach acids but soluble in alkaline intestinal fluids. Development of liquid-absorbing surgical dressings saturated with water-soluble carboxymethylcellulose have been reported (*93*).

Protective colloid action of the water-soluble salts of carboxymethylcellulose has found application in dentifrices, wave set compositions, hand lotions, and other types of pharmaceutical and cosmetic emulsions (*62*). Their ease of dispersion in hot or cold water makes them valuable as ointment bases in the drug field. Their grease and organic solvent-resistant films are useful in protective hand creams. Dental impression materials might contain various salts of carboxymethylcellulose.

Stains from copying inks or pencils or from typewriter ribbons, it is claimed, may be removed by compositions of pasty consistency containing carboxymethylcellulose swollen by water, with or without the addition of soap or glycerol (*38*).

CERAMICS

Ceramic bodies, especially for electrical purposes, can be more readily manufactured by mixing with the ceramic material carboxymethylcellulose which swells or dissolves in water, then molding the ceramic body and sintering it at a temperature of about 1500° C. (*70*).

LEATHER

Lilienfeld (*50*) described in early patents the use of alkali-soluble water-insoluble carboxymethylcellulose as a leather dressing. This type can also be used, it is said, for impregnating leather to increase its waterproofness (*46*). A leather coating and coloring composition has been reported which contains 100 grams of a 5% solution of a carboxymethylcellulose salt, 3 grams of Turkey red oil, 2 grams of glycerol, 15 grams of dyestuff, and 30 grams of water (*72*). The water-soluble salts are being used to control adhesiveness in the leather-pasting operation.

PAINTS AND LACQUERS

Because of its film-forming properties, carboxymethylcellulose has been proposed for many types of protective coatings. Lilienfeld (*50*) disclosed coatings of the alkali-soluble type resistant to water and most chemicals; he also recommended a heat-treated carboxymethylcellulose for this purpose (*57*).

The water-soluble salts of carboxymethylcellulose have been suggested by Köhler (*44*) for the priming of interior walls, particularly when coloring matter is desired in the prime coat.

Medl (*61*) described an aqueous composition particularly suitable for coating iron and other surfaces; his composition contained sodium carboxymethylcellulose with water-soluble nonacid salts of phosphoric, boric, and other polybasic acids to prevent rusting by the solution. These coatings are said to be impervious to grease and oil. He also suggested (*62*) a complex ester condensation product of a polyhydric alcohol with boric acid as a modifier to plasticize films of carboxymethylcellulose which are used as coatings for paper, cardboard, plaster or concrete surfaces, iron structural members, and black iron sheets.

The epichlorohydrin-treated carboxymethylcellulose of Maxwell (*58*) was reported as a thickening agent in emulsion-type paints. Sodium carboxymethylcellulose was also suggested for emulsion paints and lacquers (*69*). Carboxymethylcellulose may be used, it is said, to extend white pigments and improve their hiding power in flat paint formulations (*28, 29*).

Reichel and Craver (*77*) reported carboxymethylcellulose as a hydrophilic colloid thickener in a coating composition containing a cellulose derivative and a wax in an organic solvent. The water-insoluble polyvalent metal salts of carboxymethylcellulose (*26*) also have been recommended for coatings.

Water-soluble salts of carboxymethylcellulose are being used to control viscosity and brushing properties, and to protect the emulsion in resin emulsion paints.

Slightly soluble crystalline materials, useful as pigments, extenders, fillers, or bases, such as calcium sulfate, may be treated, it is said, with water-soluble salts of carboxymethylcellulose to inhibit crystalline growth (*83*).

ADHESIVES

Voss (*87*) disclosed both the water-soluble and alkali-soluble types of carboxymethylcellulose as adhesives. A viscous aqueous solution containing 3 to 8% of sodium, potassium, ammonium, triethanolamine, or triethylammonium carboxymethylcellulose, alone or with soluble starches, was reported as forming adhesives suitable for hanging wallpaper or pasting paper products such as boxes (*44*). Robie (*79*) reported the use of carboxymethylcellulose to bond abrasive particles to a base in the manufacture of sandpaper and various abrasive articles.

The alkali-soluble type was proposed as an adhesive by Lilienfeld (*50*), Maxwell and Larson (*60*), and others. It has also been suggested as a cement for laminating nonfibrous sheets (*88*).

Meyer (*67*) disclosed a specially dried and powdered water-soluble carboxymethylcellulose or its sodium salt as an adhesive, and Medl (*61*) reported the use of a sodium carboxymethylcellulose with alkaline salts of phosphoric, boric, or other polybasic acid in adhesives.

The aluminum salt of carboxymethylcellulose as an adhesive for pasting paper and wallpaper was described by Sichel (*81*).

FILMS AND FILAMENTS

Films of carboxymethylcellulose, particularly the alkali-soluble type, have been proposed for "cellophane-type" wrappings. Such films are said to be tough and difficultly combustible (*40*).

Lilienfeld (*50*) disclosed films prepared by coagulating an alkaline solution of a water-insoluble carboxymethylcellulose with 10 to 20% sulfuric acid, 25% acetic acid, 30% ammonium chloride solution, 20% tannin, or 40% formaldehyde solution, or by the usual viscose precipitating bath. The solidified film was washed with water and dried. Flexibility may be increased, it was said, by plasticizing with 10% glycerol. Ellsworth (*20, 21*) coated alkali-soluble films of carboxymethylcellulose with a composition of a synthetic resin with wax and plasticizer to increase moisture resistance. A coating or surface size of nitrocellulose or other cellulose derivative emulsion may be used with water-sensitive films according to Kojevnikoff (*45*). In preparing a wrapping tissue of carboxymethylcellulose carrying a moistureproofing coating, Müller and Herrmann (*68*) used an intermediate coating of the polymerization product of maleic anhydride and vinyl methyl ether. For wrapping frozen foods, a carboxymethylcellulose film plasticized with water, glycerol, and diethylene glycol was recommended (*75*).

It is reported that alkali-soluble films of carboxymethylcellulose may be treated with deformation-restricting agents (*63, 64, 86*). A film of mixed structure (*84*) was prepared by precipitating 20 parts of a polyamide dissolved in 6 *N* hydrochloric acid in a bath consisting of a solution of 10 parts of carboxymethylcellulose in 80 parts of 6 *N* sodium hydroxide.

MISCELLANEOUS

Miscellaneous proposed uses of carboxymethylcellulose include a coating for the inside of metal molds used for the polymerization of resin-forming liquids (*24*), sticking agents for insecticides (*60*), clarifying agents for liquids (*60*), crystallization inhibitors (*60*), boiler compounds (*31*), creaming and thickening latex (*31, 66, 80*), oil drilling muds (*31*), can-sealing compounds (*31*), antistick compounds to prevent blocking, and emulsifiers in the photographic field (*43*). The water-soluble salts may also be used as suspending agents in tungsten wire-drawing compounds.

The molding of insulating blocks has been patented, using 1.5 to 5% of a polyvalent metal salt of carboxymethylcellulose as the binder for exfoliated vermiculite (*73*). The aluminum, copper, zinc, iron, tin, nickel, and chromium salts were said to be suitable.

Substances found to be compatible with carboxymethylcellulose, which may be used in conjunction with it, include hydrated cellulose or hydrocellulose soluble in alkalies; viscose (cellulose xanthate) in the crude form or purified by any known process; albuminous substances, proteins, and glue (gelatin); amyloid, starch, and starchlike materials; tragasol; resins soluble in alkalies; resinous condensation products (soluble in alkalies) obtained by the condensation of a phenol or an aromatic amine or of a urea with an aldehyde; shellac; glycerol, diglycerol, polyglycerol, glycols, and sugars and sirups; soaps, fats, ammonium or alkali-metal derivatives of fatty sulfonic acids such as Turkey red oil (*50*); drying or nondrying oils; and halogen derivatives of polyhydric alcohols, particularly halohydrins (*57*).

Carboxymethylcellulose, it is said, may be plasticized with polyhydric alcohols (*47*) or special *N*-hydroxyalkyl amides (*92*). Aluminum carboxymethylcellulose in combination with wax in an ammoniacal solution has been disclosed (*94*).

Since carboxymethylcellulose was first developed during World War I as a substitute for scarce natural products, it has attained a position based on its own virtues. Unique among cellulose derivatives, it acts both as a film former and as a stabilizer and emulsifier for aqueous systems. This combination of properties makes carboxymethylcellulose potentially useful in fields in which gums, glues, and gelatins have so far not been used.

Neither the highly substituted organic-soluble type of carboxymethylcellulose (*10*) nor its many derivatives, with the exception of the metallic salts, have been discussed in this paper. The numerous possibilities for derivatives are illustrated in part in patents which show xanthate derivatives (*22*, *51-53*, *54*, *55*); nitrogen-containing derivatives (*11*, *16*); acid halides of carboxymethylcellulose (*12*, *13*); derivatives containing carboxy and amine groups (*17*); and mixed ethers (*56*). Mixtures of carboxymethylcellulose with viscose have also been suggested (*52*, *59*).

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PHYSICAL TESTING OF GLUE COMPOSITIONS

Sorbitol and Glycerol in Printers Rollers

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Viscosity, tensile strength, and gel strength data on a wide range of glue compositions are presented. A comparison of glycerol and sorbitol as softeners is presented, along with data on combinations of the two. Physical properties deteriorate rapidly with an increase in water content. Generally speaking, sorbitol gives a stronger composition—i.e., higher viscosity and tensile and gel strengths; these physical properties are very sensitive to water content of the composition. In general, compositions softened with sorbitol show higher viscosity, higher gel strength, and higher tensile strength than those softened with glycerol.

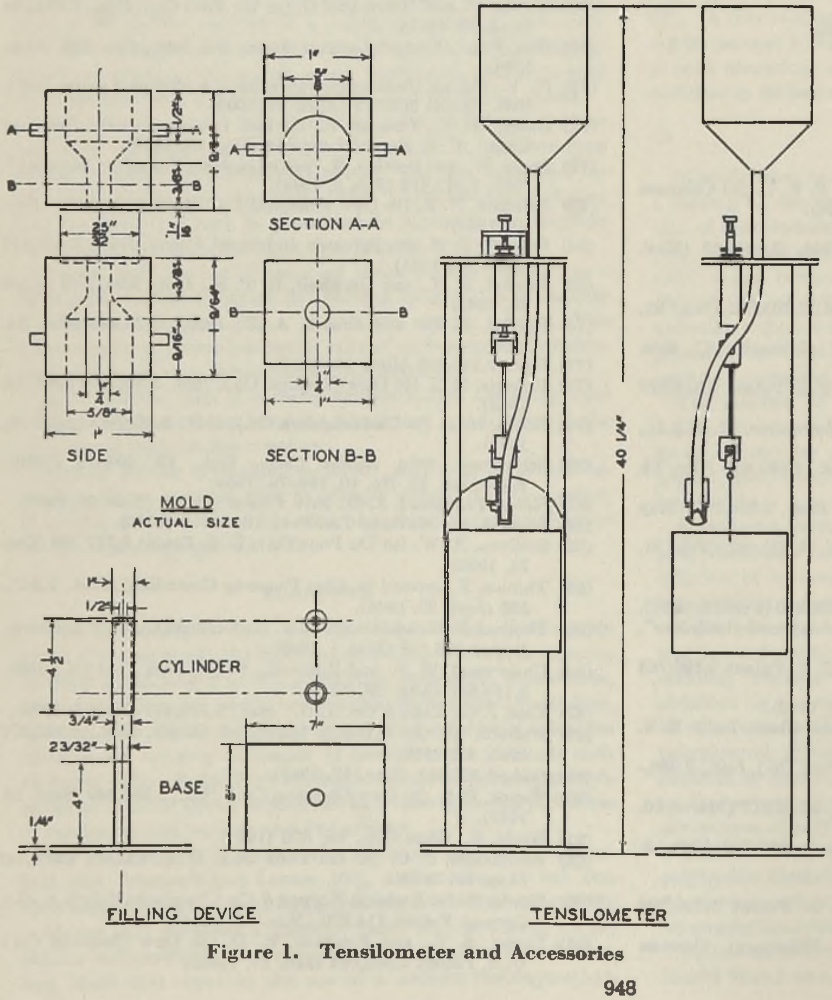


Figure 1. Tensilometer and Accessories

SEVERAL years ago the operating characteristics of various glue formulations were improved by using as a plasticizer a mixture of glycerol and commercial sorbitol solution. In order to establish rules for formulation, the physical properties of glue composition were studied. Formulations chosen for the work embraced printers roller compositions and extended into flexible glues and to hectograph compositions on either side.

Of primary importance in the manufacture of softened glue rollers is the relation between viscosity, temperature, and composition of the mass. This relation was investigated in some detail. The performance characteristics of a roller composition may be divided into two classes: those influencing the length of the operating life of the roller, such as toughness and heat resistance; and those affecting the quality of the printing, such as surface tack and resilience.

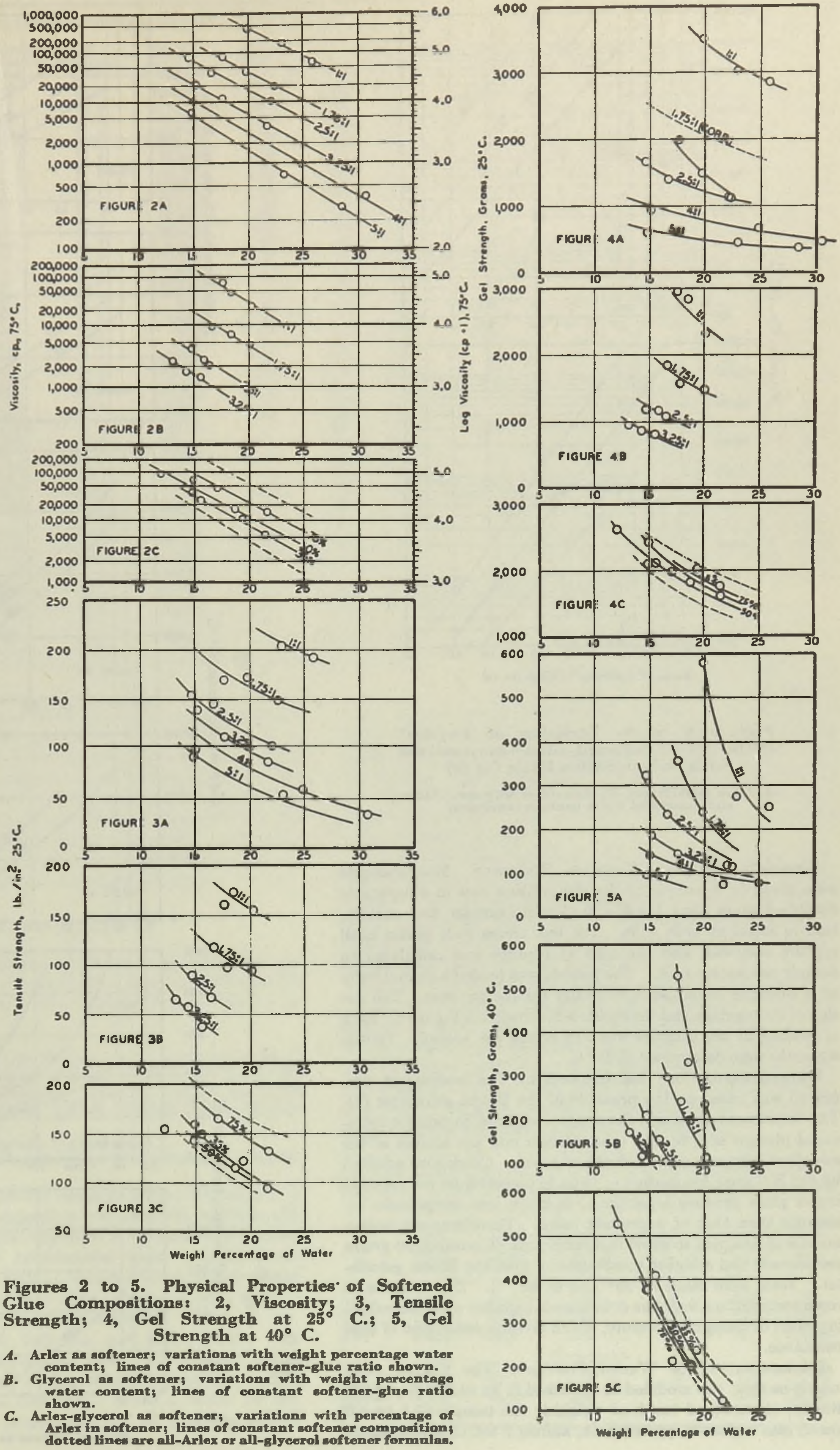
Tensile and gel strengths of the roller composition were found to correlate reasonably well with operating life in the field. By measuring gel strength at two temperatures, some idea was obtained of the resistance of the roller to softening due to heat. During field trials with formulas devised to obtain the above correlations, the indications were that the tack and resiliency characteristics of sorbitol-glycerol roller composition were satisfactory. Laboratory evaluation of these properties was not undertaken.

The physical properties of a roller composition depend upon the water content which, under operating conditions, is a function of the hygroscopicity of the composition (*4*) and the atmospheric conditions. This paper describes the methods and apparatus used to determine the viscosities of gel, and tensile strengths of glue composition plasticized with sorbitol, with glycerol, and with mixtures of the two over a considerable range of water contents. The ratios of softener to glue studied varied from 1:1 to 5:1, which covers the range of formulations commonly employed in the printers roller industry and includes formulas employed in the flexible glue, hectograph, and adhesive industries. Formulations containing tanning or insolubilizing agents are not included in this study.

Standard methods of testing glue were adopted by the National Association of Glue Manufacturers in 1934 (*1, 3*), utilizing the Bloom gelometer and a pipet-type viscometer. However, little has been published concerning the testing of plasticized glue compositions at low water contents. It was therefore necessary to devise suitable methods of testing. The dependence of these properties on water content is so great that it was necessary to know accurately the moisture content of each composition under test. The rapid titrimetric method for determining water (*2*) developed in this laboratory made possible the requisite control analyses.

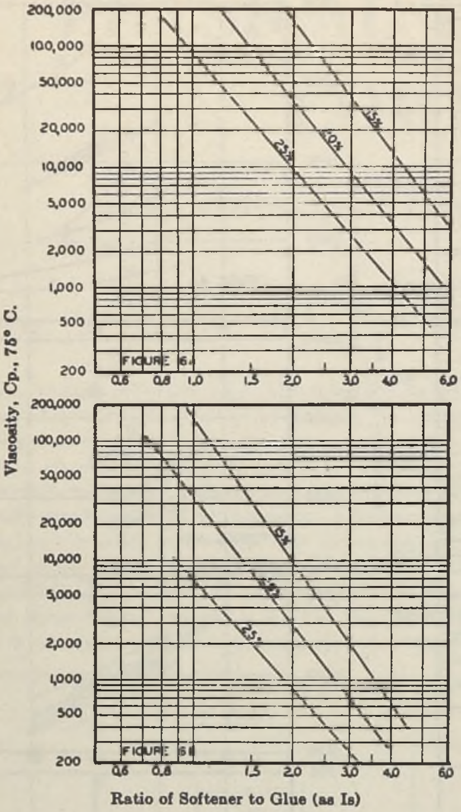
METHODS OF TESTING

Determination of Viscosity. A Hoeppler falling-ball viscometer (*5, 6*) was used for the roller compositions. Viscosities were determined at 75° C. (167° F.) which is in the range of casting temperature for printers roller compositions. The liquid density was assumed to be 1.3 grams per cc. in all tests. Maximum deviation from this value would be 0.1 gram per cc., which would introduce an error of less than 2%. This is within the reproducibility of the compositions.



Figures 2 to 5. Physical Properties of Softened Glue Compositions: 2, Viscosity; 3, Tensile Strength; 4, Gel Strength at 25° C.; 5, Gel Strength at 40° C.

A. Arlex as softener; variations with weight percentage water content; lines of constant softener-glue ratio shown.
B. Glycerol as softener; variations with weight percentage water content; lines of constant softener-glue ratio shown.
C. Arlex-glycerol as softener; variations with percentage of Arlex in softener; lines of constant softener composition; dotted lines are all-Arlex or all-glycerol softener formulas.



Figures 6 to 9. Variation of Physical Properties of Softened Glue Compositions with Softener-Glue Ratio (as Is)

A, Arlex as softener; B, glycerol as softener. Lines show constant water content (analyzed).

Determination of Tensile Strength. Measurements were made on a sample of the composition cast in a separable dumbbell mold that freed a 0.25-inch-diameter test section, held in metal at both ends. The test pieces were pulled until rupture occurred, and the load at rupture was calculated to pounds per square inch. The sample was loaded automatically on a machine developed specifically for the purpose. The design of the machine and the molds is illustrated in Figure 1. Rate of loading of the samples was 215 grams per second. Tensile strengths were determined at 25° C.

Determination of Gel Strength. The instrument employed was based on the principle of the Bloom gelometer (*1*). The instrument measures the weight required to press a cylindrical plunger of 1 sq. cm. cross section into the surface of the sample of composition to a depth of 4 mm. Conditions adopted by the National Association of Glue Manufacturers for the testing of glues produce a gel that has much less compression resistance than that of a printers roller. Therefore, our instrument was designed to provide a faster rate of loading (76 grams per second) and a higher total capacity than the Bloom gelometer. Tests were made at 25° and at 40° C. The firmness at room temperature was thus determined, together with the softening effect of rising temperature, which gives an indication of heat resistance.

Determination of Water Content. The Fischer volumetric method was modified as described in an earlier paper (*2*). Briefly, the method involved weighing the sample (0.5 to 1.0 gram) into a glass-stoppered flask, adding 5 ml. of glacial acetic

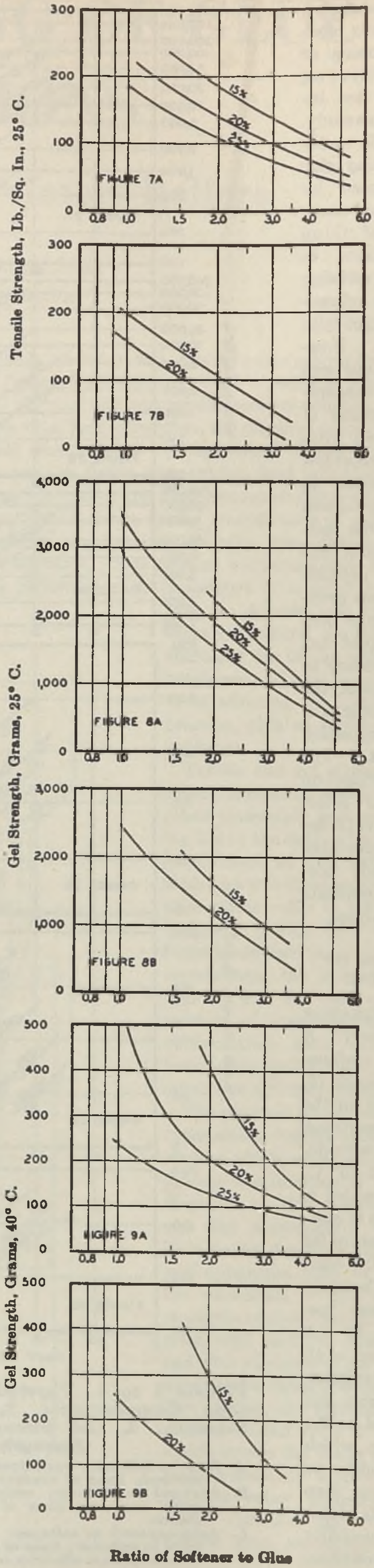


TABLE I. ANALYSES OF PRINTERS ROLLER COMPOSITIONS

Glue No.	Softener	Softener: Glue Ratio (as Is)	% Analyzed Water	Viscosity at 75° C., Centipoises	Tensile at 25° C., Lb./Sq. In.	Gel Strength, Grams	
						25° C.	40° C.
A-1	Arlex	1:1	19.9	396,000	...	3500	578
A-2	Arlex	1:1	22.9	177,000	204	3040	275
A-3	Arlex	1:1	25.8	61,500	193	2890	250
A-4	Arlex	1.75:1	17.6	82,700	171	2000	356
A-5	Arlex	1.75:1	19.8	37,500	173	1500	240
A-6	Arlex	1.75:1	22.4	19,200	149	1140	114
A-7	Arlex	2.5:1	14.6	79,700	155	1690	323
A-8	Arlex	2.5:1	16.7	36,400	146	1400	235
A-9	Arlex	2.5:1	22.1	10,350	100	1120	117
A-10	Arlex	3.0:1	16.7	16,100	84	968	146
A-11	Arlex	3.25:1	15.2	20,400	137	950	187
A-12	Arlex	3.25:1	17.6	11,650	108	900	142
A-13	Arlex	3.25:1	21.7	3,570	83	700	75
A-14	Arlex	3.5:1	16.0	11,530	91	792	123
A-15	Arlex	3.5:1	23.2	1,960	75	845	Liquid
A-16	Arlex	4.0:1	15.0	10,000	96	968	142
A-17	Arlex	4.0:1	24.9	958	60	670	80
A-18	Arlex	4.0:1	80.7	360	34	480	Liquid
A-19	Arlex	5.0:1	14.8	6,490	88	620	98
A-20	Arlex	5.0:1	23.1	664	53	460	Liquid
A-21	Arlex	5.0:1	28.5	296	7	390	Liquid
G-1	Glycerol	1:1	17.6	75,000	161	2945	530
G-2	Glycerol	1:1	18.5	44,800	174	2850	430
G-3	Glycerol	1:1	20.2	23,100	156	2340	234
G-4	Glycerol	1.75:1	16.7	9,250	118	1863	297
G-5	Glycerol	1.75:1	17.9	6,970	97	1520	244
G-6	Glycerol	1.75:1	20.1	4,550	94	1480	113
G-7	Glycerol	2.5:1	14.8	3,790	89	1190	211
G-8	Glycerol	2.5:1	15.9	2,510	58	1175	159
G-9	Glycerol	2.5:1	16.5	2,145	67	1085	104
G-10	Glycerol	3.25:1	13.2	2,480	65	975	171
G-11	Glycerol	3.25:1	14.3	1,646	57	860	116
G-12	Glycerol	3.25:1	15.6	1,423	37	820	110
AG-1	50% Arlex–50% glycerol	1.75:1	12.1	88,400	155	2620	528
AG-2		1.75:1	14.8	35,300	143	2100	376
AG-3		1.75:1	18.7	16,900	115	1805	200
AG-4	75% Arlex–25% glycerol	1.75:1	14.9	77,400	160	2435	375
AG-5		1.75:1	17.1	42,500	165	1990	216
AG-6		1.75:1	21.6	14,560	131	1605	119
AG-7	35% Arlex–65% glycerol	1.75:1	16.6	25,700	150	2120	408
AG-8		1.75:1	19.3	11,160	122	2015	237
AG-9		1.75:1	21.5	5,600	93	1760	117

acid, allowing the sample to stand overnight at room temperature to effect solution, adding an excess of modified Fischer reagent, and titrating with water-alcohol solution. The acetic acid introduces water for which a correction must be made. On occasion, samples very low in water, or tanned to an insoluble state, were found which would not disperse completely with this treatment. In such case the sample was heated gently after standing overnight in acid. No compositions have been encountered that would resist this combined treatment.

GLUE COMPOSITIONS

Several series of compositions were prepared, tested, and analyzed: (*a*) all-sorbitol, (*b*) all-glycerol, and (*c*) soribtol-glycerol softened compositions. The ingredients are listed with specifications:

GLUE. A balanced grade of hide glue containing approximately 16% water (analyzed 15.3%); 410 to 415 grams gel strength (Bloom), 135-millipoise viscosity, ground to 24–26 mesh, pH 5.9 in 20% solution (pH of plasticized glue mixture was found to be 6.0 ± 0.2).

GLYCEROL. Dynamite grade, 1% water.

SORBITOL. Commercial solution (Arlex) containing 16% water.

The ratio of softener to glue was varied between the limits of 1:1 and 5:1. Each basic composition was prepared at three different water contents so that the effect of varying water content on the properties under consideration could be determined. At one softener-glue ratio (1.75:1), the composition of the softener was varied from 100% Arlex to 100% glycerol in 25% steps to study the effects of this progressive substitution.

The liquid ingredients, including any added water, were weighed into a tared round-bottom flask. The amount chosen was one third to one half of the volume of the flask. The mixture was warmed to 65–75° C. (with a steam or hot water jacket), and the proper quantity of glue was added. A tared aluminum stirrer, anchor type, was inserted, and the glue was mixed with the liquid by swirling and brief hand stirring until all of the glue was wetted by the liquid medium. The neck of the flask was covered with an inverted one-hole rubber stopper, fitting loosely about the stirrer shaft. The stirrer was then driven at a speed of approximately 100 r.p.m. Heating was continued in the water bath (at 75° C.) until there were no detectable swollen undispersed glue particles. A uniform cooking time could not be established since the dispersion and degradation of the glue at the cooking temperature are a function of time, water content, and softener-glue ratio. Thus, in a high-ratio or high-water-content composition the glue is dispersed in appreciably less time than in a low-ratio or low-water-content formula; if the two are heated the same length of time, the higher rate of degradation for the former composition would result in too great a change in physical properties. One and a half hours were sufficient for complete cooking of a majority of the compositions. Thirty minutes and 4 hours represent extremes in time of cooking. Good agreement of data were obtained on duplicate preparations.

PHYSICAL PROPERTIES

The data are summarized in Table I. It must be kept in mind that softener-glue ratios and softener percentage compositions are based on the ingredients as commercially available. The water contents (column 4) are, on the other hand, analyzed values and include the moisture of the ingredients as well as the added water. In computing the formulas, it was necessary to allow for the water of the ingredients in order to bring the analyzed water values within the desired range.

The physical properties given in Table I are plotted as a function of water content (at constant softener-glue ratios) in Figures 2 to 5. A satisfactory graph for viscosity *vs.* water content, essentially linear throughout the working range, was obtained by plotting the empirical function log-log (cp. + 1), where cp. represents the Hoeppler viscosity in centipoises.

Besides being considered from the standpoint of varying water content, the data may be expressed as a function of the softener-glue ratios (at constant water contents) in Figures 6 to 9. In plotting viscosity *vs.* softener-glue ratio (Figure 6), linear curves were obtained if logarithmic scales were used for both ordinate and abscissa. For the other properties no true linear relations were found. However, the use of the logarithm of softener-glue ratio in these curves was found to be advantageous.

TABLE II. COMPARISON OF PROPERLY COOKED AND OVERCOOKED SORBITOL-SOFTENED COMPOSITIONS

No.	Softener: Glue Ratio (as Is)	% Analyzed Water	Viscosity at 75° C., Centipoises	Tensile at 75° C., Lb./Sq. In.	Gel Strength, Grams	
					25° C.	40° C.
			Properly Cooked			
A-17	4.0:1	24.9	958	60	670	80
A-18	4.0:1	30.7	360	34	480	Liquid
A-20	5.0:1	23.1	664	53	460	Liquid
A-21	5.0:1	28.5	296	7	390	Liquid
			Overcooked			
A-17-a	4.0:1	24.7	414	7	250	Liquid
A-18-a	4.0:1	30.6	129	7	160	Liquid
A-20-a	5.0:1	24.9	318	7	270	Liquid
A-21-a	5.0:1	30.2	159	7	240	Liquid

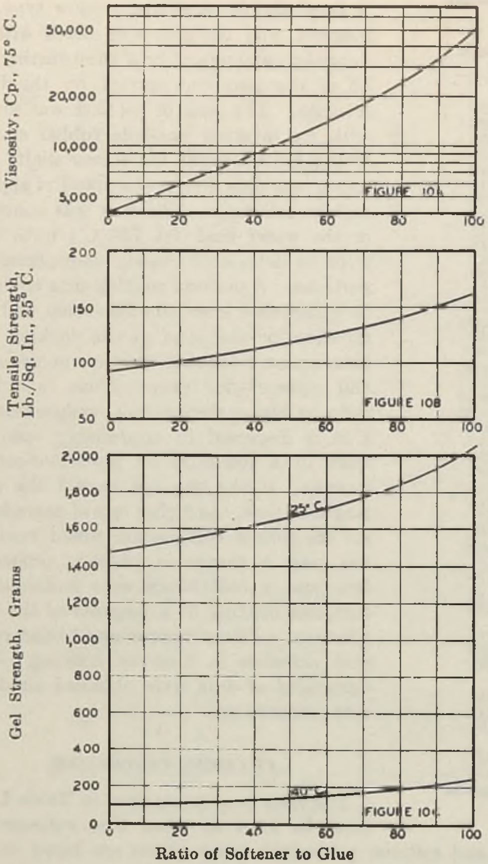


Figure 10. Variation of Physical Properties of Glue Compositions with Composition of Softener at 20% Water Content and 1.75-1 Softener-Glue Ratio

Figure 10 illustrates the variation of physical properties with changing composition of softener (at constant softener-glue ratio and at constant water content).

It is generally conceded that, with prolonged heating, glue compositions undergo deterioration. In the present work it was not feasible to standardize on a single heating time for all compositions since the time required for complete dispersions of the glue was much shorter at high softener–high water contents than when the glue content was high. Furthermore, it was evident that the degradation was more severe when the water content was high so that the practice throughout this study was to pour each batch as soon as there were no detectable particles of swollen glue in it. Serious degradation by overcooking is illustrated in the following experiments.

Compositions corresponding to formulas A-17, -18, -20, and -21 of Table I were prepared, and heating was continued for approximately 4 hours after the glue had been dispersed. Table II lists the properties of the overcooked compositions and those prepared in the standard manner.

The difference in results is most noticeable in the gel strength determinations. The degradation of the glue in this fashion, at a constant pH, is apparently a function of time, temperature, and concentration of glue. Thus, certain of the 1:1 compositions were cooked for a long time without noticeable degradation, but high-softener or high-water-content glue formulas seem to be greatly affected by such treatment. The discrepancies noted in the 25° C. gel strength (Figure 4*A*) are probably traceable to this trouble. Apparently, for the same reason the 25° C. gel strengths for sorbitol-glycerol compositions were too erratic to plot.

The present data are based on glue having a gel strength of 415 grams and are therefore strictly applicable to the preparation of formulas from such a glue. However, they have been used for comparative purposes with some success for glues with gel strength ranging from 200 to 465 grams.

CONCLUSIONS

The curves show that the replacement of glycerol by sorbitol in glue compositions increases the viscosity, tensile strength, and gel strength. In most applications, these are desirable trends.

Thus, in printers rollers, higher tensile and gel strengths, particularly at elevated temperatures, permit higher press speeds and operating temperature. The higher viscosity of sorbitol-containing compositions may necessitate modification of operating procedure and formulation. In printers roller formulas, particularly, it is undesirable to increase the fluidity for ease in casting by increasing the water content since this would increase the risk of roller shrinkage. The proper modification is to raise the casting temperature or to increase the softener-glue ratio (or a combination of the two).

It was not feasible to include in this study all of the properties pertaining to the quality of a roller. Thus, resiliency, tack, etc., are important factors. In general, it has been found in plant tests that a roller of excellent wearing properties combined with good printing characteristics is obtained when approximately equal quantities of glycerol and sorbitol are used.

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(2) Almy, Griffin, and Wilcox, Ind. Eng. Chem., Anal. Ed., **12**, 392–6 (1940).
(3) Government Printing Office, *Tech. Bull.* 24 (1942).
(4) Griffin, Ind. Eng. Chem., to be published.
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Correlating Vapor Compositions and Related Properties of Solutions—Correction

A mistake in this paper which appeared in the September, 1944, issue has been called to my attention. In the discussion under "Partial Heats of Solution" on page 860, the second sentence reads: "The heat required to vaporize one mole of one component (L) from a solution is equal to the latent heat of the pure component ($L°$), plus its partial heat of solution (H), etc." This sign should be *minus* rather than *plus*, as well as those in the corresponding formulas of Table I, the second line for p_1. This line should read as follows:

$$p_1 \;\Big|\; p_1^\circ \;\Big|\; \frac{d \log p_1}{d \log p_1^\circ} = \left(1 - \frac{H_1}{L_1^\circ}\right) \;\Big|\; \log p_1 = \left(1 - \frac{H_1}{L_1^\circ}\right) \log p_1^\circ + C \;\Big|\; p_1 = cp_1^{\circ\left(1 - \frac{H_1}{L_1^\circ}\right)} \;\Big|\; 1 - \frac{H_1}{L_1^\circ}$$

D. F. Othmer

Tall Oil Esters as Plasticizers for GR-S

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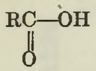
Tall oil is a rich source of resin and fatty acids. Previous work has shown that this material exerts a plasticizing effect on GR-S. The structure of tall oil was modified by esterification with alcohols. Most interesting were those esters derived from hydroxy compounds related to GR-S unit structure. They were superior to tall oil in rate of incorporation into the GR-S and general plasticizing action. For a comprehensive picture of the properties of tall oil esters, data are also given for esters of aliphatic, phenolic, cycloaliphatic, and polyhydroxy alcohols.

TALL oil is a by-product of the pine wood paper industry. It consists of approximately equal amounts of fatty and resin acids plus 6–10% of unsaponifiable matter. It would be expected to have the general properties of resin and fatty acids; tests made in these laboratories indicated that tall oil exerted a plasticizing action in GR-S. However, when added to GR-S on the laboratory mill it produced greasiness and incorporated into the mix rather slowly. Furthermore, the tall oil tended to bleed out of the stock on curing, and the stock was sticky when hot. It seemed desirable, therefore, to seek ways of improving the properties of this material.

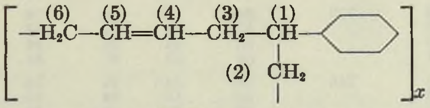
The simplest chemical modification which was considered practical was to convert the tall oil to its esters. In this manner the chemical constitution of the material could be brought closer to that of GR-S. In the following formulas R represents the aliphatic-phenanthrene residue of tall oil:

Tall oil:

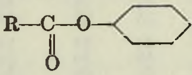


$$RC(=O)-OH$$

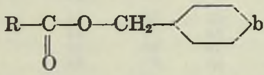
GR-S unit:



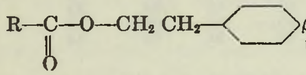
Tall oil esters:



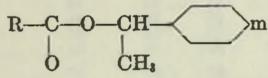
phenyl (GR-S unit less groups 1–6)



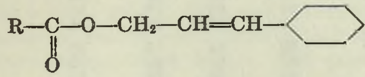
benzyl (GR-S unit less groups 2–6)



β-phenyl ethyl (GR-S unit less groups 2, 4, 5, 6)



methyl phenyl carbinyl (GR-S unit less groups 3–6)



cinnamyl (GR-S unit less groups 1–3)

Effecting this change should result in greater solubility of the tall oil in GR-S and, consequently, more rapid incorporation and enhanced plasticizing action. These effects at best would be produced only moderately because whatever the change in the carboxyl group of the tall oil, the contribution of the long-chain aliphatic residues of the fatty acids and the phenanthrene residue of the resinic acids continue to be of major importance.

While those esters of tall oil which are related to the structure of GR-S are of more importance, it was considered of interest to prepare esters of other classes in order to present a complete picture of the value of tall oil esters in plasticizing GR-S. The following basic formula for tire tread stock was used in comparing the properties of the tall oil esters with tall oil and commercial plasticizers:

GR-S	100	Witco No. 12 channel black	50
Mercaptobenzothiazole	1.5	Sulfur	2
Stearite	2	Softener	15
Zinc oxide	5		

The esters were prepared either by direct reaction of the tall oil and the hydroxy compound, or by conversion of the tall oil to its acid chlorides and reaction of these with the hydroxy compounds.

ESTER PREPARATION AND RUBBER TESTING

POLYHYDROXY ALCOHOL ESTERS OF TALL OIL. The preparation of the glycerol ester illustrates the procedure: A 3-liter three-necked flask was equipped with a glass inlet tube, thermometer, and air-cooled reflux condenser at the top of which was a water-cooled take-off condenser and receiver. In the flask were placed 879 grams (3 moles) of Indusoil (distilled tall oil), 110 grams (1.2 moles) of glycerol, and 0.5 gram of litharge catalyst. The flask was heated in a graphite bath while nitrogen was bubbled through the reaction mix. Heating was continued at 250° C. for 4 hours at which time the acid number of the product dropped to 2.1. During heating, the water of reaction passed through the air condenser and was collected in the receiver. At the end of the reaction time the temperature of the flask was raised above the boiling point of the glycerol to remove any unreacted material. The yield was quantitative.

ESTERS OF OTHER CLASSES. Esters other than those of polyhydroxy alcohols were prepared from the tall oil acid chlorides and the hydroxy compound. The preparation of the cresyl esters illustrates the procedure: A 1-liter Claisen flask was equipped with a dropping funnel, and through the other neck was placed a short air condenser which was, in turn, connected to a hydrochloric acid–water trap. The distilling tube of the flask was plugged with a glass rod. In the flask were placed 104 grams (0.5 mole) of phosphorus pentachloride. Through the dropping funnel were added slowly 145 grams (0.5 mole) of Indusoil. After the initial vigorous reaction had subsided, the reaction was brought to completion by warming on the steam bath for 30 minutes. The flask was then equipped for vacuum distillation (water pump) and heated in an oil bath, and the phosphorus oxychloride was removed. As soon as decomposition was noted in the flask (around 110° C.), heating was stopped. The flask was

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[1] Present address, Brown Rubber Company, Lafayette, Ind.

Table I. Properties of Plasticized GR-S Stocks

Softener	Plasticizer Incorporation Time, Sec.	Williams Plasticity at 70° C., Cm.	Cure at 307° F., Min.	Tensile Strength, Lb. per Sq. In.	Modulus at 300%, Lb. per Sq. In.	Elongation at Break, %	Tear Resistance[a], Lb./In. Thickness	Hardness (Shore) Instantaneous	Hardness (Shore) 30-sec.	Rebound (Bashore) 25° C.	Rebound (Bashore) 100° C.	Flex Cracking at 25° C.[b], Kilocycles per Cm.
Control (no softener)	None	0.473	60	2740	1650	410	249	66	62	31	42	155
			80	2810	1840	490		67	64	31	42	
			100	2645	1970	360		68	65	30	41	
			120	2655	1970	350		69	65	30	41	
Tall oil (Indusoil)	275	0.368	60	2500	630	670	330	60	55	26	37	435
			80	2790	740	660		61	56	26	37	
			100	2830	800	630		62	57	27	37	
			120	2820	850	610		61	58	28	38	
Esters of Aromatic-Aliphatic Alcohols												
Benzyl alcohol	225	0.366	60	2200	620	700	339	58	52	31	35	316
			80	2730	780	650		60	55	31	35	
			100	2930	870	640		60	55	30	34	
			120	2830	930	600		60	55	30	34	
β-Phenyl ethyl alcohol	185	0.340	60	2390	480	770	307	55	50	27	32	744
			80	2320	570	690		56	51	27	33	
			100	2570	600	700		58	52	28	34	
			120	2550	630	660		58	52	28	34	
Methyl phenyl carbinol	130	0.368	60	2250	520	710	304	62	55	27	31	1039
			80	2320	600	690		62	55	28	32	
			100	2400	660	640		64	60	28	32	
			120	2420	710	640		64	58	27	31	
Cinnamic alcohol	125	0.363	60	1990	380	800	240	60	51	25	30	1888
			80	2090	390	790		60	51	25	31	
			100	2220	420	750		61	54	26	31	
			120	2100	440	700		63	57	27	32	
Esters of Aliphatic Alcohols												
Methyl alcohol	200	0.391	60	1930	450	690	280	55	49	31	36	294
			80	2230	490	670		57	49	31	35	
			100	2320	610	660		57	50	29	34	
			120	2660	630	660		57	52	29	34	
Isopropyl alcohol	225	0.341	60	2310	540	720	287	55	50	27	36	468
			80	2500	640	690		57	52	28	37	
			100	2600	720	650		57	52	28	38	
			120	2660	770	640		58	53	27	37	
Butyl alcohol	225	0.363	60	2320	530	710	293	55	50	29	38	466
			80	2250	660	620		59	54	30	38	
			100	2530	750	620		60	55	29	37	
			120	2590	820	600		60	55	29	37	
Allyl alcohol	275	0.320	60	1930	600	670	347	59	55	29	34	...
			80	2280	610	690		60	55	29	34	
			100	2410	670	660		60	55	28	33	
			120	2370	720	650		61	56	28	33	
Esters of Polyhydroxy Alcohols												
Ethylene glycol	...	0.318	60	2430	390	730	285	56	51	28	33	...
			80	2300	410	670		57	52	28	33	
			100	2350	420	660		59	54	28	33	
			120	1620	440	560		59	55	28	34	
Diethylene glycol	...	0.336	60	2480	630	670	252	55	50	28	34	...
			80	2510	760	640		57	52	29	34	
			100	2610	810	610		58	54	29	34	
			120	2620	820	610		58	53	29	35	
Tetraethylene glycol	...	0.341	60	2630	850	600	248	56	51	29	36	364
			80	2820	880	600		56	53	29	36	
			100	2780	920	590		56	53	29	36	
			120	2730	920	580		57	55	28	35	
Nonaethylene glycol	225	0.381	60	2850	850	620	239	56	54	25	34	117
			80	2850	860	600		57	55	26	34	
			100	2610	930	550		59	56	26	35	
			120	2660	930	560		57	55	26	34	
Glycerol	...	0.328	60	2060	420	730	267	55	50	25	31	...
			80	2170	580	660		59	54	26	32	
			100	2160	620	620		60	55	27	32	
			120	1820	620	600		60	55	27	33	
Pentaerythritol	...	0.332	60	2260	400	770	314	55	50	24	32	...
			80	2260	480	700		59	53	25	33	
			100	2460	560	700		60	55	25	33	
			120	2530	570	660		60	54	24	32	
Esters of Phenols												
Phenol	...	0.330	60	2310	610	670	258	56	51	28	33	445
			80	2520	730	660		58	55	29	34	
			100	2800	790	650		59	55	30	35	
			120	2600	860	610		61	58	29	35	
p-Chlorophenol	200	0.394	60	2340	670	640	330	67	60	30	37	133
			80	2860	820	640		68	61	29	36	
			100	2800	970	600		69	62	29	35	
			120	2780	1020	570		70	63	28	35	
Cresol	335	0.358	60	2130	520	700	304	59	54	28	32	420
			80	2700	700	690		60	55	28	33	
			100	2830	760	650		61	56	28	32	
			120	2860	830	620		60	55	29	33	
Thymol	225	0.374	60	2130	620	670	314	57	53	29	34	545
			80	2460	640	650		57	62	29	34	
			100	2820	800	630		60	55	29	34	
			120	2760	860	600		60	55	30	34	
p-*tert*-Amylphenol	200	0.358	60	2060	450	690	302	57	53	26	33	390
			80	2500	620	680		60	56	27	31	
			100	2440	760	610		60	57	28	32	
			120	2670	820	620		61	58	28	32	

Table I. Properties of Plasticized GR-S Stocks (*Continued*)

Softener	Plasticizer Incorporation Time, Sec.	Williams Plasticity at 70° C., Cm.	Cure at 307° F., Min.	Tensile Strength, Lb. per Sq. In.	Modulus at 300%, Lb. per Sq. In.	Elongation at Break, %	Tear Resistance[a], Lb./In. Thickness	Hardness (Shore) Instantaneous	Hardness (Shore) 30-sec.	Rebound (Bashore) 25° C.	Rebound (Bashore) 100° C.	Flex Cracking at 25° C.[b], Kilocycles per Cm.
2-Chloro-4-*tert*-amylphenol	230	0.368	60	2060	530	710	303	60	52	26	32	380
			80	2440	650	670		60	55	26	32	
			100	2400	800	620		60	55	26	32	
			120	2640	840	620		61	56	26	32	
p-Phenylphenol	150	0.348	60	2400	490	740	336	60	53	24	32	...
			80	2450	600	690		61	56	24	33	
			100	2780	660	690		61	56	25	34	
			120	2800	720	680		62	58	25	34	
β-Naphthol	225	0.361	60	2410	400	800	324	60	54	24	29	26'
			80	2610	560	730		61	55	25	30	
			100	2750	600	730		63	57	25	30	
			120	2920	650	710		64	60	25	30	
Esters of Cycloaliphatic Alcohols												
Cyclohexanol	175	0.320	60	2040	590	650	324	59	54	29	34	..
			80	2390	640	670		60	55	29	35	
			100	2460	750	640		60	55	29	35	
			120	2350	770	600		60	55	28	36	
Borneol	225	0.320	60	1960	610	630	283	58	54	27	34	...
			80	2250	680	600		60	54	28	35	
			100	2380	750	580		60	55	28	35	
			120	2310	780	570		60	55	29	36	
Ester of Miscellaneous Alcohol												
Tetrahydrofurfuryl alcohol	225	0.374	60	2790	580	720	308	60	55	27	32	245
			80	2910	680	680		61	58	27	32	
			100	2910	800	630		61	59	27	31	
			120	2790	810	630		62	60	27	32	
Commercial Plasticizers												
Witco MR No. 38	25	0.368	60	2590	570	740	321	60	55	25	31	498
			80	2810	620	720		60	55	25	32	
			100	2940	690	700		60	56	25	32	
			120	2960	750	690		61	57	25	31	
Bardol	275	0.363	60	2200	890	520	255	60	57	29	39	182
			80	2200	960	510		60	56	29	39	
			100	2190	1010	490		60	56	28	38	
			120	2200	990	490		60	56	28	38	
Witco No. 20	200	0.330	60	2610	600	710	299	55	50	27	32	...
			80	2540	620	680		57	51	28	33	
			100	2800	730	690		57	52	27	33	
			120	2960	760	690		59	53	27	33	
Witco SR	60	0.325	60	2660	520	750	283	55	50	26	33	...
			80	2510	590	690		55	50	26	33	
			100	2780	650	690		56	51	26	34	
			120	2850	780	670		57	52	25	35	
Pine tar	200	0.419	60	2070	370	810	290	59	52	22	31	...
			80	1950	410	740		60	57	23	32	
			100	2060	480	720		60	55	24	33	
			120	2440	540	730		60	56	24	33	
Turgum	125	0.354	60	1810	280	860	293	61	58	29	36	...
			80	2380	410	800		61	59	29	37	
			100	2710	480	790		61	59	30	38	
			120	2850	500	770		60	58	30	38	

Average of four cures. [b] Based on optimum cure.

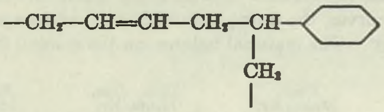
again equipped as at first, and to the crude acid chlorides were added slowly 54 grams (0.5 mole) of U.S.P. cresol. The flask was warmed on the steam bath until hydrogen chloride evolution ceased. This required about 2 hours. The product was cooled to room temperature, taken up in ether, washed with 500 ml. of 5% sodium hydroxide, then washed twice with saturated salt solution. The ether solution was dried over calcium chloride. After removal of solvent, a dark brown liquid (acid number 6.2) remained. The yield was 170 grams (89%).

Rubber Testing Methods. Stress-strain measurements were made by A.S.T.M. Method D412–41. The cures were 60, 80, 100, and 120 minutes at 307° F. Tear resistance was determined by A.S.T.M. Method D624–41T. Hardness was determined with a Shore type A durometer; 30-second reading was obtained after the durometer had rested on the test piece with a 2-pound weight for that length of time. Flex cracking was determined by making an initial nick in the sample and noting the number of kilocycles of flexing needed to extend a crack to a width of 1 cm. The following was devised as a combination of the essential features of the test methods reported by Vila (*4*), Carlton and Reinbold (*2*), and Breckley (*1*): A standard De Mattia test sample as provided in A.S.T.M. Method D430–40B was mounted in a National Rubber Machinery flexing machine, model D. An initial nick 0.2 cm. long was made, and the sample was flexed at 460 cycles per minute from 0° to 90° until a crack of 1.2 cm. was obtained (*3*).

BEHAVIOR OF ESTERS IN GR-S

The GR-S tread stock was highly loaded (15 parts) with the plasticizers under investigation so that their effects on physical properties would be more easily noted. Hence the properties of the stocks listed in Table I are not intended for comparison with commercial tread stocks. They are of value only in comparison with one another.

The esters in Table I which are directly related to the GR-S unit structure



$$—CH_2—CH{=}CH—CH_2—CH(C_6H_5)—CH_2—$$

fall into the class of aromatic-aliphatic alcohol esters since the GR-S unit is aromatic-aliphatic. When aromatic-aliphatic alcohols were attached to the tall oil carboxyl group, marked changes occurred in the vulcanizates. The time required to incorporate these esters was the lowest of any of the classes studied. The more rapid dispersion of these plasticizers may be attributed to their similarity in structure to the GR-S unit. The esters of the aromatic-aliphatic alcohols had the same order of plasticity for the uncured stocks as had tall oil, but the moduli of the cured stocks were lower than the cured tall oil stocks. This was especially outstanding with the cinnamyl ester which produced a cured stock having half the modulus of the tall oil stock. The aromatic-aliphatic esters gave higher ultimate elongations than the tall oil stocks. These observations indicated a generally greater softening of the cured stocks. The marked superiority of the aromatic-aliphatic esters in flex-crack resistance may have indicated that the esters most closely related to the GR-S unit have the property of reducing the tendency for cracking under dynamic flex. However, it may be argued that stocks plasticized with esters of aromatic-aliphatic alcohols showed greater resistance to flex cracking because these stocks had low moduli. Hence the work done per flexing cycle on each test piece was less for these lower-modulus stocks. This argument does not appear to apply in the case where the methyl phenyl carbinyl ester is compared with Witco MR No. 38, for here the moduli of the stocks are of the same order yet the ester is superior in flex crack resistance. While the lowering in modulus of the aromatic-aliphatic esters on the cured stocks was greater than tall oil, these stocks retained their hardness and did not lose their resilience. In tensile strength and tear resistance the aromatic-aliphatic esters gave poorer results than tall oil but still compared favorably with some of the commercial types of plasticizers.

With respect to the other classes of esters in Table I the aliphatic esters were found to be about as greasy on the mill as tall oil. There was some decrease in plasticizer incorporation time. In general there was no significant improvement in the physical properties of the stocks. These remarks apply about as well for the esters of polyhydroxy alcohols.

Attaching phenolic types to the tall oil molecules did tend to improve the plasticizing action of this material. In general they were less greasy on the mill and easier to incorporate. Otherwise the physical properties of the stocks were of the same order as tall oil. The physical properties of the cycloaliphatic esters were of the same order as the phenols.

ACKNOWLEDGMENT

The authors wish to thank H. F. Schwarz and H. R. Spielman for their help in obtaining the data on the physical properties of the stocks.

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Two-Component Equilibrium Curves for Multicomponent Fractionation

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A GRAPHICAL method for the solution of multicomponent fractionation problems was presented in an earlier paper (*2*). A modification of the graphical solution using a two-component structure is presented whereby equilibrium curves are drawn which simulate the McCabe-Thiele structure for two-component systems.

Figures 1 and 2 show the new form of equilibrium curve for multicomponent problems which is based on plotting the mole fraction of the light key component and lighter in the vapor phase, y, against the mole fraction of the light key component and lighter in the liquid phase, x. Figure 1 shows the equilibrium curve and operating lines for the theoretical minimum reflux ratio of example 1, for which a detailed algebraic solution is available (*2*). Figure 2 presents equilibrium curves for reflux ratios varying from the theoretical minimum to total or infinite reflux.

METHOD OF CONSTRUCTION

To illustrate the method used in constructing two-component equilibrium curves, the example given in the previous paper is reviewed briefly. The material balance on the column follows:

	Feed, Moles/Hr.	Dist. Gas, Moles/Hr.	Bottoms, Moles/Hr.
CH_4	26	26	....
C_2H_6	9	9	....
C_3H_8	25	24.6	0.4
NC_4H_{10}	17	0.3	16.7
NC_5H_{12}	11	....	11.0
NC_6H_{14}	12	....	12.0
	100	59.9	40.1

The light key component in this separation is C_3H_8 and the heavy key component is NC_4H_{10}. "Light key component and lighter" is defined here as the summation of CH_4, C_2H_6, and C_3H_8.

A complete solution of the problem at a reflux ratio of 1.5 to 1 gave the following equilibrium values for the concentrations of the light key component and lighter throughout the column:

	Light Key Component and Lighter	
	x	y
Stripping section		
Reboiler	0.0100	0.0274
Tray B-1	0.0218	0.0516
Tray B-2	0.0380	0.0865
Tray B-3	0.0615	0.135
Tray B-4	0.0940	0.195
Tray B-5	0.1341	0.268
Tray B-6	0.1838	0.350
Tray below feed tray	0.259	0.460
Feed tray	0.316	0.555
Fractionating section		
Tray above feed tray	0.416	0.707
2nd tray above feed tray	0.518	0.772
Tray A-4	0.686	0.872
Tray A-3	0.792	0.924
Tray A-2	0.873	0.957
Tray A-1	0.931	0.979
Condenser	0.968	0.995

These values are plotted as curve *b* of Figure 2. The values in the region of the feed tray are slightly different from those presented in the original paper because the feed tray temperature has been changed from 205° to 210° F. in order to obtain a more optimum feed tray location.

Figure 1 shows that at the theoretical minimum reflux ratio the operating lines touch the equilibrium curve at two distinct points, one in the fractionating or enriching section, point *A*, and the

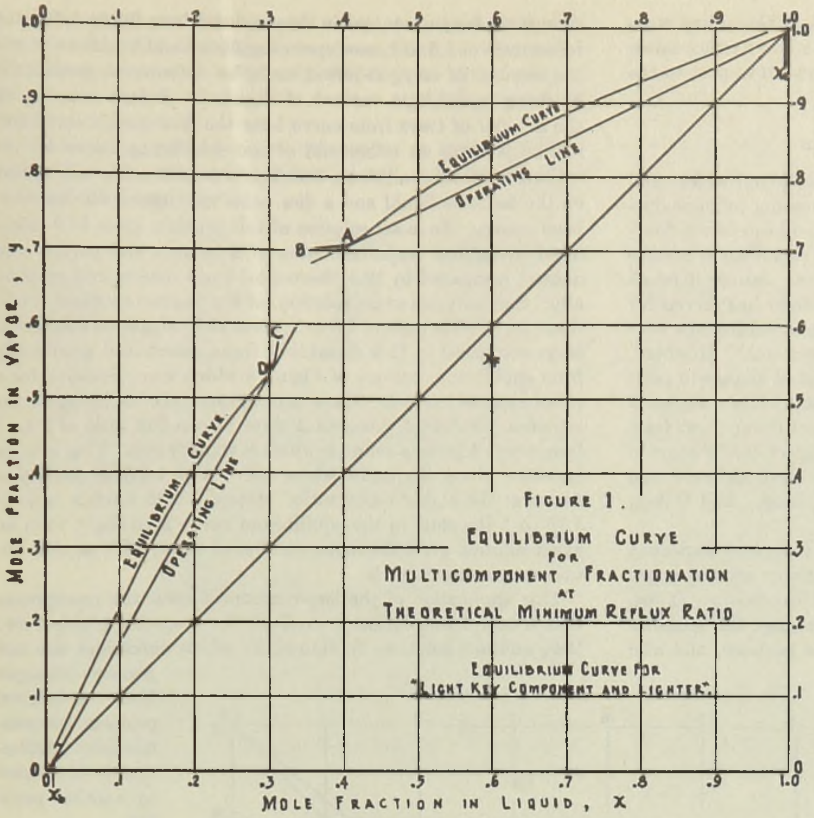

Figure 1. Equilibrium Curve for Multicomponent Fractionation at Theoretical Minimum Reflux Ratio

Equilibrium Curve for "Light Key Component and Lighter".

other in the stripping section, point *D*. Between these two points is a region representing the fractionation in the vicinity of the feed tray. Point *C* corresponds to equilibrium on the feed tray and point *B* corresponds to equilibrium on the bottom tray of the fractionating section. Section *AB* corresponds to the bottom trays of the fractionating section in which section components heavier than the heavy key component are refluxed back completely. At point *A*, the heavy key component goes through its theoretical maximum concentration. Section *CD* corresponds to the top trays of the stripping section in which section components lighter than the light key component are completely stripped. At point *D* the light key component goes through its theoretical maximum concentration. The equilibrium curve is discontinuous between points *B* and *C*, representing the crossover from the stripping to the fractionating section.

Figure 2 shows the effect of reflux ratio on the position of the equilibrium curve at constant total pressure. For the example illustrated, at total reflux the equilibrium curve (*d*, Figure 2) approximates the equilibrium curve for a two-component system

A new method of plotting equilibrium curves for multicomponent systems is based on the use of equilibrium values for the "light key component and lighter". This method simulates the McCabe-Thiele structure for two-component systems. It has been in use for over five years, and its application to the solution of industrial problems has been useful and time saving. Illustrative examples are included. The proposed method of applying the two-component structure presupposes that a complete solution is available for a specific problem and that another solution is desired in which conditions are not greatly changed from the original problem.

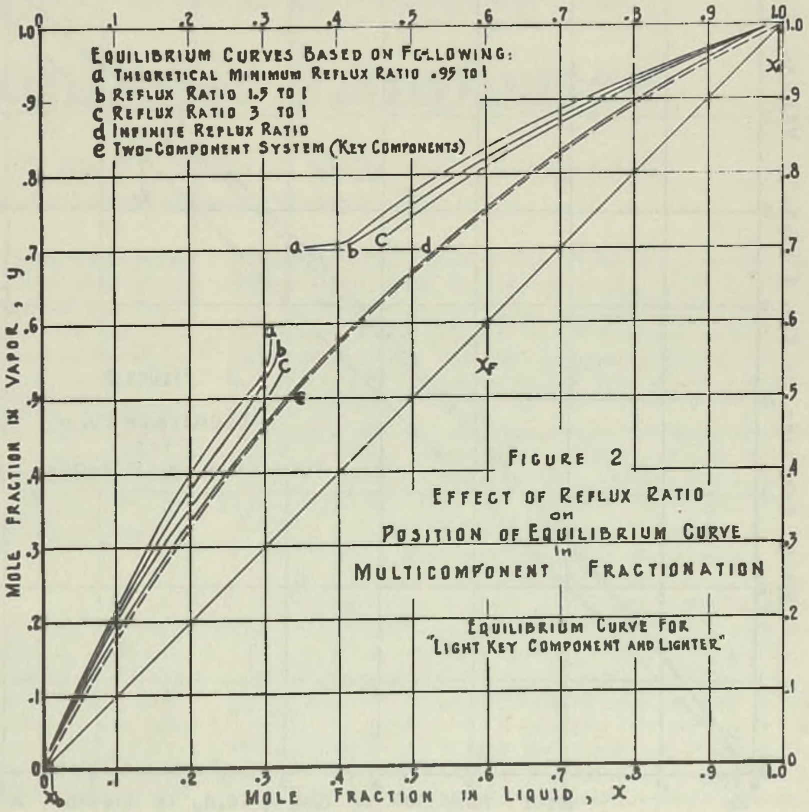

Figure 2. Effect of Reflux Ratio on Position of Equilibrium Curve in Multicomponent Fractionation

Equilibrium Curve for "Light Key Component and Lighter" in which the two components are the light and heavy key components of the multicomponent problem. At lower reflux ratios the equilibrium curve becomes more concave with respect to the diagonal.

APPLICATION OF CURVES

The proposed two-component structure has found widespread application in the design of industrial fractionating columns during the past five years. The method has also been of considerable merit in aiding students of distillation to visualize the mathematical significance of multicomponent tray calculations in much the same manner as the McCabe-Thiele method has served for strictly two-component systems. Shiah (*4*) also published a two-component method for multicomponent systems. However, Shiah did not include in his method the effect of change in position of equilibrium curve with changing reflux ratio. Figure 2 illustrates that for the general problem of multicomponent fractionation, it is not always permissible to neglect this change in position of the equilibrium curve. Similar methods were also proposed by Obryadchakoff (*3*) and Brown, Singer, and Wilson (*1*).

An obvious and useful application of the two-component structure is in determining the effects of relatively small changes in reflux ratio and/or changes in terminal conditions. Thus, in the example given, if it were desired to change the terminal conditions from 1.0 to 2.0% propane in the bottoms, and also change the butane content in the overhead from 0.5 to 1.0% at a reflux ratio of 1.5 to 1, new operating lines could be drawn in and the number of trays required could be determined graphically by using equilibrium curve *b* of Figure 2. Before stepping off the number of trays from curve *b* for the new case, a small correction is made at either end of the equilibrium curve for the revised terminal conditions, based on a bubble point calculation on the bottoms liquid and a dew point calculation on the overhead vapor. An exact solution of this problem gives 11.9 calculated theoretical trays (exclusive of a reboiler and partial condenser) compared to 12.1 theoretical trays determined graphically. Similarly, an exact solution for the original terminal conditions, for a reflux ratio of 2.0 to 1, gives 12.7 calculated theoretical trays compared to 11.9 theoretical trays determined graphically from equilibrium curve *b* of Figure 2 which was calculated for a reflux ratio of 1.5 to 1. The short-cut method of stepping off the required number of theoretical trays at a reflux ratio of 2 to 1 from curve *b* gives a solution which is slightly low. This is to be expected since the equilibrium curve will become somewhat flatter at the higher reflux ratio. Actually with a reflux ratio of 1.75 to 1 the shift in the equilibrium curve is so slight than an exact solution gives the same number of trays, 13.6, as that obtained by using curve *b*.

This application of the two-component structure presupposes that a complete solution is available for a specific problem and that another solution is desired in which conditions are not greatly changed from the original problem. A commercial application is illustrated by another problem.

In an alkylation unit the effluent from the reactor contains a considerable percentage of isobutane since the alkylation reaction is favored by a large excess of this component. This stream is generally charged directly to an isobutane column where substantially all the isobutane in a high degree of purity is taken overhead and recycled to the reactor. Since the fractionation required is a relatively sharp one between close-boiling key components (iso- and *n*-butane), the isobutane column is generally a large and expensive tower, and its high consumption of utilities is an important factor

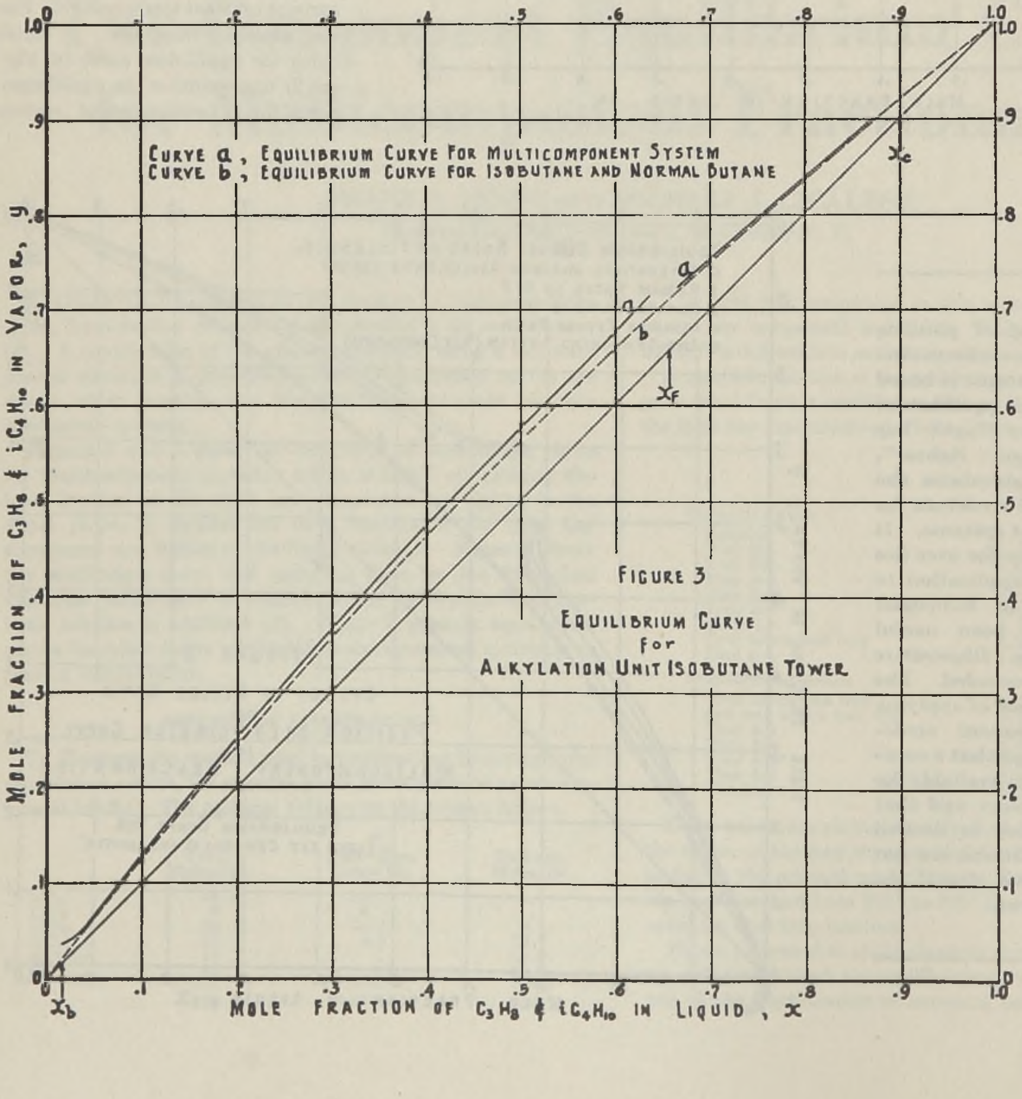

FIGURE 3
EQUILIBRIUM CURVE
FOR
ALKYLATION UNIT ISOBUTANE TOWER

in the over-all economic picture. Consequently, considerable attention is paid to the design of such a column in the selection of the optimum reflux ratio. By utilizing the two-component equilibrium curves, much of the tedious algebraic calculations have been eliminated.

The following molal material balance for an isobutane tower, taken from the design of a commercial unit, is used to illustrate the method of application:

	Feed, Moles/Hr.	Overhead, Moles/Hr.	Bottoms, Moles/Hr.
C_3H_8	98.9	98.9	....
iso-C_4H_{10}	1272.8	1263.5	9.3
n-C_4H_{10}	467.4	151.1	316.3
Alkylate	251.0	....	251.0
	2090.1	1513.5	576.6

To illustrate this case, the following simplifying assumptions are made: (*a*) Feed enters as liquid at the boiling point; (*b*) constant molal reflux is assumed in each section of the column; (*c*) constant relative volatility, α, is used as follows:

	α
C_3H_8	2.5
iso-C_4H_{10}	1.29
n-C_4H_{10}	1.0
Alkylate	0.05

For the solution of this problem, a two-component diagram is drawn first, using equilibrium data for iso- and *n*-butane. This is curve *b* of Figure 3. This curve is then used as a guide in the selection of a preliminary reflux ratio since the true multicomponent equilibrium curve will be outside this curve but close to it. A reflux ratio of 4 to 1 is selected, and several equilibrium points are calculated for the top and bottom sections of the column by direct equilibrium calculations. Equilibrium points corresponding to the feed tray and the bottom tray of the fractionating section are now calculated in the manner explained in the previous paper, making use of the fact that alkylate and propane will be essentially at their theoretical minimum concentrations on the feed tray and tray above the feed, respectively. The calculated points for the light key component and lighter (propane plus isobutane) are now plotted on an $x - y$ diagram as in Figure 3. If deemed advisable, additional equilibrium points in the vicinity of the feed tray may also be calculated directly in order to define accurately the position of the equilibrium curve in this section. With the equilibrium curve completely defined and drawn in (curve *a* of Figure 3), the theoretical number of trays is stepped off in the conventional manner. The solution of the reference problem showed thirty-one theoretical trays plus a reboiler and total condenser which checked exactly with a stepwise algebraic solution.

Other solutions within the accuracy of the equilibrium data can be determined for moderate changes in reflux ratio, using the previously determined equilibrium curve.

The examples used for illustration in the present paper are based on problems in which a relatively sharp separation is desired between adjacent components. The method has also been applied successfully to problems involving a split key component.

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Cellulose Compounds in Thermoplastic Laminates

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Thermoplastic laminates prepared by bonding fillers such as cloth and paper with cellulose acetate and ethyl cellulose plastics were evaluated in direct comparison to commercial phenolic-bonded laminates. They were found to possess an unusual degree of toughness, and were readily drawn into complex shapes with inexpensive equipment when softened by heat. They have the additional advantages of quick and easy fabrication and an unlimited range of color possibilities. Properties such as low-temperature flexibility, impact strength, modulus of elasticity, water absorption, and electrical insulation behavior can be controlled by proper selection of the bonding plastic and the filler material.

THE art of combining plastic materials with fibrous fillers is old, for some three decades ago fabric-filled phenolics were developed and placed on the market for electrical insulating and mechanical uses. Other thermosetting binders, such as the ureas and melamines, have expanded into laminar constructions, and during the war the so-called contact resins have come into prominence. All of these materials have their individual sets of properties and characteristics which tend to direct them into specific end uses where they logically belong. However, even though they differ in many respects, they have one thing in common; that is, they are thermosetting and must be polymerized by heat or a combination of heat and pressure. Furthermore, being three-dimensional polymers, they have relatively low impact strength and must depend to a large extent on the filler for impact strength or shock resistance.

During the past year this company has investigated combinations of cellulose derivative plastics, which are noted for their inherent toughness, and various types of fillers, such as fabric, paper, and asbestos paper. The purpose of this article is to present some of the results of this investigation. Two different types of laminar constructions were examined; the differences were primarily in the methods of preparation rather than in the materials employed. Low-pressure combinations of thermoplastics and cloth, which were studied in some greater detail, were prepared by pressing a sandwich lay-up of plastic sheeting and filler. A simultaneous application of heat softens the plastic sufficiently to allow it to flow into and adhere to the cloth under the exerted pressure. These are called low-pressure constructions to distinguish them from the other type which is based upon the successive lay-up of several plies of wet-plastic-impregnated cloth over a form, and which depends upon solvent release for setting

TABLE I. PHYSICAL PROPERTIES OF THERMOPLASTIC LAMINATES

(Ratio of plastic to cloth, 70:30; type of cloth, 8-ounce drill)

	Cellulose Acetate				Ethylcellulose				Phenolic Grade C
	Formula 1, soft		Formula 3, hard		Formula 4, soft		Formula 6, hard		
	P	*L*	*P*	*L*	*P*	*L*	*P*	*L*	
Izod impact strength, ft.-lb./in. notch, edgewise	4	7.3	2.9	5.5	+	5.8	4.0	5.4	3.9
Flexural strength, lb./sq. in.	680	1600	9600	10400	400	1900	5000	5900	13000
Modulus of elasticity in flexure, lb./sq. in. $\times 10^3$	14	41	230	260	5.7	62	108	150	440
Tensile strength, lb./sq. in.	500	4300	7200	8040	460	2940	3100	5370	8000
Elongation, %	75	10	26	8	37	7	15	7	1.3
Modulus of elasticity in tension, lb./sq. in. $\times 10^3$	16	79	260	390	9	59	140	337	850
Water absorption, %									
100% relative humidity, 168 hr., 77° F.	..	..	4.36	6.80	3.66	7.99	4.30	5.78	4.93
24-hr. immersion[a]	..	..	..	3.30	..	..	..	2.00	..
Thermal conductivity, cal./sec./sq. cm./° C./cm. $\times 10^{-5}$	..	74	..	54	..	71	..	54	43
Thermal expansion, in./in./° C. $\times 10^{-5}$	..	6	..	3	..	5	..	7	2.9
Sp. gr. at 77° F.	1.26	1.31	1.32	1.33	1.06	1.16	1.09	1.13	1.35
Dimensional stability, % change at 80% R.H., 168 hr. 140° F.									
Lengthwise	..	..	..	−0.34	..	..	..	−0.36	+0.18
Edgewise	..	..	..	−0.49	..	..	..	−0.49	+0.20
Flatwise	..	..	..	+3.0	..	..	..	+0.60	+0.67

[a] Determined by A.S.T.M. D570–42; edges were sealed.

into a rigid unit. The latter type will be discussed later in this report.

LOW-PRESSURE LAMINATES

Three primary factors are recognized as having an influence on the properties of thermoplastic laminates: plastic composition, type of filler, and ratio of plastic to filler. The broad range of properties obtainable by variation in plastic composition is founded on the ability of thermoplastics to be modified with high or low percentages of plasticizer giving soft and flexible or hard and rigid plastics.

In the examination of the effect of formulation on the properties of laminates several plastic compositions, based upon cellulose acetate and ethylcellulose of varying degrees of plasticization, were combined with an 8-ounce drill fabric under pressure and heat. This drill cloth weighed 7.7 ounces per square yard, with a 72/60 thread count, 61.5% of the weight being in the warp threads. The cellulose acetate, type PH-1, had a combined acetic acid content of 52–53.5% and a viscosity of 85–120 seconds by the conventional falling-ball method in a 20% solution with 90:10 acetone:ethanol. The ethylcellulose (type N-100) had an ethoxyl content of 46.8–48.5% and a viscosity of 100 centipoises in a 5% solution, the solvent being 80:20 toluene:ethanol. These two cellulose derivatives are standard materials used in commercial plastic work. The ratio of plastic to cloth was held constant at 70 parts plastic to 30 parts cloth by weight, which was found to represent an optimum combination of properties.

The materials to be laminated, consisting of alternate layers of plastic sheeting and fabric, were placed between $^3/_{16}$-inch, polished, chrome-plated steel platens in a heated press which was closed, but no pressure was applied during the initial heating period of 6 minutes. The temperature ranged from 275° F. for the very soft formulas to 350° F. for the hard formulas. Pressure was then applied and maintained while the press was cooled. This required from 10 to 12 minutes. Pressures ranged from 100 pounds per square inch for the soft formulas to as high as 400 pounds for the hard formulas. The alternate layers of cloth were cross-laid in order to obtain balanced physical properties in both directions.

As far as possible, A.S.T.M. tests were employed. In tests requiring specimens with a greater thickness than $^1/_8$ inch, composite specimens were used in accordance with A.S.T.M. practice.

EFFECT OF PLASTIC COMPOSITION ON PROPERTIES

Table I presents some properties of thermoplastic laminates and compares the unfilled plastics, designated *P*, and the laminates based on these plastics, designated *L*. The data obtained on a commercial Grade C phenolic laminate are also included. "Grade C" is the National Electric Manufacturer's Association designation for the high-impact cloth-phenolic combination which is generally recommended for mechanical uses.

One method of interpreting the data in Table I is to observe the effect of cloth when combined with the different plastic binders. Whether the plastic formulation is hard or soft, or whether the binder is based on cellulose acetate or ethylcellulose, the general effect of the fabric filler is one of increasing the impact, flexural, and tensile strengths, the modulus of elasticity in flexure and in tension, and the thermal conductivity. On the other hand, thermal expansion and percentage elongation decrease as cloth is combined with plastic.

Water absorption, as would be expected, is greater in the laminates than in the unfilled plastic. Data on all compositions were obtained by subjecting the test specimens to 100% relative humidity for 168 hours at 77° F. This procedure was used because a broad range of plastics was being tested; some contained large percentages of plasticizer while others had very little. Immersion of these materials in water, as required by A.S.T.M. Method D570-42, would result in relatively large amounts of plasticizer loss for some of the soft specimens, with the possibility

TABLE II. EFFECT OF FABRIC TYPE ON PROPERTIES OF THERMOPLASTIC LAMINATES

(Ratio of cellulose acetate PH-1 to Santicizer M-17, 75 to 25; Ratio of plastic to cloth, 70 to 30)

Type of cloth	Airplane	Balloon Basket Weave	Chafer Duck	Chafer Duck	Hose Duck	Harvester Duck	Drill Cloth
Count	80 × 80	104 × 98	35 × 25	23 × 23	26 × 22	32 × 16½	...
Breaking strength							
A.S.T.M. raveled strip method	80 × 80	120 × 120	...	...	...	...	...
A.S.T.M. grab method	...	...	92 × 61	201 × 191	119 × 122	546 × 432	...
Weight, oz./yd.	4.0	5.6	5.6	14.0	9	31.5	8
No. of layers of cloth	8	6	6	2	3	1	4
Izod impact strength, ft.-lb./in. notch, edgewise	2.7	3.4	2.5	3.6	3.5	5.2	5.5
Flexural strength, lb./sq. in.	16,500	17,200	14,000	12,400	12,100	12,700	10,400
Tensile strength, lb./sq. in.	11,200	15,100	8,700	7,300	8,000	7,400	8,040
Elongation, %	6.9	3.5	4.5	7.6	6.6	11.9	8
Elastic modulus in tension, lb./sq. in. $\times 10^3$	900	1000	610	430	440	350	390
Water absorption (100% R.H., 168 hr. 77° F.), %	5.7	6.4	7.0	7.2	7.2	6.5	6.8

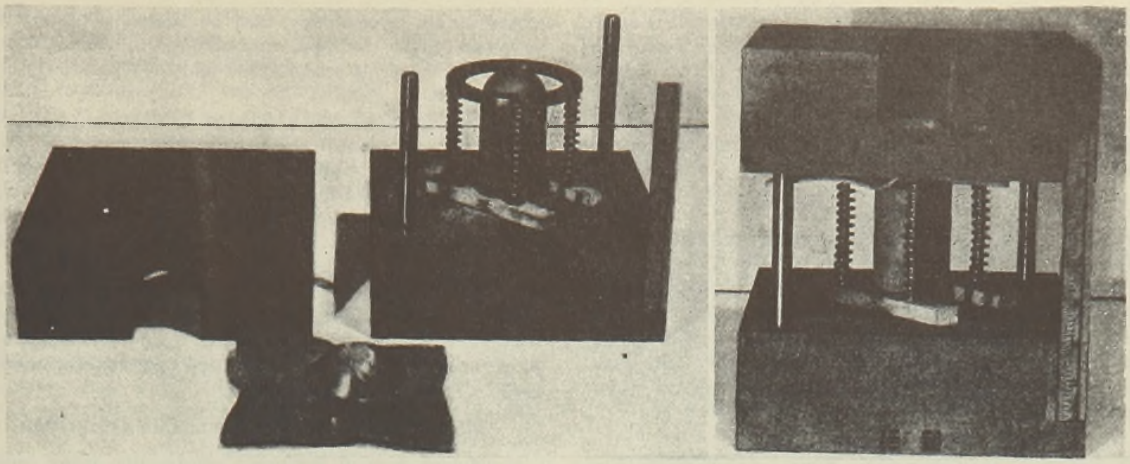

Figure 1. Parts of Drawing Mandrel (*left*) and Assembled (*right*)

that water absorption data would not be correct even though the procedure described in D570–42 is supposed to compensate for such loss. However, limited data were obtained on formulas 3 and 6 according to D570-42 in order to obtain comparative values. The edges of the specimens subjected to the high humidity test were not sealed so that the specimens would come to equilibrium with the humid atmosphere within the test period of 168 hours. Sealing the edges by coating them with a solvent solution of the plastic with which the laminate was made would greatly lower water absorption by reducing the wicking action of the fabric.

Another interpretation of Table I is the analysis of the effect of plastic formulations on physical properties. This is done by comparing the two *L* columns under formulations 1 and 3 for cellulose acetate or the *L* columns under formulas 4 and 6 for ethylcellulose. The general effect of decreasing the plasticizer content, or increasing the cellulose derivative in the bonding plastic, is to lower impact strength and thermal conductivity; on the other hand, flexural and tensile strengths and elastic moduli in flexure and in tension increase substantially.

The thermoplastic laminate which shows the closest degree of similarity with the Grade C phenolic laminate is based upon the hard cellulose acetate formulation. The phenolic structure has higher flexural strength, higher modulus, lower water absorption, and slightly lower thermal conductivity while the thermoplastic construction has greater impact strength and higher elongation The two are comparable from the standpoints of tensile strength and thermal expansion.

TABLE III. ELECTRICAL PROPERTIES OF THERMOPLASTIC LAMINATES

	Cellulose Acetate		Ethylcellulose		Phenolic, Grade LE
	Formula 1, soft	Formula 3, hard	Formula 4, soft	Formula 6, hard	
Dielectric strength (25° C., 60 cycles), volts/mil (step bystep)					
Dry	320	360	370	480	360
Wet[a]	27	210	82	68	78
Power factor (25°C.)					
60 cycles					
Dry	0.299	0.080	0.038	0.071	0.34
Wet	>0.70	0.109	0.135	0.045	0.66
1,000,000 cycles					
Dry	0.0509	0.0434	0.0443	0.0289	0.0570
Wet	0.132	0.133	0.100	0.107	0.122
Dielectric constant (25° C.)					
60 cycles					
Dry	8.2	5.6	4.5	4.3	12.9
Wet	>30.0	16.4	13.1	13.8	>30.0
1,000,000 cycles					
Dry	6.0	4.4	4.2	3.6	5.2
Wet	13.1	9.6	6.6	8.1	6.8

[a] Signifies 7 days' immersion in water at 25° C.

In concluding this phase of investigation where plastic formulation and its effect on physical properties have been covered, it is pertinent to point out that the range of plastic compositions, from soft to hard, is not complete. The limit on the soft end of the range has been approached and is determined by plasticizer retention. Since the maximum temperature available in our laboratory equipment is approximately 350° F., and since this is also the maximum with large commercial laminating presses, the hard formulations contain as little plasticizer as possible, consistent with proper impregnation at 350° F. and up to 400 pounds per square inch pressure. Attempts to obtain impregnation of harder plastics with greater pressure were unsuccessful due to lateral flow of the plastic and tearing of the fabric. When higher temperatures are made available in commercial equipment, the use of harder formulations will result in greater tensile and flexural strengths and greater elastic moduli, all of which are important properties in many end uses. However, research with fabrics other than 8-ounce drill cloth has resulted in considerable improvement in these properties (Table II).

EFFECT OF FABRIC TYPES ON PROPERTIES

With plastic composition and ratio of plastic to cloth held constant, results in Table II indicate that the type of fabric has a definite bearing on the physical properties of the laminated structure. For instance, the use of balloon cloth resulted in laminates having greatly increased tensile and flexural strengths and an elastic modulus in tension of more than twice that obtained with 8-ounce drill. However, these properties are increased at the expense of impact strength which is considerably lower than that obtained with the drill cloth. The four duck weaves fall in between the two extremes when strength qualities are examined, and all of the fabrics give water absorption results within a fairly narrow range.

ELECTRICAL PROPERTIES

The electrical properties of thermoplastic laminates (Table III) were determined on soft and hard combinations by standard A.S.T.M. methods. For comparison, tests were conducted at the same time on a Grade LE phenolic laminate which is commonly used for electrical applications requiring toughness. Both the thermoplastic and thermosetting compositions break down rather badly after soaking in water. In the dry state, however, the thermoplastic laminates are good insulating materials. For dielectric strength the cellulose acetate structures are roughly comparable to the Grade LE phenolic laminate while the ethylcellulose is far superior. The power factor of ethylcellulose laminates is vastly superior to the thermosetting compound; cellulose acetate is somewhat better. Both cellulose acetate and ethylcellulose laminates show a much better dielectric constant at 60 cycles, with ethylcellulose again being the best. At 1,000,000 cycles the superiority of the cellulosic compositions is still noticeable but by a closer margin.

EFFECT OF FILLERS

Physical properties obtained on combinations of thermoplastics with fillers other than cloth are shown in Table IV. Asbestos paper produced a laminate with remarkable properties in all respects; the significant value is the elastic modulus of nearly 2,000,000. Glass fabric also produced an outstanding laminate; extraordinarily high impact strength was combined with high tensile strength and high modulus, and a relatively low water absorption value.

Table IV. Effect of Miscellaneous Fillers on Properties of Laminates

Type of Filler	Asbestos Paper	Glass Fabric	Kraft Paper
Number of layers	30	3	25
Izod impact strength, ft.-lb./in. notch, edgewise	3.7	>14.9	1.7
Flexural strength, lb./sq. in.	19400	8500	17900
Tensile strength, lb./sq. in.	23100	25800	14500
Elongation, %	1.86	2.8	2.5
Modulus of elasticity in tension, lb./sq. in. × 10^3	1890	1160	1000
Water absorption (100% R.H., 168 hr., 77° F.), %	4.4	3.34	5.6

The laminate based on kraft paper also has exceptional strength properties with the exception of impact. However, this value is quite good when compared with similar values for paper-base phenolics. These determinations are edgewise and would, therefore, be considerably greater if flatwise specimens were tested. The best results to date have been achieved with an absorbent type of kraft furnished by the Forest Products Laboratory. The values in Table IV are based on a laminate prepared with this paper.

OTHER CHARACTERISTICS

One of the most important qualities of thermoplastic laminates with cloth fillers is their adaptability to easy and economical fabrication. They can be formed and drawn into complex shapes when heated, and component parts may be sealed together quickly by solvents or heat (Figure 1). In examining the drawability of various fabric fillers, a drawing mandrel was used. The apparatus consists of a base block to which is attached a ram 2 inches in diameter. This ram is guided into an opening 2$^5/_{16}$ inches in diameter in the upper block. The clamping ring, supported by springs, serves to prevent wrinkling around the edge of the draw; pressure is adjusted to the extent that the hot laminate can slide over the ring and into the mold to increase the ultimate depth of draw. The procedure followed in evaluating the draw characteristics of different fabrics was to heat 6 × 6 inch laminates, based on these fillers, to a predetermined temperature and to transfer them immediately from the heating unit to the drawing device. The pressure for drawing was supplied by a small hydraulic press. Motion was stopped when the first sign of rupture occurred, as seen from the opening in the upper block. The value for drawability was taken as that depth to which the unit was drawn to cause rupture.

The deepest draws were obtained with a high-twist open-weave fabric such as bootleg duck or with very high-tensile-strength fabrics such as balloon cloth. The drawing characteristics of laminates bonded with either a cellulose acetate or an ethylcellulose plastic were comparable.

There is practically no limit to color versatility with thermoplastic laminates. The plastic binder may be dyed or pigmented, or the surface layer of cloth may be colored or printed with a design and given the appearance of depth by the use of a clear plastic binder. This advantage should be important in civilian applications.

The proper selection of plastic composition is important for low-pressure laminates. For instance, where extreme low-temperature flexibility or good electrical properties are desired, formulations based on ethylcellulose are indicated. On the other hand, if delicate shades of color or high grease resistance is wanted, it would be advisable to choose a plastic based on cellulose acetate.

In conclusion, the addition of cloth to cellulosic plastics increases all of the strength properties of the thermoplastic compositions themselves and contributes other factors which may direct them into applications where they have not previously been used.

NO-PRESSURE (SOLVENT-RELEASE) LAMINATES

A different type of laminated construction using cellulosic thermoplastics as binders is based upon solvent release for obtaining rigid constructions, and has been used in a limited number of applications for many years. The basic advantages of solvent-process laminating lie in the ease of fabricating large or complicated laminates without the need for expensive equipment or skilled labor. They differ from other no-pressure methods of laminating where thermosetting resins are used, in that no heat is required since the cellulosic plastic binders need not be cured.

The equipment and materials necessary for no-pressure construction are simply a wood or plaster mold or a skeleton frame, a dope solution containing the plastic binder, an open-weave fabric which lends itself to easy impregnation, and brushes for application of the dope solution to the fabric. The method of application consists in cutting the fabric to the shape required to cover the mold uniformly, laying the cloth over the mold, and impregnating it with the plastic solution. This procedure is repeated with successive plies of treated cloth until the desired thickness is attained. An interlayer of cellophane between the mold and the first layer, or a coat of wax on the mold, ensures quick release when the laminated unit is ready to be removed. The time interval for solvent release may range from several minutes to several hours, depending on the thickness of the construction.

Table V. Physical Properties of No-Pressure Thermoplastic Laminates

	A.S.T.M. Test No.	Value
Izod impact strength, ft.-lb./in. notch, edgewise	D256–41T	6–10
Tensile strength, lb./sq. in.	D638–42T	1300–4400
Modulus of elasticity in tension, lb./sq. in.	D638–42T	15000–170000
Elongation, %	D638–42T	8–15
Water absorption, %		
24-hr. immersion[a]	D570–42	6–12
100% R.H., 168 hr., 77° F.	.....	10–12

[a] Edges were sealed.

In examining no-pressure thermoplastic laminates, the primary consideration has been the study of physical properties obtained when various binders such as ethylcellulose, cellulose acetate, and cellulose nitrate were employed. The over-all results are described in Table V. Specimens for these tests carried varying percentages of cloth ranging from 30 to 64%. The amounts of plasticizer in the cellulose bonding agents also were adjusted from 15 to 30% of the plastic composition. Osnaburg cloth with a weight of 8 ounces per yard was used throughout.

In general, as the ratio of cloth to plastic is increased, the impact strength, per cent elongation, and water absorption values show corresponding increases while the values for tensile strength and elastic moduli go down. The range found most workable for the wet method of lamination was 45–65% fabric content:

the optimum solids content of the dope solutions from the standpoint of application by brush was 10-15%. Cellulose acetate binders were dissolved in a 90:10 mixture of acetone and ethanol; the solvent for ethylcellulose was ethyl acetate.

The effect of increasing the percentage of plasticizer in the bonding plastic was to lower water absorption and elastic moduli while the percentage elongation increases. Impact and tensile strength values showed no consistent trend and were quite comparable. Water absorption values were determined both by direct immersion in water for 24 hours in accordance with A.S.T.M. recommended procedure and by exposure to 100% relative humidity at 77° F. for 168 hours. It was considered satisfactory to immerse the no-pressure solvent-release specimens, since the plastic binders had relatively low amounts of plasticizer and therefore plasticizer loss would not be significant.

In comparing the resulting products of two methods of lamination with cellulosic binders—that is, the low-pressure type which was first discussed and this solvent-release build-up type—the following facts are apparent: The pressure types with comparable plastic formulations have greater tensile and flexural strengths and much higher moduli; they also have lower water absorption. On the other hand, solvent-release no-pressure constructions are superior in impact strength and are lighter in weight, having densities around 0.8 to 1.0 as against 1.15 for ethylcellulose low-pressure structures and 1.3 for cellulose acetate low-pressure types.

The method of producing low-pressure laminates, involving mechanical cloth treating and pressing equipment, indicates that they lend themselves to volume production. On the other hand, no-pressure, solvent-release laminations do not lend themselves so easily to mechanization but do have the advantages of requiring simpler and lower-cost equipment for fabrication, and can be built up into larger units.

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Aconitic Acid from Citric Acid by Catalytic Dehydration

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ACONITIC acid is the common name of propene-1,2,3-tricarboxylic acid. This unsaturated acid occurs in nature in *Aconitum napellus*, *Equisetum fluviatile*, sugar cane, beet root (*13*), and sorghum (*11*). Aconitic acid has been suggested as a possible ingredient of modified alkyd resins. Esters of aconitic and tricarballylic (dihydroaconitic) acids have been employed as plasticizers for plastics and Buna-type synthetic rubbers, and in the manufacture of wetting agents (*10*). Aconitic acid can be readily decarboxylated to itaconic acid (*7*), whose esters can be polymerized to produce plastics (*2*).

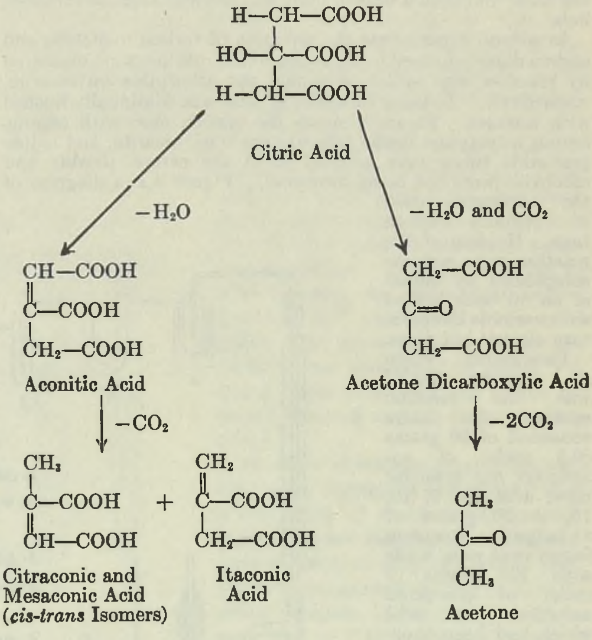
Previously reported methods for aconitic acid include recovery from sugar cane sirup residues (*8*), dehydration of citric acid by sulfuric acid (*3, 12*), hydrochloric and hydrobromic acids (*5*), and H_3PO_4 (*3*), and direct synthesis from sodium malonic and acetylene dicarboxylic esters (*9*).

Because citric acid is relatively cheap and, in normal times, is abundant, most aconitic acid produced in the past has been derived from citric acid by the mineral acid dehydration process. Rather low yields (41-44% with sulfuric acid, *3*) and extremely corrosive conditions in the mineral acid processes were responsible for the present investigation.

Three general methods were employed: (*a*) homogeneous systems in which the citric acid and catalyst were dissolved in a suitable organic solvent; (*b*) heterogeneous systems in which the citric acid was suspended and the catalyst suspended or dissolved in an organic liquid; and (*c*) a vacuum fusion process in which the citric acid and catalyst in intimate mixture were heated under 23-24 mm. mercury absolute pressure; in this process fusion occurred at the temperatures employed which were always below the normal melting point of citric acid (153° C.).

Because of the relative instability of aconitic acid above 150° C., the work was limited to the range between 150° and 120° C. (the minimum temperature at which citric acid could be dehydrated even under the influence of a catalyst).

Previous investigation (*7*) showed that the pyrolysis of citric acid can proceed in two directions; both liberate water but only one produces aconitic acid:



The decomposition products of aconitic acid are the isomeric acids itaconic (methylene succinic), and citraconic (methyl maleic) and mesaconic (methyl fumaric). Acetone and carbon dioxide are the decomposition products of acetone dicarboxylic acid.

DEHYDRATION PROCEDURE

APPARATUS. The reaction apparatus consisted of a three-neck flask with the center neck containing a motor-driven agitator and one side neck containing a Dean-Stark tube and total condenser. In the case of runs made at atmospheric pressure, the water liberated during the course of the reaction was measured by collection in the Dean-Stark tube. In vacuum fusion ex-

Aconitic acid has been prepared in limited quantities in the past by the mineral acid dehydration of citric acid. This paper describes the preparation of aconitic acid by the catalytic dehydration of citric acid, a noncorrosive process. In one technique a nonsolvent for citric and aconitic acid is used as the suspension medium for the acids and catalyst; in the second method citric acid is mixed with the catalyst in the dry state, and the mixture is heated under vacuum at temperatures sufficient to fuse the reaction mass. In either case the reaction is continued until approximately half of the citric acid is converted. Carrying the reaction past this point results in too high a decomposition of citric and aconitic acids to give such products as acetone, itaconic acid, and citraconic acid. A preliminary investigation indicates that aconitic and unconverted citric acid can be separated by the solvent extraction of a water solution of the two acids.

periments the Dean-Stark tube was supplemented by two calcium chloride tubes in series, interposed between it and the water aspirator used as the source of vacuum. A thermometer inserted in the second side neck of the flask measured the temperature of the reaction mass.

In heterogeneous systems good agitation was achieved by a semicircular anchor-type agitator large enough to wipe the inner surface of the reaction flask almost completely. The paddle was made of three pieces of stainless steel spot-welded to a threaded hub. The paddle was inserted through one of the side necks of the flask, and then a bronze shaft was screwed into the threaded hub.

In several experiments the amounts of carbon monoxide and carbon dioxide formed in the course of the reaction were measured by reaction with iodine pentoxide and absorption on ascarite, respectively. In these runs, the system was continually flushed with nitrogen. Figure 1 shows the system used with organic liquids as reaction media (the dry ice trap, ascarite, and iodine pentoxide tubes were omitted when the carbon dioxide and monoxide were not being measured); Figure 2 is a diagram of the apparatus used in vacuum fusion runs. Heating of the reaction mass was accomplished by means of an oil bath heated with variable temperature electric hot plate.

PROCEDURE. When an organic liquid was the reaction medium, the charge consisted of 96 grams (0.5 mole) of anhydrous, fine granular citric acid and 5, 10, 15, or 20 grams of catalyst. Vacuum fusion runs were made with 192 grams (1 mole) of powdered anhydrous citric acid which had been thoroughly mixed in a mortar with 10, 20, or 40 grams of catalyst.

The time required for the contents of the flask to reach reaction temperature was usually less than 30 minutes. Readings of temperature and the amount of water collected in the Dean-Stark tube were taken every 10 minutes from the time the reaction mass reached the desired temperature or from the time the first droplet of water appeared in the Dean-Stark tube, whichever occurred first. In the case of vacuum fusion runs, the weight of water collected in the calcium chloride drying tubes located between the Dean-Stark tube and aspirator was added to that found in the Dean-Stark tube in order to determine the water evolved in the course of the experiment.

At the completion of a run, water was added to the reaction flask in order to dissolve the product; when organic solvent was used, it was removed by decantation in the case of nonsolvents for citric or aconitic acids, or by steam distillation when the material was a solvent for the acids. The water solution was filtered, and the water was removed by azeotropic distillation with benzene. In this manner it was often possible to recover the reaction product as a finely divided material. The entire recovery process was often carried out in 3–4 hours.

METHODS OF ANALYSIS. Because of the lack of a suitable quantitative method of analysis, the aconitic acid content of the reaction product was determined by difference. The mixture of acids obtained in a run was titrated for total acidity, and analyzed for citric acid by the pentabromoacetone method (*6*) and for itaconic and citraconic acids by noncatalytic bromination, employing acid bromate-bromide as the source of bromine (*8*). The acidity due to citric, itaconic, and citraconic acids was calculated and expressed as milliequivalents per gram of product and was subtracted from total acidity, and the residual acidity was ascribed to aconitic acid.

Although the limitations of such a method are obvious, it did serve to indicate the amounts of aconitic acid that might be expected in the reaction product. Furthermore, Seuffert (*14*) used the Heyrovsky-Shikata polarograph for a quantitative estimation of aconitic acid in our reaction product, and verified the amounts found by the method of difference. Unfortunately, difficulties encountered by Seuffert did not permit the analysis of all the reaction products, but representative data follow:

Run No.	% Aconitic Acid By difference	 By polarographic analysis
88	42.3	42.3
92	40.8	40.4

The temperatures involved in the dehydration experiments were generally above the decomposition temperature of acetone dicarboxylic acid, but several determinations were made to ascertain whether any of this material was present in the reaction product. Since acetone dicarboxylic acid is unstable in hot mineral acid solutions, the total amount of citric and acetone

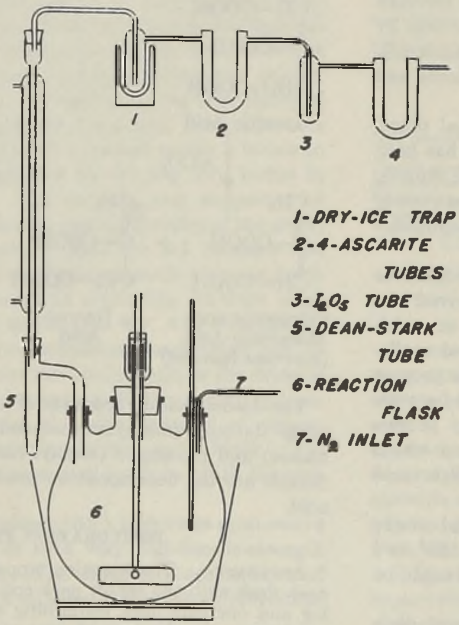


Figure 1. Apparatus Used in Runs with a Withdrawing Agent

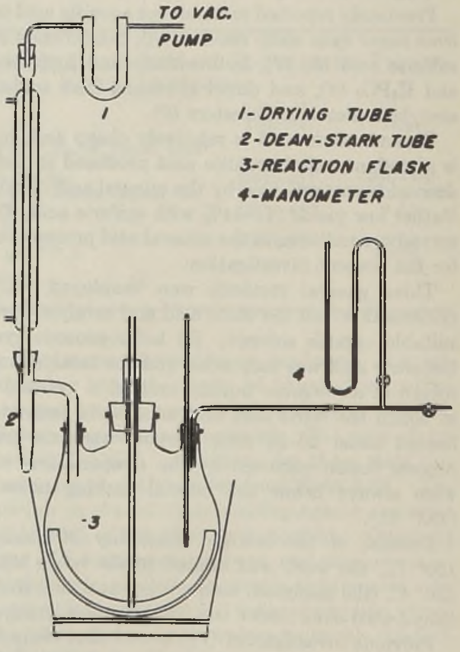


Figure 2. Apparatus Used in Vacuum Fusion Runs

dicarboxylic acids in the product was determined as pentabromoacetone; then a separate sample of the product was boiled in dilute sulfuric acid solution for one hour, and the citric acid alone was determined by precipitation as pentabromoacetone. Because of the time required to make the analysis and because check runs showed comparatively little acetone dicarboxylic acid in the reaction product, this determination was run only when a complete analysis was desired.

DATA. A total of 142 runs was carried out. A few of the reaction products obtained were not analyzed because it was obvious from the weights of the material recovered that the catalyst had caused excessive pyrolysis of the citric acid and the products of the reaction. Representative data are listed in Tables I and II.

ORGANIC LIQUIDS AS REACTION MEDIA

In these runs orthophosphoric acid, ethyl phosphoric acid (a mixture of approximately 65% monoester and 35% diester, as received from Monsanto Chemical Company), and a mixture of phosphoric acid and fuller's earth supplied by Universal Oil Products Company were found to be good catalysts.

The most suitable media for the reaction were the nonsolvents for citric and aconitic acids. The selection of such a reaction medium depended solely on its boiling point. The solvents for citric acid, such as the ketones and diethyl Cellosolve were of little value as reaction media because it was impossible to control the pyrolysis to obtain the desired aconitic acid. These runs were all characterized by low recovery of a reaction product containing 10 to 25% of itaconic and citraconic acids.

Of the nonsolvents, aromatic hydrocarbons were used as reaction media because they were readily available and had the desired boiling points. It was found that the reaction could be carried out from 120° to 150° C. In this temperature range and with the catalysts mentioned, it was possible to obtain good conversions of citric acid to aconitic acid provided the reaction was only 50% complete. If the reaction was carried beyond the 50% point, recoveries of reaction products decreased markedly and greatly increased formation of itaconic and citraconic acids and nonacidic tarry materials. For every mole of citric acid dehydrated, 2 moles of water were formed. Only half of the water liberated was due to the pyrolysis of the citric acid; it was probable that the extra water formed in the dehydration reaction was due to the formation of acid anhydrides.

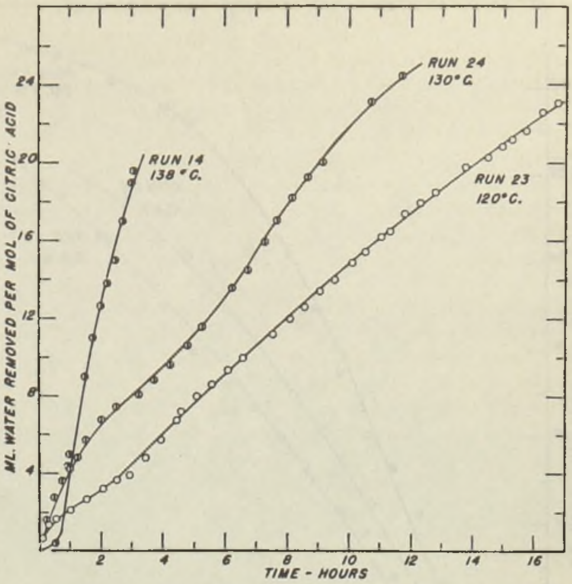


Figure 3. Effect of Reaction Temperature on Rate of Water Removal in Runs Made with a Withdrawing Agent and 5.2% Phosphoric Acid as Catalyst

Figure 3 illustrates the effect of temperature on the rate of reaction. Three runs were made using 5.2% orthophosphoric acid as catalyst and either xylene or a blend of xylene and toluene as reaction medium. The xylene boiled at 138° C., and the blends had boiling points of 130° and 120° C. under total reflux. The run with xylene as reaction medium was completed in about 3¼ hours; those employing the blends required about 9 and 14 hours, respectively.

The effect of catalyst concentration on the rate of reaction is less marked than is the effect of reaction temperature. Figure 4 shows the effects of increasing concentrations of ethyl phosphoric acid, which is completely soluble in the reaction medium in the concentrations used, and of U.O.P. catalyst, which is insoluble in the reaction medium. The soluble catalyst is, of course, more intimately associated with the citric acid than is U.O.P. No. 2 and, therefore, the effect of catalyst concentration on the rate of reaction is more marked than for the U.O.P. catalyst. However, tripling the catalyst concentration had far less effect on the rate of reaction than increasing the temperature from 130° to 138° C.

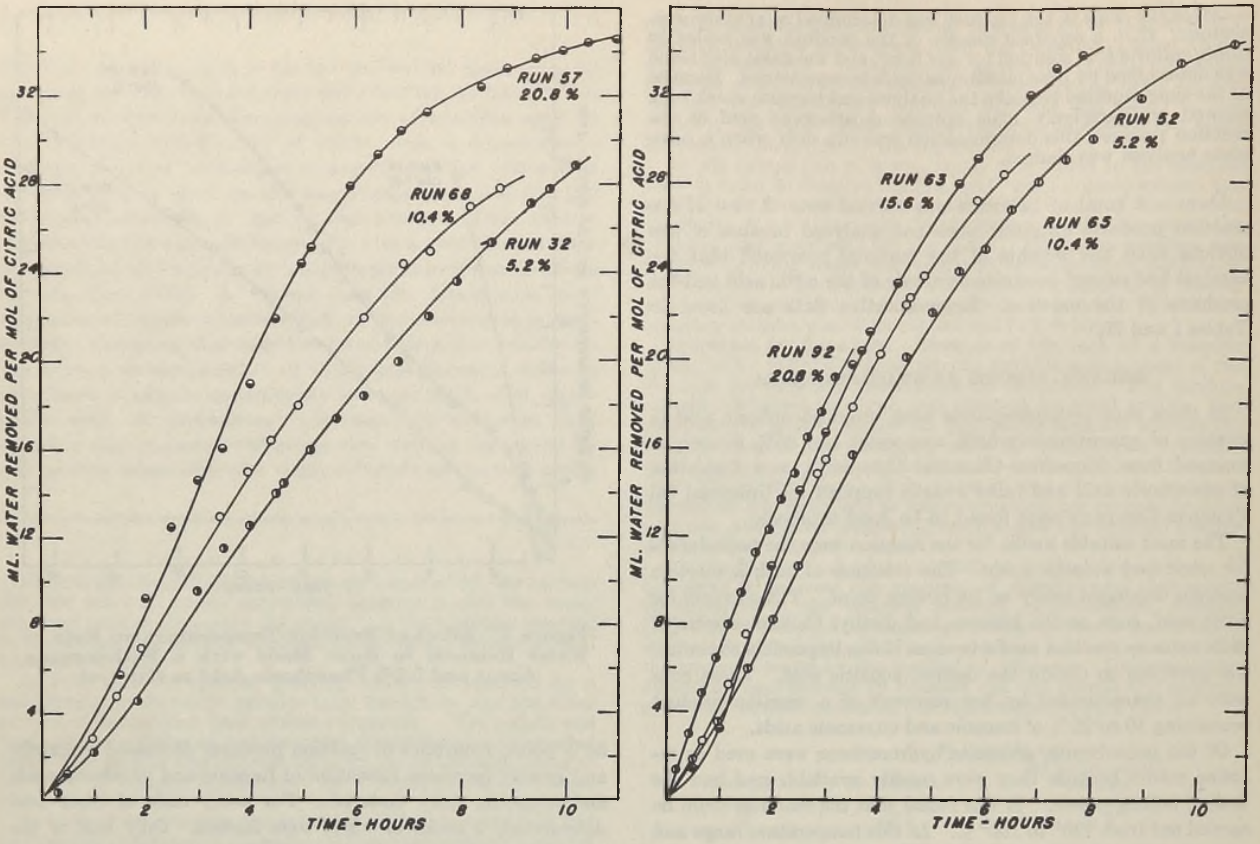
TABLE I. DATA FROM RUNS WITH AN ORGANIC LIQUID AS REACTION MEDIUM

Run No.	Catalyst, %	Reaction Medium (B.P. in ° C.)	Ml. H_2O Removed per Mole Citric Acid	Reaction Time, Hr.:Min.	Compn. of Product, % Citric acid	 Aconitic acid	 Itaconic acid[a]
23	H_3PO_4, 5.2	50% xylene + 50% toluene (120)	23.6	17:45	41.7	51.5	3.1
24	H_3PO_4, 5.2	75% xylene + 25% toluene (130)	30.8	21:15	Not analyzed		
14	H_3PO_4, 5.2	Xylene (138)	19.6	3:55	Not analyzed		
16[b]	H_3PO_4, 5.2	Xylene	19.8	6:30	48.9	44.1	0.2
32	E.P.A.[c], 5.2	Xylene	14.0	4:30	68.0	24.5	3.0
			28.8	10:50	9.2	72.3	8.9
68	E.P.A., 10.4	Xylene	30.0	8:5	11.8	67.2	6.1
57	E.P.A., 15.6	Xylene	34.6	11:15	0.2	74.9	11.0
52	U.O.P. 2[d], 5.2	Xylene	36.0	13:10	1.8	67.2	14.1
65	U.O.P. 2, 10.4	Xylene	28.2	6:15	21.5	58.8	9.7
63	U.O.P. 2, 15.6	Xylene	33.8	7:40	7.3	72.0	9.8
72	U.O.P. 2, 10.4	Xylene	18.0	4:30	55.4	34.7	3.6
74	U.O.P. 2, 10.4	Xylene-cymene (142)	18.8	3:20	48.4	40.0	8.8
92	U.O.P. 2, 20.8	Xylene	19.2	3:10	52.5	40.8	2.9
M-1	H_2PO_4, 5.2	Methyl isobutyl ketone	16.8	9:20	66.0	6.4	27.7
M-6	H_3PO_4, 5.2	Methyl *n*-amyl ketone	36.0	10:0	13.4	63.0	23.4
M-12	H_3PO_4, 5.2	Diisopropyl ketone	31.0	25:5	23.4	51.8	17.0

[a] Includes citraconic acid.
[b] 2.5 moles of citric acid were used in this run, 0.5 mole in all other runs.
[c] Ethyl phosphoric acid from Monsanto Chemical Company.
[d] Universal Oil Products Company catalyst.

TABLE II. EFFECT OF WATER REMOVAL ON CONVERSION OF CITRIC ACID IN VACUUM FUSION RUNS WITH 20.8% U.O.P. CATALYST

Run No.	Ml. H_2O Removed per Mole Citric Acid	Pressure, Mm. of Hg	Temp., ° C.	Compn. of Product, % Citric acid	 Aconitic acid	 Itaconic acid	% Recovery	% Conversion
83	12.7	10	132	75.2	24.0	0.8	99.2	94.8
88	18.5	12	137	55.8	42.7	1.5	96.7	99.2
85	25.0	12	136	38.7	55.8	5.5	93.8	81.5
95	30.7	19	144	6.5	76.5	17.0	81.4	65.5



Ethylphosphoric acid as catalyst

U.O.P. No. 2 as catalyst

Figure 4. Effect of Catalyst Concentration on Rate of Water Removal Using Xylene as Withdrawing Agent

Figure 5. Effect of Concentration of U.O.P. No. 2 on Water Removal in Vacuum Fusion Runs

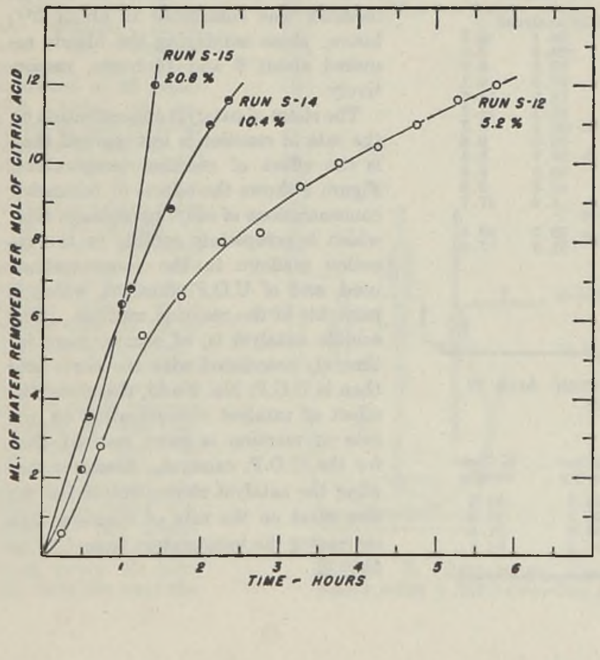
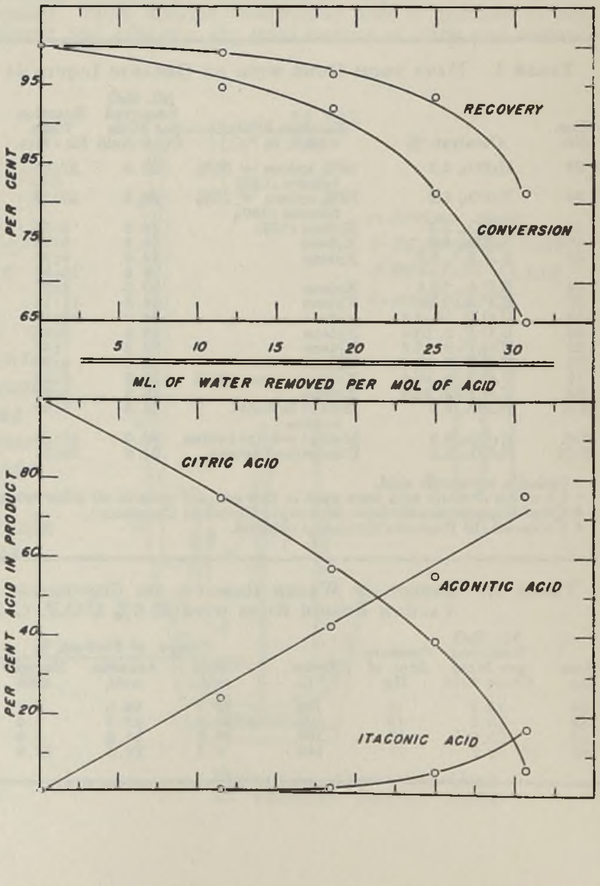


Figure 6. Effect of Water Removal on Conversion of Citric Acid



Raising the temperature caused an increase in reaction rate and a decrease in the amount of itaconic acid formed, since prolonged heating converted aconitic acid to itaconic acid. Raising the temperature beyond 140° C. resulted in diminished returns because at that point the rate of conversion of aconitic to itaconic acid increased rapidly. This point was shown in run 74; a reaction medium of cymene and xylene having a boiling point of 142° C. was used, and other conditions were similar to those of run 72. Although the same amount of water was removed, the higher temperature resulted in a product containing almost 9% itaconic acid, as compared to about 3.6% in run 72.

VACUUM FUSION RUNS

In this series the catalyst had to be nonvolatile at a temperature of about 140° C. and a pressure of not more than 25 mm. of mercury. Of the catalysts available, only the metallic phosphates and oxides and U.O.P. No. 2 met this requirement. Because of the work previously carried out with organic liquids as reaction media, only U.O.P. No. 2, aluminum phosphate, and various grades of alumina were investigated. U.O.P. No. 2 was found to be most effective from the standpoint of higher conversion of citric to aconitic acid and decreased reaction time.

Five grades of alumina were tried; all of them caused considerable decomposition of aconitic to itaconic acid, and also resulted in lower recoveries (due presumably to greater pyrolysis of the citric acid and its decomposition products).

Experiments were run on the U.O.P. catalyst to determine the effect of catalyst concentration on the rate of reaction. The results are shown in Figure 5; comparison with Figure 4 shows that catalyst concentration has a greater effect in the vacuum fusion process than in the organic liquid process. This difference is probably due to the fact that agitation was better in the case of the runs made with an organic liquid as reaction medium, and, consequently, contact between the catalyst and fresh citric acid was more complete.

The effect of the extent of water removal on the formation of aconitic and itaconic acids and on the percentage conversion and recovery is illustrated by runs 83, 85, 88, and 95 (Table I and Figure 6). Figure 6 shows that, although in the vacuum fusion process a product can be obtained which is substantially free of citric acid, a considerable part of the aconitic acid formed is converted to itaconic acid. The curves also indicate that, in addition to the loss of aconitic acid through its pyrolysis to itaconic acid (and possibly citraconic and mesaconic acids), there is further loss due to more complete pyrolysis of citric and aconitic acids. The latter, more complete pyrolysis results in the formation of dark colored, noncrystalline materials of unknown composition which are partially insoluble in water. Thus, at least with the catalysts thus far investigated, it is not feasible to attempt complete dehydration of the citric acid in the charge. Fifty per cent dehydration (i.e., one mole of water removed per mole of citric acid charged) was chosen as the end point of the reaction. At this point the amount of itaconic acid found in the product is still less than 1%; only 3% of the citric acid charged is lost through the formation of gaseous products of decomposition such as acetone, carbon monoxide, and carbon dioxide; and 92% of the citric acid converted is present as aconitic acid. Of the above mentioned curves, the curve in Figure 6 representing percentage conversion is based on the grams of aconitic acid present in the reaction product divided by the number of grams that would be present if all the citric acid decomposed had been converted to aconitic acid. The percentage recovery refers to the weight of citric acid and reaction products recovered, divided by the total weight of citric acid charged to the reactor.

Several large-scale runs were made using a charge of 3 moles of citric acid. The recoveries in these experiments were slightly lower, and slightly more itaconic acid was formed than in the case of the smaller charges. However, both of these points could probably be improved by better agitation and heating.

CATALYSTS

A large number of materials were investigated as possible catalysts (*1*, *4*) for the production of aconitic acid. They are listed below according to the degree of activity demonstrated in the course of a large number of experiments:

GOOD CATALYSTS. U.O.P. No. 2, ethyl phosphoric acid, orthophosphoric acid.

FAIR CATALYSTS. Kaolin, fluorite, tungstic oxide, sodium bisulfate, dichloroacetic acid, pyrophosphoric acid, metaphosphoric acid, polyphosphoric acid.

POOR CATALYSTS. Cyanoacetic acid, bentonite, chloroacetic acid, zinc chloride.

NONCATALYSTS. Sulfuric acid and paratoluene sulfonic acid (complete pyrolysis of citric acid); aluminum chloride and triethyl phosphate (no catalytic activity).

Good catalysts are designated as those which gave high yields of a product containing only aconitic acid and unreacted citric acid; fair catalysts gave low yields of product; poor catalysts, low yields of aconitic acid mixed with citric acid and other decomposition products; and noncatalysts are either without catalytic activity or those which resulted in complete pyrolysis of the citric acid.

SEPARATION OF ACONITIC AND CITRIC ACIDS

Because yields of aconitic acid are highest when the reaction is only partially complete, a method of separating the two acids was necessary. These acids are so similar in chemical properties and solubilities that most of the usual methods for separating organic acids were of little use. However, investigations now underway indicate that the extraction of aconitic acid from a water solution of the mixed acids by an organic solvent may be possible. The most promising solvent found to date is methyl isobutyl ketone.

To identify aconitic acid in the reaction product, small-scale separations were carried out by precipitation of the aconitic acid from water solutions by saturation with hydrogen chloride. The product precipitated from the cooled solution was recrystallized from acetic acid and found to possess the acid valu calculated for aconitic acid—17.1 (calculated 17.24).

ACKNOWLEDGMENT

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Esterification of Butanol and Acetic Acid

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Knowledge of the kinetics of the reaction of butanol and acetic acid catalyzed by sulfuric acid, coupled with vapor-liquid equilibrium data, should allow the calculation and design of the distillation unit for the combined steps of reaction and separation. The densities of butanol, acetic acid, and butyl acetate at temperatures from 20° C. to their respective boiling points were determined to allow estimations of the volumes at reaction temperatures. The esterification reaction was more complex than that given by the customary equation. The reaction of butanol and sulfuric acid is probably the controlling factor at room temperature, but at the temperatures used in continuous processing (100–120° C.), the esterification reaction was the controlling factor. With an excess of butanol as solvent, the reaction rate was proportional to the square of the acetic acid concentration, up to 75–85% conversion. The theoretical aspects of the mechanism are discussed and compared with the generally accepted Goldschmidt equation for catalytic esterifications. The effect of catalyst concentration, proportions of reactants, and temperature on the reaction rate constant were also studied. The results correlated into a single empirical equation for predicting the rate constant from these three quantities within an accuracy of about 8% in the range studied.

TWELVE years ago Keyes (*14*) pointed out the desirability of carrying out esterification reactions continuously inside ordinary fractionating columns, but no theoretical considerations of such processes have been published. The patents in this field (*1, 4, 16*) have been based on general principles rather than on specific design data.

By applying kinetics to an esterification process and then combining these results with distillation, it should be possible to estimate what occurs in a continuous esterification system after steady-state conditions are attained. From the initial studies, it was evident that the following data were needed: (*a*) variation of density of the various components with temperature; (*b*) knowledge of the kinetics of the esterification reaction—i.e., the order and mechanism of the reaction; (*c*) variation of the rate constant of esterification with temperature, catalyst concentration, and proportions of reactants, and a general correlation of these factors; (*d*) equilibrium constant for the esterification; (*e*) vapor-liquid equilibria data for the system.

The first four items were studied for the system butanol-acetic acid-sulfuric acid, chosen as a typical medium-boiling ester for continuous esterification. The experimental work on this system involved catalyst concentrations of 0.03 to 0.13% sulfuric acid and five moles of butanol per mole of acetic acid feed, with a total contact time of 24.4 to 46.7 minutes (*15*).

VARIATION OF DENSITY WITH TEMPERATURE

To correct for volume at elevated temperatures, the variation of density of butanol, acetic acid, and butyl acetate with temperature up to their normal boiling points was determined with a thin-walled Cassia flask, which had a bulb of about 100 ml. capacity and a long, thin, graduated neck of 10 ml. capacity. The Cassia flask was equipped with a tight-fitting cork, which bore a short air-cooled reflux tube, and was immersed in a rapidly stirred oil bath. The bath temperature was held to within ±0.1° C. of the desired temperature until the volume in the neck of the flask was constant to ±0.01 ml. over a 3-minute period. About 30 minutes were required for each temperature reading.

Since the variation of density of water is known (*11*), the flask was calibrated with water to correct for the thermal expansion of glass. A relation was obtained to allow for the expansion of the flask, using the best straight-line relation calculated by the method of least squares between a plot of true and determined values:

$$d = (1.000073 - 0.0000287\ T)d' \qquad (1)$$

where T = temperature, ° C.
d = corrected density
d' = apparent density

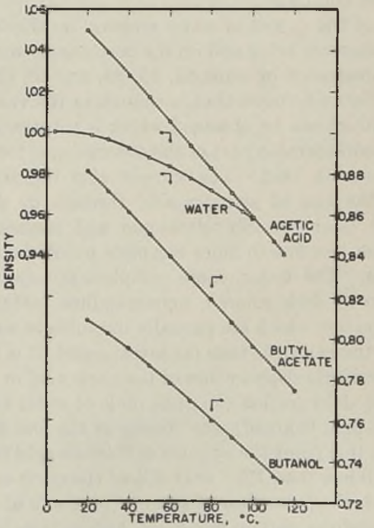

Figure 1. Variation of Density (d_4) with Temperature

MATERIALS USED. Acetic acid was recrystallized three times from commercial C.P. glacial acid; it was 99.66% pure by titration and had a melting point of 16.6° C. The butanol used was 99.92% pure, and had a water content of 0.080% and a boiling range of 116.6–117.7° C. Butyl acetate was prepared from commercial ester by treatment with acetyl chloride, followed by distillation and phosphorus pentoxide purification (*3*) and redistillation; its boiling point was 125.5° C. and its ester content was 99.80% by saponification in the cold with aqueous alkali.

Table I. Variation of Density with Temperature

Temp. T, ° C.	Indicated Expansion, Ml.	Indicated Volume, Ml.	Apparent Density, d′	Corrected Density, d	Literature Value[a], d_c	Difference, $(d - d_c)$
Acetic Acid, 99.6042 Grams at 20° C., 99.66% Pure						
20	0.00	94.86	1.0500	1.0495	1.0498	−0.0003
30	0.98	95.84	1.0393	1.0385	1.0387	−0.0002
40	1.98	96.84	1.0285	1.0274	1.0274	0.0000
50	2.97	97.83	1.0181	1.0167	1.0160	+0.0007
60	4.10	98.96	1.0065	1.0048	1.0046	+0.0002
70	5.25	100.11	0.9949	0.9929	0.9931	−0.0002
80	6.32	101.18	0.9844	0.9822	0.9816	+0.0006
90	7.51	102.37	0.9730	0.9705	0.9699	+0.0006
100	8.78	103.64	0.9611	0.9584	0.9582	+0.0002
110	10.00	104.86	0.9499	0.9470	...	...
115	10.7	105.56	0.9436	0.9405	...	...
						±0.0003
Butanol, 76.7361 Grams at 20° C., 99.92% Pure						
20	0.00	94.86	0.8089	0.8085	0.8086	−0.0001
30	0.76	95.62	0.8025	0.8019	0.8000	+0.0019
40	1.60	96.46	0.7955	0.7946	0.7908	+0.0038
50	2.61	97.47	0.7873	0.7862	0.7810	+0.0052
60	3.63	98.49	0.7791	0.7778	...	...
70	4.70	99.56	0.7707	0.7692	...	...
80	5.98	100.84	0.7610	0.7593	...	...
90	7.05	101.91	0.7530	0.7511	...	...
100	8.20	103.06	0.7446	0.7425	...	...
110	9.69	104.55	0.7339	0.7316	...	...
115	10.2	105.06	0.7304	0.7280	...	...
Butyl Acetate, 83.5792 Grams at 20° C., 99.80% Pure						
20	0.00	94.86	0.8811	0.8807	...	...
30	1.00	95.86	0.8719	0.8712	...	...
40	2.13	96.99	0.8617	0.8608	...	...
50	3.28	98.14	0.8516	0.8504	...	...
60	4.43	99.29	0.8418	0.8404	...	...
70	5.78	100.64	0.8305	0.8289	...	...
80	7.02	101.88	0.8204	0.8186	...	...
90	8.41	103.27	0.8093	0.8073	...	...
100	9.80	104.66	0.7986	0.7964	...	...
110	11.2	106.06	0.7880	0.7856	...	...
120	12.67	107.53	0.7773	0.7747	...	...

[a] Calculated from density-temperature equations (*12*).

Table I and Figure 1 summarize the data. Those for acetic acid are in good accord with the literature, but the values for butanol are considerably higher.

RATE OF REACTION

The mechanism of esterification depends on such variables as the concentration of reactants, concentration of catalyst, and temperature. To study these variables, batches of 50 to 135 grams total were weighed out in the order sulfuric acid, acetic acid, butanol, and were cooled in ice water. Approximately 5-ml. samples were pipetted into drawn-down soft glass test tubes (13 × 100 mm.), which were sealed and inserted into a constant-temperature bath. Tubes were removed at various times, cooled, and dried. Then the tips were broken off, and 2 to 5 ml. of the contents were weighed out into a tared 250-ml. Erlenmeyer flask. Each sample was diluted with 50 ml. of distilled water and titrated immediately with 0.1 *N* sodium hydroxide, using phenolphthalein to determine the free acidity. The time was measured from insertion in the bath (the maximum elapsed time from the addition of butanol to insertion in the sealed tube in the bath was 8 to 10 minutes). Some reaction undoubtedly occurs in this treatment, but it is insignificant compared with the amount of reaction at the elevated temperatures (for example, see Figure 9).

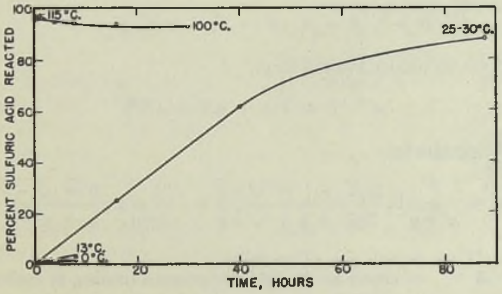

Figure 2. Reaction of Butanol and Sulfuric Acid at Various Temperatures

Materials Used. Acetic acid for runs *B* through *R* was commercial c.p. glacial acid, 99.51% pure by titration, with a melting point of 15.5° C. For runs *S* through *Z*, the acid was recrystallized three times; 99.66% by titration and a melting point of 16.6° C. were obtained. Commercial butanol was used throughout; it had no acidity, a water content of 0.080%, and a boiling range of 116.6–117.7° C. The sulfuric acid was reagent grade, titrated 97.19 to 97.45% as sulfuric acid using phenolphthalein, and gave 97.42% when assayed as barium sulfate. The average value of 97.38% was taken.

REACTION OF BUTANOL AND SULFURIC ACID

To obtain the acetic acid present, the free acidity must be corrected for the presence of the catalyst. There is, however, a reaction between the alcohol and sulfuric acid (*19*, *20*). The butyl monosulfate formed has a different equivalent weight from that of sulfuric acid in titration (154.18 compared to 49.04). Since the total number of moles of sulfate radical in the system is constant, the amount of butyl sulfuric acid formed can be determined from a single titration value, and the known amount of sulfuric acid:

$$\text{grams butyl sulfuric acid formed} = (154.18/1000)\ (2M - \text{ml. } N)$$

$$\text{grams sulfuric acid remaining} = \frac{98.08}{1000}\,(\text{ml. } N - M)$$

where M = millimoles sulfuric acid originally present
ml. N = titration equivalents used (ml. base × normality)

Table II and Figure 2 give the results of tests with approximately 2% sulfuric acid in butanol. The reaction of butanol and sulfuric acid varies greatly with temperature. At 0° and 13° C. the rate is scarcely measurable up to 8 hours, at 25° to 30° C. the reaction proceeds over a period of days, and at 100° and 115° C. the reaction is so rapid (95 to 96% complete in 15 to 30 minutes) that the rate cannot be followed accurately. After 4 hours at 100° C. the amount of butyl sulfuric acid present decreases con-

Table II. Reaction of Butanol and Sulfuric Acid

Time, Hr.	Sample, Grams	Titration, Ml. *N*	Millimoles H_2SO_4 Original	Millimoles H_2SO_4 Remaining	% of H_2SO_4 Combined	Apparent Milliequivalent, *E*
0° C., 1.9230% H_2SO_4						
1	3.2860	1.2799	0.6443	0.6356	1.35	49.37
2	3.7144	1.4543	0.7283	0.7260	0.31	49.12
3	3.2866	1.2902	0.6444	0.6458	−0.22	48.99
5	3.9314	1.5312	0.7708	0.7604	1.35	49.37
8	3.7262	1.4543	0.7306	0.7237	0.94	49.27
13° C., 1.9230% H_2SO_4						
0	3.9902	1.5640	0.7823	0.7817	0.08	49.06
1	3.9472	1.5466	0.7739	0.7727	0.15	49.08
2	3.9720	1.5487	0.7788	0.7699	1.14	49.32
3	3.9243	1.5292	0.7694	0.7598	1.25	49.35
5	3.9989	1.5569	0.7840	0.7729	1.42	49.39
8	4.0511	1.5702	0.7943	0.7759	2.31	49.61
168	3.5623	1.3107	0.6984	0.6123	12.34	52.26
25 to 30° C., 1.9440% H_2SO_4						
16	4.0012	1.4248	0.7931	0.6317	20.34	54.59
16	3.9720	1.3439	0.7873	0.5566	29.31	57.46
40	3.9631	1.0923	0.7855	0.3068	60.94	70.53
40	4.2303	1.1616	0.8386	0.3230	61.48	70.80
88	4.0962	0.9128	0.8119	0.1009	87.57	87.24
768	4.0646	0.8477	0.8056	0.0421	94.77	93.21
100° C., 1.9230% H_2SO_4						
0.25	4.1889	0.8554	0.8213	0.0341	95.85	94.17
0.5	4.3815	0.9005	0.8590	0.0415	95.17	93.57
1	4.2160	0.8625	0.8266	0.0359	95.66	94.00
1.5	4.1123	0.8410	0.8063	0.0347	95.70	94.03
2	4.5070	0.9210	0.8837	0.0373	95.78	94.10
4	4.7260	0.9825	0.9266	0.0559	93.97	92.50
8	4.6386	0.9630	0.9095	0.0535	94.12	92.63
16	4.1962	0.8772	0.8227	0.0545	93.37	91.99
30	3.8925	0.8174	0.7632	0.0542	92.89	91.57
115° C., 1.9230% H_2SO_4						
0.5	3.8350	0.7805	0.7519	0.0286	96.20	94.49

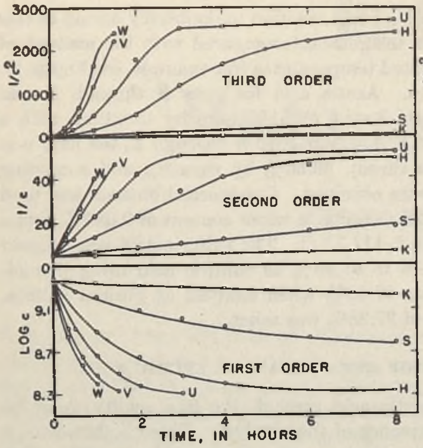

Figure 3. Determination of Order of Reaction for Catalyst Series at 100° C. and Approximately 5 Moles Butanol per Mole Acetic Acid

Run	Wt. % H_2SO_4
K	0.000
S	0.0147
H	0.0316
U	0.0679
V	0.1032
W	0.1373

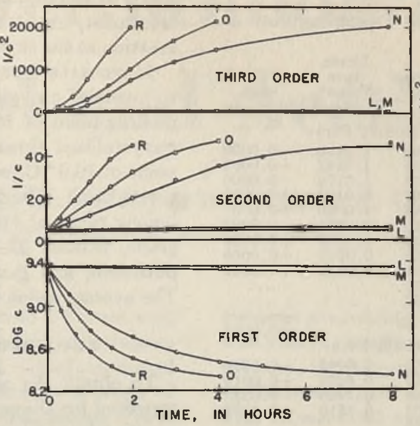

Figure 4. Determination of Order of Reaction for Temperature Series with 0.03% Catalyst and Approximately 5 Moles Butanol per Mole Acetic Acid

Run	Temp., ° C.
L	0
M	30
N	100
O	110
R	120

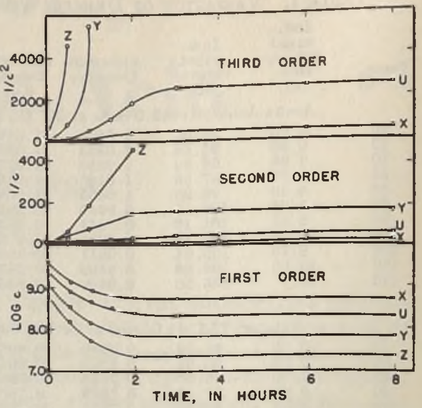

Figure 5. Determination of Order of Reaction for Proportion Series at 100° C. and Approximately 0.07% Catalyst

Run	Moles Butanol/ Mole Acetic Acid
X	2.991
U	4.992
Y	10.03
Z	19.62

siderably. A similar change in acidity has been reported in the reaction of ethanol and sulfuric acid (*5*, *19*). This complication has no bearing upon this research, however, since after 4 hours at 100° C. most of the esterification rate curves deviate from straight lines. Furthermore, the amount of catalyst used in such esterifications is in the order of 0.03 to 0.13% by weight, as compared with 2% in these experiments. Thus for samples kept at room temperature or below, all of the catalyst can be assumed to be present as sulfuric acid; for samples heated to 100° C. or above, all of the catalyst can be assumed to be present as a mixture of butyl sulfuric and sulfuric acids, having a titration equivalent of 94.0. It was impossible to study the reaction of sulfuric acid and butanol in the presence of the other components; in any case it seems unlikely that there would be any important change if the other components were present.

ORDER OF ESTERIFICATION REACTION

The order of the esterification reaction can be most readily determined graphically (*6*). Log *c vs.* time gives a straight line for a first-order reaction; $1/c$ *vs.* time gives a straight line for a second-order reaction; and $1/c^2$ *vs.* time gives a straight line for a third-order reaction. Figures 3, 4, and 5 are qualitative plots for a few of the runs, based on the concentration of acetic acid in moles per 100 grams.

Figure 3 shows the effect of catalyst concentration at 100° C. With no catalyst (run *K*) straight-line plots are obtained for all three cases. With low catalyst concentrations (0.0147%, run *S*), a second- or third-order reaction is indicated. With catalyst concentrations above 0.015%, well defined straight lines are obtained for the second-order plot up to about 70–80% conversion, after which the curves flatten out.

Figure 4 shows that at low temperatures (runs *L* and *M*) with only limited reaction, the order is not ascertainable. At 100° C. or higher the reaction is bimolecular up to about 80 to 85% completion, as shown by the straight-line relation between $1/c$ and time.

Figure 5 indicates that the runs at 100° C. and constant catalyst concentration are not first- or third-order reactions. With molar ratios of 3 to 1 and 5 to 1, the curves are sensibly straight lines for the plot of $1/c$ *vs.* time. With a 10 to 1 ratio (run *Y*) a straight-line relation is also obtained up to 2-hour reaction time. In the case of a 20 to 1 ratio (run *Z*) the points for 0.5, 1, and 2 hours fall on a straight line which does not pass through the point for zero time; possibly this indicates an induction period.

It is apparent that the reaction between butanol and acetic acid in the presence of excess butanol and sulfuric acid as a catalyst, at temperatures above 100° C., follows a second-order (quadratic) equation up to a conversion of about 75 to 85% of the acetic acid present.

REACTION RATE EQUATION

The actual equation which governs the rate of esterification may be determined by trial and error; those generally given for esterification reactions were tested first. Assuming a nonreversible reaction,

$$dX/dt = k(A - X)(B - X) \tag{2}$$

which integrates into

$$kt = \frac{1}{A - B} \ln \frac{B(A - X)}{A(B - X)} \tag{3}$$

Assuming a reversible reaction,

$$dX/dt = k_1(A - X)(B - X) - k_2X(W + X) \tag{4}$$

which can be reduced to the form,

$$dX/dt = k(a + bX + cX^2)$$

This integrates into

$$kt = \frac{1}{\sqrt{-q}} \ln \frac{2cX + b - \sqrt{-q}}{2cX + b + \sqrt{-q}} - \frac{1}{\sqrt{-q}} \ln \frac{b - \sqrt{-q}}{b + \sqrt{-q}} \tag{5}$$

where dX/dt = velocity of reaction
A = acetic acid originally present (moles, or moles per liter)
B = butanol originally present (same units as A)
W = water originally present (same units as A)

X = amount of acetic acid transformed in interval (same units as A)
k, k_1 = reaction rate constants
k_2 = reverse reaction rate constant
K = equilibrium constant = k_1/k_2
a = AB
b = $(A + B + W/K)$
c = $1 - 1/K$
q = $4ac - b^2$, where $b^2 > 4ac$

None of these equations correlated all of the experimental data, but after a number of trials it was found that the equation

$$dX/dt = k(A - X)^2 \qquad (6)$$

fitted the experimental data for all of the runs very well, up to a conversion of about 75 to 85% (as in the second-order reaction plot).

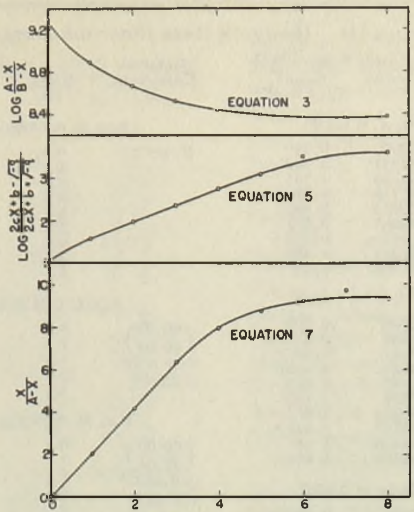

Figure 6. Reaction-Rate Equation Tests for Run *B*

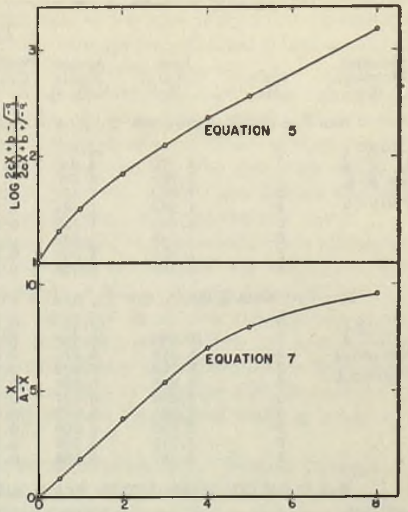

Figure 7. Reaction-Rate Equation Tests for Run *N*

Integration of Equation 6 gives

$$\frac{1}{A - X} = kt + I$$

Evaluating I by setting $X = 0$ when $t = 0$,

$$kt = \frac{X}{A(A - X)} \qquad (7)$$

The proper form of the rate equation may be determined graphically by plotting various functions against time and noting which gives a straight-line relation: For Equation 3, log $(A - X)/(B - X)$ *vs. t*; for Equation 5, log $(2cX + b - \sqrt{-q})/(2cX + b + \sqrt{-q})$ *vs. t*; for Equation 7, $X/(A - X)$ *vs. t*.

The data for run *B* for these tests are plotted in Figure 6. Equation 3 gives a well defined curve and hence does not apply. The last six points on the curve for Equation 5 appear to fall on a straight line; on a larger scale, however, these points show a definite curve, and the initial point (zero time) falls far off the straight-line relation. Equation 7, however, shows a straight-line relation from 0 to 3 hours, with the point for 4 hours slightly low.

As a further illustration the data for run *N*, using Equations 5 and 7, are plotted in Figure 7. With a larger scale and a check point at 0.5 hour, it is apparent that during the early stages the rate equation does not correspond to the mechanism proposed by Equation 5, but Equation 7 does give a straight line.

At the 3-hour point run *N* is 84.5% completed and run *B* is 86.3% completed. At the 4-hour point and above, Equation 7 no longer holds; the mechanism changes apparently to one approaching Equation 5 since the reverse reaction, saponification, is beginning to have an effect. This is indicated by the straight-line portion of the log plot above 4 hours, which shows that the normal esterification equilibrium law is setting in and is obeyed. However, in the continuous column esterification studies reported elsewhere (*15*), it was desired to reduce the time of contact to about 30 minutes; hence Equation 7, which gives a straight-line relation for the early stages of reaction, applies in the continuous esterifications. Long times of contact and attainment of esterification mass law equilibrium on a given plate are not needed for a high over-all extent of conversion.

Table III summarizes the complete calculations for the experimental data testing Equation 7. Figure 8 shows the relation between $X/(A - X)$ and t for the runs at 100° C. with a molar ratio of butanol to acetic acid of approximately 5 to 1 and with varying catalyst concentration. The degree of completion of the esterification of acetic acid is indicated on the right-hand scale. Up to 2 hours at 100° C. all of the lines are straight and pass through the origin. Run *C* with 0.00614% catalyst appears to be slightly irregular, showing a deviation at 3 hours. With 0.03% catalyst or higher, a conversion of 85 to 90% of the acetic acid is possible before the curves deviate from Equation 7, as equilibrium sets in and Equation 5 becomes valid.

Figure 9 gives the effect of temperature on conversion. Here again, at temperatures over 100° C., straight-line relations are obtained up to about 85% conversion. It will be noted that the points determined with heating times of 20 and 30 minutes are slightly low; this is probably because of the time required to heat the samples up to the reaction temperature.

Figure 10 illustrates effect of proportions of reactants at 100° C. At low catalyst concentrations (0.03% or less), these runs show fairly good agreement with Equation 7. With 0.07% sulfuric acid, however, the curves for run *Y* (10 to 1 ratio) and run *Z* (20 to 1 ratio) do not pass through the origin; evidently a slight induction effect occurs here. Practically all of these data deviate from straight lines after 2 hours at 100° C., but below 75% conversion, the agreement is good.

REACTION RATE CONSTANT

Determination. In a bimolecular reaction the value for k is dependent upon the numbers expressing the concentration; for uniformity, the concentrations are expressed in moles per liter and k in liters/mole-minutes. Equation 7 can be rearranged to give

$$kA_0t = X/(A - X)$$

If the units are substituted for each term,

$$\frac{\text{(liter)}}{\text{(mole)(min.)}} \; \frac{\text{(moles)}}{\text{(liter)}} \; \text{(min.)} = \text{dimensionless ratio}$$

so that if A_0 in the left-hand member is expressed in moles per liter, the quantities on the right hand, X and $A - X$ (i.e., the amount of acid reacted and the amount of acid unreacted) can be expressed in any units, such as moles, mole fractions, or moles per liter, provided the same units are used for each.

TABLE III. REACTION RATE EQUATION DATA

Catalyst Correction, %	Time, Hr.	Free Acidity, %	Actual Acetic Acid, %	Acetic Acid, Moles/100 G.	
				Converted, X	Ratio, $X/(A - X)$
Run *B*, 0.0309% H_2SO_4, 100° C., B/A = 4.978, A = 0.2327					
$\left(\frac{60.05}{94}\right)$ ×0.0309 0.0197%	0	...	13.97	0.0000	0.000
	1	4.673	4.652	0.15521	2.003
	2	2.730	2.710	0.18756	4.155
	3	1.912	1.892	0.20118	6.383
	4	1.584	1.564	0.20665	7.933
	5	1.452	1.432	0.20885	8.757
	6	1.388	1.368	0.20991	9.211
	7	1.327	1.307	0.21093	9.689
	8	1.378	1.358	0.21008	9.287
Run *C*, 0.00614% H_2SO_4, 100° C., B/A = 4.984, A = 0.2325					
$\left(\frac{60.05}{94}\right)$ ×0.00614 0.00392%	0	...	13.96	0.0000	0.000
	1	10.441	10.437	0.0587	0.3377
	2	8.374	8.370	0.0931	0.6679
	3	7.743	7.739	0.1036	0.8037
	4	6.806	6.802	0.1192	1.052
	5	6.541	6.537	0.1236	1.135
	6	5.931	5.927	0.13379	1.355
	7	5.710	5.706	0.13747	1.447
	8	5.211	5.207	0.14578	1.681
	9	5.167	5.163	0.14651	1.704
Run *D*, 0.0198% H_2SO_4, 100° C., B/A = 5.029, A = 0.2307					
$\left(\frac{60.05}{94}\right)$ ×0.0198 0.0127%	0	...	13.86	0.0000	0.000
	1	6.258	6.245	0.12675	1.219
	2	3.937	3.924	0.16539	2.532
	3	2.857	2.844	0.18336	3.873
	4	2.301	2.288	0.19262	5.058
	5	1.904	1.891	0.19922	6.328
	6	1.624	1.611	0.20388	7.602
	8	1.400	1.387	0.20761	8.991
	9	1.334	1.321	0.20871	9.491
Run *E*, 0.0307% H_2SO_4, 100° C., B/A = 5.079, A = 0.2287					
$\left(\frac{60.05}{94}\right)$ ×0.0307 0.0196%	0	...	13.73	0.0000	0.000
	1	5.624	5.604	0.13535	1.450
	2	3.454	3.434	0.17150	2.998
	3	2.373	2.353	0.18951	4.836
	4	1.896	1.876	0.19745	6.318
	5	1.624	1.604	0.20198	7.559
	6	1.484	1.464	0.20431	8.377
	7	1.409	1.389	0.20556	8.883
	8	1.380	1.360	0.20605	9.097
Run *F*, 0.1608% H_2SO_4, 100° C., B/A = 4.993, A = 0.2318					
$\left(\frac{60.05}{94}\right)$ ×0.1608 0.103%	0	...	13.92	0.0000	0.000
	1	1.514	1.411	0.20830	8.864
	2	1.358	1.255	0.21090	10.09
	3	1.357	1.254	0.21092	10.10
	4	1.382	1.279	0.21050	9.883
	5	1.371	1.268	0.21065	9.960
	6	1.343	1.240	0.21115	10.22
	7	1.363	1.260	0.21082	10.05
Run *G*, 0.0490% H_2SO_4, 100° C., B/A = 2.998, A = 0.3535					
$\left(\frac{60.05}{94}\right)$ ×0.0490 0.0314%	0	...	21.22	0.0000	0.000
	1	6.934	6.903	0.2385	2.074
	2	4.540	4.509	0.27838	3.706
	3	3.722	3.691	0.29201	4.749
	4	3.442	3.411	0.29668	5.221
	5	3.345	3.314	0.29829	5.403
	6	3.312	3.281	0.29884	5.467
	7	3.282	3.251	0.29934	5.527
	8	3.298	3.267	0.29908	5.496
Run *H*, 0.0316% H_2SO_4, 100° C., B/A = 5.087, A = 0.2284					
$\left(\frac{60.05}{94}\right)$ ×0.0316 0.0202%	0	...	13.72	0.0000	0.000
	1	4.637	4.617	0.15154	1.972
	2	2.663	2.643	0.18440	4.191
	3	1.765	1.745	0.19935	6.862
	4	1.491	1.471	0.20391	8.326
	5	1.353	1.333	0.20621	9.293
	6	1.299	1.279	0.20711	9.728
	7	1.256	1.236	0.20782	10.10
	8	1.245	1.225	0.20801	10.20
Run *I*, 0.0211% H_2SO_4, 100° C., B/A = 8.030, A = 0.1524					
$\left(\frac{60.05}{94}\right)$ ×0.0211 0.0135%	0	...	9.151	0.0000	0.000
	1	3.682	3.668	0.09131	1.495
	2	2.117	2.104	0.11740	3.354
	3	1.267	1.253	0.13153	6.302
	4	1.053	1.039	0.13510	7.809
	5	0.797	0.783	0.13936	10.69
	6	0.731	0.717	0.14046	11.76
	7	0.670	0.656	0.14148	12.96
	8	0.629	0.615	0.14216	13.88
Run *J*, 0.0179% H_2SO_4, 100° C., B/A = 9.619, A = 0.1292					
$\left(\frac{60.05}{94}\right)$ ×0.0179 0.0114%	0	...	7.756	0.0000	0.000
	1	3.390	3.379	0.07291	1.295
	2	2.028	2.017	0.09560	2.845
	3	1.298	1.287	0.10776	5.026
	4	0.886	0.875	0.11462	7.861
	5	0.693	0.682	0.11784	10.37
	6	0.612	0.601	0.11919	11.91
	7	0.540	0.529	0.12039	13.66
	8	0.506	0.495	0.12095	14.66
Run *K*, 0.000% H_2SO_4, 100° C., B/A = 4.965, A = 0.2332					
None	0	...	14.05	0.0000	0.000
	1	13.06	13.06	0.01636	0.07545
	2	12.40	12.40	0.02732	0.1327
	3	11.84	11.84	0.03662	0.1863
	4	11.32	11.32	0.04525	0.2408
	5	10.79	10.79	0.05405	0.3017
	6	10.38	10.38	0.06086	0.3531
	7	9.933	9.933	0.06833	0.4144
	8	9.591	9.591	0.07398	0.4646
Run *L*, 0.0322% H_2SO_4, 0° C., B/A = 4.972, A = 0.2329					
$\left(\frac{60.05}{49.04}\right)$ ×0.0322 0.0394%	0	...	13.99	0.0000	0.000
	2	13.62	13.58	0.00682	0.03017
	4	13.53	13.49	0.00842	0.03749
	6	13.41	13.37	0.01032	0.04636
	8	13.35	13.31	0.01132	0.05109
Run *M*, 0.0322% H_2SO_4, 30° C., B/A = 4.972, A = 0.2329					
$\left(\frac{60.05}{49.04}\right)$ ×0.0322 0.0394%	0	...	13.99	0.0000	0.000
	1	13.35	13.31	0.01132	0.05109
	2	13.03	12.99	0.01664	0.07694
	4	12.46	12.42	0.02613	0.1264
	6	11.95	11.91	0.03462	0.1746
	8	11.44	11.40	0.04311	0.2271
Run *N*, 0.0322% H_2SO_4, 100° C., B/A = 4.972, A = 0.2329					
$\left(\frac{60.05}{94}\right)$ ×0.0322 0.0206%	0	...	13.99	0.0000	0.000
	0.5	7.695	7.674	0.10514	0.8229
	1	5.151	5.130	0.14750	1.727
	2	3.035	3.014	0.18272	3.641
	3	2.221	2.200	0.19627	5.358
	4	1.777	1.756	0.20367	6.968
	5	1.594	1.573	0.20671	7.893
	8	1.345	1.324	0.21086	9.567
Run *O*, 0.0322% H_2SO_4, 110° C., B/A = 4.972, A = 0.2329					
$\left(\frac{60.05}{94}\right)$ ×0.0322 0.0206%	0	...	13.99	0.0000	0.000
	0.5	5.943	5.922	0.13431	1.362
	1	3.502	3.481	0.17495	3.019
	1.5	2.422	2.401	0.19293	4.827
	2	1.915	1.894	0.20137	6.387
	3	1.493	1.472	0.20839	8.502
	4	1.319	1.298	0.21129	9.777
	9	1.188	1.167	0.21347	10.89
Run *P*, 0.0322% H_2SO_4, 115° C., B/A = 4.972, A = 0.2329					
$\left(\frac{60.05}{94}\right)$ ×0.0322 0.0206%	0	...	13.99	0.0000	0.000
	0.33	6.356	6.335	0.12744	1.206
	0.67	3.927	3.906	0.16787	2.581
	1	2.743	2.722	0.18758	4.139
	1.5	1.952	1.931	0.20075	6.244
	2	1.616	1.595	0.20635	7.772
	3	1.293	1.272	0.21172	9.996
Run *R*, 0.0322% H_2SO_4, 120° C., B/A = 4.972, A = 0.2329					
$\left(\frac{60.05}{94}\right)$ ×0.0322 0.0206%	0	...	13.99	0.0000	0.000
	0.33	5.637	5.616	0.13940	1.491
	0.67	3.280	3.259	0.17864	3.292
	1	2.201	2.180	0.19661	5.418
	1.5	1.623	1.602	0.20623	7.733
	2	1.378	1.357	0.21031	9.310
	5	1.186	1.165	0.21351	11.01
Run *S*, 0.0147% H_2SO_4, 100° C., B/A = 4.960, A = 0.2355					
$\left(\frac{60.05}{94}\right)$ ×0.0147 0.0094%	0	...	14.02	0.0000	0.000
	0.5	10.86	10.85	0.05279	0.2921
	1	9.532	9.523	0.07489	0.4722
	2	7.308	7.299	0.11194	0.9209
	3	6.003	5.994	0.13367	1.339
	4	5.060	5.051	0.14938	1.776
	6	3.891	3.882	0.16885	2.612
	8	3.567	3.558	0.17424	2.940
Run *T*, 0.0418% H_2SO_4, 100° C., B/A = 5.001, A = 0.2318					
$\left(\frac{60.05}{94}\right)$ ×0.0418 0.0267%	0	...	13.92	0.0000	0.000
	0.5	6.402	6.375	0.12564	1.183
	1	4.045	4.018	0.16489	2.464
	2	2.297	2.270	0.19400	5.132
	3	1.614	1.587	0.20537	7.770
	4	1.454	1.427	0.20804	8.756
	6	1.264	1.237	0.21120	10.25
	8	1.221	1.194	0.21192	10.66
Run *U*, 0.0679% H_2SO_4, 100° C., B/A = 4.992, A = 0.2321					
$\left(\frac{60.05}{94}\right)$ ×0.0679 0.0434%	0	...	13.94	0.0000	0.000
	0.5	4.970	4.927	0.15007	1.829
	1	2.724	2.681	0.18746	4.199
	1.5	1.896	1.853	0.20125	6.524
	2	1.452	1.409	0.20864	8.893
	3	1.239	1.196	0.21219	10.66
	4	1.234	1.191	0.21227	10.70
	6	1.212	1.169	0.21264	10.93
	8	1.217	1.174	0.21255	10.87

(*Continued on page 973*)

Table III. (*Continued*)

Catalyst Correction, %	Time, Hr.	Free Acidity, %	Actual Acetic Acid, %	Acetic Acid, Moles/100 G. Converted, X	Acetic Acid, Moles/100 G. Ratio, $X/(A - X)$
Run *V*, 0.1032% H_2SO_4, 100° C., B/A = 4.925, A = 0.2347					
$\left(\frac{60.05}{94}\right)$ ×0.1032 0.0661%	0	...	14.09	0.0000	0.000
	0.33	5.082	5.016	0.15115	1.809
	0.67	2.744	2.678	0.19009	4.261
	1	1.819	1.753	0.20550	7.038
	1.5	1.341	1.275	0.21346	10.05
	2	1.354	1.288	0.21325	9.942
	3	1.319	1.253	0.21383	10.25
	4	1.311	1.245	0.21396	10.32
	8	1.307	1.241	0.21403	10.35
Run *W*, 0.1373% H_2SO_4, 100° C., B/A = 4.975, A = 0.2326					
$\left(\frac{60.05}{94}\right)$ ×0.1373 0.0878%	0	...	13.96	0.0000	0.000
	0.33	4.237	4.149	0.16347	2.365
	0.67	2.339	2.251	0.19509	5.201
	1	1.571	1.483	0.20789	8.413
	2	1.305	1.216	0.21234	10.48
	3	1.345	1.257	0.21166	10.11
	4	1.328	1.240	0.21194	10.26
	8	1.341	1.253	0.21172	10.14
Run *X*, 0.0690% H_2SO_4, 100° C., B/A = 2.991, A = 0.3542					
$\left(\frac{60.05}{94}\right)$ ×0.069 0.0441%	0	...	21.27	0.0000	0.000
	0.5	7.845	7.801	0.22429	1.726
	1	5.191	5.147	0.26849	3.132
	2	3.307	3.263	0.29986	5.518
	3	2.994	2.950	0.30507	6.209
	4	2.849	2.805	0.30749	6.583
	6	2.835	2.791	0.30772	6.620
	8	2.801	2.757	0.30829	6.715
Run *Y*, 0.0711% H_2SO_4, 100° C., B/A = 10.03, A = 0.1242					
$\left(\frac{60.05}{94}\right)$ ×0.0711 0.0455%	0	...	7.458	0.0000	0.000
	0.5	2.104	2.058	0.08993	2.624
	1	0.8573	0.811	0.11069	8.195
	2	0.4413	0.395	0.11762	17.88
	3	0.4297	0.384	0.11781	18.44
	4	0.4131	0.367	0.11809	19.33
	6	0.4254	0.379	0.11789	18.68
	8	0.4067	0.361	0.11819	19.67
Run *Z*, 0.0692% H_2SO_4, 100° C., B/A = 19.62, A = 0.06593					
$\left(\frac{60.05}{94}\right)$ ×0.0692 0.0442%	0	...	3.959	0.0000	0.000
	0.5	0.9368	0.893	0.05106	3.434
	1	0.3620	0.318	0.06063	11.44
	2	0.1740	0.130	0.06377	29.52
	3	0.1678	0.124	0.06387	31.00
	4	0.1762	0.132	0.06373	28.97
	6	0.1641	0.120	0.06333	24.36
	8	0.1828	0.139	0.06362	27.54

The method of least squares was used to calculate the equation for the best straight line through the indicated points, and k was determined from the least squares value for $X/(A - X)$ at a selected value for time for all runs made with a 5 to 1 molar ratio of butanol to acetic acid. In the proportion series this method was not used because of the indicated curvature at short reaction times with high catalyst concentrations and high ratios of butanol to acetic acid (Figure 5). Here it was deemed advisable to use the actual observed data with short reaction times.

Table IV summarizes calculations for reaction rate constant k. The initial concentration of acetic acid was calculated from Figure 1. The values for $X/(A - X)$ are the results of least squares calculations, together with the corresponding time values, except in the proportion series where the observed data have been employed with shorter time intervals. It is apparent from Table IV that the value of k varies with the amount of catalyst, the temperature, and the ratio of moles of butanol to moles of acetic acid.

Effect of Catalyst Concentration. Various investigators have found that the rate of esterification with acid catalysts is proportional to the acid concentration (*13, 21*) or to the hydrogen-ion concentration (*7*). Figure 11 shows a linear relation between the rate constant for the runs at 100° C. with approximately 5 moles of butanol per mole of acetic acid and between 0 and 0.14% sulfuric acid as catalyst.

Effect of Temperature. Figure 12 is a plot of the logarithm of 10^5 k against the reciprocal of the absolute temperature for data of Table IV, where variables other than temperature were constant. For the range 0° to 120° C. this curve indicates that the esterification reaction is not simple but consists of at least two different consecutive reactions with different temperature coefficients (*10*). However, over the range 100° to 120° C., used in the continuous-column esterification runs, the relation between log k and $1/T$ may be regarded as a straight line; the controlling reaction is given by Equation 6.

Effect of Proportion. According to Watson (*21*), the rate of esterification is proportional to the concentration of alcohol and acid as well as catalyst. A plot of the rate constants for runs X, U, Y, and Z against the molal ratio of butanol to acetic acid

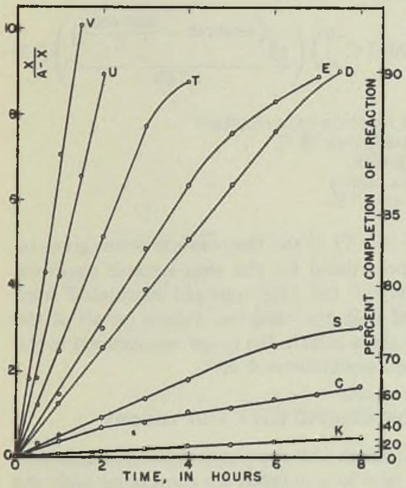

Figure 8. Relation between $X/(A - X)$ and Time for Catalyst Concentration Series at 100° C. and B/A = 5 Approximately

Run	Wt. % H_2SO_4	Run	Wt. % H_2SO_4
K	0.000	*E*	0.0307
C	0.0061	*T*	0.0418
S	0.0147	*U*	0.0679
D	0.0198	*V*	0.1032

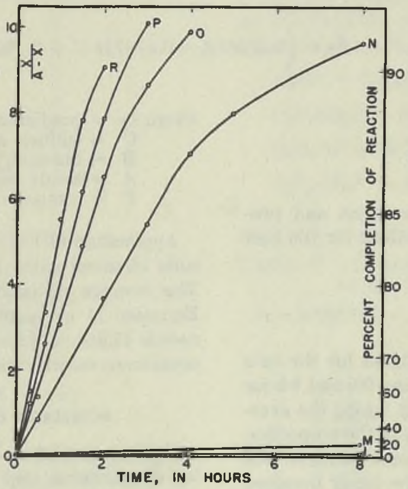

Figure 9. Relation between $X/(A - X)$ and Time for Temperature Series at 0.0322 Weight % Catalyst and B/A = 4.972

Run	Temp., ° C.	Run	Temp., ° C.
L	0	*O*	110
M	30	*P*	115
N	100	*R*	120

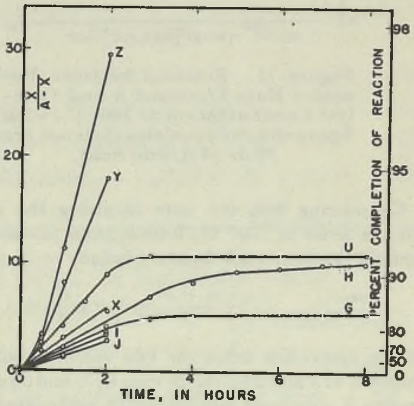

Figure 10. Relation between $X/(A - X)$ and Time for Proportion Series at 100° C.

Run	Wt. % H_2SO_4	Moles B/A
G	0.0490	2.998
H	0.0316	5.087
I	0.0211	8.030
J	0.0179	9.619
X	0.0690	2.991
U	0.0679	4.992
Y	0.0711	10.03
Z	0.0692	19.62

indicated a distinct linear relation; but the catalyst concentrations varied about 5%. However, from the catalyst series the rate constant is directly proportional to the amount of catalyst. Hence, by dividing the rate constant by the weight per cent of catalyst and plotting this quotient against the molar ratio of reactants, the effects caused solely by the catalyst might be expected to be eliminated. Figure 13 shows a linear relation for all of the runs in the proportion series.

RATE CONSTANT EQUATION

From the relations indicated in Figures 11, 12, and 13, the following empirical equation was deduced to define the constant in terms of catalyst concentration, proportions of reactants, and temperature for application in the continuous esterification runs:

$$k = \left(a + bC + c\frac{B}{A}C\right)\left(e + \frac{f}{T}\right)$$

The first parenthesis indicates the effect, at 100° C., of catalyst concentration and proportion, with the second parenthesis taken as unity. The second parenthesis gives the temperature effect, and is evaluated from the data at constant proportions and catalyst concentration. At 100° C., a should represent the rate of the uncatalyzed esterification—i.e., the rate constant due to acetic acid alone; hence, if the value for k obtained with no catalyst (run K) is assumed equal to a, the other four constants can be evaluated from the straight-line relations.

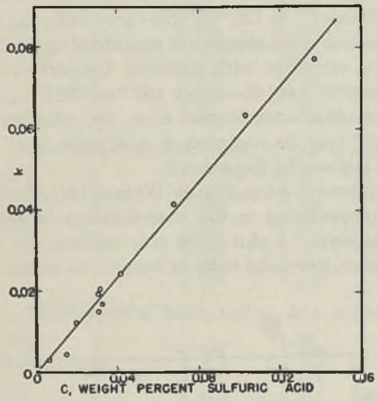

Figure 11. Relation between Reaction Rate Constant k and Catalyst Concentration at 100° C., with Approximately 5 Moles Butanol per Mole of Acetic Acid

Considering first the term involving the catalyst and proportion series at 100° C., least-squares calculations for the best straight line were made by the relation:

$$\frac{k - a}{C} = b + c\frac{B}{A}$$

In the proportion series the two values calculated for the rate constant at 1 and 2 hours for runs G, I, and J, and 0.5 and 1 hour for run X were used independently, rather than taking the average values in order to give more equal weight to the proportion and catalyst series. Run K with zero per cent catalyst was omitted from these calculations since it was previously involved in determining constant a. The relation obtained for the least-squares best straight line for these data is:

$$k = 0.000618 - 0.376724\,C + 0.180917\,C\frac{B}{A} \tag{8}$$

To check the validity of Equation 8, the values of k were recalculated from the molar ratio of butanol to acetic acid and the catalyst concentration, as summarized in Table V. All of the calculated values for k are in good agreement with the experimental values, with the exception of run S (96.8% too high). The average deviation between the calculated and experimentally determined rate constants is 17.65%. Discounting the runs with catalyst concentrations below 0.015% sulfuric acid (runs K, C, and S) and those with 3 moles of butanol per mole of acetic acid (runs G and X), the average deviation is 8.92%.

To tie in the results of the temperature series with the proportion-catalyst term, it is necessary to use the calculated value for the rate constant for run N (calculated value is 6.03% higher than observed). If a least-squares treatment on the straight-line relation

$$\log 100\,k_T = e + f/T \tag{9}$$

is applied, using the data for the runs at 100° to 120° C., the following results are obtained, using $e = 9.140142$ and $f = -3320.0564$:

Run	Temp., ° C.	Rate Constant: Actual k	Rate Constant: k_T from Eq. 9	Rate Constant: Difference	Rate Constant: Deviation, %
N	100	0.01745[a]	0.01744	−0.00001	−0.06
O	110	0.03004	0.02978	−0.00026	−0.86
P	115	0.03775	0.03851	+0.00076	+2.00
R	120	0.04999	0.04947	−0.00052	−1.04
					±0.99

[a] From Equation 8.

If the rate of reaction at 100° C. is taken as the basis for this series,

$$100\,k_T = 10^{\left(9.140142 - \frac{3320.0564}{T}\right)}$$

Then by proportion,

$$\frac{k_T}{k_{100}} = \frac{10^{\left(9.140142 - \frac{3320.0564}{T}\right)}}{(100)(0.01745)} \tag{10}$$

Where $T = 100°$ C. (373.1° K.), Equation 10 reduces to unity and thus represents the temperature factor. Multiplying Equation 8 by Equation 10, the final empirical equation for predicting the reaction rate constant is obtained:

$$k_T = \left(0.000618 - 0.376724\,C + 0.180917\,C\frac{B}{A}\right)\left(\frac{10^{\left(9.140142 - \frac{3320.0564}{T}\right)}}{1.745}\right) \tag{11}$$

where k_T = predicted reaction rate constant
C = sulfuric acid, weight %
B = butanol, moles
A = acetic acid, moles
T = temperature, ° K.

Application of Equation 11 to the temperature series gives results identical with those listed for the least-squares equation. The average deviation for the rate constant calculated from Equation 11 compared with the observed values for all of the runs is 15.3%, and for those runs in the range encountered in the continuous esterification experiments, 7.46%.

SUMMARY OF KINETIC DATA AND THEORY

Goldschmidt (*8*) and Smith (*18*) showed that the free hydrogen ion of a mineral acid acts as a catalyst by combining with the alcoholic hydroxyl to form a complex:

$$RCOOH + R_1OH_2^+ = RCOOR_1 + H_2O^+$$

They expressed the rate of formation of ester by the equation:

$$\frac{(RCOOR_1)}{dt} = k(RCOOH)(R_1OH_2^+)$$

However, as water is formed, it competes with the alcohol for the hydrogen ion, cutting down the number of alcohol complexes. By defining a quantity r as

$$r = \frac{(R_1OH_2^+)(H_2O)}{(\text{total } H^+) - (R_1OH_2^+)}$$

based on the equilibrium between the alcohol and water complexes, solving this relation for $(R_1OH_2^+)$, and substituting in the original rate equation:

$$\frac{dx}{dt} = \frac{kr(\text{catalyst})(a - x)}{r + x} \tag{12}$$

where a is the original concentration of organic acid, x is the concentration of ester formed after time t, and the catalyst is a strong mineral acid.

Integrating Equation 12 and setting $x = 0$ when $t = 0$ gives:

$$k = \frac{(r + a) \ln \dfrac{a}{a - x} - x}{(\text{catalyst})\ rt} \tag{13}$$

Goldschmidt tested this equation for a number of esterification reactions at 25° C. and found constant values of k up to about 80 to 90% reaction; then the reverse hydrolysis reaction became appreciable, and the value of k fell off. Smith (*18*) confirmed the Goldschmidt equation over the temperature range 20° to 50° C., using normal aliphatic acids in methanol catalyzed by hydrochloric acid, with an initial acid concentration of 0.5 mole per liter and a catalyst concentration of 0.005 mole. Thus, although the catalyst concentration is in the range employed in these experiments, the initial concentration of acetic acid is considerably less. The molar ratio of methanol to acetic acid used by Smith was 51.22, or more than twice that of the highest ratio of butanol to acetic acid used in these studies.

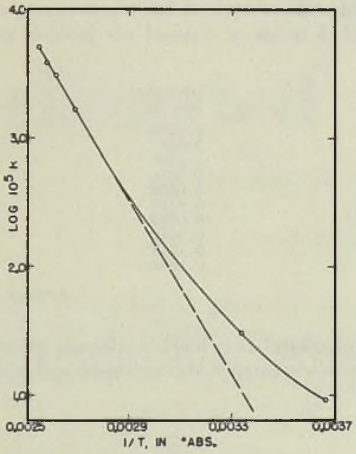

Figure 12. Relation between Reaction Rate Constant *k* and Temperature with 0.0322% Catalyst and 4.972 Moles Butanol per Mole Acetic Acid

Dotted line is an extrapolation of the straight-line portion.

Application of the Goldschmidt equation to these experiments was unsuccessful because the value of r at the temperatures involved was unknown. However, substitution of Smith's data for the formation of methyl acetate at 50° C. with hydrochloric acid fits Equation 7 very well up to about 50% conversion, as Table VI shows.

Up to 16.75 minutes, the values of k (in liters per mole-second), calculated by Equation 7, are in excellent accord with those obtained by Smith using the Goldschmidt equation (Equation 13). With times of reaction greater than 16.75 minutes, Equation 7 does not apply as shown by a plot of $X/(A - X)$ against time; an excellent straight line is obtained for the first four points with the 16.75-minute point slightly high and the longer times considerably higher.

TABLE IV. CALCULATION OF RATE CONSTANT k, WHERE

$$k = \frac{1}{A_0t} \cdot \frac{X}{A - X}$$

Run	A_0, Moles/ Liter	Time, Min.	$\frac{X}{A - X}$	k	Wt. % Catalyst	$\frac{B}{A}$	Temp., ° C.
			Catalyst Series				
K	1.7880	120	0.1327	0.0006185	0.0000	4.965	100
C	1.7817	120	0.5894	0.002757	0.00614	4.984	100
S	1.7897	120	0.9051	0.004214	0.0147	4.960	100
D	1.7677	120	2.5326	0.01194	0.0198	5.029	100
E	1.7520	120	3.1204	0.01484	0.0307	5.079	100
B	1.7836	120	4.0948	0.01913	0.0309	4.978	100
H	1.7497	120	4.2700	0.02034	0.0316	5.087	100
N	1.7853	120	3.5275	0.01646	0.0322	4.972	100
T	1.7766	120	5.1341	0.02408	0.0418	5.001	100
U	1.7792	120	8.785	0.04115	0.0679	4.992	100
V	1.8002	120	13.595	0.06293	0.1032	4.925	100
W	1.7838	60	8.207	0.07668	0.1373	4.975	100
			Temperature Series				
L	1.9797	120	0.02119	0.0000892	0.0322	4.972	0
M	1.9299	120	0.06877	0.0002969	0.0322	4.972	30
N	1.7853	120	3.5275	0.01646	0.0322	4.972	100
O	1.7637	120	6.3570	0.03004	0.0322	4.972	110
P	1.7522	120	7.9374	0.03775	0.0322	4.972	115
R	1.7418	60	10.4498	0.04999	0.0322	4.972	120
			Proportion Series				
G_1	2.7567	60	2.074	0.01254	0.0490	2.998	100
G_2	2.7567	120	3.706	0.01120	0.0490	2.998	100
H	1.7497	120	4.270	0.02034	0.0316	5.087	100
I_1	1.1550	60	1.495	0.02157	0.0211	8.030	100
I_2	1.1550	120	3.354	0.02420	0.0211	8.030	100
J_1	0.9759	60	1.295	0.02212	0.0179	9.619	100
J_2	0.9759	120	2.845	0.02429	0.0179	9.619	100
$X_{0.5}$	2.7628	30	1.726	0.02082	0.0690	2.991	100
X_1	2.7628	60	3.132	0.01889	0.0690	2.991	100
U	1.7792	120	8.785	0.04115	0.0679	4.992	100
Y	0.9378	30	2.624	0.09327	0.0711	10.03	100
Z	0.4938	30	3.434	0.2318	0.0692	19.62	100

The Goldschmidt equation was derived from purely theoretical considerations for low concentrations of acids, whereas Equation 7 was obtained empirically at higher concentrations and also higher temperatures, but both give results in substantial agreement up to about 50% complete reaction.

In accordance with the known complexity of the reaction, shown by the deviation of the plot of log k against the reciprocal of absolute temperature (Figure 12) and the peculiar temperature sensitivity of the reaction of butanol and sulfuric acid, the following series of reactions appear probable:

$$H_2SO_4 + C_4H_9OH = C_4H_9SO_4H + H_2O \tag{14}$$

$$C_4H_9SO_4H + H_2O = C_4H_9SO_4^- + H_3O^+ \tag{15}$$

$$C_4H_9OH + H_3O^+ = C_4H_9OH_2^+ + H_2O \tag{16}$$

$$C_4H_9OH_2^+ + HOOCCH_3 = C_4H_9OOCCH_3 + H_3O^+ \tag{17}$$

TABLE V. COMPARISON OF ACTUAL AND CALCULATED VALUES OF k AT 100° C. BY EQUATION 8 WHERE

$$k = 0.000618 - 0.376724C + 0.180917C\left(\frac{B}{A}\right)\frac{\text{Liters}}{(\text{Moles})\ (\text{Min.})}$$

Run	C, Wt. %	$\frac{B}{A}$	k Calcd.	k Actual	Difference	Deviation, %
K	0.000	4.965	0.000618	0.000618	0.000000	0.0
C	0.00614	4.984	0.003841	0.002757	+0.001084	+39.32
S	0.0147	4.960	0.008271	0.004214	+0.004057	+96.28
D	0.0198	5.029	0.01118	0.01194	−0.00076	− 6.36
E	0.0307	5.079	0.01726	0.01484	+0.00242	+16.31
B	0.0309	4.978	0.01681	0.01913	−0.00232	−12.13
H	0.0316	5.087	0.01780	0.02034	−0.00254	−12.49
N	0.0322	4.972	0.01745	0.01646	+0.00099	+ 6.03
T	0.0418	5.001	0.02269	0.02408	−0.00139	− 5.77
U	0.0679	4.992	0.03636	0.04115	−0.00479	−11.64
V	0.1032	4.925	0.05369	0.06293	−0.00924	−14.68
W	0.1373	4.975	0.07247	0.07668	−0.00421	− 5.49
G	0.0490	2.998	0.008736	0.01187	−0.00313	−26.36
I	0.0211	8.030	0.02332	0.02288	+0.00044	+ 1.94
J	0.0179	9.619	0.02503	0.02320	+0.00183	+ 7.87
X	0.0690	2.991	0.01196	0.01986	−0.00790	−39.78
Y	0.0711	10.03	0.10285	0.09327	+0.00958	+10.27
Z	0.0692	19.62	0.2202	0.2318	−0.0116	− 5.00

Reaction 14 is particularly temperature sensitive, requiring days at low temperatures and only a few minutes at elevated temperatures. Reaction 15 cannot proceed until after reaction 14 has occurred but then probably takes place instantly. Reaction 16 should also occur extremely rapidly; free hydrogen ions can scarcely be expected to exist in the neighborhood of polar alcohol molecules because of their tendency to become solvated, especially since the alcohol molecules are present in large excess. Reaction 17 can now occur; this will be recognized as the Goldschmidt equation. At low temperatures, therefore, it is likely that reaction 14 controls the rate of esterification, whereas at elevated temperatures (100° C. or higher) reaction 17 is the controlling factor with sulfuric acid catalyst.

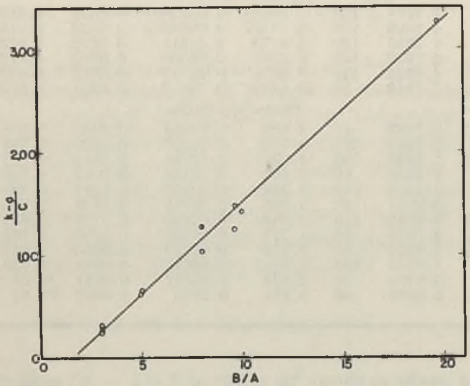

Figure 13. Relation between Ratio of Reaction Rate Constant to Catalyst Concentration, $(k - a)/C$, and Proportions of Reactants B/A, at 100° C.

However, it is well known from latent heat determinations and surface tension measurements (*2*) over the range of 15° to 150° C. that acetic acid exists largely as a double molecule, $(C_2H_4O_2)_2 = 2C_2H_4O_2$, independent of temperature. On this basis, reaction 17 should be represented by

$$C_4H_9OH_2^+ + (CH_3COOH)_2 = C_4H_9OOCCH_3 + HOOCCH_3 + H_3O^+ \quad (18)$$

The rate of formation of the ester, according to this mechanism, becomes

$$\frac{d(\text{ester})}{dt} = k'(CH_3COOH)_2(C_4H_9OH_2^+)$$

The concentration of the alcoholic complex will remain constant because of the rapidity of reaction 16; as soon as a molecule has reacted, the liberated hydrogen ion immediately will take up another alcohol molecule. The rate of esterification will therefore be proportional only to the concentration of acetic acid. The reduction of the concentration of the alcoholic complex by the hydronium ion can probably be neglected in these considerations in view of the small water concentrations involved and of the trend indicated in the value of k shown in Smith's data with longer times of reaction.

Let us assume that only the acetic acid molecules existing in the dimeric form contain sufficient energy of activation to react with the alcoholic complex; this seems probable because resonating systems have the property of concentrating energy over a few atoms instead of having the energy scattered over the whole molecule. Then, since two molecules of acetic acid are involved per mole of activated complex, the rate must be proportional to the square of the acetic acid concentration:

$$\frac{d(\text{ester})}{dt} = k(CH_3COOH)^2$$

Table VI. Esterification of Methanol and Acetic Acid at 50° C. (*18*) with 0.005 *M* Concentration of Hydrochloric Acid as Catalyst

t, Min.	$A - X$	X	$\frac{X}{A - X}$	k from Eq. 7	k (Goldschmidt) from Eq. 13
0	0.500	0.000	0.000	...	...
1	0.467	0.033	0.0707	0.2356	0.236
5.5	0.365	0.135	0.370	0.2240	0.224
9	0.308	0.192	0.623	0.2306	0.224
16.75	0.223	0.277	1.24	0.2466	0.221
24.5	0.170	0.330	1.94	0.2640	0.215
38.5	0.110	0.390	3.55	0.3073	0.207

where rate constant k now includes the concentration of activated alcoholic complex. Since the moles of ester formed must be exactly equal to the amount of acetic acid reacted, X, and if A is taken as the initial concentration of acetic acid, the above equation reduces to $dX/dt = k(A - X)^2$, which is Equation 6.

EQUILIBRIUM CONSTANTS

The equilibrium constant is defined as the ratio of the concentrations of products divided by the concentrations of reactants:

$$K = \frac{(\text{ester})(\text{water})}{(\text{butanol})(\text{acetic acid})}$$

To determine the equilibrium constant for the esterification, extra test tubes of the various runs used in the rate studies were heated for additional lengths of time (16, 24, and 32 hours, in general), and the free acidity was determined. After correction for the catalyst, the amount of unreacted acetic acid remaining could be calculated, which fixed the other compositions. The average values for the equilibrium for the longer time intervals are summarized in the following tables.

The concentration of catalyst has no effect on the equilibrium constant, with 5 moles of butanol per mole of acetic acid at 100° C.: •

Run	Catalyst, Wt. %	K
D	0.0198	2.38
E	0.0307	2.26
B	0.0309	2.21
H	0.0316	2.40
N	0.0322	2.38
T	0.0418	2.42
U	0.0679	2.48
V	0.1032	2.40
W	0.1373	2.31
F	0.1608	2.32
	Average	2.36

Similarly, temperature has no marked influence on the equilibrium constant at constant catalyst concentration and proportions:

Run	Temp., ° C.	K
N	100	2.38
O	110	2.58
P	115	2.32
R	120	2.58
	Average	2.46

The equilibrium constant is markedly affected by the proportions of reactants employed, however:

Run	Molal Ratio, Butanol/Acetic Acid	K
G	2.998	2.25
H	5.087	2.40
I	8.030	2.12
J	9.619	2.01
X	2.991	2.87
U	4.992	2.48
Y	10.03	2.12
Z	19.62	1.66

A similar decrease in the equilibrium constant for the reaction of acetic acid and ethanol was reported by Poznanski (*9, 17*) who cites a variation in K from 1.0 to 6.8, depending upon the proportions of reactants used. The average value for the equilibrium constant for the esterification of butanol and acetic acid from the above summary is about 2.35, which is considerably lower than the value of 4.24 reported by Menschutkin (*9*) for the uncatalyzed reaction at 155° C.

CONCLUSIONS

The controlling reaction involved in the catalytic esterification of butanol and acetic acid at elevated temperatures (100° C. or higher) is of the second order kinetically and is proportional to the square of acetic acid concentration up to 75 to 85% completion. The rate constant is a linear function of the catalyst concentration and the molar ratio of butanol to acetic acid. At temperatures in the range 100° to 120° C., the logarithm of the rate constant is proportional to the reciprocal of absolute temperature.

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Viscosity of Carbonated Aluminate Solutions

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Viscosity data are presented for plant solutions that have been encountered in the development of an alkaline process for the production of alumina. The solutions represent aqueous mixtures of sodium carbonate, sodium aluminate, sodium hydroxide, and minor constituents. Viscosities were measured at 15°, 30°, 45°, 60°, 75°, 90° C. and at 0–30% dissolved solids. The composition of the dissolved solids was varied from about 43% carbon dioxide–0% alumina to 0% carbon dioxide–43% alumina, with the sodium oxide nearly constant at 57%. Viscosity increased as the ratio of sodium oxide to carbon dioxide increased.

IN THE course of an extended investigation of a lime-soda sintering process for alumina from low-grade bauxites and clays, a need arose for viscosity data on the plant liquors. Such data were desired for calculations of heat transfer, fluid flow, etc., for purposes of engineering design. The solutions involved were aqueous mixtures of sodium hydroxide, sodium aluminate, and sodium carbonate with small amounts of impurities. For simplicity, the solutions can be considered part of the four-component system Na_2O–CO_2–Al_2O_3–H_2O. The range of compositions encountered in plant operation falls approximately along the line shown in Figure 1, which neglects the component water. Sodium oxide is nearly constant at 56–58%; carbon dioxide and alumina vary reciprocally from 0 to about 43%. This corresponds to sodium carbonate at one extreme and a mixture of sodium aluminate and sodium hydroxide at the other end. No viscosity data on the four-component system and relatively little data on related alkaline solutions were found in the literature. Values for solutions containing sodium hydroxide and sodium carbonate together were reported by Hitchcock and McIlhenny (*2*). The measurements of viscosity in the present work were carried out with sufficient accuracy for design purposes. The data obtained should be useful for application to similar industrial processes.

An Ostwald-type viscometer was mounted in a water bath consisting of a 4-liter glass beaker, motor stirrer, electric immersion heater, and calibrated thermometer. The temperature was controlled within ±0.1° C. Time was measured to 0.1 second with a precision electric stop clock. The test solutions were prepared from plant liquors by concentrating to a point just preceding saturation at 100° C. (compare the system $NaOH$–Na_2CO_3–H_2O, *1*) and by diluting subsequently with water in the ratios 1:1/3, 1:1, and 1:3 by weight. Five-milliliter samples were pipetted into the viscometer. Each determination was repeated three or four times. Weighed samples of the solu-

Table I. Viscosity and Density of Carbonated Aluminate Solutions[a]

Solution No.	15° C. η	15° C. d	30° C. η	30° C. d	45° C. η	45° C. d	60° C. η	60° C. d	75° C. η	75° C. d	90° C. η	90° C. d
1-A	[b]	[b]	9.52	1.370	5.36	1.356	3.49	1.343	2.45	1.329	1.84	1.315
1-B	6.84	1.283	4.00	1.270	2.61	1.257	1.84	1.244	1.32	1.231	1.06	1.218
1-C	3.13	1.182	2.04	1.171	1.36	1.159	1.06	1.147	0.84	1.135	0.69	1.123
1-D	1.73	1.082	1.15	1.071	0.88	1.060	0.68	1.049	0.54	1.039	0.44	1.028
2-A	[b]	[b]	13.79	1.395	7.39	1.381	4.50	1.366	3.05	1.352	2.19	1.338
2-B	9.11	1.302	4.99	1.289	3.14	1.276	2.16	1.262	1.57	1.249	1.21	1.236
2-C	3.60	1.195	2.30	1.183	1.58	1.171	1.16	1.159	0.91	1.147	0.73	1.135
2-D	1.82	1.088	1.23	1.077	0.91	1.066	0.70	1.055	0.55	1.044	0.46	1.033
3-A	[b]	[b]	13.75	1.386	7.34	1.372	4.47	1.358	3.02	1.344	2.19	1.330
3-B	9.12	1.294	5.02	1.281	3.14	1.268	2.16	1.255	1.55	1.242	1.19	1.229
3-C	3.63	1.191	2.30	1.179	1.58	1.167	1.16	1.155	0.89	1.143	0.72	1.131
3-D	1.84	1.086	1.23	1.075	0.90	1.064	0.70	1.054	0.55	1.043	0.45	1.032
4-A	[b]	[b]	16.44	1.394	8.53	1.380	5.07	1.366	3.37	1.352	2.42	1.338
4-B	10.42	1.302	5.59	1.289	3.45	1.276	2.33	1.262	1.67	1.249	1.26	1.236
4-C	3.91	1.195	2.45	1.183	1.67	1.171	1.21	1.159	0.93	1.147	0.75	1.135
4-D	1.88	1.087	1.26	1.076	0.93	1.065	0.71	1.055	0.57	1.044	0.46	1.033
5-A	115.7	1.472	39.3	1.457	17.74	1.442	9.43	1.428	5.82	1.413	3.97	1.398
5-B	19.43	1.350	9.37	1.336	5.31	1.323	3.39	1.309	2.38	1.296	1.74	1.282
5-C	5.22	1.226	3.12	1.214	2.08	1.202	1.45	1.189	1.11	1.177	0.87	1.165
5-D	2.10	1.104	1.39	1.093	1.01	1.082	0.76	1.071	0.60	1.060	0.50	1.049

[a] Viscosity, η, in centipoises; density, d, in grams per ml.
[b] Solution crystallized at 15° C.

tions were analyzed for carbon dioxide, sodium, and aluminum by standard gravimetric procedures. Densities were calculated by an empirical equation developed in another study on the same type of solutions (*4*):

$$\text{density} = (0.0129\,W + 0.938)\,[1 + 0.0007\,(80 - t)]$$

where W = solids in solution, %
t = temperature, ° C.

The viscometer was calibrated by the method of Fenske *et al.* (*5*). Aqueous glycerol solutions were used as standards as recommended by Sheely (*8*). Seven solutions ranging from 25 to 95% were prepared from c.p. glycerol and checked by density. The pipet constant, k, was determined at 20° and 30° C. for each solution. Pure water at temperatures from 15° to 90° C. was also used for calibration. For times of efflux greater than 35 seconds, the value of k was constant within ±0.6%. Corrections for all sources of error other than liquid head were included in the pipet constant by the method of calibration.

Figure 1. Composition of Dissolved Solids in Solutions Used for Viscosity Tests (Weight Per Cent)

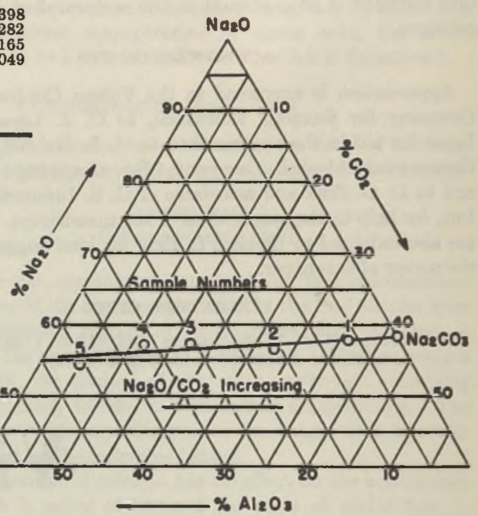

Table II. Composition of Solutions Used in Viscosity Tests

Solution No.[a]	Na_2O	CO_2	Al_2O_3	Total
	Composition, % by Weight			
	Na_2O/CO_2 = 1.614			
1-A	17.32	10.73	1.85	29.90
1-B	12.99	8.05	1.39	22.42
1-C	8.68	5.38	0.93	14.98
1-D	4.34	2.69	0.46	7.49
1-S	57.9	35.9	6.19	100.0
	Na_2O/CO_2 = 2.060			
2-A	17.94	8.71	5.07	31.73
2-B	13.46	6.53	3.80	23.80
2-C	8.98	4.36	2.54	15.89
2-D	4.49	2.18	1.27	7.94
2-S	56.6	27.5	16.0	100.0
	Na_2O/CO_2 = 3.385			
3-A	17.84	5.27	7.98	31.09
3-B	13.36	3.95	5.98	23.29
3-C	8.93	2.64	3.99	15.56
3-D	4.48	1.32	2.00	7.80
3-S	57.4	17.0	25.7	100.0
	Na_2O/CO_2 = 5.095			
4-A	18.19	3.57	9.97	31.73
4-B	13.64	2.68	7.47	23.79
4-C	9.12	1.79	5.00	15.90
4-D	4.56	0.90	2.50	7.96
4-S	57.3	11.3	31.4	100.0
	Na_2O/CO_2 = 11.28			
5-A	19.85	1.76	14.85	36.46
5-B	14.91	1.32	11.16	27.39
5-C	9.94	0.88	7.43	18.25
5-D	4.97	0.44	3.72	9.12
5-S	54.5	4.83	40.7	100.0

[a] Numerals refer to original five samples. Letters refer to dilutions: A = concentrated solutions; B, C, D = dilutions of solution A by weight factors of approximately 1.3, 2, and 4, respectively; S = solids basis.

Table III. Interpolated Values of the Viscosity of Carbonated Aluminate Solutions

Solids, % by Wt.[a]	15° C.	30° C.	45° C.	60° C.	75° C.	90° C.
	Viscosity, Centipoises					
		Na_2O/CO_2 = 1.614				
5	1.47	1.00	0.754	0.594	0.480	0.394
10	2.06	1.38	0.993	0.777	0.616	0.508
15	3.13	2.04	1.40	1.06	0.824	0.669
20	5.23	3.15	2.11	1.52	1.13	0.905
25	9.47	5.31	3.31	2.28	1.62	1.28
30	...	9.14	5.40	3.53	2.48	1.85
		Na_2O/CO_2 = 2.060				
5	1.49	1.02	0.772	0.594	0.473	0.397
10	2.12	1.41	1.04	0.791	0.616	0.514
15	3.30	2.12	1.47	1.09	0.839	0.690
20	5.64	3.39	2.22	1.58	1.19	0.944
25	10.6	5.71	3.53	2.40	1.75	1.32
30	...	10.7	6.02	3.81	2.63	1.91
		Na_2O/CO_2 = 3.385				
5	1.51	1.03	0.762	0.594	0.477	0.391
10	2.18	1.44	1.03	0.800	0.625	0.505
15	3.41	2.18	1.50	1.12	0.855	0.685
20	5.94	3.50	2.30	1.62	1.20	0.950
25	11.5	6.12	3.70	2.47	1.77	1.36
30	...	11.6	6.44	4.00	2.72	2.00
		Na_2O/CO_2 = 5.095				
5	1.52	1.05	0.779	0.601	0.481	0.397
10	2.20	1.47	1.07	0.805	0.636	0.518
15	3.53	2.23	1.54	1.13	0.875	0.700
20	6.32	3.37	2.37	1.68	1.24	0.976
25	12.2	6.56	3.91	2.61	1.85	1.40
30	...	12.7	6.91	4.24	2.86	2.05
		Na_2O/CO_2 = 11.28				
5	1.54	1.04	0.774	0.587	0.476	0.400
10	2.25	1.47	1.08	0.793	0.634	0.525
15	3.62	2.23	1.58	1.12	0.880	0.708
20	6.40	3.70	2.46	1.68	1.27	0.982
25	13.0	6.80	4,06	2.66	1.91	1.43
30	30.4	13.8	7.22	4.46	3.02	2.18
35	83.1	30.7	14.2	7.94	5.01	3.47

[a] $Na_2O + CO_2 + Al_2O_3$.

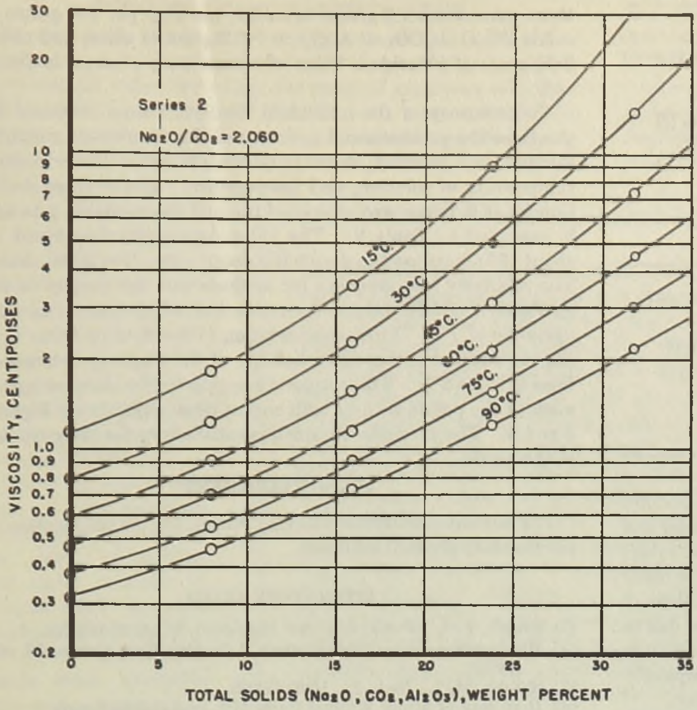

Figure 2. Effect of Concentration on Viscosity of Carbonated Aluminate Solutions

Table I gives the data obtained in 120 viscosity tests on the five series of solutions at 15°, 30°, 45°, 60°, 75°, and 90° C. The corresponding solution compositions are listed in Table II. The composition of the dissolved solids in each series, corresponding to a point in Figure 1, is also given. Composition is expressed on a weight basis in order to make it independent of temperature. For brevity, solution composition can be expressed in terms of per cent dissolved solids and Na_2O/CO_2 ratio. The Na_2O/CO_2 ratios are weight rather than mole ratios.

The measured viscosities may be considered a function of temperature, per cent solids, and Na_2O/CO_2 ratio. The data of Table I were plotted as log η against per cent solids. The points fell along smooth curves of slight curvature, concave upward and terminating for each temperature at the logarithm of the viscosity of water. The six curves for series 2 are shown in Figure 2. The interpolated viscosity values of Table III were read from these and similar curves. At the highest Na_2O/CO_2 ratio (namely, 11.28) the solubility was greater so that viscosities can be reported up to 35% solids. In order to obtain viscosities at other temperatures by interpolation, log η was plotted against t° C. as shown in Figure 3. Again the points fell closely on smooth curves. By plotting log η against $1/t$° K., curves were obtained with less curvature but this method is not so convenient to use. Log η was also plotted against log absolute temperature. In none of these three cases was a linear relation obtained. The relation between viscosity and Na_2O/CO_2 ratio is illustrated in Figure 4. As the Na_2O/CO_2 ratio increased from 1.614 to 11.28, the viscosity at 30° C. increased by 4.0% at 5% solids up to 52% at 30% solids. At 90° the corresponding increases in viscosity were 1.5% and 18%. With pure solutions of sodium hydroxide and sodium carbonate also, the viscosity increases with increasing Na_2O/CO_2 ratio, as shown by Hitchcock and McIlhenny's data (*2*) after recalculation to the present basis.

No data were found in the literature for comparison with the present results. However, by converting the analytical values for

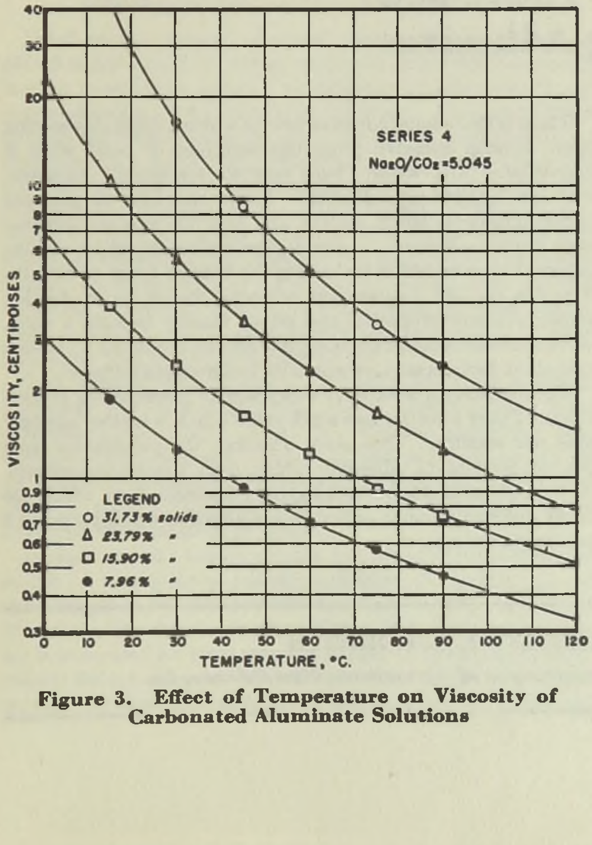

Figure 3. Effect of Temperature on Viscosity of Carbonated Aluminate Solutions

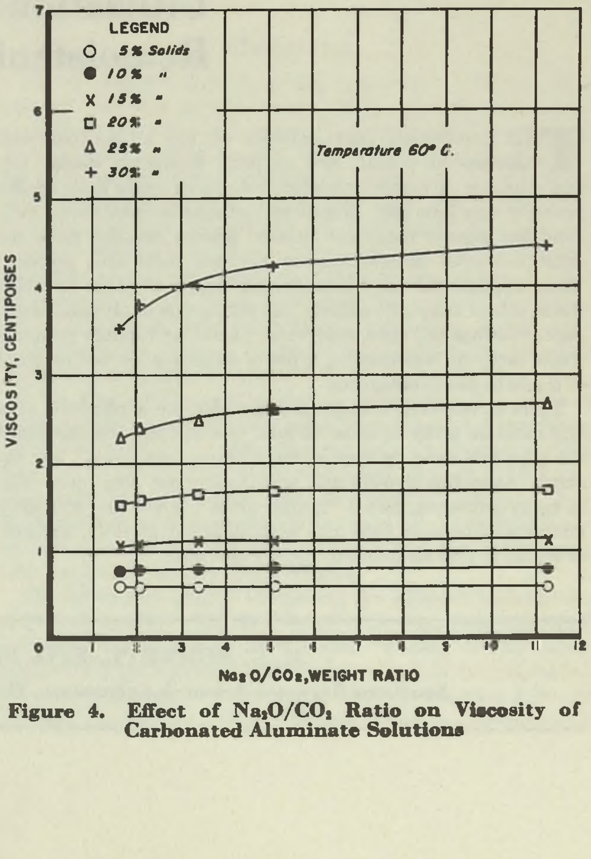

Figure 4. Effect of Na_2O/CO_2 Ratio on Viscosity of Carbonated Aluminate Solutions

TABLE IV. COMPARISON OF THE VISCOSITY OF SODIUM CARBONATE–SODIUM HYDROXIDE SOLUTIONS, WITH AND WITHOUT DISSOLVED ALUMINA

Solution No.	Viscosity at 30° C., Centipoises	
	Present data	Hitchcock data (2)
1-A	9.52	8.28
1-D	1.15	1.17
2-A	13.79	8.43
2-D	1.23	1.17
4-B	5.59	3.21
5-B	9.37	3.78
5-D	1.39	1.16

TABLE V. PRECISION OF MEASUREMENTS IN VISCOSITY DETERMINATIONS

Component Measurement	Av. Deviation from Mean
Time of efflux	0.04–0.5%
Density	0.7%
Calibration	0.6%
Analysis	2%
Temperature	0.1° C. or less

sodium oxide and carbon dioxide into concentrations of sodium hydroxide and sodium carbonate as gram equivalents per liter and neglecting the alumina, a comparison may be made with the data of Hitchcock and McIlhenny (*2*). Such a comparison is made for a range of compositions in Table IV. The higher values of our results may be attributed to the higher solids content due to the presence of alumina and impurities. Further interpretation of the data does not seem warranted, because of the complexity of the solutions studied, and is not the purpose of this paper.

The solutions used in this work were not prepared from pure reagents but contained small amounts of several minor elements commonly found in clays. Besides the three major constituents, there were about 1.8 grams of sulfate (as SO_3) per 100 grams of solids ($Na_2O + CO_2 + Al_2O_3$), 0.1–0.2 gram of silica, and about 0.05 gram of chloride. Other elements were present as traces only.

The accuracy of the individual viscosity values obtained depends on the precision and accuracy of the component measurements: time of efflux, density, calibration curve of viscometer, composition of solution, and temperature. The average deviation for each factor was computed from all the available data and is presented in Table V. The value for density was based on about 100 points used to derive the density equation given above. The relatively low precision for analysis was due largely to the gravimetric carbon dioxide determination, which had an average deviation of 1%. From consideration of the data in Table V, it may be concluded that the reliability of the viscosity determinations is 1.5 to 2%. This estimate is supported by the close agreement of the points with smooth curves when plotted as in Figures 2 and 3. The precision obtained is satisfactory for the purposes of this work.

ACKNOWLEDGMENT

The authors are indebted to Guy Ervin, Jr., for preparation of the standard glycerol solutions.

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PEANUT PROTEIN HYDRATES

Utilization as Tacky and Remoistening Adhesives

THE peptization characteristics of the nitrogenous constituents of peanut and soybean meals are similar (*5*), and solutions of proteins isolated from these meals have similar viscosity relations (*3*). These and related investigations indicate that peanut meal and isolated peanut proteins have the same industrial applications as soybean meal and proteins. These applications have been limited largely to those to which casein is best adapted—namely, the production of plywood glues, paper coatings and sizes, cold water paints, and similar products where tacky or remoistening types of adhesives are not required or would be disadvantageous.

There is, however, a large field in which the applied wet glue film must be tacky in order to hold two surfaces together until the glue film dries to form a more permanent bond. For example, paper-box makers and bookbinders use large quantities of tacky adhesives, called "flexible glues", which are ordinarily mixtures of bone or hide glue with sufficient glycerol, sorbitol, or sugars to give flexibility to the dry glue film.

There is also a large adhesive field in which a dried glue coating must develop adhesive properties and form a bond when it is moistened with water. Such varieties are called "remoistening" or "gumming" adhesives. Large amounts of gummed paper suitable for labels, stamps, and envelope seals are prepared with dextrin adhesives. Animal glues are employed for making gummed tape or fabric for sealing the heavier types of cartons. For this use the remoistened adhesive coating must develop strong adhesive properties and set up rapidly to form a bond. About 20 million pounds of bone glue and an estimated 25 million pounds of dextrins are used annually for gumming purposes.

These adhesives must have tacky and/or remoistening properties, and they must possess a pH value which is neither strongly acid nor alkaline. This paper describes the preparation from peanut proteins of adhesives which meet these requirements. A description of peanut and soybean hydrates from which the tacky and remoistening adhesives are prepared was reported in a previous article (*1*).

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DEWATERED PEANUT PROTEIN CURDS

Protein curds obtained by precipitation at pH 5.0 contain practically all the protein which was in the peanut meal extract, since this pH value lies within the range of minimum solubility of the peanut proteins (*2*, *5*). Furthermore, the curds obtained by precipitations at pH 5.0 can be dewatered more readily to yield the protein hydrate than can curds obtained by precipitation at pH 4.5. Dewatering is accomplished by heating the curds to about 50° C., at which temperature the jelly-like particles of curd coalesce and exclude water present in excess of that bound by the protein molecules. This was discussed in a previous publication (*1*).

Glues have been prepared from peanut protein, isolated from both solvent-extracted and hydraulic-pressed peanut meals, which are suitable for making gummed tape and paper and for making flexible glues of the type used by the setup paper-box maker and the bookbinder. Preliminary investigations have shown that gummed tapes with relatively good adhesive strengths can be prepared from peanut protein glues. Peanut protein flexible glues are relatively free of difficulties encountered with certain other types because they can be applied cold and become tacky immediately. Readily soluble glues can be prepared from isoelectric peanut protein curds by neutralizing the curds before they are dried. Dewatering peanut protein curds to the amount of water in the hydrate reduces drying costs and provides a glue of relatively uniform ash content. The characteristics of these peanut protein glues described, particularly rewettability, tackiness, and flow properties, render them suitable for certain gluing purposes for which vegetable proteins have previously been considered unsuitable.

There are two advantages of dewatering the protein curds before drying. First, by lowering the water content to about 42.5 %, this method reduces the cost of drying the filtered curds which originally may contain as much as 80% water. Second, it results in dried protein of uniform ash content, since the water content of two batches of dewatered curds prepared by the same method is approximately the same. Any variation in the amount of water retained by the curds would produce a variation in the soluble nonprotein content of the dried protein.

PREPARATION OF PROTEINS FOR ADHESIVES

Dried peanut proteins obtained from curds precipitated at pH 4.5 to 5.0 must be dissolved at pH values between 6.0 and 9.0 in order to obtain sol hydrates which have viscosities suitable for use as adhesives of the type under discussion. This procedure is difficult and time consuming, and requires the use of control instruments and supervision by technical personnel, which are generally unavailable even in factories where adhesives of this type are used on a large scale. The difficulties may be circumvented by neutralizing the dewatered, acidic curds with sodium hydroxide solution before drying. The dried protein is readily soluble, provided water is not present in excess of the amount which can be bound by the protein at any given pH value. These "preneutralized" proteins are referred to here as glues. They have aptly been called "goober glues" (*4*).

Two series of experimental glues were prepared for gumming purposes. One was made from protein curds isolated from solvent-extracted peanut meal; the other was made from protein curds isolated from a hydraulic-pressed meal prepared in the pilot plant under mild cooking conditions—that is, at meal temperatures not exceeding 215° to 218° F. Details of the preparation of the glues are given in Table I.

In each case the peanut protein was extracted from the meal at pH 7.7 with aqueous sodium hydroxide, the meal to solvent ratio being 1 to 10. Since it is not necessary to clarify the protein extract completely prior to precipitation of the protein, if the latter is to be used for preparation of adhesives, the extract and insoluble residue were separated by a solid basket centrifuge. The extract was then allowed to stand about an hour to permit the small amount of suspended matter to settle, the supernatant solution was separated, and the protein was precipitated by the addition of sufficient sulfur dioxide to bring the pH to 5.1.

The curds obtained from the two meals were dewatered, and each dewatered curd was divided into three portions. Each of the three portions was adjusted to a different pH (Table I), and the curds were finally dried in an oven at 50° C. These neutralized curds are difficult to dry, since they consist of thick solutions which cannot be subjected to temperatures above 50° to 60° C. without affecting the protein, as indicated by a change in the viscosity characteristics of solutions prepared from the protein. It is probable that this material can be efficiently spray-dried or vacuum-drum-dried. However, the neutralized, dewatered peanut protein curds can be used advantageously without prior drying when the glue is used by the manufacturer or when the cost of shipping the 30–35% excess water in the glue is equal to, or less than, the cost of drying. Plasticizer, when needed, may be added by either the manufacturer or by the user. Most of the animal flexible glues now on the market contain 25 to 50% water and need only to be diluted and melted before being used. A flexible glue made from neutralized and plasticized peanut protein curds would need only to be diluted before being used.

GUMMED TAPE

The six peanut glues described above were used to make gummed tape in a gummed paper factory. Regular commercial equipment was used for all steps in the process, with the exception of the glue mixer, which was too large for the experimental material available. The glue solutions were prepared by soaking 6 parts of glue with 4 parts of water for 1 hour. The thick pastes thus obtained were then diluted with water until they appeared to be of suitable consistency for application. After dilution, these solutions contained from 40 to 45% protein. No viscometer was available at the plant to measure the resulting solutions, but from previous work it was known that peanut protein solutions having this range of concentration usually have viscosities of approximately 30 to 40 poises.

Each glue solution was poured on a traveling belt of kraft gumming paper just before the paper passed under a doctor blade which had been set to give approximately the desired coating thickness. The gummed paper was passed through drying tunnels where the glue film was dried by a blast of warm air. The dried gummed paper was made into a single roll, which was finally cut into rolls of smaller widths, including 2-inch rolls for adhesion tests and 3-inch rolls for gluing cartons.

The device and method for making the adhesion tests are described as follows: The instrument was a manually operated McLaurin gummed tape tester which "consists of two tables about 6 × 8 inches placed side by side. Each table is hinged at the outer edge on the underside so that the adjacent ends are free to move in an arc. In testing, these are moved by the action

Table I. Preparation and Tests of Peanut Protein Glues[a] and Gummed Tape

Glue No.	Meal Used as Source of Protein	pH of Extn.	pH of Pptn.	pH of Dewatered Curd before Drying	pH of Dried Glue	Coating Wt.[b]	Average McLaurin Adhesive Strength	Practical Test by Taping No. 102 Cartons
1	Solvent-extd.	7.7	5.1	7.3	7.1	9.1	75	Better than 2 or 3
2				8.6	8.2	10.0	36	Trifle slow setting
3				9.6	8.8	12.2	11	Trifle slow setting
4	Hydraulic-pressed	7.7	5.1	7.3	7.3	11.6	66	Little slower setting than 5 & 6
5				8.4	8.0	10.7	72	Better tack than any of others
6				9.5	9.3	10.0	60	Same as 5 except slight tendency of tape to let go at edges

[a] For comparison, gummed tape prepared with animal glue had a coating weight of 7.0 and an adhesive strength of 92.

[b] "Folio base", pounds per ream of 500 sheets, 17 × 22 inches.

of a cam on the end of a weighted level arm. The action of the tables is intended to duplicate the action of the flaps of a corrugated case after they have been closed and then the pressure removed, allowing them to spring back to the partially open position. In addition to the above, the machine is equipped with suitable trip levers, graduated scale, brackets to hold the test specimen, and frame to hold the entire assembly. In making the tests a sheet of the test paper about 6 × 10 inches is placed across the top of the two tables, and the holding clamps are tightened down securing the ends of the sheet. The test sheet is then slit through the center or directly over the position where the two tables come together. A piece of gummed tape to be tested is moistened and then placed on this test sheet, and after the proper interval of time the machine is tripped and the adhesive strength taken directly from the scale reading" (*6*).

Further details are given in the paper from which the preceding is quoted and in the recently issued TAPPI Tentative Standard for testing gummed paper tape (*7*).

Results of the tests conducted on the tapes gummed with peanut protein glues are given in Table I. Results of a practical test made by actually gluing cartons with the experimental gummed tapes are also given in this table. In general, results of the carton gluing tests agree with those of the McLaurin tests.

Results obtained with peanut protein glue approach closely those obtained with animal glue, but it would be unsafe to conclude that any one of the peanut glues was superior to another, as a large number of factors in this preliminary test were not controlled, and any one of them may have adversely affected the results. For example, differences in the viscosities of the glue solutions may have caused variations in the amount of glue absorbed by the paper, which would, in turn, cause variations in the amount of available glue on the surface of the tape. The results may have been affected also by variations in the glue coating applied; too much glue may be as detrimental as too little.

Although all the advantages and disadvantages of peanut protein glues as compared with other gumming adhesives have not yet been investigated, the following advantages of peanut protein glues are apparent: uniformity of product; superiority of color, especially when produced from special varieties of peanuts (*2*), hence preferable for gumming white paper; less hygroscopicity than is found in animal glues or dextrins and, consequently, less tendency of the gummed paper to stick in the roll or stack when it is stored in hot humid atmospheres; highly sanitary product, which is especially important where the glue is remoistened with saliva.

A disadvantage of the peanut protein glues tested so far is the tendency for the tape prepared with these glues to blister after it has been on the carton for some time. This tendency is also exhibited by tapes gummed with dextrins and is disadvantageous primarily from the point of view of appearance rather than of utility.

It is evident, then, that a peanut protein gummed tape with good adhesive strength can be made from the proteins of both solvent-extracted and hydraulic-pressed peanut meals. A systematic investigation of all the factors involved will probably result in an increase in the adhesive strength of the tapes until they are comparable with those made with animal glue.

Peanut glues in their present state of development, however, are suitable for gumming purposes where dextrins are now employed and for many purposes where animal glue is used.

FLEXIBLE OR NONWARP GLUES

Solutions of the glues used in the gummed tape tests were employed in experimental gluing of the paper wraps on setup paper boxes. Candy boxes were used for the tests, and the glue solutions were applied to the paper wraps by means of a small table gummer, ordinarily employed by the bookbinder and paper-box maker in hand operations. These boxes showed a tendency to warp when stored in a relatively dry atmosphere (32% relative humidity). However, when 50% sorbitol (dry glue basis) was added to the glue solution, the boxes did not warp when stored under the same conditions. The warping tendency of the boxes prepared with unplasticized peanut glues was much less than that of boxes prepared with unplasticized animal glue. Accordingly, peanut nonwarp glues may be expected to require less plasticizer than animal glues.

An important advantage of flexible peanut protein glues, as compared with flexible animal glues, lies in the fact that peanut protein glues can be applied cold, are tacky as soon as they are applied, and remain tacky long enough to complete a given gluing job. Animal flexible glues must be applied hot and are not tacky until they have cooled sufficiently to start gelling. Furthermore, animal glues allowed to cool too much lose their tackiness, owing to complete gelling of the glue film. For this reason users of flexible animal glues experience considerable difficulty whenever changes occur in the atmospheric temperature or relative humidity of sufficient magnitude to affect the rate of cooling of the glue film.

Although no extensive investigation has been made with soybean protein, protein hydrates having properties and uses similar to those of peanut protein can probably be produced from solvent-extracted soybean meal.

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CATALYTIC CRACKING OF PURE HYDROCARBONS

Cracking of Olefins

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Cracking over a silica-zirconia-alumina catalyst at 350–500° C. of seven aliphatic olefins, two diolefins, two cyclic olefins, and two aromatic olefins was studied. The principal conversions of aliphatic mono-olefins were isomerization, cracking, saturation, and formation of higher-boiling materials and coke. Diolefins and aromatic olefins were extensively saturated and transformed to higher-boiling materials and coke. Catalytic and thermal cracking of olefins at 400–500° C. are compared. The catalyzed reactions, which are of the order of 1,000 to 10,000 times as fast, yield larger fragments, involve much more isomerization, and lead to greater saturation of product.

CRACKING of paraffins over a silica-zirconia-alumina catalyst under conditions similar to those employed in the commercial cracking of petroleum fractions was described in the first article of this series (*6*). The behavior of olefins was also studied because olefins are important primary products of the cracking of saturated hydrocarbons, and because olefin-containing fractions from either thermal or catalytic cracking are sometimes reprocessed over a cracking catalyst.

The first tests with olefins over a cracking catalyst showed them to be very reactive, in accord with the findings of Egloff and co-workers (*4*). Because of this high reactivity, the relatively low temperature of 400° C. was employed for most of the experiments with olefins, rather than 500° C. which was used for cracking paraffins. The apparatus, catalyst, procedure, and terminology were the same as described previously (*6*). The catalyst, obtained from Universal Oil Products Company, analyzed 86.2% silica, 9.4% zirconia, and 4.3% alumina by weight. As stated before (*6*), it has been found to give essentially the same results as the synthetic silica-alumina catalysts used in present commercial practice.

Properties and sources of hydrocarbons follow, with compounds arranged in the order of increasing molecular weight. Bromine numbers are grams bromine per 100 grams hydrocarbon by the Rosenmund method. Ethylene (Ohio Chemical Company) was over 99% by gas analysis. Butadiene (Shell Development Company's pilot plant) contained 98.3% conjugated dienes. *n*-Butenes were made by dehydration of *sec*-butyl alcohol; they analyzed 8.0% 1-butene, 92.0% 2-butenes, and 0.0% above C_4. Isoprene was a crude material containing 70% conjugated diolefins and 26% other olefins. *n*-Pentenes were from the dehydration of *sec*-amyl alcohol over alumina; the boiling range was 30–37° C., d_4^{20} 0.6519, n_D^{20} 1.3792, bromine number 233. Cyclopentene was derived from cyclopentyl chloride, obtained by chlorination of a petroleum C_5 fraction. It had a boiling point of 44.4° C., d_4^{20} 0.7701, n_D^{20} 1.4217, and bromine number 237. Cyclohexene (Dow Chemical Company) had a boiling range of 83.1–84.2° C., d_4^{20} 0.8107, n_D^{20} 1.4467, and bromine number 195. Styrene (Dow Chemical Company) had a boiling point of 145.5° C., d_4^{20} 0.9055, n_D^{20} 1.5455, and bromine number 150.5. Diisobutenes were from "cold acid" polymerization (Shell Chemical Company). The A.S.T.M. 5 and 95% distillation temperatures were 101.4° and 104.3° C., d_4^{20} 0.7204, n_D^{20} 1.4105, and bromine number 123. *n*-Octenes (Eastman Kodak Company) were fractionally redistilled. The boiling range was 123.4–126° C., d_4^{20} 0.7205, n_D^{20} 1.4135, and bromine number 144. Indene (Kahlbaum) was freshly distilled; it boiled at about 177–182° C., d_4^{20} 0.9952, n_D^{20} 1.5748, and bromine number 135. Triisobutenes were from "cold acid" polymerization (Shell Chemical Company); they had a Cottrell boiling point of 183° C., d_4^{20} 0.768, n_D^{20} 1.4325, and bromine number about 86. Cetene (Bataafsche Petroleum Maatschappij laboratories, Delft) had a boiling point of about 280° C., melting point of 4.05° C., d_4^{20} 0.7813, n_D^{20} 1.4409, and bromine number 69.3.

CRACKING BEHAVIOR

Aliphatic olefins with carbon numbers from 2 to 16 were examined, as well as several diolefins and cyclic olefins. The term "carbon number" is employed to designate the number of carbon atoms per molecule. A temperature of 400° C. was normally used for aliphatics and of 500° C. for others. Discussion of results with the diolefins and cyclics follows that for the aliphatic olefins. The basic data for aliphatic mono-olefins are given in Tables I and II, and those for the remaining compounds in Table III.

ETHYLENE. Ethylene did not react extensively at 400° C.; there was about 6% saturation and 3% polymerization to C_4. No liquid product was obtained. The carbon deposit was high, 9.6% by weight of the feed. Thus the chief reactions were decomposition to carbon, saturation, and polymerization.

***n*-BUTENES.** Experiments with mixed *n*-butenes agreed in a general way with those reported by Egloff and co-workers (*4*). The reactions over the catalyst involve cracking, isomerization, saturation, and formation of higher-boiling materials. The run at 500° C. is of interest in showing extensive conversion to isobutane. Isomerization and saturation were less marked at 400° C. and the longer process period.

***n*-PENTENES.** Data for the cracking of *n*-pentenes show extensive reaction. Olefin contents of the 20–30° C. and 35–38° C. fractions were 42 and 91%, respectively; since these fractions were 18 and 25 volume % of the total liquid, there was substantial production of isopentane and much less of *n*-pentane. This provides another example of preferential saturation of iso-olefins (*6*). The higher-boiling liquid product above 90° C. was 20% of the total liquid and had n_D^{20} of 1.4733, which indicates the presence of aromatics. In general, reactions of pentenes resemble those of butenes.

***n*-OCTENES.** Products from *n*-octenes were about equally divided among gas, lower-boiling liquid, and higher-boiling material. Decomposition was extensive, since only 28% of C_8 material was recovered. The main gas products were propylene, butenes, and butanes. The large amount of isobutene is noteworthy. Lower-boiling liquid was largely C_5, 72% olefinic. The uncracked C_8 fraction was 40% saturated and boiled below the original octenes, which indicates isomerization as well as saturation. Material above C_8 had the moderately high refractive index of 1.4534, indicative of aromatics.

Cracking characteristics of the *n*-octenes are rapid decomposition under mild conditions, saturation of uncracked octenes and cracked products, isomerization, and formation of higher-boiling hydrocarbons. The experiments of Egloff and co-workers (*4*) led to similar conclusions, except for the saturation which was not examined. A later paper from the same laboratories by Thomas demonstrates the extensive saturation in detail (*14*).

TABLE I. CATALYTIC CRACKING OF LOWER ALIPHATIC OLEFINS

	Ethylene	*n*-Butenes		*n*-Pentenes	*n*-Octenes
Temperature, ° C.	400	400	500	400	400
LHSV[a]	...	0.77	0.63	0.74	1.07
Flow rate, moles/l./hr.	7.05	8.3	6.8	6.9	6.9
Process period, min.	60	30	15	60	60
Gaseous product					
Moles/mole charge	...	...	...	0.222	0.497
Vol. % H_2	0.5	1.4	9.5	10.4	1.7
CH_4	1.0	0.2	13.7		0.9
C_2H_4	91.3	0.2	3.3		0.7
C_2H_6	5.5	0.0	3.7		1.3
C_3H_6	0.2	6.1	18.3	33.6[b]	26.6
C_3H_8	0.3	1.3	7.2	56.0[c]	2.4
iso-C_4H_8	1.2	7.2	4.1		17.5
n-C_4H_8		75.7	8.3		26.5
iso-C_4H_{10}		7.9	24.9		22.4
n-C_4H_{10}			7.0		
Material balance, wt. % of charge					
Lower C No., as gas	0.5	4.4	22.8	15.4	22.4
Lower C No., as liquid	...	...	...	...	18.6
Unchanged C No.	87.0	69.2	38.2	51.2	28.0
Higher C No., liquid or gas	2.9	20.3	20.7	27.4	19.5
Carbon	9.6	6.1	14.4	6.0	3.8
Loss	d	d	3.9	d	7.7

[a] Liquid hourly space velocity.
[b] Total olefins, C No. 3.7.
[c] Total saturates, C No. 3.8.
[d] Input not known accurately; balance on output basis.

DIISOBUTENES. Several experiments were made with diisobutenes, which are chiefly 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. At 450° C. and a flow rate of 6.6 moles per liter of catalyst per hour, decomposition exceeded 90%. Table II gives data for another run at 400° C. with a flow rate of 12.9 moles per liter per hour. Even under these milder conditions, decomposition to gas was extensive, and the liquid recovery was only 20.4% by weight. The principal product was isobutene, but a moderate amount of higher-boiling product was also formed.

TRIISOBUTENES. At the low temperature of 350° C. triisobutenes (presumably 2,2,4,6,6-pentamethylheptenes) were almost entirely decomposed. The chief product was gas, largely isobutene. There was also a moderate amount of lower-boiling liquid, distilling mostly in the C_6–C_7 range and containing 90% olefins. Remaining liquid above 150° C. was only 7.7% by weight of the charge and could have contained little unchanged triisobutenes because the refractive index, n_D^{20}, was 1.5002.

CETENE (*n*-HEXADECENE). Table II shows results of cracking at 400° and 450° C. Data obtained by Egloff and co-workers (*4*) are also given. Using higher flow rates and a longer process period, they observed a similar extent of cracking, but their conditions caused a lower production of gas, a higher olefin content in the gas, and greater formation of gasoline. Cetene cracks readily over the catalyst and is much more susceptible to the catalysis than the corresponding paraffin, cetane.

Olefin contents of fractions from cetene cracking show an overall decline as the molecular weight increases. Table IV gives the distributions and olefin contents of fractions. Of particular significance is the low olefin content of the recovered C_{16} fraction. Saturation of cetene evidently proceeded concurrently with the cracking, and the major portion of the cetene not saturated was cracked. This is interpreted as meaning an extensive saturation of higher olefins, together with rapid decomposition of the higher olefins which have not been saturated.

The presence of isobutene in the gas again indicates extensive isomerization accompanying the cracking process. Further evidence is found in the lowered and wider boiling range of the recovered C_{16} fraction. In distillations at 15 mm., cetene boiled at 156° C. and cetane at 158° C.; but 60 to 80% of the recovered C_{16} material from cetene cracking experiments boiled at 135–150° C. Such isomerization does not occur with paraffins; when cetane was cracked, the recovered C_{16} material boiled at the same temperature as the feed.

The study of cetene cracking by Egloff and co-workers (*4*) yields more information on the branched compounds, which usually exceed 70% of the individual product fractions. Their work indicated that the isomerized C_{16} olefin cracks more rapidly than cetene, and led to a proposed description of the cracking involving isomerization to a branched olefin, cracking of the isomer at all bonds except those near to the extremities, and further reaction and isomerization of cracked products.

BUTADIENE. The reactions of 1,3-butadiene at 400° C. (Table III) were extensive, and only 4.8% of the butadiene charged was recovered as such. Saturation, carbon formation, and polymerization were pronounced. The liquid product (33% of the charge) was about 50% C_8 material, and the C_8 material contained 36% olefins, computed as mono-olefins (perhaps the butadiene dimer, 4-vinylcyclohexene) and about 50% aromatics.

TABLE II. CATALYTIC CRACKING OF HIGHER ALIPHATIC OLEFINS

	Diisobutenes	Triisobutenes	Cetene		
Origin of data	This work	This work	This work		(4)
Temperature, ° C.	400	350	400	450	450
LHSV	2.0	2.9	2.0	2.0	4.0
Flow rate, moles/l./hr.	12.9	13.4	6.8	6.8	13.9
Process period, min.	60	60	60	60	167
Gaseous product					
Moles/mole charge	1.27	1.80	0.384	0.935	0.615
Vol. % H_2	0.3	0.2	2.2	2.8	0.0
CH_4	0.6[a]	0.4	4.7	2.2	0.0
C_2H_4	0.1		1.4	1.5	0.0
C_2H_6	...		1.0	2.0	0.0
C_3H_6	4.0		23.6	29.2	32.8
C_3H_8	0.5		4.9	5.1	3.2
iso-C_4H_8	73.0	31.4	11.7	14.8	27.4
n-C_4H_8	7.5	13.6	22.7	22.6	29.8
C_4H_{10}	14.0	4.4	27.8	19.8	6.9
Material balance, wt. % of charge					
Gas	63.1	61.2	8.5	20.2	14.1
Liquid, lower C No.	5.4	25.1	49.4	59.4	67.5
Liquid, unchanged C No.	7.9	7.7	26.3	9.8	14.1
Liquid, higher C No.	7.1		9.9	4.8	
Carbon	1.8[b]	2.2	1.2[b]	1.1[b]	...
Loss	14.7	3.8	4.7	4.7	4.3

[a] Including C_2H_6.
[b] Not including CO.

ISOPRENE. An isoprene-olefin mixture containing 70% conjugated diolefins likewise underwent extensive reaction when treated over the cracking catalyst at 400° C. The recovered C_5 material was 31.7% of the charge but contained no conjugated diolefin and 64.5% mono-olefin. The higher-boiling material (32.1% of the charge) consisted of 25% C_6–C_9, evidently a mixture of olefins, saturates, and aromatics; 55% C_{10} with n_D^{20} of 1.4980 and containing only 5% olefins; and about 20% above C_{10} with n_D^{20} of 1.5980. The complete disappearance of all diolefin, the heavy carbon formation, and the high yield of aromatic condensation products are the chief features of interest in this experiment.

STYRENE. When styrene was passed over the catalyst at 500° C., a small amount of gas was produced and some benzene resulted, but the principal reactions were deposition of carbon on the catalyst and saturation of styrene to ethylbenzene, together with formation of higher-boiling condensation products.

TABLE III. CATALYTIC CRACKING OF CYCLIC OLEFINS, STYRENE, AND DIOLEFINS

	Cyclohexene	Cyclopentene	Styrene	Indene	Butadiene	Isoprene
Temperature, ° C.	500	500	500	500	400	400
LHSV	1.4	1.2	1.6	1.4	0.65	0.72
Flow rate, moles/l./hr.	13.9	13.8	14.1	12.0	7.3	7.2
Process period, min.	60	60	60	48	60	60
Gaseous product						
Moles/mole charge	0.410	0.253	0.036	0.097	0.456	0.191
Vol. % H_2	39.5	43.0	41.7	55.1	1.2	9.3
CH_4	16.3	12.0	....	....	3.0	....
C_2H_4	4.9	6.7	....	....	1.8	....
C_2H_6	5.8	7.8	....	....	5.6	....
C_3H_6	9.4	9.4	....	....	7.3	....
C_3H_8	7.2	7.8	....	....	2.9	....
C_4H_6	....	....	....	....	10.4	....
iso-C_4H_8	1.4	1.5	....	....	2.6	....
n-C_4H_8	3.9	1.8	....	....	54.3	....
C_4H_{10}	11.6	10.0	....	....	10.9	....
Total olefins	....	....	15.8	13.3	....	35.6
Total saturates	....	....	42.5	31.6	....	55.1
Material balance, wt. % of charge						
Lower C No., as gas	11.7	8.3	0.4	1.2	5.9	12.4
Lower C No., as liquid	5.1	0.0	4.8	2.9	....	....
Unchanged C No.	37.0	36.8	66.7	48.8	37.3	31.7
Higher C No.	38.1	40.0	9.2	10.8	33.0	32.1
Carbon	5.0	6.8	13.4	>19.3	>13.0	14.0
Loss	3.1	8.1	5.5	<17.0	<10.8	9.8

The product boiling from 135° to 150° C. was 67% by weight of the charge and contained 42% styrene and 58% ethylbenzene, according to analyses by refractive index or bromine number. The higher-boiling material was a tarry solid at 20° C.

INDENE. When passed at 500° C., this compound proved to be more resistant to cracking to lower-boiling materials than styrene and at the same time gave even more carbon. The carbon deposit was above 19% of the weight of the charge, or over 30% of the weight of catalyst. Saturation of uncracked indene was pronounced; olefin analysis showed that the fraction boiling at 175–180° C. (49% of the weight of the charge) contained only 34% indene. The material of higher carbon number than the charge (10.8% by weight) was a tarry solid.

CYCLOHEXENE. Products from cracking at 500° C. included a considerable amount of gas rich in hydrogen, a little C_5 liquid, much uncracked but largely saturated C_6 material which was mostly methylcyclopentane, and a surprising amount of higher-boiling highly aromatic material. The carbon deposit was moderately large (5% by weight of the charge). The recovered C_6 material (37% of the charge) consisted chiefly of a fraction boiling from 70° to 73° C., which contained 15% olefins, 2.5% aromatics, 2.5% paraffins, and 80% naphthenes. Properties of the washed (with 98% sulfuric acid) and redistilled (70–73° C.) C_6 fraction were: n_D^{20} 1.4089, d_4^{20} 0.7467 (methylcyclopentane 1.4099, 0.7488; and boiling point 71.8° C.). Products above C_6, in weight per cent of charge and with n_D^{20} as shown, were: 75–105° C., 5%, 1.4264; 105–165° C., 8%, 1.4850; bottoms, 25%, 1.5859.

Isomerization, saturation, formation of higher-boiling materials, and cracking were the most important reactions in the treatment of cyclohexene over the cracking catalyst. Cracked products were distributed over the range C_1 to C_4, but there was no C_5 material. The experiments of Bloch and Thomas (*1*) supply information on the reactions of cyclohexene over a similar catalyst under less severe conditions. Reactions observed by them were the same as outlined here, but because of the milder conditions the initial isomerization products (methylcyclopentenes) were obtained in quantity.

CYCLOPENTENE. The reactions of cyclopentene at 500° C. were in part quite similar to those of cyclohexene. Cracking to gas was not extensive, polymer formation was marked, and the carbon deposit was fairly large. Differences relative to cyclohexene were evident in the lack of isomerization and the lesser degree of saturation of uncracked C_5 material. The fraction boiling at 45–50° C. contained 48% olefins, whereas the uncracked fraction from cyclohexene contained only 15%. The material boiling above 110° C., recovered in yield of 32%, was quite aromatic (n_D^{20} 1.5508) and had a bromine number of 20.

REACTIVITY OF OLEFINS

The normal aliphatic olefins are remarkably reactive over the cracking catalyst, and it is clear that, when formed as primary products from the cracking of saturates, they must undergo extensive secondary reaction. Figure 1 shows the variations of reactivity and products within the homologous series of n-olefins, C_nH_{2n}. Under the fixed conditions employed—namely, temperature of 400° C. and flow rate of about 6.8 moles per liter per hour—formation of products with a lower carbon number than the feed increased rapidly with molecular weight. The formation of products with a higher carbon number reached a maximum at about C_5. Carbon formation was relatively high throughout but the percentage of the feed converted to carbon declined with increasing carbon number. As the molecular weight of the feed stock rose, the olefin content of the recovered material with unchanged carbon number decreased rapidly, as shown below:

Carbon No. of Olefin Treated, n	C_n Product as Wt. % of Charge	Wt. % Olefin in C_n Fraction	Fate of C_nH_{2n}, Wt. %			
			Satd., same C No.	Unchanged	Products of smaller C No.	Products of larger C No.[a]
2	87	94	5	82	0.5	12.5
4	69	91	6	63	4.5	26.5
5	51	*ca.* 65	18	33	15.5	33.5
8	31	61	12	19	44	25
16	28	28	20	8	61	11

[a] Including carbon.

This is explained by the combined effects of greater rates of saturation and cracking for the higher olefins. The increases of these rates with increasing n are not fully brought out by the above table, for in the experiments represented, little unchanged olefin remained to react in the case of the higher homologs. Saturation is ascribed to hydrogen transfer from those olefin molecules that react to form products of low hydrogen content, such as the coke on the catalyst or aromatics, usually C_8 or above. Possible sources of hydrogen for saturation in the catalytic treatment of n-octene were discussed by Thomas (*14*).

TABLE IV. CATALYTIC CRACKING OF CETENE

Fraction	Cracking at 400° C.		Cracking at 450° C.	
	Fraction as vol. % of total liquid	Olefin in fraction, wt. %	Fraction as vol. % of total liquid	Olefin in fraction, wt. %
C_5	11	68	20	72
C_6	10	69	18	68
C_7–C_{10}	28	..	33	..
C_{11}	5	43	4	33
C_{12}–C_{15}	9	34	8	36
C_{16}	28	28	12	31
Above C_{16}	(9)	..	5	..

Compared to the paraffins previously discussed (*6*), the olefins react much more rapidly. Disappearance of the initial material was more rapid with olefins at 400° than with paraffins at 500° C. A direct comparison of cetene and cetane is available from experiments at 450° C., and a flow rate of 6.8 moles per liter of catalyst per hour. Under these conditions cetene was 97% reacted to other products, while cetane was only 25% reacted. The olefins not only react faster, but they also undergo reactions which do not occur directly with paraffins—namely, isomerization to give chain branching, and polymerization and condensation to give higher-boiling products rich in aromatics.

Under suitable reaction conditions, the chain-branching isomerization of *n*-olefins, followed by saturation by hydrogen transfer, leads to the production of isoparaffins. In similar fashion the formation of methylcyclopentane from cyclohexene is explained. That an actual hydrogen transfer .and not simply direct hydrogenation is involved has been proved by showing the complete ineffectiveness of molecular hydrogen for the saturation of olefins over cracking catalysts. These data will be given in a subsequent paper.

An effect of the structure of olefins on the reactivity over the catalyst is seen by comparing results with *n*-octenes and diisobutenes. The rate of reaction of diisobutenes was considerably higher; at 400° C. less than 8% of the diisobutenes was left unchanged after treatment at a flow rate of 12.9 moles per liter per hour, while 19% of *n*-octenes remained after treatment at half that flow rate. Diisobutenes cracked principally to isobutene, and the gas production in the run at 400° C. was 63% by weight of the feed. The *n*-octenes did not crack so selectively to any single product, and with them the gas production was only 22% by weight even though the molar flow rate was lower. It is believed that the high reactivity of diisobutenes is related to the presence of a tertiary olefinic carbon atom. The behavior of triisobutenes was like that of diisobutenes.

Although the number of olefinic cyclic compounds tested was not large enough to permit much generalization, some significant features may be noted. The cyclic olefins showed the high degree of reactivity associated with all olefins. They also gave exceptionally large amounts of higher-boiling products, which might have been expected from styrene and indene but not from cyclopentene and cyclohexene. With cyclohexene the rapid initial isomerization to methylcyclopentenes (*1*) was followed by extensive saturation to give methylcyclopentane as a principal product. The hydrogen for saturation of the methylcyclopentenes came from formation of catalyst coke and high-boiling aromatics, and there was little dehydrogenation of cyclohexene to benzene. Styrene and indene, being compounds which cannot by simple cracking yield fragments of their nonbenzenoid portions with a hydrogen-carbon ratio of 2 or more, produced large amounts of carbon on the catalyst.

The diolefins, butadiene and isoprene, were extremely reactive over the catalyst, and it is concluded that any such compounds formed in catalytic cracking must be largely transformed by secondary reactions. Like styrene and indene, the diolefins gave a large amount of high-boiling product and of carbon.

COMPARISON WITH THERMAL REACTIONS

The reactions of olefins are complex, both in thermal and catalytic treatment, and depend strongly on the conditions employed. It is therefore difficult to present a close comparison of thermal and catalytic reactions on the basis of the data available. Nevertheless, some important effects of catalysis may be demonstrated. Compared to the thermal reactions under comparable conditions, catalytic cracking of olefins is found to (*a*) be much faster, with a rate factor of the order of magnitude of 1000 to 10,000 between 400° and 500° C., (*b*) give marked isomerization where otherwise very little occurs, (*c*) cause much more extensive saturation of any olefins in the system, whether part of the feed or produced by cracking, (*d*) induce preferential rupture to yield fragments of three or more carbon atoms instead of rather indiscriminate rupture, and (*e*) favor polymerization or condensation.

Evidence follows for these items for the individual olefins.

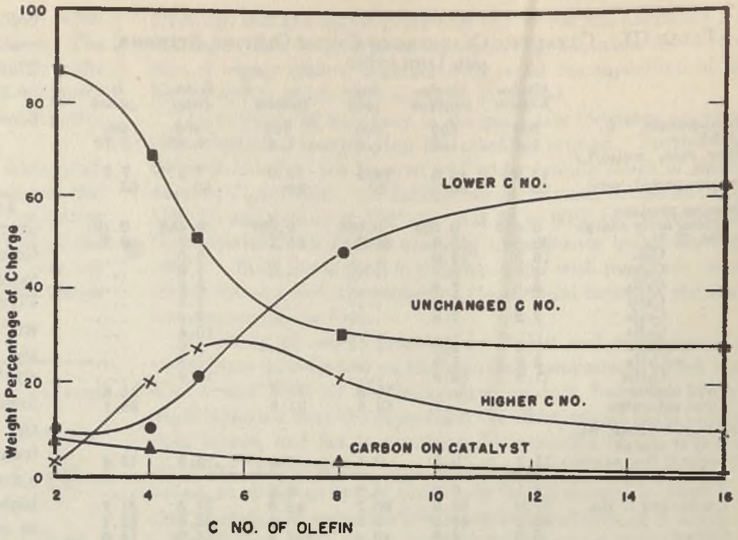

Figure 1. Distribution of Products Obtained by Treating *n*-Olefins over Silica-Zirconia-Alumina Catalyst at 400° C. for One-Hour Process Period at a Flow Rate of 6.8 Moles per Liter per Hour

Relative velocities of catalytic and thermal reactions have been estimated by means of rate constants calculated from the first-order equation

$$k_1 = (1/t)\ln(100/100 - C)$$

where t = time, seconds
C = per cent converted to material of different carbon number or to saturates

Actually, catalytic cracking does not follow this equation exactly under any conditions, and thermal cracking of olefins follows it only at high temperatures (say above 500° C.) and pressures not substantially above atmospheric; nevertheless the values of k_1 give rough measures of the velocities of the reactions and are used in the absence of a more precise formulation. Activation energies for computing temperature coefficients of thermal reactions were taken from the literature (*3*, *13*, *15*), and where exact data were lacking were assumed to be 60,000 calories per mole.

ETHYLENE. The thermal reactions are manifold and include all those observed with the catalyst, although they are far slower under similar conditions. At 400° C. and one atmosphere pressure the chief thermal reaction is polymerization to butene (*3*),

TABLE V. CATALYTIC AND THERMAL CRACKING OF *n*-BUTENES AT 600° C.

Type of cracking	Catalytic		Thermal		Thermal		
Citation	(*4*)		(*17*)		(*11*)		
Hydrocarbon	*n*-Butenes		1-Butene	2-Butene	2-Butene		
Contact time, sec.[a]	5.9	1.05	~30	~30	7.6	12.2	40.5
% converted	49	32	(45.0)[b]	(34.2)[b]	9.4	15.3	43.7
$k_1 \times 10^3$	114	370	20	14	13	14	14
Wt. % of charge							
Below C_4	31.4	15.7	(32.1)[b]	(29.0)[b]	3.5	7.1	17.8
C_4	59.7	71.6	55.0	65.8	90.6	84.7	56.3
Above C_4	8.9	12.7	12.9	5.2	5.9	8.2	25.9
Gas analysis, vol. % below C_4							
H_2	29.8	5.1	3.7	10.2	7.9	7.7	14.4
CH_4	31.6	12.1	37.5	31.8	34.0	37.8	39.3
C_2H_4	4.8	1.6	14.8	14.8	10.0	10.7	10.4
C_2H_6	5.8	6.3	8.8	13.6	6.0	..	4.1
C_3H_6	23.8	67.8	35.2	29.6	42.1	39.4	31.8
C_3H_8	4.2	7.1	...	...	..	..	..

[a] Assuming catalyst 100% void and taking gas flow rate as average of inlet and outlet.
[b] By difference.

but it is only about one thousandth as fast as catalytic polymerization or saturation.

n-BUTENES. The results of Egloff and co-workers (*4*) from catalytic cracking at 600° C. are compared to thermal results (*11, 17*) in Table V. At this temperature thermal cracking reactions follow the first-order law, and the product composition is not much changed with a change in the conversion. In catalytic cracking, the first-order rate law is not followed, and product composition depends on conditions. The comparisons outlined in Table V are valid for high flow rates or the lower range of temperatures in catalytic cracking. The catalytic reaction, compared to the thermal, gives less methane, less ethylene, more propylene, more butane, and more isobutene. The data further show that the catalytic rate is six to twenty-nine times the thermal even at the high temperature of 600° C. For these reactions at 400° C. it is estimated that the ratio of rates is roughly 1000. This follows from a comparison of the observed catalytic rate with the thermal rate computed from the Arrhenius equation.

n-PENTENES. From the scanty thermal data at 400° C., it may be said that the catalytic reactions are much more rapid. Isomerization is prominent in catalytic treatment but not in the thermal (*4*).

n-OCTENES. Table VI compares data from a rather limited pyrolytic investigation (*8*) and from catalytic cracking. The catalytic reaction is much faster. Assuming an activation energy of 60 kg.-cal. per mole, k_1 (thermal) at 400° C. is about 0.02×10^{-3}. Since k_1 (catalytic) is 170×10^{-3}, the catalytic reaction is indicated to be about eight thousand times as fast.

TABLE VI. CATALYTIC AND THERMAL CRACKING OF *n*-OCTENES

Type of cracking Citation	Catalytic This work	Thermal (*8*)	
Temperature, ° C.	400	440	485
Contact time, sec.[a]	9.5	240	190
% converted[b]	81.4	12	32
$k_1 \times 10^3$	170	0.53	2.03
Material balance, wt. % of charge[c]			
Gas	24.2	7.3	27
Liquid below C_8	20.1		
C_8	30.5	88.0	68
Above C_8	25.2	4.7	5
Olefins in gas, vol. %	71.3	8.5	20.5

[a] Assuming catalyst 100% void.
[b] To material other than C_8 olefins.
[c] Yields corrected to no-loss basis.

Other comparisons are: (*a*) In thermal treatment the total gas contains a higher percentage of saturates. This may be ascribed to preferential splitting out of methane and ethane, rather than by saturation of produced olefins. (*b*) Polymerization and formation of hydrocarbons of increased carbon number are prominent in catalytic treatment. (*c*) Isomerization of uncracked octenes is observed in both types of reaction. Thus, in thermal cracking at 440° and 485° C. (*8*), 15–20% of the C_8 fraction was said to distill from 105° to 121.5° C. This example of thermal isomerization has not been verified elsewhere as far as is known. In catalytic experiments 80–100% of the C_8 fraction was lower boiling. (*d*) The unsaturation of the C_8 fraction recovered from thermal cracking was equal to that of the feed, while in catalytic cracking the C_8 fraction was partially saturated.

CETENE (*n*-HEXADECENE). Table VII compares results from catalytic cracking with thermal results (*5*). The ratio of thermal rates at 500° and 450° C. corresponds to an activation energy of 51 kg.-cal. per mole, and from this, k_1 (thermal) at 400° C. = 5×10^{-5}. Thus the catalytic rate is of the order of six thousand times the thermal at 400° C. and eight hundred times the thermal at 450° C.

Other important differences appear. A greater ratio of liquid to gas, at equal or greater depth of cracking, can be obtained in catalytic cracking. At low temperatures the olefin content of the thermal gas is much lower than the catalytic, as with octenes. However, the thermal gas is chiefly methane and ethylene, whereas the catalytic gas is largely propylene, butenes, and butanes. The thermal liquid products are spread over the entire range from C_5 to C_{15}, while the catalytic are especially rich in C_5 and C_6. The lower-boiling liquid obtained thermally at temperatures below 600° C. contains the equivalent of more than 100% mono-olefins, the catalytic, of the order of 60%.

TABLE VII. CATALYTIC AND THERMAL CRACKING OF CETENE

Type of cracking Citation	Catalytic This work		Thermal (*5*)		
Temperature, ° C.	400	450	450	500	550
Contact time, sec.[a]	7.3	6.4	75	61.5	50.5
% converted[b]	92	97	5.0	34.1	69.7
$k_1 \times 10^3$	*ca.* 340	*ca.* 550	0.67	6.8	23.6
Material balance, wt. % of charge[c]					
Gas	8.9	21.2	0.3	11.5	37.5
Liquid below C_{16}	51.8	62.3	4.7	22.8	32.2
Remainder	39.3	16.5	95.0	65.7	30.3
Gas analysis, % vol.					
H_2	2.2	2.8	0	3	5
Olefins	59.4	68.1	29	58	65
Saturates	38.4	29.1	71	39	30
Mol. wt. of gas	49	48	...	28	31

[a] Assuming catalyst 100% void, and correcting for expansion with 2 moles product per mole cracked.
[b] To material other than C_{16} olefin.
[c] Corrected to no-loss basis.

DIISOBUTENES. The thermal decomposition of diisobutenes was observed (*12*) at 492–641° C. The data give a first-order rate constant of 0.01 at 492° C. If an activation energy of 60 kg.-cal. per mole is assumed, k (400° C.) = 4.5×10^{-5}. This is of the order of 1/14,000, the rate found in catalytic cracking. Hence the acceleration by the catalyst seems to be about the same for both *n*-octenes and diisobutenes, a factor of roughly 10,000 appearing in the rates. There are indications that the catalytic acceleration is greater for diisobutenes than for *n*-octenes, but the comparisons are not direct enough to make this certain.

Other differences between thermal and catalytic cracking of diisobutenes are not pronounced, as far as can be judged. The gas analyses are much alike (*12*). Possibly formation of higher-boiling materials is less prominent and of C_6 and C_7 a little more so in thermal treatment at 492° C., compared to catalytic at 400° C.

CYCLIC OLEFINS. Data on the thermal treatment of styrene and cyclopentene under conditions comparable to those used for catalytic cracking are not available. The thermal cracking of indene, like the catalytic, leads to condensation products and indan (*7, 16*), but the relative amount of indan is less. Carbon formation appears to be more pronounced in catalytic treatment.

The rate of disappearance of cyclohexene is much slower without a catalyst, for in thermal treatment at 450° C. only 7% was decomposed in 6 hours (*2*). Comparison with a kinetic study at 485° to 565° C. (*10*) indicates that the catalytic reaction is faster by a factor of about 1000 at 500° C. The thermal treatment leads to the formation of ethylene and butadiene, but in catalytic treatment the products are quite different.

DIOLEFINS. Again there is a marked contrast between catalytic and thermal reactions. Under the conditions of the catalytic experiments there would be little thermal reaction. At somewhat higher temperatures butadiene and isoprene dimerize thermally to cyclohexene derivatives.

While some dimer may form catalytically, there is also marked formation of aromatics and saturates, which are not obtained thermally except at much higher temperature. The thermal rate of disappearance of butadiene at about 400° C. (*9*) is estimated to be about 1/600 of the catalytic rate, comparing second-order rate constants for each.

ACKNOWLEDGMENT

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Redwood Products as Inhibitors of Oxidation in Petroleum Hydrocarbons

INHIBITION OF OXIDATION IN MINERAL OILS

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Redwood tannin preparations are shown to be effective inhibitors of the oxidation of mineral oil. The active inhibiting principles are present in the ethyl acetate–soluble part of the tannin fraction and appear to be absent in the ethyl acetate–insoluble part. The ether-soluble tar and the phenol fraction obtained by a vacuum destructive distillation of redwood phlobaphene are both effective inhibitors for mineral oil. Redwood, on destructive distillation, yields a tar differing in composition from the hardwood tars. The resulting total tars from redwood are effective inhibitors. There appears to be no advantage in separating the phenolic fractions from the tar.

AUTOXIDATION of paraffin hydrocarbons by oxygen has been known and investigated for many years. The reaction involves, first, an "induction period", during which measurable absorption of oxygen does not occur; at the end of this time oxygen is absorbed at a definite rate for the particular material. The rate is constant for a given temperature and rate of oxygen flow and is independent of the length of the induction period. Small amounts of certain materials lengthen the induction period, others shorten it. The former are oxidation inhibitors, the latter, oxidation catalysts.

Although a great deal of work on this autoxidation has been carried out with gasolines and related compounds, the phenomenon is not confined to these specific products. In an early paper Haslam and Frölich (*4*) studied the oxidation of purified mineral oils. Their technique consisted in bubbling oxygen through the oil at an elevated temperature and titrating the acid formed. Viscosity, color changes, and gum formation were found to be equally valuable as a measure of the rate of oxidation. Not all the oxygen is consumed in the acid formation; the remainder apparently enters into resinous polymerized reaction products. Dornte (*2*) showed that the oxidation of white oils is autocatalytic. Among the oxidation products are peroxides (which form in the first stage), acids, and water.

Many compounds have been described in the literature as inhibiting oxidation of paraffin hydrocarbons. The wide range of materials was discussed in some detail by Ellis (*3*). The compounds include many amines and phenols and derivatives of both phosphorus and sulfur. Specific reference to the use of hardwood tars or particular fractions thereof as inhibitors of gum formation in gasolines is made by Lowry and Dryer (*5*). These authors refer especially to the fraction of the tar distilling between 240° and 280° C.

In general, the oxidation of refined mineral oil is attended by a rancid odor. The reaction is easily followed by use of the technique of Haslam and Frölich, and the relative value of various agents in inhibiting the formation of acids and their subsequent odors may be determined.

In this investigation, inhibiting power was determined for tannin from redwood (*Sequoia sempervirens*) and for derivatives resulting from the destructive distillation of the tannin fraction and the redwood itself. The test method was that of Haslam and Frölich; the oil used for the test was the grade sold as Carnation White mineral oil. Blanks were run on unprotected oil to furnish basic information on the period of inhibition of the oil.

The chemical nature of redwood tannin was discussed at some length by Buchanan, Lewis, and Kurth (*1*). Alkaline fusion of the tannin yields only protocatechuic acid and catechol; vacuum distillation gives catechol and a smaller amount of phenol. Since catechol is a good inhibitor, redwood tannin was also expected

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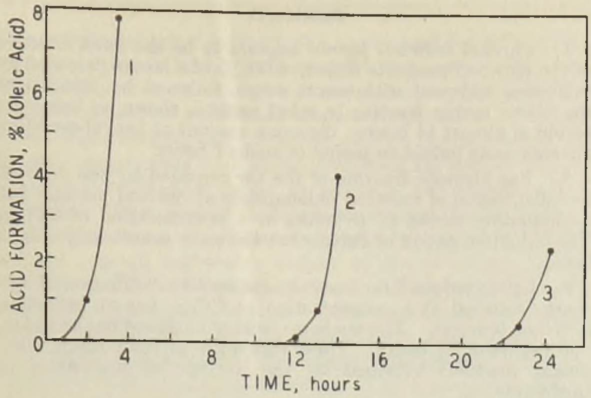

Figure 1. Catechol and Redwood Tannin as Inhibitors of Oxidation in Mineral Oil

1. No inhibitor. 2. 0.01% Catechol. 3. 0.002% Redwood tannin.

to be. Work reported here not only indicates the ability of redwood tannin to inhibit formation of acids in mineral oil, but also demonstrates a similar activity of the distillation products of both wood and tannin. In this regard, the various redwood products have activities in the range of those shown by catechol; the tannin itself appears to be as active as benzyl-*p*-aminophenol.

EXPERIMENTAL PROCEDURE

The oxidation-inhibiting power of the various redwood products was determined as follows: A sample of the oil to be tested (75 grams) was placed in a 35 × 190 mm. test tube in a constant-temperature bath maintained at 135° C., and oxygen was bubbled through the oil from a 20-mm. fritted glass gas dispersion tube at a rate of 10 liters per hour. The rate of acid formation was estimated on samples withdrawn at periodic intervals. Free fatty acid was determined by dissolving 2 to 3 grams of the oil in 25 cc. of neutral isopropyl alcohol, warming to 30–35° C., and titrating with 0.05 *N* sodium hydroxide until a phenolphthalein end point remained on vigorous shaking. The acidity was calculated as free oleic acid. The inhibitor to be tested was dissolved in ethyl acetate, ether, or acetone, and added to the mineral oil in an amount sufficient to make the desired concentration in the oil.

For illustration, data from runs on mineral oil alone, and with 0.01% catechol and redwood tannin, respectively, are included in Table I and plotted in Figure 1. The induction period for the mineral oil is about 2 hours; for 0.01% catechol, 13 hours; and for 0.002 redwood tannin, about 23 hours.

The following redwood products were investigated: redwood tannin, ether-soluble oil from the vacuum distillation of redwood phlobaphene, and tars from the destructive distillation of redwood stumpwood and rootwood and the phenolic oil fractions from these tars.

REDWOOD TANNIN

Redwood chips were extracted with alcohol in a large metal continuous extractor. The extract was concentrated and steam-distilled to remove the last trace of alcohol. The phlobaphenes separated on dilution with distilled water, whereas the tannins and other water-soluble substances remained in solution. The aqueous solution was decanted from the phlobaphene and concentrated in vacuo to a thick sirup, which was extracted with ethyl acetate. Two "tannin" fractions resulted; one was soluble, the other insoluble in ethyl acetate. The solvent was removed from the soluble fraction, and the products were dried to a fluffy mass in a vacuum oven at 50° C. The insoluble tannin in aqueous solution was concentrated to a viscous gum which was dissolved in acetone, and the cycloses were allowed to crystallize. After it had been filtered, the acetone-soluble material was evaporated. The residue was powdered and is termed "ethyl acetate–insoluble tannin".

Other samples of redwood tannin tested included the product extracted from wood by warm distilled water followed by an extraction of the ethyl acetate-soluble portion. An ethyl acetate–soluble portion was recovered also from the phlobaphene precipitate and was included in the test.

No attempt will be made to indicate other than the approximate induction periods in concentrations as listed. The induction period is the time required for appreciable amounts of acid to appear in the oil. The rate of acid formation increases sharply, and the slope of the curve changes completely as Figure 1 shows. The induction periods for 0.001% solutions of the tannins follow:

Material Used as Inhibitor	Induction Period, Hr.
None	2
Ethyl acetate–soluble tannin	8.5
Ethyl acetate–insoluble tannin	2
Tannin from aqueous extract	10
Total tannin from alcohol extract	2
Ethyl acetate–soluble phlobaphene	6.5
Benzyl-*p*-aminophenol	7

The ethyl acetate–soluble tannin and phlobaphene appear to be the best inhibitors of the group for mineral oils. The ethyl acetate–insoluble fraction has no activity; from the test on the total tannin, it appears that compounds might actually be present in the insoluble fraction which could neutralize the activity of the soluble fraction. The redwood tannins compare favorably with benzyl-*p*-aminophenol and with catechol as inhibitors of acid formation in mineral oil.

ETHER-SOLUBLE OIL FROM DISTILLATION OF PHLOBAPHENE

The so-called phlobaphene fraction of the redwood extract represents the material which is soluble in alcohol but insoluble in water. The relation between the tannin fraction and the phlobaphene fraction in redwood was considered earlier (*1*). The phlobaphene fraction from the redwood, on vacuum destructive distillation, yields about 25% by weight of an ether-soluble tar which consists of 75% by weight of phenolic material (with catechol predominating among the phenols).

Table I. Inhibiting Action of Redwood Tannin and Catechol in Mineral Oil as Measured by Acid Formation

Time, Hr.	Acid Formation as % Oleic Acid: Mineral oil	Mineral oil + 0.01% catechol	Mineral oil + 0.002% redwood tannin
1	0.07	...	...
2	0.99	...	...
3.5	7.8	...	...
12	...	0.09	...
13	...	0.82	...
14	...	4.08	...
22.8	...	...	0.47
24.3	...	...	2.32

Both the total ether-soluble tar and the phenolic fraction have been investigated as inhibiting agents. The ether-soluble tar had an induction period of about 10 hours in a concentration of 0.01%, whereas the induction period of the phenolic fraction was approximately 18 hours at the same concentration. Catechol at 0.01% concentration had an induction period of more than 13 hours.

TARS FROM DESTRUCTIVE DISTILLATION OF REDWOOD

Reference has already been made to the patents of Lowry and Dryer who used fractions from hardwood tars as inhibitors of gum formation in gasoline. Redwood differs from the hardwoods specified, both in the extent and nature of the tannins and in the type of lignin. Hardwood lignin contains both syringyl and vanillyl radicals; redwood contains only the latter. In view of the inhibiting activity of the destructive distillate from the phlobaphenes, the tars from the destructive distillation of redwood

Table II. Induction Periods of Redwood Tars and Phenolic Fraction (0.01% Concentration)

Material Used as Inhibitor	Induction Period, Hr.
Stumpwood tar (tar 3)	11
Phenolic fraction 195–203° C.	9–10
203–210° C.	7–8
210–220° C.	9–10
Above 220° C.	9
Redwood tar (tar 5)	16–17
Middle oil	7
Phenolic oil	10
Catechol	13

might be expected to possess the same inhibiting power. This proved to be the case. A number of distillations were carried out with redwoods of varying extractive contents. The wood with the highest extractive contents (rootwood) gave the highest yield and, in general, the most active tar.

For illustration, results (Table II) are given for two tars—one from rootwood (tar 5) and the other from stumpwood (tar 3). In the case of tar 3, the middle oil (fraction of tar boiling above 150° C.) and the phenolic oil from the middle oil were tested. In the second case, the phenolic oil was separated into four fractions. The crude redwood tars as such appear to be as satisfactory antioxidants as catechol in inhibiting acid formation in mineral oil.

SUMMARY

1. Purified redwood tannin appears to be the most effective of the redwood products tested; 0.001% of a tannin prepared by extracting redwood with warm water, followed by solution of the active tannin fraction in ethyl acetate, shows an induction period of almost 11 hours; the same amount of benzyl-*p*-aminophenol has an induction period of about 7 hours.

2. The phenolic fraction of the tar prepared by the destructive distillation of redwood phlobaphene at reduced pressure has an induction period of 18 hours at a concentration of 0.01%. The induction period of catechol at the same concentration is 13 hours.

3. Crude redwood tar from the destructive distillation of redwood rootwood at a concentration of 0.01% has an induction period of 16 hours. The crude tar from stumpwood has an induction period of 11 hours. These tars differ in composition from similar products obtained by the destructive distillation of hardwoods.

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Nomographs for Enthalpies of Pure Hydrocarbons and Their Mixtures

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ONE of the most important calculations in the process design of petroleum refining equipment is the preparation of heat balances. For these heat balance calculations, it is necessary to know the thermal properties of the hydrocarbons and, more particularly, the thermal properties of mixtures of hydrocarbons. Considerable data are available in the literature on specific heats, latent heats, and pressure-volume-temperature relationships of pure hydrocarbons. During recent years additional data on binary mixtures containing methane have been found (*1*, *2*, *3*, *13*, *15*). Thermal data on multicomponent mixtures are virtually nonexistent. The multicomponent mixtures encountered in practice are unlimited in number, and in the preparation of universal total heat charts for such mixtures, some generalization of properties is necessary.

For gaseous mixtures Kay (*9*) proposed the concept of a pseudo critical temperature and pressure. General correlations have shown that a gaseous mixture can be considered as a pure component with a critical temperature and pressure equal to the pseudo critical properties of the mixture. The pseudo critical constants have been found to be nearly equal to the molal average of the critical constants of the components of the mixture.

Edmister (*5*) presented a general correlation of the specific heat data based on a linear variation of specific heat with temperature. More recent correlations (*6*) indicated a definite curvature at high temperatures. However, over the range of temperatures used in these nomographs, the correlation of Edmister was considered of sufficient accuracy to justify its use. The vapor enthalpy determined from Edmister's correlation agreed fairly well with that found by the correlation recommended by Fallon and Watson (*6*). The cumulative deviations up to 800° F. varied from less than 1% for methane to about 5% for pentane. This error might appear to be large if considered as B.t.u. per pound. but it applies only to the calculated differences on a percentage basis.

Edmister (*5*) also correlated the pressure-volume-temperature data based on the reduced temperatures and pressures of the pure hydrocarbons. Through the application of this correlation, it was possible to develop enthalpy charts for the pure hydrocarbons. Study of these enthalpy charts revealed that, if the temperature scale were calibrated empirically so the vapor enthalpy curve of any of the hydrocarbons at atmospheric pressure was a straight line, the enthalpy curves of all other hydrocarbons were nearly straight. It was also found that at a constant enthalpy the pressure was approximately a linear function when plotted against this empirical temperature scale.

PURE HYDROCARBONS

The nomograph for the enthalpy of pure hydrocarbons was constructed using a temperature scale calibrated from the enthalpy of *n*-butane vapor and a uniformly calibrated pressure scale. The enthalpy scales for the normal saturated paraffins were located and calibrated empirically. The nomograph covers

Three nomographs[1] present the vapor and liquid enthalpies of individual hydrocarbons and hydrocarbon mixtures. The first gives the enthalpies of normal saturated paraffins from methane to *n*-octane; the construction is such that at a single setting the enthalpy can be found for all the liquid components at a given temperature and of all the components in the vapor at a given temperature and pressure. The second nomograph shows the liquid and vapor enthalpies of mixtures of light hydrocarbons based on the average molecular weight of the mixture. Joule-Thomson effects determined from this nomograph agree with all available data on hydrocarbon mixtures within the limits of precision of the nomograph and within the accuracy of the data. The third nomograph gives the liquid and vapor enthalpies of the heavier petroleum fractions. It is based on a correlation of the properties of the various fractions of an oil with a characterization factor of 11.8. The nomograph is accurate within the limits of reliability of the basic correlation.

the range of conditions usually encountered in petroleum work—namely, pressures up to 1000 pounds per square inch and temperatures from −100° to +800° F. To avoid negative enthalpy values in the heat balances, the datum enthalpy condition chosen for these charts was that of liquid at −200° F.

It was also found that at temperatures appreciably below the critical, the enthalpy of a liquid hydrocarbon was nearly a straight line when plotted against the empirical temperature scale. A nomograph based on this principle would be the simplest to construct. However, such a nomograph is not the most convenient to use since it requires several settings to obtain the enthalpy of all components present in the liquid mixture. It is also possible to have a component present in the liquid as a dissolved gas at temperatures much greater than the critical, and these dissolved gases follow a different relationship. Accordingly, a nomograph was constructed whereby the liquid enthalpy could be determined for all components at a given temperature by a single setting of a line on the nomograph.

The vertical enthalpy scales for the liquid hydrocarbons shown in Figure 1 were calibrated for pure liquids up to a temperature 50° F. below the critical. These scales are shown above the dashed line on Figure 1. The calibration of the scales below this locus gives the enthalpy of the absorbed gas.

Othmer and White (*11*) showed that heat of absorption can be calculated from the slope of the partial pressure curve of the component at given concentrations when plotted against the vapor pressure of water at the same temperature on log paper. The slope of this curve is equal to the ratio of the molal heat of absorption to the molal latent heat of evaporation of water at the given temperature. This can be derived from the Clausius-Clapeyron equation. However,

$$y = p/P = Kx$$

or

$$p = KPx$$

where y = mole fraction of given component in vapor
p = partial pressure of component
P = total pressure on system
K = vaporization constant
x = mole fraction of component in liquid

Thus the partial pressure is proportional to the K value at constant total pressure and constant liquid concentration. The heats of absorption of the hydrocarbons were therefore calculated from the slopes of curves obtained by plotting the K values for the components at different pressures against the vapor pressure of water at the same temperature. This method is based on the same principle as that of Holcomb and Brown (*8*) and yields essentially the same result. It is, however, somewhat simpler in application.

The enthalpy of the dissolved gas was the same within the limits of accuracy of the calculations when computed for different total pressures on the system. Extrapolation of this enthalpy curve below the critical temperature showed that in the critical region there is an apparent heat of solution of liquids which is a function of concentration. Therefore, in setting up this nomograph, it was arbitrarily decided to draw a smooth curve for the absorbed gas which intersected the enthalpy of pure liquid 50° F. below the critical. Where the component is considered as a dissolved gas, the quantity actually present in the liquid will be so small that an error in the enthalpy will have a minor effect on the enthalpy of the total liquid.

USE OF NOMOGRAPH. The enthalpy of a hydrocarbon in the liquid state is determined in Figure 1 by connecting the proper point on the temperature scale at the right with the focal point at the left and reading the intersection of this line with the proper hydrocarbon scale. A single setting gives the enthalpy of all the hydrocarbons on the different scales.

The enthalpy of a hydrocarbon in a vapor is determined by connecting the proper point on the temperature scale at the right with the proper value on the pressure scale at the left. The enthalpy of vapor is read on the proper component scale.

The heats of absorption determined from the nomograph were compared with the data of Budenholzer, Sage, and Lacey (*4*) on propane and ethane and with the calculations of Sage and Olds on methane (*14*). At temperatures above the critical, the heat of absorption agreed with the data at very dilute concentrations. At temperatures below the critical, the heat of absorption corresponds to the data for larger concentrations in the liquid. The nomograph thus covers the range of concentrations as they would probably be encountered in practical design calculations on mixtures.

The enthalpy of the hydrocarbon vapor given by Figure 1 agreed with the original charts almost within the precision of interpolating the scale and certainly within the limits of accuracy of the basic enthalpy correlation.

HYDROCARBON MIXTURES

The most reliable method for determining the enthalpy of gaseous mixtures is to calculate the enthalpy of all the components at the given temperature and zero pressure and subtract from this value the Joule-Thomson effect determined from a correlation such as that of Edmister, using the pseudo critical conditions recommended by Kay.

The nomograph of Figure 1 is valuable in this respect since a single setting at zero pressure and the given temperature gives the enthalpy of all the components on the proper scales. The determination of the Joule-Thomson effect as described is fairly tedious. Thus, the over-all calculation requires considerable time, and other generalizations have been developed which eliminate this work.

In all process calculations the molecular weight of all the streams is either known or readily calculable, and it has been found very convenient to use this property as a basis for an enthalpy correlation. To this end it would be desirable to draw lines of constant enthalpy on Figure 1. However, these lines would not yield a readable grid. Thus, it was necessary to adjust the datum enthalpy for all the hydrocarbons. The resulting nomograph is shown in Figure 2. The datum enthalpies for the different mixtures are shown on the scale at the top. The variable datum enthalpy of the individual components does not alter the final heat balances because in any operation where there is no chemical reaction, the same components enter and leave the system, and the datum enthalpies cancel one another. The datum quantities used in the construction of the nomograph are exactly additive for mixtures of components heavier than propane as can

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[1] Full-size reproductions (approximately 18 × 22 inches) of the three nomographs described here may be obtained from the authors upon request.

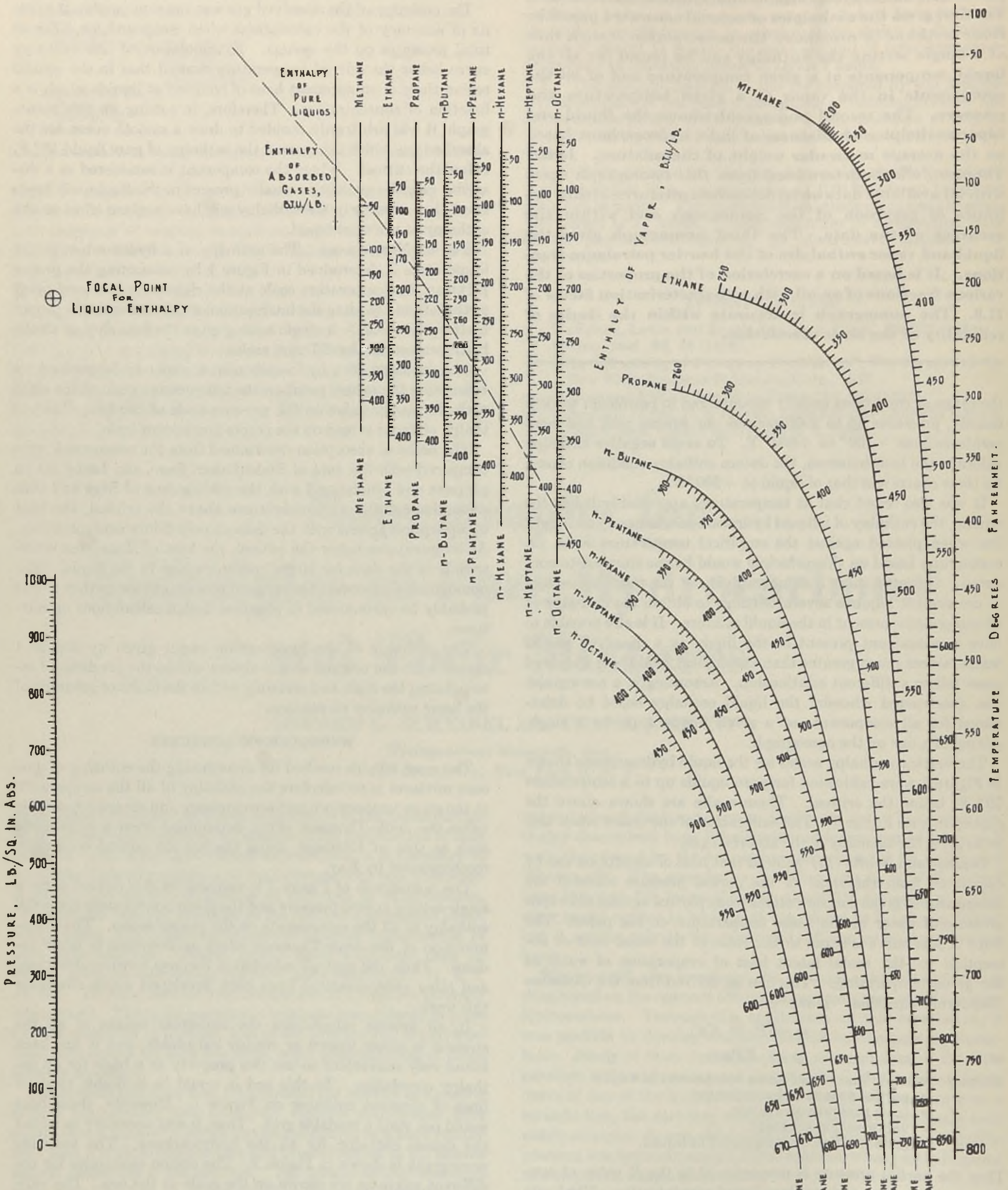

Figure 1. Enthalpy Nomograph for Pure Hydrocarbons

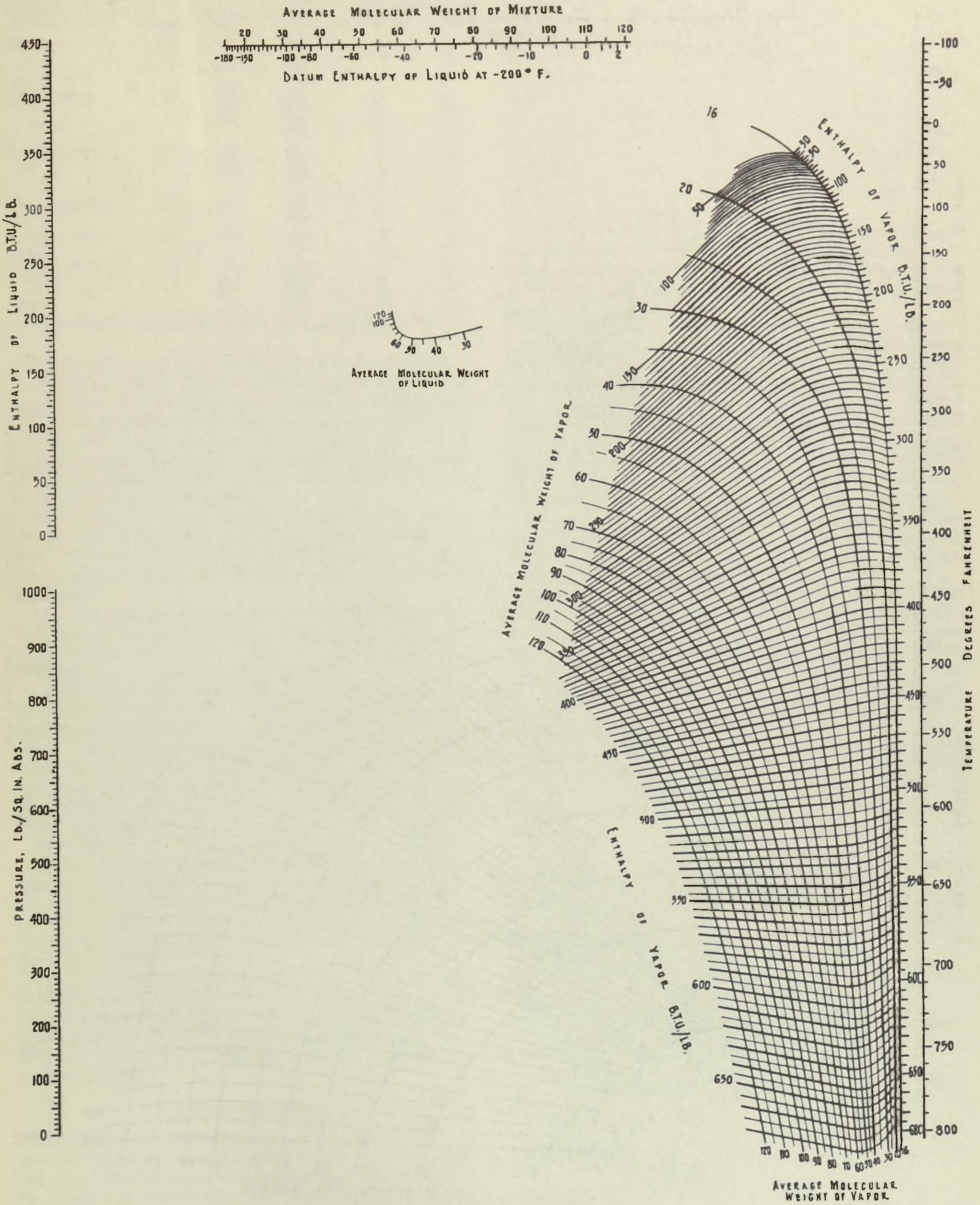

Figure 2. Enthalpy Nomograph for Light Hydrocarbons

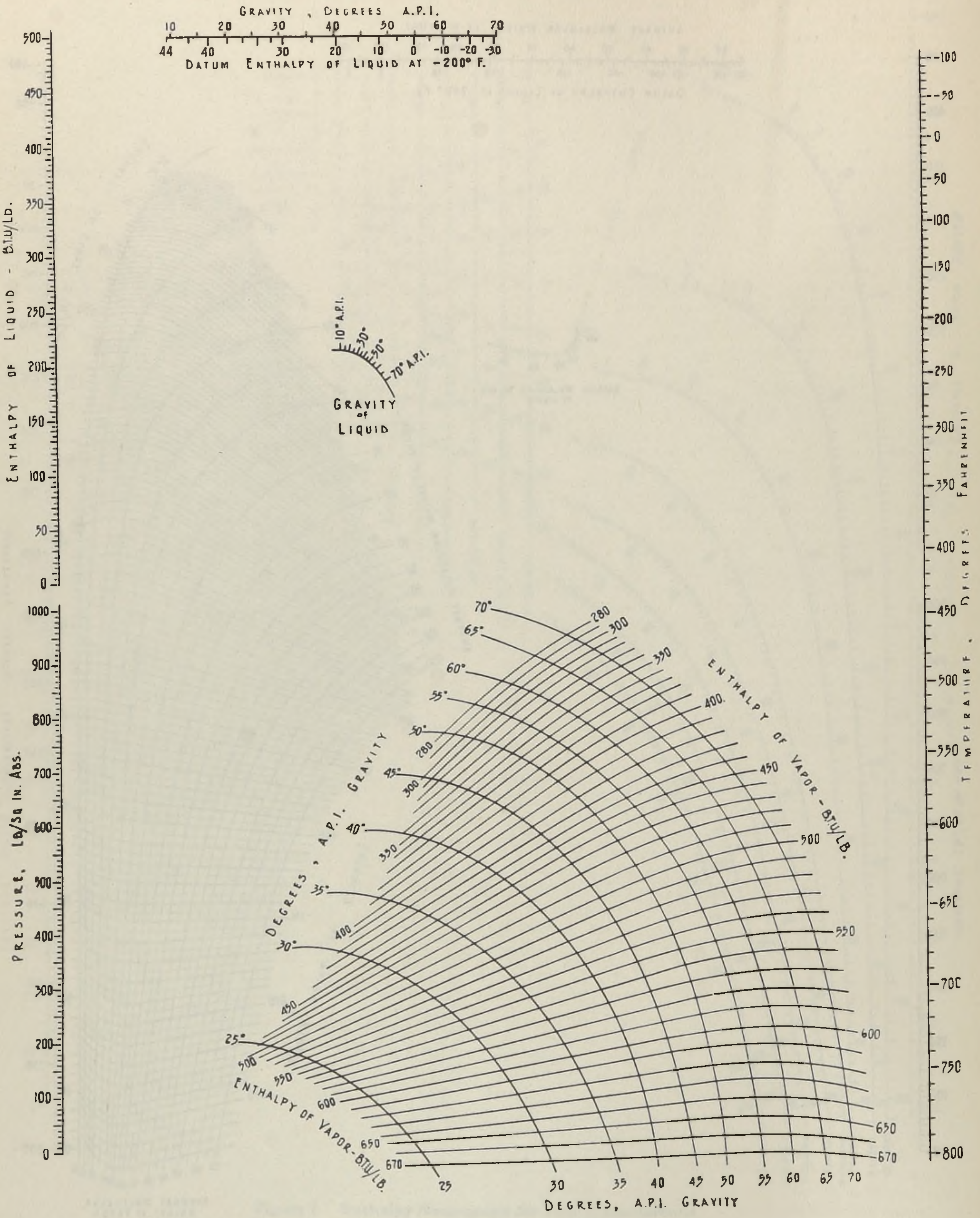

Figure 3. Enthalpy Nomograph for Petroleum Fractions (Based on Characterization Factor 11.8)

TABLE I. COMPARISON OF JOULE-THOMS N EFFECTS FROM FIGURE 2 WITH OBSERVED DATA ON METHANE MIXTURES

Mole Fraction of Second Component in Methane Mixt.	Citation	Temp., ° F.	Pressure, Lb./Sq. In. Abs.	Joule-Thomson Effect, B.T.U./Lb.	
				Nomograph	Obsvd.
0.50 ethane	(*2*)	70	250	11	11
			750	39	39
		220	250	7	6
			750	22	20
0.528 propane	(*1*)	70	200	13	13
		190	600	26	26
		310	200	5	5
			800	24	22
0.116 *n*-butane	(*3*)	70	250	10	8
		190	500	11	14
		310	250	5	5
			750	14	15
0.261 *n*-pentane	(*15*)	280	200	6	6
			600	19	18
0.536 *n*-pentane	(*15*)	400	200	6	6
			600	23	21
Natural gas (mol. wt. 20)	(*12*)	70	200	7	7
			600	22	22
		310	200	3	3
			600	10	10

be seen by plotting the datum enthalpies against the reciprocal of the molecular weight. Points for methane and ethane deviate from a straight line, an indication that mixtures containing large fractions of very light and very heavy components have a slightly different datum from that given by the curve. However, in practice, such mixtures are rarely encountered in the same phase so that in general the errors involved in this variable datum are negligible for all reasonable mixtures.

The enthalpy of the pure liquids was previously found to give straight lines when plotted against the empirical temperature scale. Thus, the liquid enthalpy was drawn at the left of Figure 2 and calibrated uniformly. The molecular weight scale was located empirically.

The vapor enthalpy was plotted by drawing constant enthalpy lines through the pure component scales after adjusting the datum values. The molecular weight lines were drawn by interpolating between the pure component scales.

USE OF NOMOGRAPH. The liquid enthalpy is found by projecting a line from the desired temperature on the scale at the right of Figure 2 through the average molecular weight and reading the enthalpy on the upper left-hand scale. The vapor enthalpy can be determined by connecting the temperature on the right-hand scale with the pressure on the lower left-hand scale and reading the enthalpy from the grid at the average molecular weight of the vapor.

Joule-Thomson effects from zero pressure given by this nomograph were compared with those calculated from the published data on binary mixtures of methane with ethane (*2*), propane (*1*), *n*-butane (*3*), and *n*-pentane (*15*), and data on two natural gases (*12*). The agreement (Table I) is almost within the accuracy of reading the nomograph and, in all probability, is within the accuracy of the data.

Thus, if an exact enthalpy is desired for special purposes, it can be calculated at zero pressure from Figure 1 and can be corrected for pressure by determining the Joule-Thomson effect at the proper molecular weight on Figure 2. However, the enthalpy values determined from the latter are sufficiently accurate for most process calculations.

PETROLEUM VAPOR

Specific heats of mid-continent petroleum oils and vapors as presented by Nelson (*10*) were based on a study of published data. Latent heat data at atmospheric molal average boiling point are also available on these oils (*10*). Thus, it is possible to develop enthalpy charts for liquid petroleum fractions of different gravities and also enthalpy charts for vapors at atmospheric pressure.

The effect of pressure at constant temperature was correlated from pressure-volume-temperature data. For Figure 3, the chart of Watson and Nelson (*16*) was used. The temperature and pressure scales of Figure 3 are identical with those of Figure 2, and the lines of constant gravity were located empirically and calibrated. The characterization factor of the oil was taken as 11.8, and from a gravity–molecular weight correlation (*10*) the molecular weight of the different fractions was determined. In order to give enthalpy values on the same basis as the molecular weight nomograph, the previous graph of the datum enthalpy against the reciprocal of molecular weight was extrapolated linearly to large molecular weights, and thus the datum enthalpy of the different petroleum fractions was established. The datum enthalpy of the different fractions is shown on the scale at the top of Figure 3. On this basis the lines of constant enthalpy were located on the nomograph.

It was also found that the enthalpy of the liquid petroleum fractions was a linear function when plotted against the same empirical temperature scale. Thus, the liquid enthalpy scale was drawn above the pressure scale as in Figure 2, and the liquid gravity scale was located empirically.

USE OF NOMOGRAPH. The enthalpy of the liquid fraction is located on Figure 3 by projecting a line from the temperature scale at the right through the proper point on the liquid gravity scale to the liquid enthalpy scale at the upper left of the nomograph. The reading on this scale gives the desired enthalpy. The enthalpy of the vapor is determined by connecting the given point on the temperature scale with the proper point on the pressure scale at the lower left. The intersection of the line with the proper liquid gravity scale gives the enthalpy of the vapor on the other set of lines on the central grid. This nomograph gives enthalpy values which are in agreement with the original calculations within the limits of reliability of the data, since other bases for calculating these same enthalpy values have been developed which differ slightly from the method of Nelson (*7*, *17*).

Figure 3 is to be used for mixtures having average molecular weights greater than 80 or 90, since the aromatics in these mixtures have different heat contents from the normal saturated paraffins and are present in sufficiently large concentrations to introduce appreciable error. For molecular weights less than 80 or 90 the molecular weight correlation of enthalpy is sufficiently accurate even though small quantities of branched-chain paraffins or unsaturated hydrocarbons may be present.

The characterization factor of 11.8 is at the center of the range of values usually encountered in crude oils; although other oils may be appreciably different, the oil upon which Figure 3 is based represents a good average for general application.

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Production of Tyrothricin in Cultures of *Bacillus brevis*

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Yields of tyrothricin in excess of 2 grams per liter of medium were obtained through the growth of *Bacillus brevis* (B.G.) in shallow layers of medium. Maximum yields were found after 10 or 16 days of incubation at about 35° C. with the medium disposed in 11-mm. layers. Complex sources of nitrogen, such as Bacto tryptone, acid hydrolyzate of casein, corn-steep liquor, tryptic digest of soybean meal, and press juice concentrates from waste asparagus butts, proved most suitable; relatively simple substances, such as glutamic acid, asparagine, or ammonium sulfate plus citric or malic acid, proved moderately effective in the presence of 0.2% Bacto tryptone. About 3 to 5% of a fermentable carbon compound, such as glucose, mannitol, or glycerol, was necessary for best yields; fructose, sucrose, lactose, and maltose proved much less effective. Requirements for calcium, magnesium, and manganese were demonstrated. Unlike the other nitrogen sources mentioned, properly processed asparagus concentrates yielded nutritionally complete media without addition of sugar or inorganic elements.

TYROTHRICIN, an antibiotic material formed during the growth of *Bacillus brevis*, is now produced commercially for medical and veterinary uses. In the course of investigations of the potential usefulness of press juices from vegetable wastes in industrial microbiological processes (*5*, *6*), shallow-layer cultures on asparagus-butt-juice media gave tyrothricin yields approaching 2 grams per liter (*5*). The yields reported elsewhere (*2*, *3*, *9*) are much lower for both shallow-layer and submerged cultures. This paper deals with the cultural and nutritional factors promoting high yields of tyrothricin in shallow-layer cultures and the use of juice concentrates from waste asparagus butts as culture media.

Almost all of the published work on tyrothricin production has been done with a strain of *Bacillus brevis* isolated and designated "B.G." by Dubos and Hotchkiss (*2*). The substock of this strain used principally in this study is identical with that discussed previously (*5*).

Stock cultures were maintained on Bacto nutrient agar slants. The slants were incubated at 35° C. for 24 hours and then stored in the refrigerator. Inoculum cultures were prepared by suspending the surface growth from a freshly incubated nutrient agar slant culture in sterile water, and transferring this to 50 ml. of asparagus juice medium (concentrate E diluted to 0.15% nitrogen was generally used, Figure 7). After incubation for 24 hours at 35° C., the inoculum cultures were pooled and used at the rate of 1 ml. per 50 ml. of experimental medium.

The experimental cultures were usually grown on 50-ml. portions of medium in 250-ml. Pyrex Erlenmeyer flasks. This method gave an 11-mm. depth of medium, which represented a compromise between the most rapid production and the need for suitable volumes of culture liquid. The cultures were incubated at 35° C. in an incubator room maintained at about 50% relative humidity to diminish evaporation. Enough flasks were set up for each treatment so that duplicates could be removed for assay at intervals. Before assays were made, evaporation losses were corrected by addition of water, so that all yield data are in terms of original volume of medium.

Two types of media were used in these investigations: media in which asparagus juice was the sole or principal component, and media based on Bacto tryptone or other nitrogenous substances, plus glucose or other fermentable carbon compounds, and inorganic ingredients. Asparagus media were sterilized at about pH 5 (the unaltered pH of the asparagus juice or diluted asparagus juice concentrate) by autoclaving for 20 minutes under 10 pounds of steam pressure. After the flasks had cooled, the medium was adjusted aseptically to pH 7.5 by the addition of predetermined aliquots of sterile 1 *N* sodium hydroxide (generally 0.5 to 3 ml. were required). Tryptone media were prepared in the same way, although no difference in results was obtained when they were sterilized at pH 7.5.

Growth was estimated turbidimetrically. Suitable dilutions of the whole culture suspension were measured in a Klett-Summerson photoelectric colorimeter with a wide-band filter, with maximum transmission at 660 millimicrons. For convenience the turbidity reading was multiplied by the dilution factor to give "Klett units" of bacterial growth. Older cultures with heavy or wrinkled pellicles could not be dispersed completely by shaking; such cultures were dispersed in a homogenizer consisting of a square-bottom glass tube and a closely fitting, mechanically driven rubber cylinder. Blanks on the pH-adjusted uninoculated medium were subtracted.

Tyrothricin was determined by a rapid method (*1*), based on the hemolytic action of tyrothricin on rat erythrocytes. The decrease in turbidity on hemolysis was measured photometrically. All results in this paper are expressed in terms of the standard described by Dimick (*1*).

Turbidity and tyrothricin determinations checked closely for replicate cultures. Calculations based on routine assays selected at random showed that the over-all variation in culturing and assaying gave the following standard deviation for individual cultures: for turbidity, 50 Klett units or 3% of the actual mean values; for tyrothricin production, 0.07 gram per liter or 7% of the actual mean values.

The hemolytic assay was checked by the isolation of tyrothricin in certain experiments. The procedure of Dubos and Hotchkiss (*2*) was conducted on a scale that would permit the isolation of tyrothricin from 40- to 100-ml. samples of culture suspension. The steps of their procedure were unchanged except that the solutions were heated to 50° C. on the steam bath after tyrothricin was precipitated with 1% saline; this modification induced rapid flocculation and aided filtration. The precipitate obtained was dried to constant weight over phosphorus pentoxide in vacuo. The hemolytic activity of this material was determined after solution in alcohol.

Yields of tyrothricin for a given treatment were fairly constant from one experiment to another. Thus a control medium containing 1.5% tryptone, 3% glucose, and inorganic salts was tested in connection with each of eight experiments carried out to obtain the comparisons given in Figures 7 and 8. The cultural work extended over a period of 9 weeks. The mean yields and standard deviations of the individual yields in grams per liter follow: 4 days of incubation, 1.23 ± 0.09; 10 days, 2.14 ± 0.11; 16 days, 2.32 ± 0.19. The turbidities developed were equally regular; the corresponding values in Klett units were: 4 days of incubation, 1440 ± 90; 10 days, 2590 ± 90; 16 days, 3110 ± 130. Nevertheless, each experiment was designed, as far as possible, to be complete within itself so that the interpretation of results would not depend on questionable differences in absolute values from one experiment to another.

Nitrogen fractions, reducing sugars, and inorganic constituents were determined by recognized methods. Asparagus press juices were found to contain no appreciable amounts of acid-hydrolyzable nonreducing sugars. Nonamino organic acids were approximated by titrating from pH 7.8 to 2.6 (*8, 10*) and correcting for the buffering effect of the amino acids and phosphate present. An arbitrary equivalent weight of 65 was used for converting the data to a weight basis. Citric acid was determined by a colorimetric pentabromoacetone method (*7*).

EXPERIMENTAL RESULTS

A general parallelism was observed between tyrothricin production, turbidity and cellular-matter production, and nitrogen utilization. These and certain other variables are plotted in Figure 1, in relation to the period of incubation for two different media which are capable of producing high yields of tyrothricin. The asparagus medium consisted of asparagus press juice concentrate 101 (Figure 7), diluted to give 0.18% nitrogen and, after sterilization, adjusted to pH 7.5 by adding 1.75% of 1 *N* sodium hydroxide. The other medium contained 1.5% tryptone, 3% glucose, and inorganic salts (footnote *a*, Table II). This medium also contained 0.18% nitrogen.

The values for cellular matter were obtained by centrifuging aliquots of the cultures without pH adjustment, and drying and weighing the precipitate. The residual turbidity in the supernatant liquors and the additional weight of material centrifugable after a preliminary acidification, as in the isolation of tyrothricin, indicate that the values for cellular matter as determined are low by about 25 and 15%, respectively, for the asparagus and tryptone media.

At each harvest period pooled cultures were centrifuged without adjustment of pH, and the liquors were clarified by filtration with the aid of a small amount of analytical-grade Celite. The culture filtrates were then analyzed for total (Kjeldahl), amide, amino, and ammonia nitrogen, reducing sugar (as glucose), pH, and nonamino organic acids. Approximately half of the total nitrogen disappeared from the culture filtrates after 14 or 18 days of incubation. Of the nitrogen taken up, about one third was converted into tyrothricin.

Amino nitrogen disappeared almost completely during the first 5 days of incubation; its disappearance was paralleled by a corresponding rise in ammonia nitrogen. Amide nitrogen remained approximately unchanged at about 6% of the original total nitrogen on the tryptone medium; on the asparagus medium it dropped parallel with the drop in amino nitrogen from 12 to about 3% of the original total nitrogen. After 5 days of incubation the ammonia nitrogen began to disappear; this loss paralleled a drop in the nonamino organic acids, which began at about this time. About 0.025 milliequivalent of ammonia per ml. disappeared in either case; the decreases in organic acids amounted to 0.024 milliequivalent per ml. of asparagus medium and 0.018 milliequivalent per ml. of tryptone medium. Only about 30% of the original organic acid content disappeared in either case. These data are of interest in connection with experiments discussed later, which show that the presence of organic acids permits the utilization of ammonia nitrogen for growth and tyrothricin production.

Sugar was utilized gradually over the whole incubation period. On the tryptone medium it was utilized almost completely after 18 days of incubation.

The pellicles became increasingly heavy throughout the incubation period in proportion to the increase in turbidity. Growth was poor on the asparagus medium the first day, and diffuse areas in the pellicles did not disappear until the fourth day. Much precipitate was formed in the tryptone cultures but not in the asparagus cultures. The pellicles of the tryptone cultures became creased with many fine intersecting wrinkles between the seventh and tenth days of incubation; this was true to a lesser degree of the pellicles on the asparagus medium. Both media permitted the development of very heavy pellicles.

EFFECT OF CULTURAL CONDITIONS

Growth and tyrothricin production were measured for seven incubation temperatures in the range 25.5° to 41.3° C., simultaneously with both asparagus-juice medium and tryptone medium (Figure 2); 35° C. proved to be a generally useful incubation temperature. Growth and tyrothricin production were measured for five depths of culture medium in the range 8 to 18 mm. simultaneously with both asparagus juice and tryptone (Figure 3). Growth and tyrothricin production increased with time of incubation, the shallowest cultures

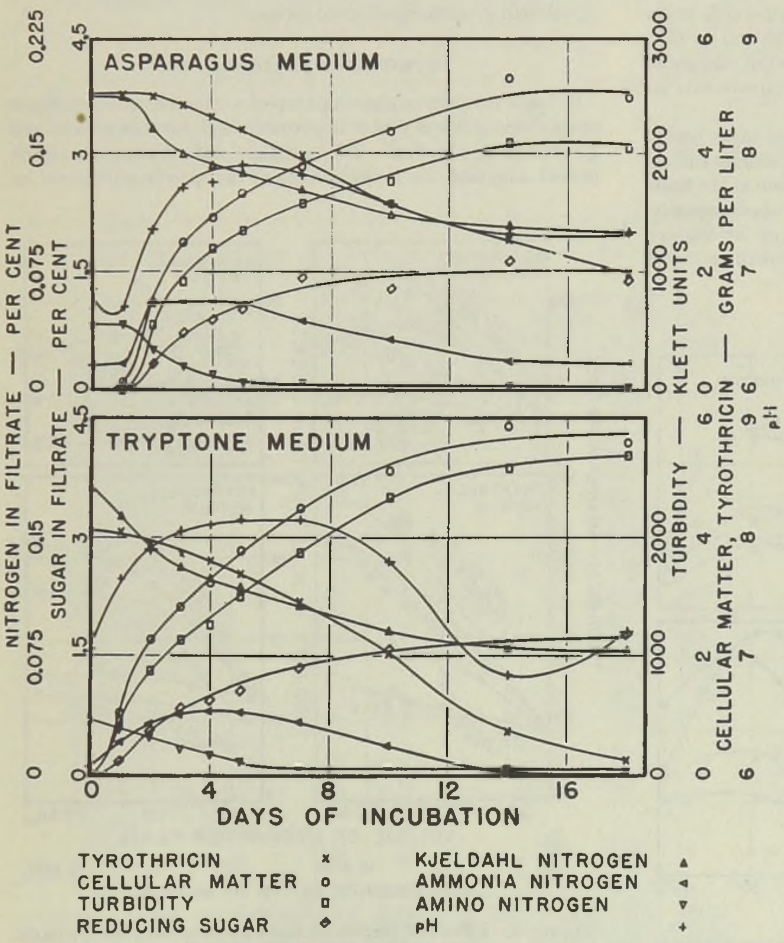

Figure 1. Growth, Tyrothricin Production, Nitrogen and Sugar Utilization, and pH after Various Periods of Incubation

Asparagus medium: Asparagus concentrate 101 diluted to 0.18% nitrogen. Tryptone medium: 1.5% tryptone, 3% glucose, and inorganic salts (0.18% nitrogen).

Table I. Effect of Oxygen Content of Atmosphere on Growth and Tyrothricin Production[a]

Medium	Composition of Atmosphere, %		Tyrothricin Production, in Grams/Liter, after Incubation for:				Growth (Turbidity), in Klett Units, after Incubation for:			
	O_2	N_2	3 days	5 days	10 days	16 days	3 days	5 days	10 days	16 days
1.5% tryptone, 3% glucose, 0.4% asparagus-concentrate ash (as HCl extract), 0.18% N	29–30	70–71	1.34	1.36	1.70	1.74	1890	2450	3200	3170
	21	79	1.32	1.22	1.67	1.70	1800	2360	3130	3200
	12–14	86–88	0.92	1.12	1.46	1.60	1350	1870	2530	3050
Asparagus concentrate E diluted to 0.16% N	29–30	70–71	0.89	0.99	1.15	1.12	840	1360	1960	1830
	21	79	0.90	0.90	1.12	1.26	770	1310	1780	1960
	12–14	86–88	0.51	0.81	1.05	1.23	550	850	1410	1910

[a] The flasks were incubated in closed wooden boxes through which the gas mixtures were passed continuously. Relative humidity was about 85%. Oxygen contents were checked by periodic gas analyses.

reaching a maximum at 5 to 10 days, while the deepest required 16 days.

Several comparisons of 50-ml. cultures in 250-ml. Erlenmeyer flasks and 280-ml. cultures in Fernbach flasks (11 mm. depth of medium in either case) failed to disclose any significant differences in rate or extent of growth or tyrothricin production for pellicles of differing areas.

Table I shows the effect of variation in the oxygen content of the atmosphere. Experiments were conducted simultaneously with asparagus and tryptone media. A reduction of oxygen content to 12–14% gave a small depressive effect for short incubation periods. An atmosphere with the oxygen content raised to 29–30% was not better than normal air. No definite differences were obtained when cultures were incubated at 45 and at 85% relative humidity. Evaporation losses were greater in the former case, but such losses have been corrected in the experiments reported in this paper.

Although the pellicle formed by *B. brevis* may be quite heavy, its cohesive strength is not high. A slight jarring usually suffices to break up the pellicle so that it sinks to the bottom of the flask. On certain relatively poor media this happens spontaneously. Cultures in which the pellicle has been broken up by shaking daily or less frequently give depressed levels of growth and tyrothricin production.

A few exploratory experiments demonstrated that this stock of *B. brevis*, unlike that studied by Stokes and Woodward (*9*), is able to produce substantial amounts of tyrothricin in submerged or shake cultures with complex sources of nitrogen. A yield of 1.4 grams of tyrothricin per liter was obtained after 48 hours of aeration on a medium containing 1.5% tryptone, 3% glucose, and inorganic salts. Fifty-milliliter portions of the same medium in 250-ml. Erlenmeyer flasks were also shaken in a reciprocating shaker with a 1.5-inch stroke at the rate of 140 cycles per minute. A yield of 0.9 gram per liter was obtained after 4 days of shaking, whereas the turbidity had reached a maximum within 24 hours of incubation. Finally, on certain asparagus juices tyrothricin production in aerated cultures lagged behind growth by one or more days. One asparagus juice, which gave excellent tyrothricin production in shallow-layer cultures, failed to permit significant tyrothricin production in submerged cultures, although as good a level of growth was obtained. Our results, like those of Stokes and Woodward, indicate that some factor or factors in addition to those that control growth are important for production of tyrothricin in submerged fermentations.

NUTRITIONAL REQUIREMENTS

A basal medium containing tryptone, glucose, and asparagus concentrate ash was found to permit a high level of growth and tyrothricin production. This medium, unlike asparagus juice, proved adaptable for investigations of the specific nutritional re-

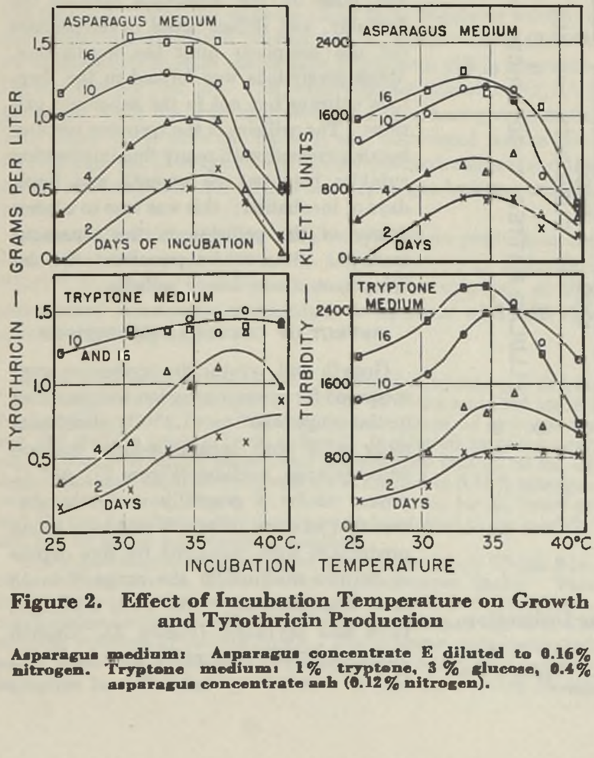

Figure 2. Effect of Incubation Temperature on Growth and Tyrothricin Production

Asparagus medium: Asparagus concentrate E diluted to 0.16% nitrogen. Tryptone medium: 1% tryptone, 3% glucose, 0.4% asparagus concentrate ash (0.12% nitrogen).

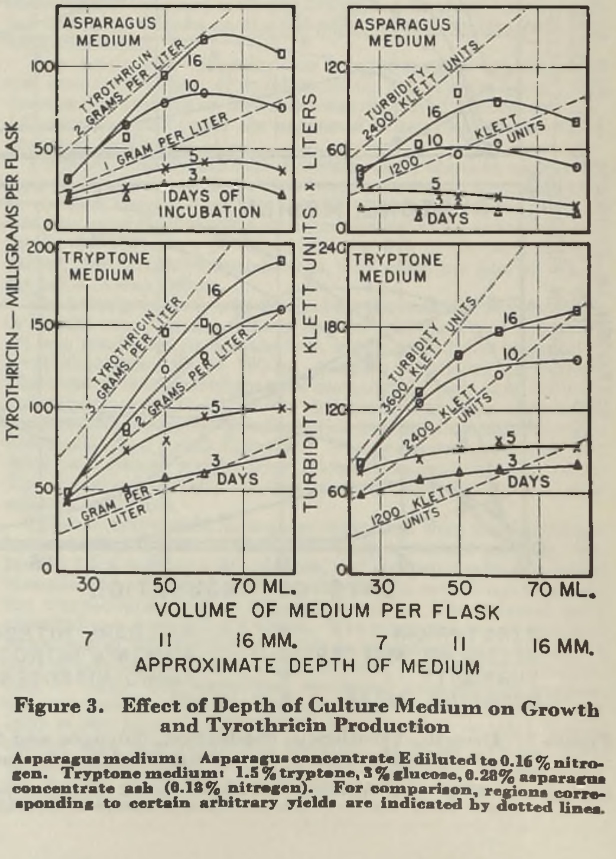

Figure 3. Effect of Depth of Culture Medium on Growth and Tyrothricin Production

Asparagus medium: Asparagus concentrate E diluted to 0.16% nitrogen. Tryptone medium: 1.5% tryptone, 3% glucose, 0.28% asparagus concentrate ash (0.18% nitrogen). For comparison, regions corresponding to certain arbitrary yields are indicated by dotted lines.

quirements of *B. brevis*, since the components could be eliminated or altered one at a time. The development of a synthetic medium was not attempted, however.

Figure 4 combines the results of several experiments which demonstrated that both the glucose and the ash were essential components of the medium. Moderate variations of the concentration of glucose or of ash were without significant effect. The maximum yield was related to the amount of tryptone supplied. The ash was added directly to the medium in these preliminary trials. Subsequent work showed that it could be replaced by a hydrochloric acid solution of the ash, though not by a hot water extract. It could also be replaced by the mixture of inorganic salts described in footnote *a*, Table II.

Some effects of variations in the inorganic salts of the tryptone-glucose-salts medium are presented in Table II. Of the elements supplied by the salt mixture, calcium, magnesium, and manganese were necessary for the highest yields; the others were either nonessential or were adequately supplied in the tryptone. Omission of calcium gave sharp reductions in tyrothricin yields, especially after 10 and 16 days of incubation. Lowering the calcium concentration to 50 p.p.m. or raising it to 200 p.p.m. have no marked effect. Asparagus ash supplied about 80 p.p.m. of calcium when it was used at the 0.4% level. After incubation about half of the calcium supplied remained in solution; the other half was removed on centrifugation of the bacterial cells. The controls without added calcium contained about 10 p.p.m. of calcium. Calcium deficiency affected growth as markedly as it did tyrothricin production, so that calcium appears to be essential for the growth of *B. brevis*, at least for maximum levels. Within the authors' knowledge this is the first time that calcium has been found to be essential for growth of a microorganism, although it has been recognized as important for other functions such as proteinase production or nitrogen fixation. The magnitude of the requirement is noteworthy.

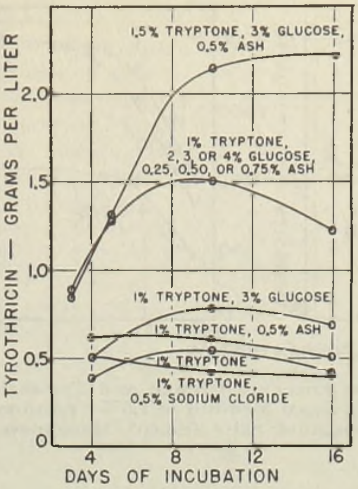

Figure 4. Tyrothricin Production on Tryptone Media

Definite depressive effects, although less marked than with calcium, were noted when magnesium was omitted from the medium. When both calcium and magnesium were omitted, growth and tyrothricin production were almost as poor as when no salts were added to the basal medium, and much poorer than when either calcium or magnesium was omitted.

Omission of manganese resulted in marked reduction of the yields of tyrothricin and bacterial cell material. Figure 5 gives the results of a study of the magnitude of manganese requirement. The tryptone supplied 0.02 p.p.m. of manganese as shown by spectrographic analysis; the addition of 0.5 to 2 p.p.m. of manganese was necessary for best results. The data suggest that, if the medium is incubated as long as 16 days, relatively low amounts of manganese suffice for tyrothricin production, though not for growth.

Figure 6 presents the influence of glucose concentration on growth and tyrothricin production. The need for sugar was most evident for the 10- and 16-day incubation periods. The sugar utilization in a similar medium (Figure 1) amounted to 0.4, 1.5, and 2.4% after 4, 10, and 16 days of incubation; these concentrations are similar to the limiting concentrations for maximum growth found in this experiment. The organism grew and produced a small amount of tyrothricin after a 4-day lag in the presence of 14% glucose.

Glucose was the only satisfactory sugar tested; fructose, sucrose, lactose, and maltose were unable to support maximum tyrothricin production (Table III). Each was tested at 1, 3, and 5% concentration; the ratios of effectiveness in comparison with glucose did not vary significantly for these concentrations. The ineffectiveness of fructose and lactose was not due to inhibitive action since combinations of glucose with these sugars gave good results.

The polyhydroxy alcohols, glycerol and mannitol, were as effective as glucose. The pellicles appeared distinctly different from those obtained with glucose and had a fluffier texture. It cannot be stated to what extent glucose, glycerol, and mannitol serve by removing ammonia and preventing high cultural pH values. However, the pH in cultures without such compounds or with non-effective sugars (fructose, sucrose, lactose, and maltose) quickly rises and stays as high as 8.8; in cultures with optimal levels of glucose, glycerol, or mannitol the pH rarely has risen above 8.2 and generally begins to fall

TABLE II. INORGANIC ELEMENT REQUIREMENTS OF *Bacillus brevis* FOR TYROTHRICIN PRODUCTION

Expt.	Addition to Basal Medium (1.5% Tryptone, 3% Glucose)	Tyrothricin Production, Grams/Liter, after Incubation for:			Relative Growth (Turbidity), Klett Units, after Incubation for:		
		4 days	10 days	17 days	4 days	10 days	17 days
A	None	0.24	0.11	...	390	410	...
	Asparagus ash (0.4%)	1.15	2.05	...	1760	3230	...
	HCl ext. of asparagus ash	1.55	2.09	...	2180	3650	...
	Salt mixt., complete[a]	1.21	2.26	...	1790	3320	...
	Ca omitted	1.02	0.96	...	1390	1400	...
	Ca content halved	1.44	1.95	...	1900	3350	...
	Ca content doubled	1.40	1.90	...	2070	3080	...
	Mg omitted	1.26	1.78	...	1630	1820	...
	Mn omitted	0.48	1.04	...	770	1200	...
	Fe omitted	1.29	2.05	...	1940	3280	...
	PO_4 omitted	1.24	2.35	...	1890	3080	...
	SO_4 omitted	1.37	2.15	...	2030	3440	...
	Cl replaced by NO_3	1.33	2.30	...	2020	3570	...
	K replaced by Na	1.29	2.15	...	2140	3400	...
B	None	0.18	0.12	0.18	160	260	660
	Salt mixt., complete[a]	1.10	1.94	2.02	1620	3150	3110
	Ca omitted	0.61	0.76	0.79	980	1430	1480
	Mg omitted	0.92	1.51	1.05	1370	2200	2640
	Ca and Mg omitted	0.20	0.35	0.25	350	800	800
	Mn omitted	0.43	1.05	1.76	740	1330	1680
C	None	0.10	0.10	...	180	460	...
	Ca (100 p.p.m.)	0.68	1.44	...	1490	1890	...
	Mn (2 p.p.m.)	0.13	0.35	...	370	720	...
	Ca (100 p.p.m.) + Mn (2 p.p.m.)	0.94	1.61	...	1730	2620	...
	Ca (100 p.p.m.) + Mn (2 p.p.m.) + Mg (50 p.p.m.)	1.06	1.95	...	1980	3170	...
	Salt mixt., complete[a]	0.93	2.24	...	1580	2760	...
	Salt mixt. + Cu (0.1 p.p.m.), Mo (0.1 p.p.m.), Zn (0.5 p.p.m.)	0.86	2.18	...	1840	2950	...
	Salt mixt. (Fe omitted)	1.02	1.88	...	1940	2980	...
	Salt mixt. (10 p.p.m. Fe added)	1.00	2.40	...	1730	2810	...

[a] KH_2PO_4 0.070%, KCl 0.035%, $MgSO_4.7H_2O$ 0.050%, $CaCl_2$ 0.025%, Fe (as sulfate) 2.0 p.p.m., Mn (as sulfate) 2.0 p.p.m. This salt mixture was used whenever "inorganic salts" are referred to in the preparation of a particular medium. The approximate amounts of ions supplied to the medium by 1.5% tryptone were: K 50, Na 400, Ca 10, Mg 5, PO_4 400, SO_4 15, Cl 50, Fe 1, and Mn 0.02 p.p.m. In addition, approximately 200 p.p.m. of Na was added during pH adjustment. Consequently the total amounts of ions in the medium were: K 400, Na 600, Ca 100, Mg 50, PO_4 800, SO_4 200, Cl 400, Fe 3, and Mn 2 p.p.m.

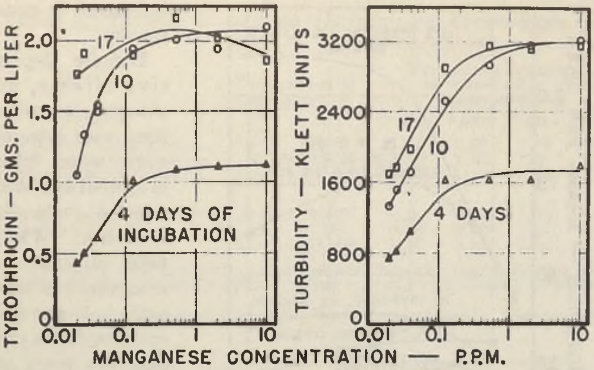

Figure 5. Manganese Effect on Growth and Tyrothricin Production with a Basal Medium of 1.5% Tryptone, 3% Glucose, and Inorganic Salts (except Manganese)

between the fourth and tenth days of incubation, as is shown in Figure 1.

Attempts to study the effect of culture pH by the addition of various buffers and by variation of the initial pH between 6.5 and 8.0 indicated that tyrothricin production was influenced more by the nature of the buffer substances added than by pH. For example, the addition to a medium containing 1.5% tryptone, 3% glucose, and inorganic salts of 0.4% veronal (sodium diethyl barbiturate) (initial pH 8.0) or of 0.4% glycine (initial pH 7.4) gave good results, while the addition of 0.4% veronal plus 0.16% sodium acetate (initial pH 8.1) gave inferior results. The overall variation in pH was from 7.6 to 8.2 in all three cases. On the other hand, almost as good results were obtained in the addition of 0.4% veronal (initial pH 6.3) or 0.75% potassium dihydrogen phosphate (initial pH 6.4) in which cases the pH varied between 5.8 and 7.4 during incubation. The choice of pH 7.5 for adjustment of various media appeared to be satisfactory.

Table IV presents results of experiments dealing with nitrogen requirements. Difco Casamino Acids was relatively ineffective when tested alone; the addition of 0.2% tryptone made it as effective as 1.5% tryptone. Fair yields were obtained with glutamic acid alone; asparagine was ineffective. Both of these nitrogen sources were improved when a small amount of tryptone was present. Ammonium sulfate was ineffective unless small amounts of both tryptone and citric or malic acid were added. The pH of the ammonium sulfate cultures dropped to about 5.0 in the absence of the organic acids and to about 5.5 in their presence. Sodium nitrate was completely ineffective.

These experiments indicate that relatively small amounts of some particular nitrogen compounds or vitamins present in tryptone are required; in addition, the main portion of the nitrogen probably must be supplied in organic form or as a combination of ammonium nitrogen and organic acids. The results are similar to those reported by Kline, MacDonnell, and Lineweaver (*6*) for *Bacillus subtilis scaber*.

Veronal was found to stimulate tyrothricin production markedly after long-continued incubation; yields above 3 grams per liter were observed (Table IV). It was wholly ineffective when used as the principal nitrogen source. The pH changes were similar to those shown in Figure 1.

NITROGENOUS MEDIA

The suitability of concentrates of asparagus-butt press juices for tyrothricin production is correlated with the nitrogen content, which is dependent on the method of processing. The highest nitrogen contents (3.4 to 4.3%, dry basis) were obtained by disintegrating the fresh butts and permitting the raw, cloudy press juice to stand for 4 hours at 50° C. and pH 5.0. Four batches of concentrate totaling 6000 pounds were prepared by this process in cooperation with a commercial canning plant. The tyrothricin yields shown for No. 101 in Figure 7 are representative for concentrates prepared by this process.

Other methods of processing were based on a preliminary blanching of the raw butts as an aid in obtaining clear juices. Concentrates of such juices had lower nitrogen contents (1.2 to 2.7%, dry basis), and proved less effective for tyrothricin production (concentrates C, D, E, and G of Figure 7). The juice obtained from blanched asparagus tips proved relatively ineffective (Figure 7), although it contained 4.5% total nitrogen, dry basis.

Concentration of the juices to thick sirups (up to 75% solids) was carried out in vacuo without detrimental effects on color or usefulness in media for *B. brevis*. The concentrates contained 14 to 39% of the total nitrogen as free amino (formol) nitrogen, 10 to 24% as amide nitrogen (more than 90% is asparagine nitrogen), and 4 to 13% as ammonia nitrogen. The reducing sugar (as glucose) generally amounted to about 65% of the solids; the total

Table III. Specificity of Carbohydrate Requirement of *Bacillus brevis* for Tyrothricin Production

Expt.	Addition to Basal Medium (1.5% Tryptone, Inorganic Salts)	Tyrothricin Production, in % of Controls[a], after Incubation for: 4 days	10 days	16 days
A	Glucose (control)[a]	100	100	100
	Fructose	94	57	57
	Sucrose	89	59	70
	Lactose	81	51	36
	Maltose	88	59	63
	Glycerol	100	102	107
	None	70	43	40
B	Mannitol	91	106	107
	Fructose (3%)	87	64	77
	Fructose (2%) + glucose (2%)	96	113	111
	Lactose (3%)	59	52	41
	Lactose (2%) + glucose (2%)	96	123	98
	None	63	50	34

[a] Except where otherwise indicated, each compound and glucose were compared at 1, 3, and 5% concentration; the data are averages of ratios calculated for each concentration. The actual assays for tyrothricin on media containing 3% glucose were approximately 0.9, 1.6, and 2 grams per liter in both experiments.

Table IV. Nitrogen Requirement of *Bacillus brevis* for Tyrothricin Production

Expt.	Addition to Basal Medium (3% Glucose, Inorganic Salts)	% N Content of Medium	Tyrothricin Production, Grams/Liter, after Incubation for: 4 days	10 days	16 days
A	Tryptone (1.5%)	0.186	0.95	1.97	1.62
	Casamino Acids (1.55%)	0.160	0.43	0.91	0.67
	Casamino Acids + tryptone (0.2%)	0.185	0.96	1.92	1.98
	Glutamic acid (1.67%)	0.160	0.36	0.63	1.26
	Glutamic acid (1.67%) + tryptone (0.2%)	0.185	0.84	1.13	1.46
	Asparagine hydrate (0.86%)	0.160	0.0	0.0	0.07
	Asparagine hydrate (0.86%) + tryptone (0.2%)	0.185	0.54	1.20	1.87
	$(NH_4)_2SO_4$ (0.86%)	0.160	0.08	0.08	0.10
	$(NH_4)_2SO_4$ (0.86%) + tryptone (0.2%)	0.185	0.16	0.15	0.16
	$(NH_4)_2SO_4$ (0.86%) + citric acid hydrate (0.5%)	0.160	0.0	0.0	0.0
	$(NH_4)_2SO_4$ (0.86%) + citric acid hydrate (0.5%) + tryptone (0.2%)	0.185	0.29	0.71	0.68
	$(NH_4)_2SO_4$ (0.86%) + malic acid (0.5%)	0.160	0.0	0.16	0.16
	$(NH_4)_2SO_4$ (0.86%) + malic acid (0.5%) + tryptone (0.2%)	0.185	0.31	0.88	1.25
	$NaNO_3$ (0.97%)	0.160	0.0	0.09	0.10
	$NaNO_3$ (0.97%) + tryptone (0.2%)	0.185	0.12	0.13	0.12
B	Tryptone (1.5%)	0.186	0.97	1.60	2.26
	Tryptone (1.5%) + veronal (0.2%)	0.216	0.95	2.06	3.20
	Tryptone (1.5%) + veronal (0.4%)	0.247	1.16	1.66	3.41
	Tryptone (1.5%) + veronal (0.7%)	0.292	1.24	1.52	2.05
	Tryptone (1.5%) + veronal (1.0%)	0.338	0.61	0.82	0.89
	Veronal (0.4%)	0.061	0.0	0.0	0.0
	Veronal (0.4%) + tryptone (0.2%)	0.086	0.0	0.0	0.01
	Veronal (0.7%)	0.106	0.0	0.0	0.01
	Veronal (0.7%) + tryptone (0.2%)	0.131	0.0	0.0	0.0

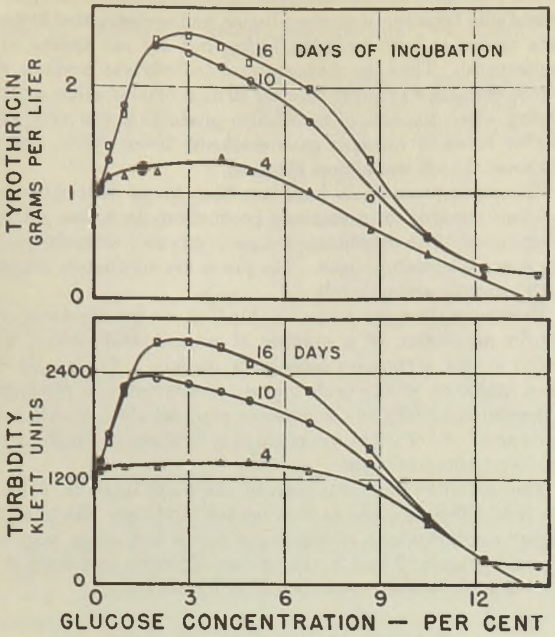

Figure 6. Influence of Glucose Concentration on Growth and Tyrothricin Production with a Basal Medium of 1.5% Tryptone and Inorganic Salts

nonamino organic acids, from 4 to 13%; citric acid, from 0.2 to 1.2%; and ash, from 8 to 12%.

Before the processing of asparagus wastes[1] had been developed to the stage where high-nitrogen juices apparently could be obtained at will, the relatively ineffective juices C and D (Figure 7) were supplemented with nitrogenous materials. Among the Bacto products, tryptone was most effective, Casamino Acids was less effective, and peptone, neopeptone, proteose-peptone, and protone were actually inhibitive at 0.4% concentration. The culture pH never rose above 8.2 with any of these supplements. Glycine, asparagine, and glutamic acid were only slightly stimulatory.

Figure 8 gives the tyrothricin-producing capacities of tryptone, corn-steep liquor, and soybean-meal hydrolyzate. The corn-steep liquor was a spray-dried commercial product containing 7.6% nitrogen, of which only 13% was present as free amino, amide, and ammonia nitrogen. The soybean-meal hydrolyzate was prepared by digestion of a solvent-extracted meal with 1% Fairchild's trypsin; the insoluble residue and heat-coagulable materials were removed. It contained 10.2% nitrogen, with 25% present as free amino, amide, and ammonia nitrogen. The tryptone, corn-steep liquor, and soybean-meal hydrolyzate were employed in varying amounts in a basal medium containing 3% of added glucose and inorganic salts in contrast to the asparagus concentrates of Figure 7, which were simply diluted to the desired nitrogen levels.

In all cases tyrothricin production was related more or less proportionately to the nitrogen supplied up to levels varying from below 0.1% for asparagus concentrate C to 0.2 or 0.3% for the best asparagus preparations, tryptone, corn-steep liquor, and soybean-meal hydrolyzate. In this region the tyrothricin yields varied from about 1 gram per gram of asparagus-tip-juice nitrogen to about 1.5 gram per gram of soybean-meal-hydrolyzate nitrogen.

Maximum yields were obtained only after 10 or even 16 days of incubation. The ranges of nitrogen concentrations at which maximum yields were obtained were relatively narrow. With low concentrations the amounts of nitrogen compounds appeared to be limiting; with high concentrations, accompanying inhibitory

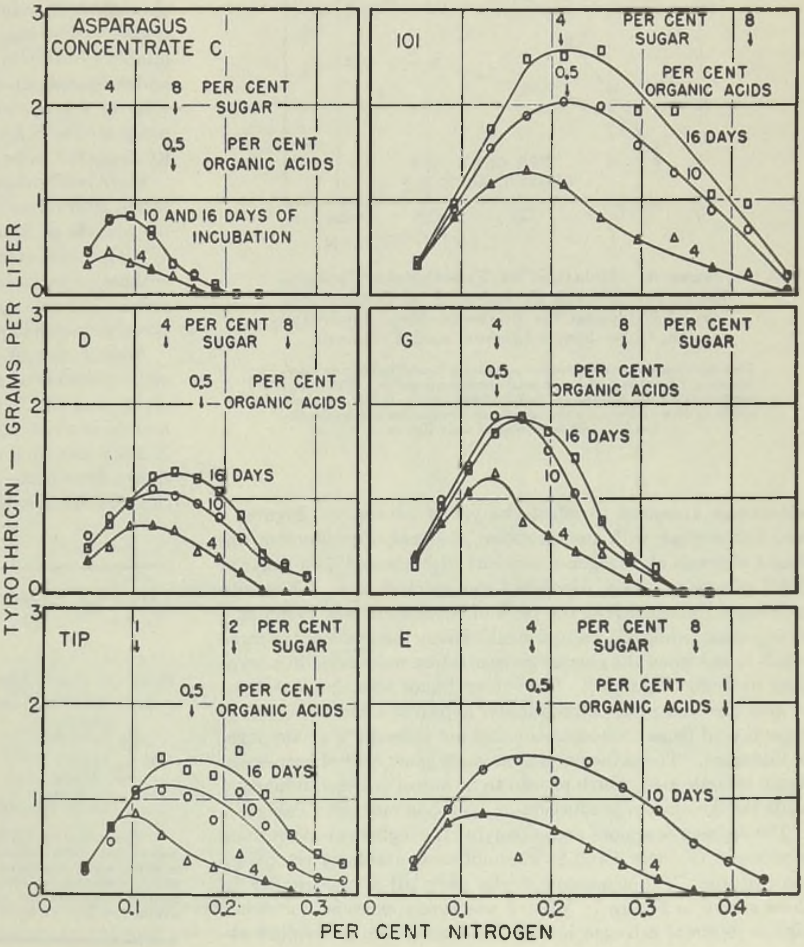

Figure 7. Relation of Tyrothricin Production to Incubation Period and to Concentration of Nitrogen for Several Asparagus Juices

The concentrations of nitrogen coincident with 4 and 8% sugar and with 0.5% organic acids in the uninoculated medium are indicated to facilitate the discussion of this figure.

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[1] A detailed presentation of asparagus-butt processing and analytical data will be made later. Mimeographed circular AIC-70, describing equipment layout and giving cost estimates for the production of asparagus concentrate by the disintegration and digestion process, is available on request to this laboratory.

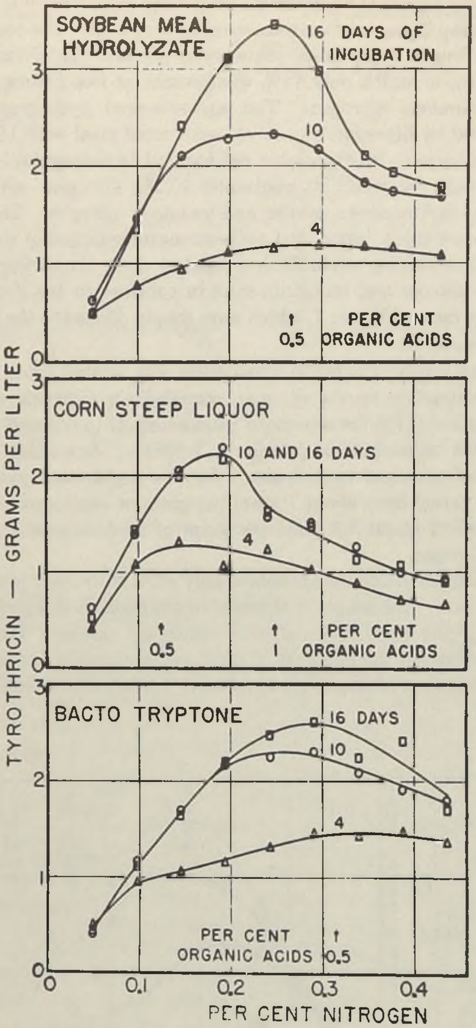

Figure 8. Relation of Tyrothricin Production to Incubation Period and to Concentration of Nitrogen for Soybean-Meal Hydrolyzate, Corn-Steep Liquor, and Tryptone

The nitrogen sources were used in a basal medium containing 3% added glucose and inorganic salts. The concentrations of nitrogen coincident with 0.5% organic acids in the uninoculated medium are indicated to facilitate the discussion of this figure.

substances appeared to affect the yields adversely. Figures 7 and 8 show that, with one exception, the peak of production was found at levels of nitrogen coincident with about 4% of sugar or 0.5% of organic acids, whichever was reached first. Thus with asparagus concentrate C the peak of production was found at 4 to 5% sugar, while 8% was quite inhibitive; this is about the same result found when the glucose concentration was varied in a tryptone medium (Figure 6). Corn-steep liquor was the exception; in this case the peak of production appeared at about 0.8% of organic acid (sugar concentration did not exceed 4% at any level of nitrogen). The principal nonamino organic acid of corn-steep liquor is lactic acid, which proved to be one of the least inhibitive acids for tyrothricin production on tryptone medium (Table V).

The depressive actions accompanying the higher concentrations of nitrogen (Figures 7 and 8) were not accountable by the pH of the cultures. The asparagus media gave pH trends similar to those shown in Figure 1; pH 8.2 was rarely exceeded for either high or optimal nitrogen levels. The maximum pH values attained with tryptone, corn-steep liquor, and soybean-meal hydrolyzate tended to run somewhat higher but did not appear to be detrimental. Thus the soybean-meal hydrolyzate medium with 0.25% nitrogen was at pH 8.5 after 10 days of incubation, a period during which the rate of tyrothricin production was very good. Higher levels of nitrogen gave markedly lower yields, but the course of the pH was almost identical.

Asparagus press juices have not been found deficient in any nutrient required for tyrothricin production other than nitrogen compounds. The predominant sugar is glucose; essentially all of the sugar is reducing sugar. The juices are adequately supplied with vitamins and minerals.

EFFECT OF ORGANIC ACIDS. Table V shows the effects on tyrothricin production of a number of organic acids which were added to the tryptone-glucose-salts medium. Citric acid was most inhibitive of the acids tested; the tyrothricin production was reduced by 50% in the presence of about 0.6% of anhydrous citric acid. All of the acids appeared to be slightly stimulatory at the lower concentrations.

The inhibitive concentrations of the acids listed in Table V are not sufficiently low to account for inhibitory effects of the higher concentrations of asparagus juices and other materials shown in Figures 7 and 8. In no case did citric acid amount to more than 20% of the total nonamino organic acids.

TYROTHRICIN-PRODUCING CAPACITY

There was a question as to whether the high yields obtained with our stock of *B. brevis* were due solely to the use of better media, or whether the strain had varied spontaneously in this laboratory. Accordingly, a second stock of *B. brevis* (B.G.) was obtained and designated as *B. brevis* (X); the supplier found that it gave yields ranging from 0.15 to 0.5 (average 0.35) gram of isolatable tyrothricin per liter of medium containing 1% tryptone and 0.5% sodium chloride in tap water at pH 7.0. Preliminary tests in this laboratory showed it to be inferior to our stock, designated as *B. brevis* (WRRL); its tyrothricin-producing capacity appeared to be only 25 to 60% of that of the WRRL strain.

The tyrothricin-producing capacity of *B. brevis* (X) was also tested after it had been carried in slant cultures in this laboratory for periods of 2 and 6 months, respectively. For each of the WRRL and X stocks, six independent lines had been established —three on nutrient agar slants and three on 1% tryptone–0.5% sodium chloride agar slants. Table VI gives typical growth and tyrothricin-production data for these lines of *B. brevis*.

After 2 months of stock culturing (involving a total of seven serial transfers at approximately weekly intervals), three X lines (1, 4, and 6) showed significant improvement. After 4 more months of stock culturing (involving twelve more serial transfers), X line 6 was equivalent to the WRRL lines; X line 4, which had shown improvement at 2 months, was now very poor. At this time WRRL line 10 also gave inferior results. The reversal, after

TABLE V. EFFECT OF ORGANIC ACIDS ON TYROTHRICIN PRODUCTION BY *Bacillus brevis*

Expt.	Acid Added	Tyrothricin, as % of Control[a], at Acid Concentration of: 0.2%	0.4%	0.7%	1.0%
A	Citric (monohydrate)	109	98	38	19
	Malonic	103	102	80	28
	Succinic	108	107	104	75
B	Maleic	111	117	110	86
	l-Malic	124	120	109	94
	d-Tartaric	110	113	109	99
	Lactic (85–90%)	107	106	104	96

[a] The yields on 1.5% tryptone, 3% glucose, inorganic salts medium without added organic acids were designated as 100%, and the yields with added organic acids compared to it. Figures are averages of ratios for tyrothricin yields determined after 4, 10, and 16 days of incubation. For these respective periods the control yields were approximately 1.2, 2.4, and 2.4 grams per liter in both experiments.

TABLE VI. EFFECT OF STOCK CULTURING ON TWO SUBSTOCKS OF *B. brevis*

Stock of *B. brevis* (B.G.)	Stock Culturing Medium	Line No.	Relative Tyrothricin Production[a], in Grams/Liter, after Stock Culturing for: 2 mo. (*A*)	6 mo. (*B*)	Relative Growth (Turbidity)[a], in Klett Units, after Stock Culturing for: 2 mo. (*A*)	6 mo. (*B*)
X	Nutrient agar	1	0.82	0.42	1470	1230
		2	0.20	<0.10	1230	920
		3	0.26	<0.10	1380	910
X	Tryptone-NaCl agar	4	1.12	<0.10	2060	930
		5	0.36	<0.10	1360	940
		6	0.98	1.28	2070	1910
WRRL	Nutrient agar	7	1.26	1.24	1950	1720
		8	1.26	1.14	1950	1720
		9	1.32	1.25	1950	1830
WRRL	Tryptone-NaCl agar	10	1.32	0.23	1930	1010
		11	1.26	1.11	1920	1670
		12	1.20	1.31	1980	1850

[a] The tests reported were made on 1.5% tryptone, 3% glucose, inorganic salts (0.4% asparagus concentrate ash in the 2-month test). The data given are for 3 days of incubation in the 2-month test, 4 days in the 6-month test. Comparable relations were obtained for longer periods of incubation and for tests on asparagus concentrate E medium.

6 months, of the trend toward improvement in tyrothricin-producing capacity on subculturing was possibly caused by the use of partially desiccated agar slants in several of the transfers during the latter part of the experiment. In all cases variations in tyrothricin-producing capacity were accompanied by similar, though less marked, variations in growth.

The differences were not correlated with the two stock-culturing media used. No further investigation was made of factors inducing variability in the stock cultures, since no difficulties have been experienced in maintaining the bacterium in a high-producing state if it is transferred monthly to fresh slants.

RELIABILITY OF HEMOLYTIC ASSAY

A large number of tyrothricin isolations were made during this investigation to check the reliability of the hemolytic assay method. Table VII presents some representative data; the examples selected illustrate that the response of tyrothricin production to various treatments was essentially similar whether hemolytic assays or isolations were used. For example, the data for experiment *A* confirm the observation that tyrothricin production decreased markedly with an increase in temperature from 36.7° to 38.7° C. on asparagus E medium but not on tryptone-glucose-ash medium (Figure 2). Likewise, isolation data (experiment *C*) confirm the strain variations described in Table VI. The X strain, substocks 2 and 3, gave much lower yields than the WRRL strain, both by hemolytic assay and by isolation. Considerably more material was isolated from these cultures than was indicated by the hemolytic assay, but the activity of the isolated material was so low that the over-all recovery of hemolytic activity was close to 100%. The results obtained with the X strain, line 6, which had improved spontaneously on continued stock culturing in this laboratory, were not distinguishable from the results obtained with the WRRL strain.

It may be noted that the hemolytic activity of the isolated tyrothricin tended to vary around a mean of about 80% of the standard for cultures grown on tryptone medium and around a mean of about 100% for cultures grown on asparagus medium. In general, the isolation values on tryptone media have exceeded the hemolytic assay values sufficiently so that the recovery of hemolytic activity on isolation has averaged between 90 and 100% for tryptone as well as for asparagus media. The hemolytic assay thus appears to give a reliable measure of the tyrothricin produced, at least for the WRRL strain of *B. brevis* and on the media tested.

DISCUSSION OF RESULTS

As pointed out in recent reviews (*3, 4*), tyrocidine is largely responsible for the hemolytic action of tyrothricin under Dimick's assay conditions (*1*). However, the suggestion (*3*) that the method actually measures tyrocidine alone and, therefore, that the method could be used for the determination of tyrocidine in crude filtrates or in preparations if pure tyrocidine were used in the preparation of the standard curve is ill-advised. Small proportions of gramicidin exert a definite synergistic effect upon the hemolytic action of tyrocidine, although pure gramicidin is relatively nonhemolytic under the assay conditions. Dimick's Table I (*1*) showed that pure tyrocidine has only about 75% of the hemolytic activity of mixtures of tyrocidine and gramicidin containing 10 to 35% of gramicidin. In this range of composition the method gives a better measure of tyrocidine plus gramicidin than of tyrocidine alone.

Obviously studies of factors affecting tyrothricin yields would have wider significance if the effects of such factors on the individual components of tyrothricin were considered separately. Unfortunately, specific assays for gramicidin and tyrocidine are

TABLE VII. COMPARISON OF TYROTHRICIN PRODUCTION DATA OBTAINED BY HEMOLYTIC ASSAY AND BY ISOLATION

Expt.	Treatment	Medium	Incubation Period, Days	Grams Tyrothricin per Liter by: Hemolytic assay	Isolation	% Activity (Hemolytic) of Isolated Tyrothricin	% Tyrothricin Recovery by Isolation[a]: Not cor. for activity	Cor. for activity
A (see Fig. 2)	Incubation at 36.7° C.	Asparagus concentrate E	10	1.22	1.31	98	107	105
	Incubation at 38.7° C.	Asparagus concentrate E	10	0.74	0.68	90	92	83
	Incubation at 36.7° C.	1% tryptone, glucose, ash	10	1.35	1.68	80	124	99
	Incubation at 38.7° C.	1% tryptone, glucose, ash	10	1.50	1.78	77	119	92
	Incubation at 36.7° C.	Asparagus concentrate E	16	1.51	1.35	105	90	95
	Incubation at 36.7° C.	1% tryptone, glucose, ash	16	1.47	1.59	90	103	93
B (see Fig. 3)	Depth of medium, 6 mm.	1.5% tryptone, glucose, ash	3	1.78	1.90	75	107	82
	Depth of medium, 6 mm.	1.5% tryptone, glucose, ash	5	1.75	2.22	82	127	104
	Depth of medium, 18 mm.	1.5% tryptone, glucose, ash	5	1.25	1.31	70	105	75
	Depth of medium, 6 mm.	Asparagus concentrate E	5	0.86	0.80	100	93	93
C (see Table VI, expt. *A*)	Regular (WRRL) strain; lines 7, 8, 10, 11, 12 (av.)	1.5% tryptone, glucose, ash	10	2.26	2.87	72	127	92
	Low-yielding (X) strain (line 2)	1.5% tryptone, glucose, ash	10	0.26	1.28	21	492	105
	Low-yielding (X) strain (line 3)	1.5% tryptone, glucose, ash	10	0.42	1.43	27	340	92
	Adapted X strain (line 6)	1.5% tryptone, glucose, ash	10	2.50	2.99	76	120	92
D	Regular test conditions	Asparagus concentrate E (0.18% N)	2	0.48	0.35	94	73	69
		Asparagus concentrate E (0.18% N)	6	0.97	0.83	100	86	86
		Asparagus concentrate E (0.18% N)	16	1.92	1.82	95	95	90
E	Regular test conditions	1% tryptone, glucose, ash	3	0.88	0.90	85	102	87
		1% tryptone, glucose, ash	10	1.45	1.55	87	106	92
		1% tryptone, glucose, ash	17	1.15	1.55	80	133	106
		2% tryptone, glucose, ash	17	2.37	3.10	75	130	98
F (see Fig. 6)	Regular test conditions	1.5% tryptone, 0.0% glucose, salts	10	0.81	1.01	79	125	99
		1.5% tryptone, 3.0% glucose, salts	10	2.16	2.76	73	128	93
		1.5% tryptone, 8.7% glucose, salts	10	0.92	1.32	74	144	106

[a] By comparison with the hemolytic assay value for the original culture suspension.

not yet available. Within this limitation the hemolytic assay has proved to be a useful and convenient method of determining combined tyrocidine-gramicidin.

Asparagus concentrate furnishes a complete medium for the production of tyrothricin in shallow-layer cultures. The asparagus juice should be processed in such a way as to yield a nitrogen content of 3% or higher on the dry-weight basis; the ratio of nitrogen to organic acids (nonamino) should be high. The concentrates deteriorate on storage at room temperature, so that refrigeration appears to be necessary. Alternative procedures, such as treatment of storage-damaged concentrates, chemical stabilization, or stabilization by complete drying, have not been investigated sufficiently.

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Factors Affecting . . . .

BOILING IN A LIQUID

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The phenomena of liquid superheat and of nucleate and film boiling in connection with heat transfer are reviewed. On the basis of wettability or interfacial free adhesion energy, a theory for the solid ebullator is evolved. An apparatus to test the theory is described, and various solids are tested for the ebullition property.

EBULLITION, or the formation of vapor bubbles within a liquid or at a liquid-solid boundary, has received little attention except in connection with the study of heat transfer to a boiling liquid (*8, 17, 26, 29, 30, 38, 50*). The prediction of heat transfer coefficients suitable for boiler or evaporator design has been difficult and has depended largely upon empirical data obtained from tests on models. Correlation of these data has been along lines suggested by dimensional analysis, and some progress has been made in simplifying and rationalizing the problem. Yet there remain some interesting observable phenomena which probably control the over-all transfer of heat to a large extent and are not well understood. Among these are the large differences in coefficient obtained with various solid heating surfaces tested under similar conditions, and the differences in manner and extent of bubble formation observed on these surfaces. From the latter have evolved the terms "nucleate" and "film boiling" which describe the phenomenon but contribute little else.

Superheating of a liquid or establishment of a metastable state, whereby the liquid exists at a temperature above the normal boiling temperature and yet does not boil, has been known since 1807, and the extraordinary phenomena of liquids existing under a negative pressure, or in tension, have been demonstrated (*42, 49, 60, 63*). Philipp and Tiffany (*45*) reported a case where this phenomenon was seriously interfering with the performance of an evaporator in a commercial refrigerator. They succeeded in solving the problem by finding the proper "ebullator", a solid substance or surface in the presence of which superheating did not occur.

In investigations of the heat transfer from heated solids to boiling liquids, this superheating has been observed but only to a slight extent (*30*). This superheat, usually less than 1° F., is probably that necessary to maintain the heat flow from the liquid to the rising vapor bubbles. However, considerably more superheat is indicated in the very thin film of liquid adjacent to the heating solid. No means of measuring the temperature of this liquid film is available, although in some cases it might be assumed nearly equal to the heating–solid surface temperature, which can be estimated from temperatures of the solid on its heated side and known coefficients of conductivity for the solid.

In the nucleate type of boiling, the over-all heat transfer coefficient increases (*38*) with the over-all temperature difference between the main body of the boiling liquid and the heating solid, and with heat transfer rate until a critical temperature difference is attained at which the coefficient begins to decrease. In general, this indicates the beginning of film boiling. The heat transfer rate subsequently decreases as a result of the decrease in coefficient with further increase in temperature of the heating solid. Experiments (*17, 26*) indicate that the position of this curve differs with different heating solid-liquid combinations, and can be shifted somewhat by various treatments of the heating surface and by the addition of a wetting agent to the liquid. In general, the wetted surface gives the highest heat transfer coefficients.

The wetting property is supposed to be indicated by the contact angle made by the bubble before being released. Physical roughening of the surface has also produced nucleate boiling, which has led to the supposition that bubbles originate in cavities having the proper curvature (*26, 30*). In this manner the peculiar phenomenon of bubbles repeatedly forming at particular spots has been explained. This concept arises from the capillary theory and the Kelvin-Helmholtz equation which has been used to explain the metastable or supersaturated vapor state (*31*). This equation relates the pressures within and without a drop (or bubble) with the normal vapor pressure, and predicts the radius of the nucleus drop in supposed equilibrium with the metastable vapor. Other possible nuclei for condensation of supersaturated vapor such as dust particles and ions have also been recognized (*4, 9, 20, 31, 39, 40, 41, 54, 59, 61, 62*).

While the supersaturated vapor state is common in the flow of steam through turbine nozzles, the occurrence of the metastable or superheated liquid state has recently been observed in flow of boiling liquids (*6*). Recognizing that cavitation, which occurs with disastrous results in hydraulic machinery, may be the result of the metastable state, van Iterson (*28*) was able to control to some extent this phenomenon in a test apparatus by using prepared surfaces and wetting agents.

THEORY OF EBULLATOR

It has been generally recognized that a vapor bubble cannot form by itself in a saturated liquid. To do so the liquid would cool in giving up the latent heat required for the bubble whose temperature would be maintained. This could constitute a violation of the second law of thermodynamics. Furthermore, a liquid-vapor interface would be created with a resultant increase in the total free energy of the system, a part of which exists in the energy of the interface.

Interfacial energy is exhibited at the boundaries of different phases of the same substance and of immiscible substances, and is given by the expression (*1, 55*):

$$u_{int} = \left(\sigma - T\frac{\partial\sigma}{\partial T}\right)A$$

The term $T(\partial\sigma/\partial T)$ is the latent heat required to maintain the temperature when area A is extended. σ is potential energy, often represented by a contractile force which requires that work be done whenever such an interface is extended.

When a vapor bubble is created within a liquid, the so-called work of cohesion is done; it has been pictured as the work required to pull apart against the forces of cohesion a cylinder of liquid of unit cross section (*1, 55*). This is equal to the free energy of interface formed and, since two liquid-vapor interfaces are formed, is given by the expression,

$$W_l = 2\sigma_{lv}$$

If the process involves forming a bubble or vapor film on an already existing liquid-solid interface, two new interfaces are formed while one disappears:

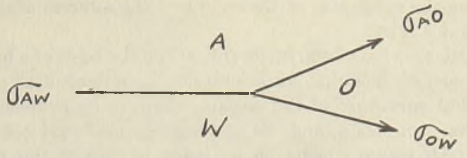
$$W_{ls} = \sigma_{lv} + (\sigma_{sv} - \sigma_{ls}) \tag{1}$$

This is the familiar Dupré (1) equation applied to a liquid-solid-vapor system.

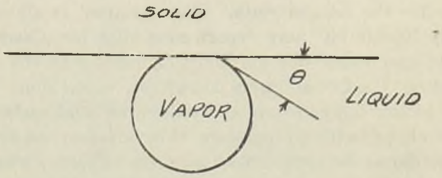
The first term on the right-hand side is the liquid-vapor surface tension and is measurable. The last two are not separately measurable but, when grouped together as shown, are called the "adhesion tension", which is assumed to be measurable through the use of the contact angle shown in Figure 1.

When three immiscible fluids are in contact at a line, the various interfaces will arrange themselves in such a way that the total free interfacial energy is a minimum. When these interfacial energies are represented by contractile forces acting along the interfaces, the Neumann equilibrium triangle of forces (*14*) is formed (Figure 1). Being vectors, the angle between these interfaces is determined by their relative values. For example, if a drop of oil is placed on the free surface of a large body of water, Figure 1*a* represents the situation at the outer edge of the oil lens formed. The extent to which the oil will spread upon the water is governed by interfacial tension; the condition for infinite spreading, or spreading at least to the extent of a monomolecular film, is when σ_{aw} is equal to or greater than $\sigma_{ao} + \sigma_{ow}$. Gravity will influence to some extent and determine the vertical arrangement according to density, and therefore a true Neumann triangle is rarely formed. When spreading occurs, the water may be said to be wetted by the oil.

If this triangle of forces is set up or assumed to act in the case of a vapor bubble in a saturated liquid adjacent to a solid, the result is Figure 1*b*, where θ is called the "contact angle". Since the solid surface is immobile, and the liquid-solid and the vapor-solid tensions are, in general, constrained to act along the plane of the solid, the conditions are not the same as before, and the contact angle is not the result of the action of the interfacial tensions alone. Only a horizontal summation of interfacial forces yields an equilibrium equation. Also, owing to the large difference in density between the liquid and the vapor, the contact angle is likely to be affected in the case of all but small bubbles. Thus, the Neumann triangle using interfacial tension can be properly set up only when the plane solid offers no constraint, as when $\theta = 0$ or $\theta = 180°$, or when gravity acts along the plane of the solid as in the case of a vertical capillary.



(a) NEUMANN TRIANGLE



(b) CONTACT ANGLE

Figure 1

It is convenient to use the contact angle as a measure of relative wettability of a solid, in which case a horizontal summation of forces (tensions) assumed to act as shown in Figure 1 yields

$$\sigma_{sv} = \sigma_{ls} + \sigma_{lv}\cos\theta$$

or

$$\sigma_{lv}\cos\theta = \sigma_{sv} - \sigma_{ls} \tag{2}$$

If Equations 1 and 2 are combined,

$$W_{ls} = \sigma_{lv}(1 - \cos\theta) \tag{3}$$

from which the following statements are possible. When the contact angle is zero, the work of separation, W_{ls}, equals or is greater than the work of cohesion, W_l:

$$\theta = 0°\text{:}\ W_{ls} \geq 2\sigma_{lv};\ (\sigma_{sv} - \sigma_{ls}) \geq \sigma_{lv}$$
$$\theta = 90°\text{:}\ W_{ls} = \sigma_{lv};\ (\sigma_{sv} - \sigma_{ls}) = 0$$
$$\theta = 180°\text{:}\ W_{ls} \leq 0;\ -(\sigma_{sv} - \sigma_{ls}) \geq \sigma_{lv}$$

If the adhesion free energy is a measure of the wettability, the negative value would measure nonwettability or could be called in contrast "repulsion" free energy. The inequalities would correspond to theoretical contact angles of less than zero and greater than 180°, and of course, are not measurable as such. The contact angle greater than 180° would not be an equilibrium state. A contact angle of 90° would represent a neutral solid with neither wetting nor nonwetting tendency, upon which the tendencies toward the formation of the liquid and vapor phases are exactly balanced (*1*). With water the terms "hydrophilic" and "hydrophobic" have been used.

When accurate measurements of σ_{lv} are made, a vertical glass capillary of sufficiently small size is used, and θ is assumed equal to zero (the glass is just completely wetted). The capillary rise (increase in potential energy) corresponds to the work of separation:

$$\text{Capillary rise} = W_{ls} = \sigma_{lv} + \sigma_{sv} - \sigma_{ls} = 2\sigma_{lv}$$

In this case the constraint of the solid and the adverse effect of gravity do not exist.

While attempts have been made (*18*, *31*) on the basis of a hypothetical model to show that surface tension σ_{lv} is dependent upon pressure and curvature of the surface, there is no evidence to support that conclusion, and the assumptions made are open to question. All measurements on σ_{lv} made by use of the glass capillary tube indicate that σ_{lv} is a function of temperature only (*47*, *55*), and that it decreases regularly, with temperature increase becoming zero at or in the region of the critical temperature. The disappearance of the meniscus has been taken to signalize the critical state. The variation is almost linear for many liquids but may depart somewhat for others. Since the liquid and vapor become indistinguishable at the critical temperature, the free adhesion energy ($\sigma_{sv} - \sigma_{ls}$) must also become zero at this temperature, and unless the solid surface characteristics change with temperature, this variation can be expected to be similar as the temperature is raised. Figure 2 was drawn from data on σ_{lv} (*27*, *34*) to represent the free energies required for vapor phase formation.

At any particular temperature 2 σ_{lv} represents the free interfacial energy that must be available if boiling or ebullition is to occur. The ebullator is assumed to be a solid surface or other substance that supplies either all or a portion of this free energy. The amount supplied is represented by the vertical distance downward from 2 σ_{lv} to any particular line. The remainder, $\sigma_{lv} + (\sigma_{sv} - \sigma_{ls})$, must come from outside the system. If the adhesion free energy is zero, represented by $\theta = 90°$, ebullition should occur immediately on heating the saturated liquid at constant pressure. If the adhesion free energy is positive, ebullition cannot take place and superheating must occur. If the adhesion free energy is negative, a vapor film should form on the surface at a temperature less than the normal boiling temperature although complete ebullition (bubble formation) would not occur until the normal boiling point was approached, or unless the pressure within the bubble was greater than the total imposed pressure.

In the case of dissolved, absorbed, or adsorbed gas or of a gas liberated because of a chemical process, complete ebullition might occur below the normal boiling point, the bubbles containing both vapor and gas. In the case of a dissolved gas, ebullition would depend upon the quantity of gas originally in solution and the solubility relation expressed by Henry's law or by Raoult's law for very soluble gases. An energy term equivalent to the adhesion free energy but dependent upon the interaction between gas and vapor, and gas and liquid molecules would govern the case and determine ebullition. Supersaturation of gas-liquid solutions is also a common occurrence (*33*).

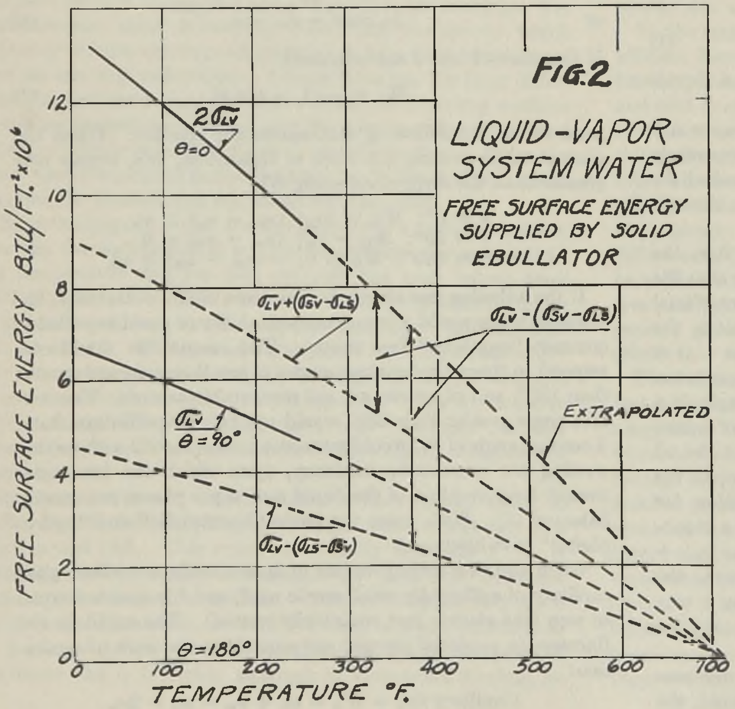


FIG. 2

LIQUID-VAPOR SYSTEM WATER

FREE SURFACE ENERGY SUPPLIED BY SOLID EBULLATOR

THEORY OF EBULLITION

The usual thermodynamic properties as listed in tables neglect the energy associated with the interface or boundary. When considering mixtures of phases, the interface is assumed plane, in which case interfacial energy is negligible because of the small interface. When the mixture is in the form of a fine suspension, the interfacial energy cannot be neglected. Thus in the case of a fog or mist, interfacial area A would be $4\pi r^2 n$ and volume V would be $4/3\pi r^3 n$, where r is the drop radius and n is the number of drops. The weight y of drops would be V/v, where v is the specific volume of the drops. The total interfacial energy per pound of drops would be

$$u_{int} = \frac{A\left(\sigma - T\frac{\partial\sigma}{\partial T}\right)}{y} = \frac{3\left(\sigma - T\frac{\partial\sigma}{\partial T}\right)v}{r}$$

The total energy of a pound of such a mixture would be given by

$$u_t = xu_g + yu_f + A\left(\sigma - T\frac{\partial\sigma}{\partial T}\right)$$

where x and y are vapor and liquid fractions. Since $x + y = 1$, we may let $y = 1 - x$ as in steam calculations:

$$u_t = xu_g + (1 - x)u_f + A\left(\sigma - T\frac{\partial\sigma}{\partial T}\right)$$

$$= u_g - (1 - x)u_{fg} + A\left(\sigma - T\frac{\partial\sigma}{\partial T}\right)$$

If all drops are the same size,

$$u_t = u_g - (1 - x)u_{fg} + (1 - x)\frac{3\left(\sigma - T\frac{\partial\sigma}{\partial T}\right)v}{r}$$

$$= u_g - (1 - x)\left[u_{fg} - \frac{3\left(\sigma - T\frac{\partial\sigma}{\partial T}\right)v}{r}\right]$$

Thus, in the case of condensation in the form of small drops, the latent heat is reduced by the interfacial energy, which depends upon the density and radius of the drops. Similarly, if ebullition occurs in the form of small bubbles,

$$u_t = u_f + x\left[u_{fg} + \frac{3\left(\sigma - T\frac{\partial\sigma}{\partial T}\right)v}{r}\right]$$

which indicates that the latent heat required is increased by the interfacial energy, of which $x\,(3v\sigma/r)$ is the free surface energy. Knowing σ, v, and r, this could be evaluated. The specific volume to use would not be the specific volume of the vapor as listed in vapor tables, which is for bubbles of infinite radius, but rather that vapor at the pressure within the bubble which, for small bubbles, according to the capillary theory would be very high. The density of such bubbles would approach that of the liquid or perhaps be even greater. The free surface energy is also expressible as $A\sigma$.

The suspensions or dispersions considered above would represent unstable states which, in the absence of some specific stabilizing restraint, would change by drop or bubble coalescence to a more stable state possessing a smaller interface, the nearest approach to the plane interface. The interfacial energy would be reduced to a minimum value, and this energy released would effect further vaporization.

SOLIDS AS EBULLATORS

In view of the foregoing theory it became desirable to test various solids experimentally as to their ability to serve as ebullators, and to determine if physical roughness of the surface was a factor. Much of the literature on flotation (*3, 14, 19, 43, 58*) was convassed for materials variously wetted by water or possessing natural floatability (large contact angle). In general, carbonaceous materials (coal, graphites, etc.) are not wetted by water but are wetted by oils or hydrocarbons. Floatability may be brought about by surface-contaminating films due to chemical reaction—oxidation, carbonation, hydration, etc. The nature of the liquid as well as the surface, whether polar or nonpolar, is given as a factor.

Some preliminary testing was done in an open beaker containing boiling predistilled water by inserting various substances selected from the literature. It was found that ebullition could be correlated with floatability, and appreciable differences in this property were observed. Physical roughness did not appear to be a factor nor did the porous nature of the substance. Silica gel was ineffective as an ebullator after the absorbed air was dissipated. Sharp points were not necessarily nuclei, inasmuch as broken glass or silica sand did not promote ebullition. Tests were also made using several hydrocarbon liquids. In general, substances known to be nonwetted proved to be good ebullators.

To measure these ebullating characteristics quantitatively, it was decided to measure the maximum amount of liquid superheat which each substance would permit. This could not be done in an open beaker. Figure 3 is a diagram of the apparatus as developed and used in these tests. It was necessary to heat from above in order to develop superheat, and to use a wetted material such as glass in contact with the superheated liquid. The substances tested were not to be heating surfaces but rather to be heated by the liquid. These substances were used in the form of smooth $^1/_8$-inch balls or pellets supported as shown in Figure 3. Temperatures of the liquid were measured by a small thermocouple, enclosed in a glass tube and mounted adjacent to the ebullator being tested. Heating was by radiation from electric heaters, several types and arrangements of shielding and insulation being used in the development.

The procedure of testing was to cleanse the apparatus and the ebullator thoroughly in order to eliminate any possible organic or other contaminating film which would cause early and false ebullition. The cleaning solution used was hot concentrated sulfuric acid saturated with sodium dichromate. This solution was corrosive to some of the ebullators, in which case a hot trisodium phosphate solution was used. This was followed by thorough rinsing. The ebullator was then inserted, and the apparatus assembled and filled with boiling double-distilled water to the level desired. In addition, the liquid in the apparatus was effectively boiled when held in a partially inverted position by applying heat from a gas burner in the vicinity of the ebullator, in order to eliminate any dissolved air. The gas burner was then removed; when boiling had ceased and all bubbles had come to the surface, the ebullator end was quickly cooled to a temperature about 10° F. below the normal boiling point. The apparatus was then quickly placed in its normal testing position, and slow heating from above was begun. The increasing temperature was observed by continuous balance of a precision-type potentiometer until the maximum or ebullition temperature was reached. If superheated this was easily detected by the rapid drop that occurred on ebullition. The time required for heating varied from about a minute up to 10 or more minutes, depending on the initial temperature and the final temperature attained. The object was to heat uniformly and to avoid steep temperature gradients in the vicinity of the ebullator.

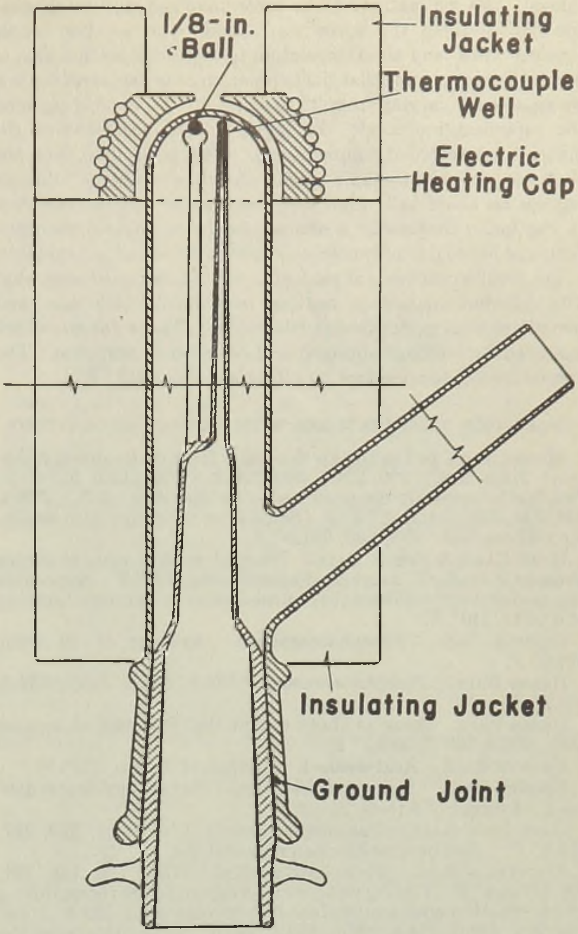


Figure 3. Apparatus for Ebullator Tests

Tests were repeated, preliminary boiling being done each time to eliminate any gases (air) that might have been absorbed at the interface with the atmosphere during the interim. In addition, the apparatus and ebullator were cleaned and recharged with fresh boiling water whenever it was desired to check for the presence of some contaminant. The ebullator was cleansed in hot trisodium phosphate solution and subsequently handled by clean forceps on insertion. Much care and patience was required in this phase to obtain reliable and consistent results. Mechanical shock in the vicinity of the apparatus sometimes caused early ebullition and hence was avoided. Ebullition temperatures less than 211° F., the average normal boiling temperature for these tests, were taken when the first small bubble appeared. For such tests the ebullator and the surrounding water were quickly chilled after preliminary boiling to a temperature about 10° F. below the ebullition temperature before heating was begun. Ebullition from highly superheated liquid was accompanied by severe shock with violent emission of the remaining liquid, the apparatus bursting on several occasions.

Since it was necessary to superheat only a small quantity of liquid due to the explosive hazard involved, a rather steep temperature gradient downward along the thermocouple wires existed. An estimation of the error involved due to thermal conduction along the wires was made by a smaller couple (smaller wires) and an extrapolation to zero cross-section area of wires. The result was that the temperatures as read were too low by an amount varying from 2° to about 10° F., depending upon the superheat indicated; the higher values accompanied the higher final recorded temperatures. The possibility that the ebullator or thermocouple might absorb enough radiation to register an abnormally high temperature was also investigated. It was found that water is almost opaque to infrared radiation (*13*), and hence this phenomenon could be dismissed as negligible.

The results obtained for particular ebullators varied somewhat with different methods of heating, occasionally with time, and sometimes with pretreatment (cleansing). These variations are indicated by readings obtained and recorded in sequence. The normal boiling temperature for all tests is about 211° F.

EBULLITION TEMPERATURES WITH VARIOUS EBULLATORS

MONEL BALL IN DISTILLED WATER. Heating by direct radiation: 219.6, 219.7, 220, 221.8, 220, 220.2, 217.9, 219.6, 219.6° F. Heating by specially designed heater at slow rate: 223.7, 226.4, 224, 224, 225, 224.3, 224.6° F. Same type of heating with ebullator acid-washed: 228, 230, 231.8° F.

HIGH-CARBON STEEL BALL. Heating at slow rate, ebullator phosphate-washed: average of eleven tests, 221° F. Apparatus cleansed and ball replaced (had turned black in interim): average of 6 tests, 210° F.

COPPER BALL. Phosphate-washed. Average of 10 tests, 214.2° F.

BRASS BALL. Phosphate-washed: 234.9, 233.5, 233.9, 234.8, 234.7° F.

BRASS BALL. Same as above except that surface had become dull: 226.8, 227.5, 226.7° F.

BRONZE BALL. Acid-washed. Average of 8 tests, 211° F.

BRONZE BALL. Same as above except that surface was roughened. Average of 8 tests, 211.2° F.

CAST IRON BALL. Phosphate-washed: 216, 218.4, 222, 217, 219.8° F. Ball became black on repeated use.

ALUMINUM BALL. Phosphate-washed: 175.1, 178, 181, 191, 192.5, 199.4° F. Testing was here interrupted for one hour, during which time the ebullator surface had become dull: 221.5, 218.8, 220, 219, 223.6, 224.8, 225.9, 226.1, 226.6° F. At this point the ball was removed and the dull surface coating was removed with emery cloth. It was subsequently washed and tested: 165.3, 165.4, 161.6, 164, 162.8° F.

ZINC BALL. Phosphate-washed. Average of 8 tests, 185° F.

LEAD BALL. Phosphate-washed. Average of 10 tests, 206.5° F.

BALL MADE FROM CARBON ELECTRODE. Average of 9 tests, 206° F.

MAGNESIUM BALL. Average of 5 tests, 112° F.

TIN BALL. Phosphate-washed: 214.2, 214.2, 217.8, 221.2, 219.5, 219.8° F.

NICKEL PELLET. Acid-washed. Average of 6 tests, 225.8° F.

MILD STEEL BALL. Phosphate-washed: 215.7, 215.9, 217.4, 217.8, 220.4, 220, 220° F. NaOH added to water to pH 10: 220.5, 228.8, 233.6, 232.4, 235.3° F. Water changed to saturated $CaCO_3$ solution (pH 8.5): 230.8, 226.5, 229.8, 234.9, 243.7, 239° F.

The following results were obtained when the surface tension of the water was changed from 72.5 to about 54 dynes per cm. by the addition of Dreft, a commercial detergent:

MONEL BALL. Average of 5 tests, 226.5° F.

COPPER BALL. Average of 7 tests, 223.5° F.

BRIGHT CARBON STEEL BALL. Average of 14 tests, 172° F.

OXIDIZED BLACK STEEL BALL. Average of 5 tests, 223° F.

BRIGHT ALUMINUM BALL. Average of 9 tests, 220.5° F.

BRIGHT BRASS BALL. Average of 5 tests, 228° F.

The following results were obtained with the glass thermocouple tube extended and bent into a spiral form completely encircling the ball ebullator at the same level. This was done to eliminate as far as possible the effect of temperature gradient on the readings. In general, stainless steel balls gave high and somewhat erratic values, depending somewhat on the pretreatment or cleansing of the ball.

STAINLESS STEEL. Acid-washed. Minimum, 228; maximum, 258; average of a great number of tests, 250° F.

ROUGHENED STAINLESS STEEL. Surface roughened with emery cloth. Average value, 253° F.

MONEL BALL. Acid-washed: 234.4, 237.2, 237, 236.3° F.

MONEL BALL. Acid-washed. Apparatus completely cleaned and recharged. Average of 5 tests, 248° F.

In an attempt to attain maximum temperature, a number of tests were conducted without an ebullator other than the glass apparatus itself. These gave a scattering of test results varying from 247° to 288.5° with an average of 263° F.

DISCUSSION OF RESULTS AND THEORY

The experimental ebullition temperatures should not be taken as precise values, but rather indicate relative values to be associated with various substances with the allowance that those above 211° F. are likely to be somewhat low. They indicate that ebullition does depend upon the presence of an ebullator whose property, assumed to be the adhesion free energy, determines the amount of superheat tolerated.

The apparent erratic test data may in some cases be explained on the basis of the nature of the ebullition phenomenon, the heterogeneous and changing nature of the solid surface, and the difficulty in controlling and duplicating test conditions and factors, some of which may be unknown. Furthermore, in a microscopic (molecular) phenomenon, fluctuations are natural (*46*).

While the theory indicates that ebullition below the normal temperature is possible, this should be examined on the basis of definition. Negative adhesion free energy indicates a nonwetted surface or preferential gas or vapor adsorption. Ebullition requires that sizable bubbles form which, in turn, requires the latent heat, and the latter may not be available unless the bubbles form at reduced pressure. This is contrary to capillary theory, which states that the pressure within a bubble is greater than the pressure of the liquid by a value $2\sigma/r$. Small values of r may make the pressure in the liquid negative (*31*). Such states of the metastable liquid have been observed (*60*) but not in the presence of detectable bubbles. However, small bubbles did appear suddenly on some substances at temperatures less than 211° F. These bubbles subsequently grew slowly, and finally grew rapidly as the normal boiling point was approached. They appeared repeatedly at the same spot on the ebullator.

It has been suggested that the cause of these bubbles was the release of some adsorbed or absorbed gas, or was the product of a chemical reaction. They appeared repeatedly on such substances as magnesium, aluminum, zinc, and lead; from their position in the electromotive series, these metals may be expected to react with water to liberate hydrogen and may, in some cases, take on an oxide coating which may inhibit the action. This probably accounts for the progressive change in the case of aluminum. One noticeable trend is that substances known to be chemically inert or resistant to corrosion support greater superheat. Thus glass, silica, and even stainless steel are not good ebullators.

The effect of additives in general upholds the theory; however, an additive (presumably a wetting agent) which also lowers surface tension σ_{lv} may result in either raising or lowering the ebullition temperature, depending upon the net difference between the effects on the terms σ_{lv} and σ_{ls}. This statement is made on the assumption that the term σ_{sv} is not affected. If no change in ebullition temperature occurs, one may assume that the wetting power (decrease in σ_{ls}) of the agent is given by the decrease in σ_{lv} which can readily be measured.

In regard to ebullition of a heated liquid (water), the following general conclusions may be stated. The ability of a surface to initiate boiling in a superheated liquid appears to depend primarily upon the adhesion free energy or adhesion tension, which has been held responsible for the wettability of this surface. The usual physical roughness does not appear to be a factor. Physical roughness in the range of molecular radii and curvatures of proper aspect may account for the heterogeneous character observed. This is in accordance with capillary theory for small bubbles. If, however, the rough surface is also a heating surface, bubble initiation can be expected to occur in surface cavities or capillaries because of the effect of such a cavity on the local superheating of the liquid contained in that cavity. The ebullition phenomenon requires that the thermodynamic requirements of the vapor phase, as it must first appear, shall be satisfied. The ebullator may supply all or a portion of the free surface energy required; the remainder must then be made up by the mechanism of superheating.

NOMENCLATURE

u_{int} = energy associated with an interface
σ = free interfacial energy per unit area of interface (surface tension)
A = area of interface
T = temperature on absolute scale
W_l = work of cohesion; free interfacial energy created when a cylinder of unit cross-section area is ruptured to produce the vapor phase between the interfaces formed
W_{ls} = work of liquid-solid separation producing the vapor phase between them, per unit of initial liquid-solid interface
σ_{lv} = free interfacial energy per unit area of liquid-vapor interface
σ_{ls} = free interfacial energy per unit area of liquid-solid interface
σ_{sv} = free interfacial energy per unit area of solid-vapor interface
θ = contact angle measured through liquid for a vapor bubble on a solid surface (Figure 1)
x = vapor fraction by weight in a mixture of liquid and vapor
y = liquid fraction by weight in a mixture of liquid and vapor
u_t = total (internal) energy of a pound of mixture
u_f = internal energy of saturated liquid per pound
u_g = internal energy of saturated vapor per pound
u_{fg} = internal latent heat per pound, $u_g - u_f$
v = volume per pound (specific volume)
V = total volume
r = radius of bubble or drop
s = entropy per pound
T = temperature
n = number of bubbles that form initially
h = enthalpy per pound
$_2(u - Ts)_3$ = change in free energy occurring in passing from state 2 to state 3
p = pressure
u_{lv} = energy of liquid-vapor interface formation per unit interfacial area

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OCCURRENCE OF METASTABLE STATES OF LIQUID AND VAPOR

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A thermodynamic theory is advanced for the requirement and mechanism of bubble formation in a heated liquid. Trial calculations using estimated thermodynamic properties of superheated water indicate that the nucleus bubble in the transformation state consists of a single molecule. The general theory is extended to condensing water vapor with similar results. The literature is reviewed for supporting evidence. The similarity between the supposed action of the ebullator and of a catalyst is pointed out.

THE preceding article pointed out that liquids are likely to superheat unless a liquid-vapor interface is already present or unless an ebullator (assumed a solid) is present, whose contact angle is 90° or more or whose adhesion free energy is zero or negative. Contact angles are difficult to measure accurately; furthermore, solid surfaces will probably be heterogeneous in this respect. Thus the contact angle is likely to be only a rough and probably inaccurate measure of adhesion free energy as the surface area is reduced. However, test results indicate that superheating does readily occur, and that the extent of superheat is dependent upon some property of the substance or surface of the ebullator, and differs with various substances. Ordinary physical roughness does not appear to be a factor. The property that limits the amount of superheat is assumed to be the adhesion free energy, given by the expression $\sigma_{sv} - \sigma_{ls}$. For thoroughly wetted substances this expression would equal σ_{lv}, the liquid-vapor free interfacial energy.

The data for this article were developed concurrently with those for the preceding article. The general theory is extended to include the supersaturated vapor state, and calculations are presented which tend to uphold the theory and give some insight into phase transformations.

THEORY OF EBULLITION

Ebullition as described above is not a smooth process, but is rather explosive as the system passes from a superheated or metastable state to a more stable state, during which an interface must be created. This transformation appears to be spontaneous and to take place without external aid.

To accomplish this change, it is postulated that the system passes through an intermediate, momentary unstable state, a mixture of liquid and small bubbles, from which it then can pass to the final equilibrium mixture state represented by a minimum-phase interface. This would require that the ebullition process consist of three steps: (1) superheating of the liquid, (2) transformation where the interface is created, assumed to take place adiabatically and reversibly, and (3) the dissipation of the high interfacial energy and subsequent expansion as the bubbles coalesce and grow.

An attempt to illustrate these changes is made in Figure 1. Numbered state points represent: 1, initial liquid at pressure p_2; 2, saturated liquid (at boiling point for pressure p_2); 3, superheated or metastable liquid at the same pressure; 4, dispersed vapor bubble mixture arising from state 3; and 5, the final stable equilibrium mixture state. State 3 would not lie on the characteristic stable state surface but on a metastable state surface. Having properties p, v, t, etc., it can properly be shown. State 4 is not shown since it is unstable although the entropy is assumed to be that of state 3. Clearly, change 3 to 4 involves the formation of a new phase at the expense of some of the liquid phase.

The free energy $(u - Ts)$ of 2 and 5 are equal since these states are in equilibrium with each other; however, 3 and 4 are states of greater free energy by amount ${}_2(u - Ts)_3$ for state 3, and by $A\sigma$ for state 4. This increase of free energy could originate only from the same source, heat absorbed ${}_2h_3$; hence they are assumed equal and equivalent[1]:

$${}_2(u - Ts)_3 = A\sigma_{lv} = \frac{A}{2} \times 2\sigma_{lv}$$

If n bubbles of radius r are formed,

$$A = 4\pi r^2 n = \frac{{}_2(u - Ts)_3}{\sigma_{lv}}$$

As a further consequence, ${}_2(Ts)_3$ will represent the latent heat required for vaporization in the form of n bubbles whose total volume V would not depend on the surface energy but rather on the bulk energy. Thus,

$$\frac{V}{v} = \frac{{}_2(Ts)_3}{u_{fg}}$$

$$V = \frac{4}{3}\pi r^3 n = \frac{{}_2(Ts)_3 v}{u_{fg}}$$

where u_{fg} is the internal bulk latent heat, and v is the volume per pound of bubbles as initially formed. Dividing volume by area,

$$r = \frac{3V}{A} = \frac{\dfrac{{}_2(Ts)_3 v}{u_{fg}}}{\dfrac{2\,{}_2(u - Ts)_3}{2\sigma_{lv}}} = \frac{3\,{}_2(Ts)_3 v\sigma_{lv}}{u_{fg}\,{}_2(u - Ts)_3}$$

which gives the particular size of bubble that serves as a nucleus when ebullition occurs in the bulk superheated liquid—i.e., in the absence of an ebullator.

With an ebullator, assumed for the present to be a solid, the amount of superheating (and hence the increase in free energy) would be governed by the adhesion free energy, $\sigma_{sv} - \sigma_{ls}$. In the above expression $2\sigma_{lv}$ would be replaced by $\sigma_{lv} + \sigma_{sv} - \sigma_{ls}$. (See Figure 2 of the preceding article.) This assumes that the adhesion free energy is known or could be estimated. Also the

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[1] The use of the free energy $(u - Ts)$ here must not be confused with its use in determining the maximum external work obtainable from a reversible isothermal change. The change pictured here is for an adiabatic system and little external work is involved. The free energy transformation is entirely internal, and $(u - Ts)$ and $A\sigma$ are the free energy functions.

adhesion latent heat, or the heat of wetting, would have to be considered as modifying u_{fg}. This modification will be taken up later. Furthermore, if a dissolved gas were to act as an ebullator the latent heat of solution would have to be considered as well.

CHECKING THE EBULLATOR THEORY

While the test results cannot be considered as precise values, various solids do exhibit the ebullating property to various degrees, and it becomes desirable to check the ebullator theory. Making substitutions previously referred to, the radius of the nucleus bubble in transition state 4 becomes:

$$r = \frac{3\,{}_2(Ts)_3\,v(\sigma_{lv} + \sigma_{sv} - \sigma_{ls})}{2\,{}_2(u - Ts)_3\,u_{fg}}$$

Values of energy u and entropy s of metastable state 3, as well as adhesion free energy $(\sigma_{sv} - \sigma_{ls})$, are required. Figure 2 gives plots made from the Keenan-Keyes steam tables. These plots indicate that at low pressures extrapolation into the metastable region is safe for a moderate degree of superheat. Estimation of the adhesion free energy may be made on the assumption that the maximum possible temperature of superheated liquid is obtained when the internal latent heat of vaporization has been absorbed. This temperature is assumed to be the critical temperature above which the vapor phase forms spontaneously. Since the added bulk free energy ${}_2(u - Ts)_3$ corresponds to the adhesion free energy $(\sigma_{sv} - \sigma_{ls})$ and for small values is proportional to the internal energy ${}_2u_3$, the estimation is made as follows:

$$(\sigma_{sv} - \sigma_{ls}) = \sigma_{lv} \times \frac{{}_2u_3}{u_{fg}}$$

A number of trial calculations were made, using the above assumptions and values of the thermodynamic properties as taken directly from the Keenan-Keyes steam tables. The results were somewhat surprising. The radius of the nucleus bubble was found to be about 0.617 × 10^{-9} ft. for an ebullator tolerating 10° F. of superheat at atmospheric pressure, 0.578 × 10^{-9} ft. for an ebullition temperature of 260° F. and 0.581 × 10^{-9} ft. for ebullition at the critical temperature. The nucleus bubble size was essentially the same for different degrees of superheat or different ebullators.

Since the difference of two Ts products is used in the calculation, it became apparent that absolute values of the entropy would be required rather than the values listed in the tables. In order to obtain these, it was necessary to determine the entropy of liquid water at 32° F. for addition to the tabular values. This was approximated by obtaining values of the specific heat of ice from data given by Dorsey (*16*)[2] from 0° to −251° C. and integrating graphically:

$$S = \int_0^T c\,\frac{dT}{T}$$

The value obtained for the entropy of ice at 32° F. was 0.496 B.t.u./lb. ° R., to which was added 0.313 as the entropy of fusion; the sum was rounded off to 0.81 as the entropy of the liquid at 32° F. Using these values in determining the absolute entropy, the size of the nucleus bubble was recalculated for a number of cases. To illustrate the method a few sample calculations will be given.

Assume ebullition to occur from water superheated only to 260° F. at atmospheric pressure due to the action of the ebullator which prevents further superheat. The values of the various properties used and the calculations follow.

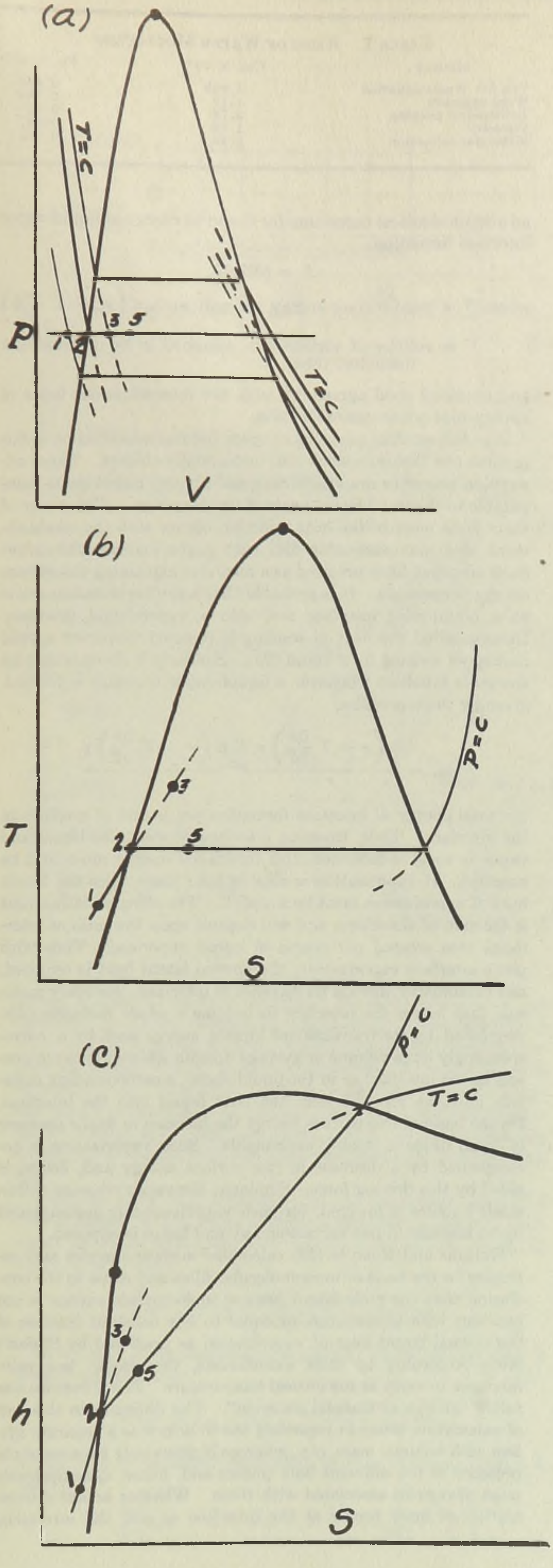

Figure 1. Metastable States of Water (Shown by Dashed Lines)

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[2] Numbers refer to bibliography at end of preceding article.

State	p	t	T	s	h	u	Ts	$u - Ts$
2	14.7	212	672	1.122	180	180	755	−575
3	14.7	260	720	1.192	228.6	228.5	859	−630

$$_2u_3 = 48.5;\ _2(Ts)_3 = 104;\ _2(u - Ts)_3 = -55$$

$$\sigma_{sv} - \sigma_{ls} = 5.03^* \times 10^{-6} \times \frac{48.5}{897.5} = 0.263 \times 10^{-6}$$

$$\sigma_{lv} + \sigma_{sv} - \sigma_{ls} = 5.29 \times 10^{-6} \text{ B.t.u./sq. ft.}$$

$$r = \frac{3 \times 104 \times 0.0167 \times 5.29 \times 10^{-6}}{2 \times 55 \times 897.5} = 0.28 \times 10^{-9} \text{ ft.}$$

Using an ebullition temperature of 222° F., the result again is essentially the same.

The calculation for ebullition from water at the critical temperature (taken as 717° F.) at 14.7 lb./sq. in. with no ebullator present follows:

State	p	t	T	s	u	Ts	$u - Ts$
2	14.7	212	672	1.122	180	755	− 575
3	14.7	717	1177	2.458	1077.5	2890	−1812

$$_2u_3 = 897.5;\ _2(Ts)_3 = 2135;\ _2(u - Ts)_3 = -1237$$

$$r = \frac{3 \times 2135 \times 5.03 \times 10^{-6} \times 0.0167}{897.5 \times 1237} = 0.485 \times 10^{-9} \text{ ft.}$$

Entropy s of state 3 was calculated on the basis:

$$s_3 = s_2 + u_{fg}/T_2$$

A similar calculation made for water at the critical temperature but at a pressure of 1 lb./sq. in. absolute yields a value $r = 0.474 \times 10^{-9}$ ft.

Loeb (*36*) gave the radii of the water molecule calculated by various methods as shown in Table I. The checks obtained are unusual. The above method of calculation is comparable with the methods of Table I, since all are based on values of statistical properties, and we encounter the result that our transition-state bubble apparently consists of only one molecule. If this is true, then the total interfacial energy of the pound of single molecule bubbles (the limiting case) is given by:

$$_2u_3 = {}_2(u - Ts)_3 + {}_2(Ts)_3 = \frac{3\left(\sigma - T\dfrac{\partial\sigma}{\partial T}\right)v}{r}$$

and $_2(Ts)_3$ corresponds to the latent heat of the interface in state 4. This suggests that the internal latent heat of vaporization could be calculated from the total interfacial energy; that is,

$$u_{fg} = \frac{3\left(\sigma - T\dfrac{\partial\sigma}{\partial T}\right)v}{r}$$

provided suitable values of v and r could be obtained. A trial calculation using the interfacial energy as determined from Landolt-Bornstein data (*34*) at 212° F. gives

$$u_{fg} = \frac{3(5.03 + 672 \times 0.88 \times 10^{-2})\,10^{-6} \times 0.014}{0.5} = 920 \text{ B.t.u./lb.}$$

which is not far from the value generally listed. Using the tabulated value 897.5 for u_{fg}, the corresponding value of r would be 0.512×10^{-9} ft.

At lower temperatures the internal latent heat as given in the standard tables exceeds the values as calculated from surface energies. This suggests that the discrepancy might be due to the presence of associated molecules, which are known to exist in low-temperature water vapor freshly formed. At higher temperatures, although accurate capillary data are not available, the opposite tendency seems to maintain; i.e., the total surface energy exceeds the listed internal latent heats. Hammick (*22*) derived an almost identical expression for the total energy of liquid-vapor interface formation:

$$L = 6SV/d$$

where S = total surface energy per unit surface $\left(\sigma_{lv} - T\dfrac{\partial\sigma_{lv}}{\partial T}\right)$

V = volume of surface film, assumed to be d (molecular diameter) thick

and obtained good agreement with the internal latent heats of twenty-nine nonassociated liquids.

Table I. Radii of Water Molecules

Method	Cm. × 10^{-8}	Ft. × 10^{-9}
Van der Waals equation	1.443	0.475
Wohl equation	1.17	0.385
Tetrahedral packing	2.74	0.90
Viscosity	1.36	0.447
Molecular refraction	1.13	0.372

It is known that gases and vapors become adsorbed on solids in films one molecule thick and occasionally thicker. These adsorption processes are exothermic and involve latent heats comparable to the usual latent heats of condensation. With many of these films most of the heat rejection occurs with the establishment of a monomolecular film with slight increase thereafter. Such adsorbed films are used as a means of explaining the surface energy phenomena. It is probable that a similar situation exists at a liquid-solid interface and also a vapor-liquid interface. Energy called the heat of wetting is rejected whenever a solid undergoes wetting by a liquid (*25*). Similarly it appears that an energy is involved whenever a liquid-vapor interface is formed. given by the expression,

$$u_{lv} = \frac{3\left(\sigma - T\dfrac{\partial\sigma}{\partial T}\right)v}{r} = \frac{6\left(\sigma - T\dfrac{\partial\sigma}{\partial T}\right)v}{d}$$

the total energy of interface formation per pound of medium in the interface. Thus, when an interface between the liquid and vapor is to be established, this interfacial energy must first be supplied. If vaporization is also to take place, then the latent heat of vaporization must be supplied. The effective latent heat is the sum of these two, and will depend upon the ratio of interfacial area created per pound of liquid vaporized. Thus with plane interface vaporization, the normal latent heat is required, and presumably there is no decrease in interface; for every molecule that leaves the interface to become a vapor molecule (distinguished by its translational kinetic energy and by a correspondingly large volume or average domain which it does not possess in the interface or in the liquid state), a corresponding molecule must be brought from the bulk liquid into the interface. On the basis of free surface energy the increase in vapor pressure of small drops is readily explainable. Such vaporization is accompanied by a decrease in free surface energy and, hence, is aided by this driving force. Similarly, the vapor pressure within small bubbles is lowered, for such vaporization is accompanied by an increase in free surface energy and hence is opposed.

Harkins and Roberts (*23*) calculated surface energies and entropies on the basis of monomolecular films and came to the conclusion that the mole latent heat or mole surface energy is not constant with temperature or equal to any constant fraction of the normal latent heat of vaporization as predicted by Stefan's law. According to their calculations, the Stefan law ratio increases to unity at the critical temperature. The difference was called "energy of thermal emission". The difficulty in this sort of calculation arises in regarding the interface as a separate system with volume, mass, etc., whereas it exists only because of the presence of the different bulk phases and, hence, quantitatively must always be associated with them. Whether actual concentration of mass occurs at the interface or not, the interfacial

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* From Figure 2 of the preceding article.

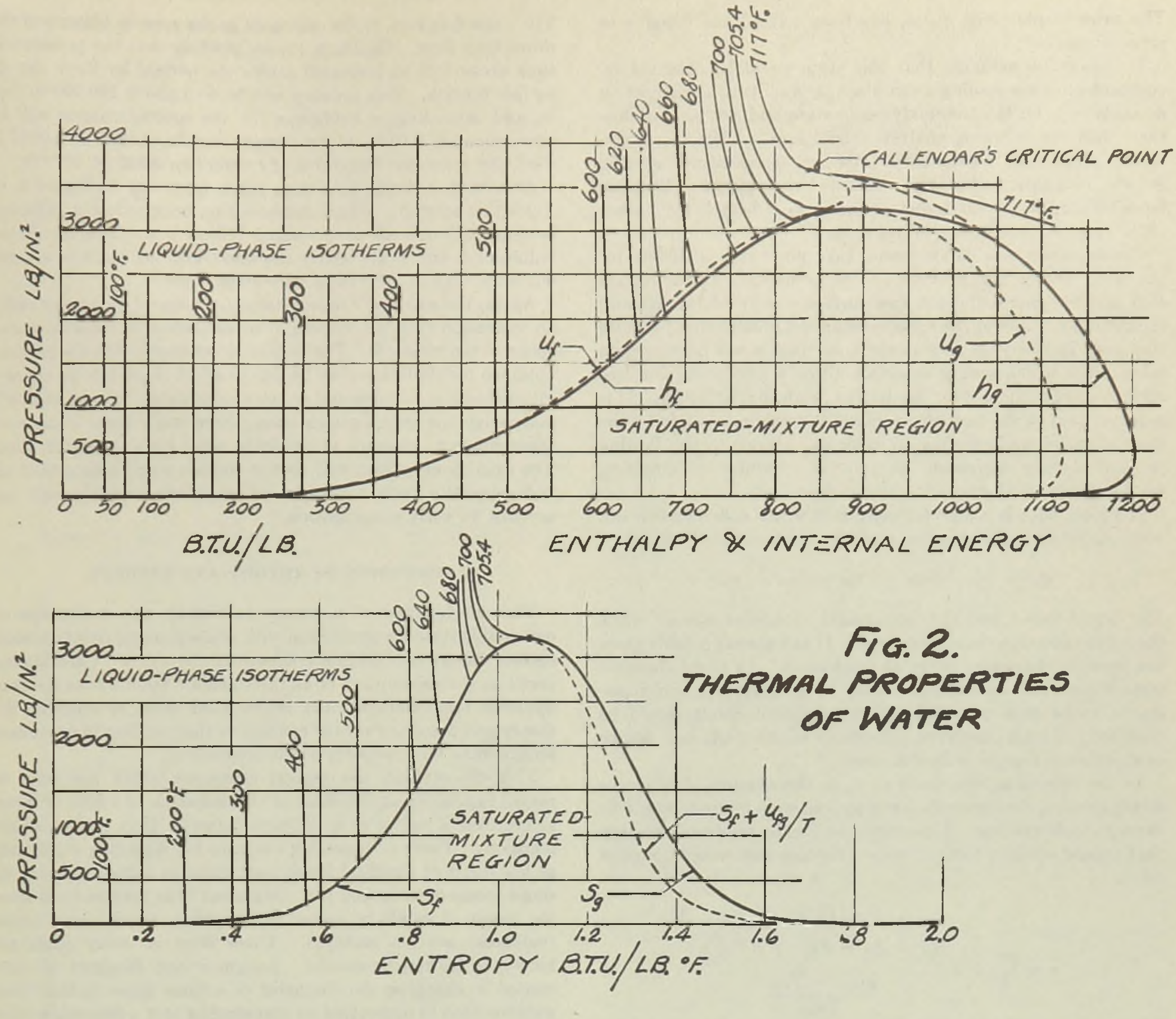

FIG. 2. THERMAL PROPERTIES OF WATER

energy is part of the total energy of all mass involved. If, as predicted by Gibbs, adsorption occurs at an interface so as to make the free interfacial energy a minimum, then one might expect the surface film to thicken with increase in temperature as expressed (*23*). Thus, one might be led to believe that adsorption occurs in more than monomolecular films at higher temperatures. If such is the case, one might expect deviations from the normal latent heat depending upon the thickening of the surface film.

From the above it is apparent that the normal internal latent heat of vaporization is approximately equal to the energy of liquid-vapor interface formation from the bulk liquid—i.e., when no ebullator is present:

$$u_{lv} = \left(\sigma_{lv} - T\frac{\partial\sigma_{lv}}{\partial T}\right) = u_{fg} \text{ (approx.)}$$

In the case of an ebullator, the thermal effect per unit area is readily expressible as

$$u = (\sigma_{lv} + \sigma_{sv} - \sigma_{ls}) - T\frac{\partial(\sigma_{lv} + \sigma_{sv} - \sigma_{ls})}{\partial T}$$

To use it in the ebullator calculation in place of u_{fg} per pound, it becomes:

$$u = \frac{3v}{2r}\left[(\sigma_{lv} + \sigma_{sv} - \sigma_{ls}) - T\frac{\partial(\sigma_{lv} + \sigma_{sv} - \sigma_{ls})}{\partial T}\right]$$

The 2 in the denominator arises from the original substitution of $(\sigma_{lv} + \sigma_{sv} - \sigma_{ls})$ for 2 σ_{lv} or the equivalent substitution of $(\sigma_{lv} + \sigma_{sv} - \sigma_{ls})/2$ for σ_{lv}. In this manner, need for missing data on integral heats of wetting, adsorption, etc., is avoided. The value of v would apparently be that of the adsorbed state, a state more condensed perhaps than that of the bulk liquid. Thus, ebullition from a liquid-solid interface would require, in general, less than the normal interfacial energy; Figure 2 shows that this would account for the low values of r obtained in the 260° and 222° F. final calculations. If $\sigma_{sv} = \sigma_{ls}$ or the contact angle is 90°, then the energy involved is half the energy of liquid-vapor interface formation. If the contact angle is zero, which is equivalent to no ebullator being present, $(\sigma_{sv} - \sigma_{ls}) = \sigma_{lv}$, then the energy involved becomes equivalent to that used in treating critical temperature ebullition.

APPLICATION OF THEORY TO CONDENSATION

Considerable data on the condensation of supersaturated steam in a turbine nozzle are available (*54*, *61*, *62*). Figure 3 is drawn to represent the various states that occur. The initial state of the superheated vapor is shown at 1′. The saturated vapor state where condensation would be expected to begin appears at 2′; this often does not occur, but expansion and cooling take place until at 3 the vapor exists in a supersaturated state and lies on the metastable pressure and temperature curves (dashed lines)

The ratio of pressures, p_3/p_s, has been termed the "degree of supersaturation".

If it may be assumed that this state could be attained by constant-pressure cooling from state 2, and that condensation depends only on the thermodynamic state and not on past history, then the following analysis should apply. The thermodynamic properties, particularly pressure, temperature, specific volume, enthalpy, and entropy, at state 3 are needed. These can be calculated with reasonable accuracy as indicated by Yellott (*61*), whose data will be used here.

Condensation of a vapor cannot take place spontaneously for the same reasons that prevent bubble formation. Condensation also involves increasing the free surface energy of the system; it cannot take place unless some substance is present that provides this and, thus, serves as a nucleus, or until some phenomenon takes place which makes available all or a portion of the free surface energy required for the drop or drops that first form. It is assumed that in the case of the nozzle the vapor does this by the mechanism of undercooling by rejecting energy to the flowing jet and thereby increasing its velocity. Similar undercooling would take place at constant pressure from state 2.

If a solid, such as a dust particle, upon which condensation can occur, is present, then the free surface energy required will be

$$\sigma_{lv} + (\sigma_{ls} - \sigma_{sv}) = \sigma_{lv} - (\sigma_{sv} - \sigma_{ls})$$

The liquid-vapor and the liquid-solid interfaces appear while the solid-vapor interface disappears. If extraneous soluble gases are present, these may serve as condensers. In cloud chamber tests Wilson (*59*) found it necessary to condense out nuclei (assumed to be dust particles) before consistent results could be obtained. He also observed differences in the maximum degree of supersaturation for different gases.

In the case of a pure vapor—i.e., in the absence of any condensing nuclei, the free surface energy $2\ \sigma_{lv}$ must be made available through undercooling. The expression for the radius of the drop that should initially form in state 4 for this case would be given by:

$$r = \frac{3V}{A} = 3\ \frac{\dfrac{{}_2(Ts)_3 v}{u_{fg} - {}_2(u - Ts)_3 + AT\,\dfrac{\partial\sigma}{\partial T}}}{\dfrac{2\ {}_2(u - Ts)_3}{2\ \sigma_{lv}}}$$

Since the total interfacial energy is combined with or is a part of the total energy of the drops formed, condensation as drops may take place with reduced latent heat, the reduction being the total interfacial energy as shown. Presumably $\sigma_{lv} - (\sigma_{sv} - \sigma_{ls})$ may be substituted for $2\ \sigma_{lv}$ when a condensing nucleus is present.

The following calculation utilizes the data of Yellott (*61*) as illustrated in his sample calculation of the properties of the supersaturated state:

State	p	t	T	h	u	s	Ts	$u - Ts$
2	12	202	662	1146.7	1074.7	2.583	1711	−636
3	12	139	599	1113.	1048.2	2.53	1516	−468
4	12	202	662	1111.4	1046.6	2.53	1675	−628

$${}_2h_3 = -33.7;\ {}_2u_3 = -26.5;\ {}_2(Ts)_3 = -195;\ {}_2(u - Ts)_3 = 168$$

$\sigma_{lv} = 5.11 \times 10^{-6}$ B.t.u./sq. ft. (Figure 2 of preceding article)

$$A = \frac{2 \times 168}{2 \times 5.11 \times 10^{-6}} = 32.9 \times 10^{6} \text{ sq. ft.}$$

$$AT\,\frac{\partial\sigma}{\partial T} = 32.9 \times 10^{6} \times 662 \times 0.88 \times 10^{-8} = -191.5 \text{ B.t.u.}$$

$$V = \frac{195 \times 0.014}{904 - 168 - 191.5} = 5.02 \times 10^{-3} \text{ cu. ft.}$$

$$r = 3\,\frac{V}{A} = \frac{3 \times 5.02 \times 10^{-3}}{32.9 \times 10^{6}} = 0.457 \times 10^{-9} \text{ ft.}$$

The value 0.014 cu. ft./lb. was used as the specific volume of the drops that form. Capillary theory predicts that the pressure in such drops will be increased above the normal by $2\sigma/r$ due to surface tension. This pressure will be well above 100,000 lb./sq. in. and, according to Bridgman (*7*), the specific volume will be approximately 0.014. If the normal specific volume of 0.0167 is used, the corresponding value of r would be 0.545×10^{-9} ft.

As a further check, data were taken from test A, Figure 9, of Yellott's paper (*61*) where condensation occurred at a different pressure but still at the so-called Wilson line. The calculated values of A and V are nearly the same, and the value of r turns out to be 0.45×10^{-9} ft., a very close check.

Again, the value of r falls within the range of molecular radii, an indication that the nucleus of condensation of supersaturated steam is the molecule. The lack of closer check with the nucleus obtained for ebullition may be due to effect of jet kinetic energy, internal friction or viscosity, or extraneous gases. To the author's knowledge the investigators from whose work these data were taken made no attempt to eliminate gases from the steam used. The usual boiler steam will always contain small amounts of air and especially carbon dioxide, which is very soluble and can account for early condensation.

DISCUSSION OF THEORY AND RESULTS

The development of a theory to explain the occurrence of metastable states in connection with phase changes points toward surface energy or capillarity effects as the cause. Calculations based on the assumption of an intermediate state whose thermodynamic requirements must be satisfied seem to confirm the theory and point toward the conclusion that capillarity or surface tension may be a property of the molecule.

This differs from the general consensus which has been to regard capillarity as the effect of the operation of a field of force, active over a region or at distances greater than molecular dimensions. There is increasing evidence for regarding capillarity as the result of chemical forces and, thus, as being expended on single atoms or molecules (*1*). Adsorbed films may be considered the result of capillary action on a surface where these forces (valences) are not satisfied. These films in many cases are known to be monomolecular. Langmuir and Blodgett (*5*) succeeded in changing the character of a clean glass surface from water-wetted to nonwetted by transferring to it a monomolecular film of the calcium salt of a fatty acid. Thus the adhesion energy was changed from positive to negative. Experiments on the relation between the tension and the thickness of stretched soap films indicate that these films could be reduced to the black state, 0.000007 to 0.000014 mm. or about two molecules thick, with essentially no change of tension (*48*). La Place's theory on capillarity was built on the supposition of "molecular forces insensible at sensible distances". Adam came to the conclusion that "the forces around the molecules which give rise to the phenomenon of capillarity are identical with those which cause chemical reaction" (*1*). Langmuir expressed the same view (*35*).

One may thus view the phase transformation in the light of a chemical reaction. Physical chemists have long regarded phase equilibrium as chemical (*52*). The ebullator may then be looked upon as a catalyst whose role is to supply either a portion or all of the free energy required for the transformation to occur in the initial step.

There is other supporting evidence (*1, 21, 53*) that this may be the role of the catalyst in general (at least in a number of heterogenous reactions), and that at temperatures below some particular temperature or at energy states below some particular energy level (*52*), such reactions do not or cannot take place at all. In the particular reactive state, the reactants have acquired, through temperature increase and by means of the catalyst, the free energy required by the product as it must initially form.

Some interesting evidence in this connection is furnished by

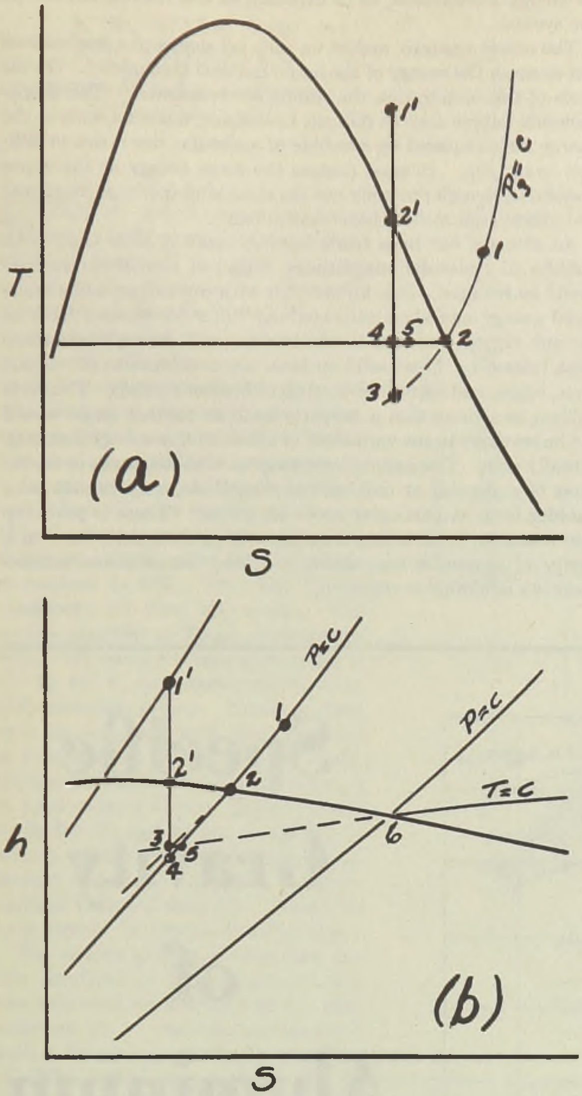

Figure 3. Condensation from Supersaturated Vapor

Baker (*2*) who succeeded in "raising" the boiling point of a number of liquids, including hexane, carbon tetrachloride, ethanol, mercury, and benzene, by large values after drying them thoroughly. Many substances appear to become chemically inert in their dry or concentrated and pure state. Water, which is ever present, may be the catalyst that makes possible many reactions considered normal.

In the calculation involving the critical temperature of water, 717° F. was used rather than the usual accepted value of 705.4° F. Callendar (*10*), trying to obtain more precise data on the thermodynamic properties of water in the critical region, found that when care was taken to eliminate air from the test specimen, considerable difference in density and enthalpy existed between the saturated liquid and the saturated vapor when the usual critical temperature 374° C. (705.4° F.) was reached. A further increase to 380.5° C. (717° F.) was required to make this difference disappear. In this region the liquid and the vapor appeared to be in an unstable equilibrium which was upset by small traces of impurity which caused them to mix or the liquid to ebullate. Maas and Geddes (*37*) observed the same phenomenon in various organic liquids; they concluded that the densities of the saturated liquid and vapor approach each other asymptotically, and become identical at a temperature higher than the usual accepted critical temperature. This has in the past been taken as the temperature at which the meniscus is observed to disappear. Since this test is usually made in a glass tube, the glass surface must be completely wetted; otherwise error is likely to result. It appears, therefore, that the usual value (705.4° F.) may be the result of both the method and the presence of impurities. The dashed lines in Figure 2 are modifications in accordance with Callendar's observations (*10, 51*).

The similarity between the total capillary energy curve and the internal latent heat curve, when plotted against temperature, has been pointed out (*64*). That one can be calculated from the other is indicated, and reasonably good checks are obtained at some temperatures. If a constant value of molecular radius is used with the generally accepted data on surface energy, the capillary energy per pound of molecules exceeds the usual latent heat at high temperatures but falls short at low temperatures. At low temperatures liquid water and also the vapor are known to be polymerized or associated. Thus, the molecular radius so used might well be a variable, subject to the degree of association. Furthermore, it is probable that the ordinary latent heat of vaporization is made up of the latent heat of dissociation of these polymers as well as the capillary energy. Again, the surface tension data available may not be sufficiently correct because of limitations inherent in the method of determination, and thus not suitable for this type of calculation.

The general theory indicates that phase changes, particularly vaporization and condensation, are not smooth processes but must be represented by a discontinuity between the properties of the bulk phases. The disturbing cause appears to be the free interfacial energy required by the new phase which must appear in definite units. That this theory can be also used to explain the development of the metastable or undercooled liquid state, or the failure of liquids to solidify when cooled to temperatures less than the usual melting point, is borne out by the following evidence (*16*). The lower limit of undercooling of water appears to be about −21° C. As a result of careful work Mayer and Pfaff (*16*) concluded that within the range 0° to −21° C. the presence of foreign substances is essential to the spontaneous freezing of water and that the limiting or freezing "temperature is a characteristic of the specimen, varying from one to another as do the foreign solids that serve as nuclei". The melting of ice below the usual melting point has been observed and attributed to the presence of impurities. Tyndall's "flowers of ice", observed when a cake of ice was subjected to light rays, are interesting. The six petals observed may indicate the common edges of the ice crystals whose interfacial energy with respect to the liquid formed may be responsible. Tyndall's explanation of the clicking sound that accompanies this phenomenon of water cavity formation now appears reasonable. The cavity is larger than the water included; hence ebullition must also occur.

The superheating of ice has been considered impossible by some investigators; however, the theory predicts such a phenomenon. Carnelly (*11*) reported heating ice to a temperature far above the normal melting point which was possible, he says, only when the pressure was maintained below the vapor pressure of water at 0° C.

All experimenters have reported that the metastable state of the liquid could be terminated by mechanical shock. Shock may be a mechanism whereby the free interfacial energy necessary for transformation is supplied. In the case of adiabatic flow of a fluid, one may expect that friction, which is the irreversible conversion of an ordered kinetic energy into internal kinetic energy, would have some effect on the termination of the metastable state. Such an effect appears to have been observed by Yellott (*62*) when a change of nozzle design away from the ideal resulted in early or "preliminary" condensation of the vapor. Again, as the back pressure in these experiments was raised above the back pressure for which the nozzle was designed, early condensation occurred. Undoubtedly the well known phenomenon called "compression shock" was brought about and, being highly irreversible, accounts for the early condensation observed.

Several excellent articles (*12*, *15*, *24*) have appeared recently which deal with gas bubble formation in a liquid. The approach is principally physical, with considerable attention given to the contact angle and surface cavities as sources of gas which serves as the nucleus for bubble formation. Bubble formation within the liquid with no ebullator is not treated.

The present discussion has been entirely thermodynamic, and the only assumption made regarding the bubble is that it must be spherical and that there may be a number of bubbles of the same size. It has been suggested (*12*, *31*) that bubbles may form in various sizes, that only those larger than a critical size will grow, and that the smaller ones will condense. For such a system the superheat would be dependent upon the bubble size, and all sizes from the critical size to infinity would be possible, with no superheat necessary for the formation of bubbles sufficiently large. Experimental observations indicate that in the absence of nuclei very large degrees of liquid superheat are possible and that bubbles are very small initially, approaching molecular magnitudes (*28*). Condensation is a similar phenomenon, and initial drops observed are of molecular magnitude (*61*). The critical size hypothesis finds its basis in statistical mechanics which allows for energy fluctuations, to be expected as one reduces the size of the system.

The above analysis makes no such allowance for fluctuations but assumes the energy of the liquid uniform throughout. On the basis of this assumption the results are reasonable. The single-molecule bubble may be difficult to imagine, but a moecule in the energy state required by a bubble of molecular size is not so difficult to imagine. It must possess the same energy as the vapor molecule although probably not the same kind (perhaps rotational and vibrational rather than translational).

An attempt has been made here to make it clear that, with bubbles of molecular magnitudes, nuclei of similar dimensions would be required. It is known that with crystalline solids interfacial energy and chemical reactivity differ for various faces of the unit crystal and may be a maximum at a corner where three faces intersect. Most solid surfaces are a composite of various faces, edges, and corners of crystals or broken crystals. Thus it is natural to assume that a property such as contact angle would not be sensitive to the variations of adhesion free energy that may actually exist. This assumption, coupled with roughness or curvatures of molecular or unit crystal magnitude, may explain why bubbles form at particular spots on a solid. There is probably also reason to believe that a bubble will preferentially form in a cavity of molecular magnitude, provided the adhesion tension there is a minimum or negative.

Specific Gravity of Aluminum Sulfate Solutions

Data on the specific gravity of aluminum sulfate solutions covering the temperature range 15° to 105° C. and concentrations from zero to saturation are presented. Specific gravity data for aluminum sulfate solutions above 45° C. or above 26% concentration were not available previously. The data are considered to be accurate within ±0.25% concentration.

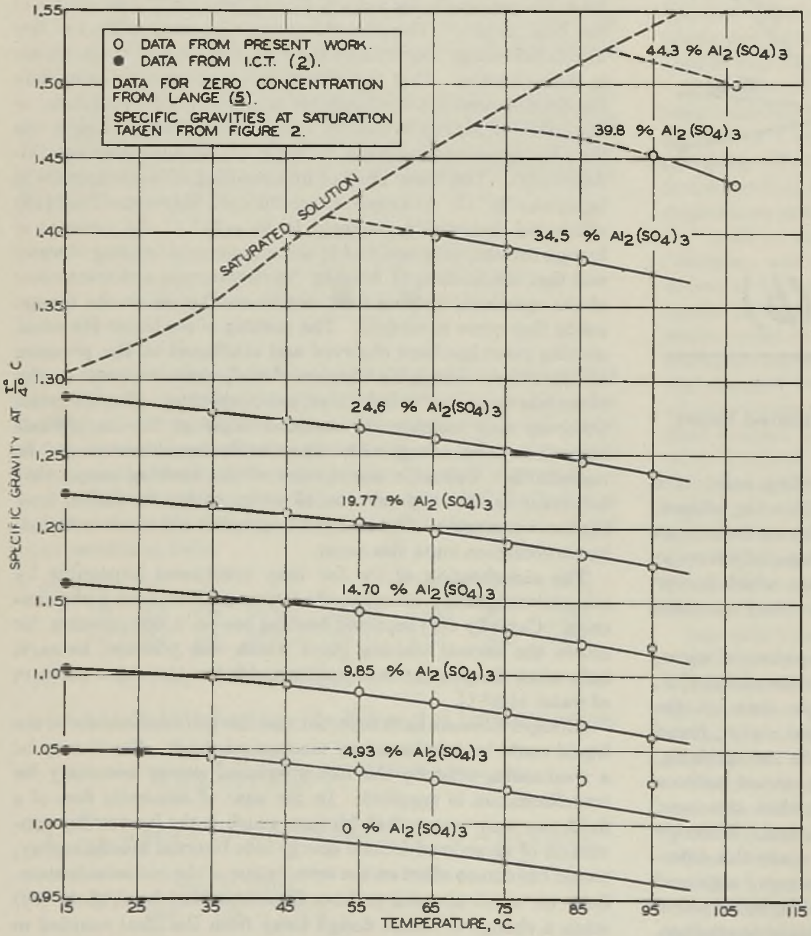

Figure 1. Experimental Values for Specific Gravity of Aluminum Sulfate Solutions

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SPECIFIC gravity data, covering concentrations of aluminum sulfate solutions from 15° to 105° C., were needed in the development of an acid process for alumina from clay (*8*). The data were intended originally for pilot-plant work; therefore experimental methods were chosen to give only the precision necessary for such work. However, a review of the data indicated that they are of sufficient accuracy to be of general interest. International Critical Tables (*2*) give specific gravities at 15° C. for concentrations to 26% aluminum sulfate and at 25° C. for concentrations to 6%. The data in the handbooks are from this source. The specific gravities of Reuss, reported by Mellor (*6*), cover a temperature range of 15° to 45° C. for concentrations up to 25% aluminum sulfate. However, these data do not agree with those reported in International Critical Tables. Solubilities of aluminum sulfate are reported in International Critical Tables (*4*) and by Seidell (*7*), and boiling points of aluminum sulfate solutions are given by Badger and France (*1*) and in International Critical Tables (*3*). These data were used in the present investigation.

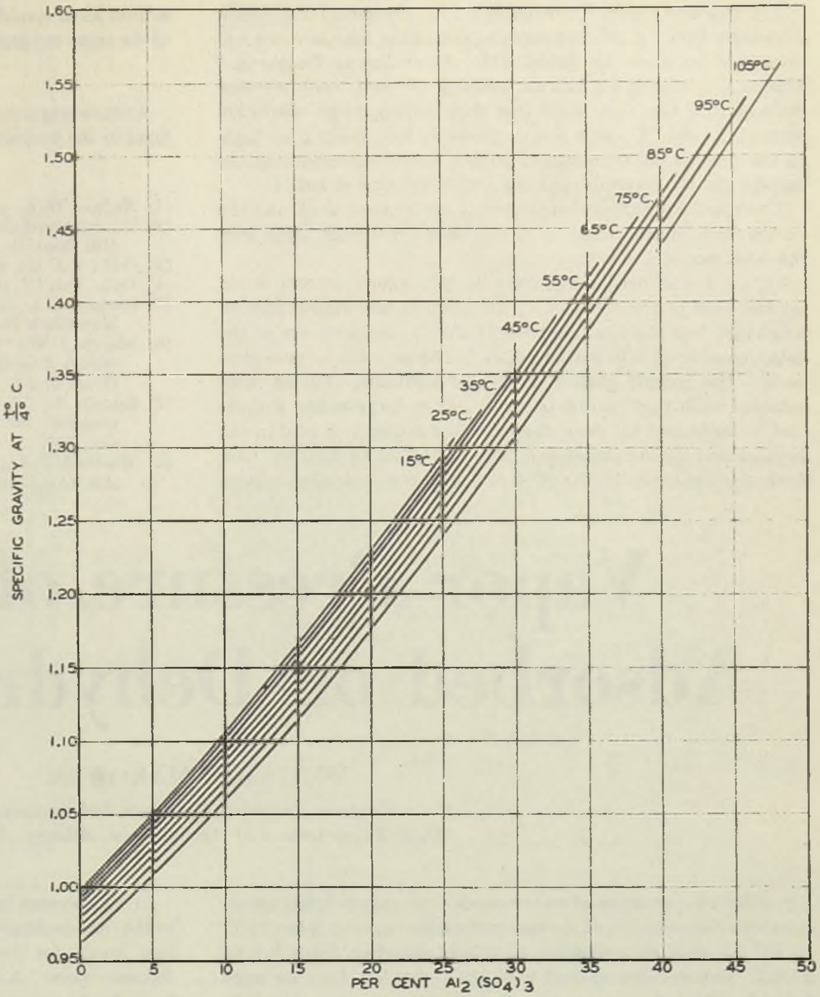

Figure 2. Isotherms of Aluminum Sulfate Solutions

The specific gravity of aluminum sulfate solutions of known concentration was measured by standard 25-ml. pycnometers in a controlled-temperature bath. Reagent-grade aluminum sulfate [$Al_2(SO_4)_3.18H_2O$] was used for the determinations. Separate solutions were made up to contain nominally 5, 10, 15, 20, 25, 30, 35, and 40% by weight of aluminum sulfate (the solutions above 25% were solid at room temperature). Determinations were made for each concentration, when possible, at approximately 35°, 45°, 55°, 65°, 75°, 85°, 95°, and 105° C. The concentration of each solution was checked by gravimetric determination of the aluminum content at the beginning, mid-point, and end of each series. The solutions were kept in glass-stoppered bottles in a constant-temperature oven, held a few degrees below the temperature at which the specific gravity was to be determined. The pycnometers were calibrated in the bath at the temperature to be used for every determination. Calibrations up to and including 85° C. were made with distilled water, and at the higher temperatures, with mercury. The specific volumes of water and mercury were taken from Lange (*5*). Temperature was measured by a thermometer checked by the National Bureau of Standards. The pycnometers were weighed to 0.1 mg., and all weights were corrected to vacuum. The specific gravities of the solutions were calculated with reference to water at 4° C. Some difficulties were experienced in keeping the solutions at constant concentration. The nominally 30% solution varied in concentration and resulted in unreliable determinations, and the entire series was therefore discarded. The discrepancies for two points on the 5% curve and one point on the 15% curve (Figure 1) are probably also due to variations in concentration of the solutions.

The experimental data are presented in Table I and Figure 1. The points shown for 15° C. on Figure 1 were obtained by interpolation from data of International Critical Tables (*2*); these points are in excellent agreement with the experimental data. The values for specific gravity of water, included for comparison, were taken from Lange (*5*). The saturation line was taken from the upper ends of the isotherms of Figure 2. The extrapolations for the 34.5, 39.8, and 44.3% aluminum sulfate curves were also taken from Figure 2.

TABLE I. EXPERIMENTAL VALUES FOR SPECIFIC GRAVITY OF ALUMINUM SULFATE SOLUTIONS

Temp., ° C.	d_4^t at $Al_2(SO_4)_3$ Concentration of:							
	4.93%	9.85%	14.79%	19.77%	24.6%	34.5%	39.8%	44.3%
34.9	1.0440	1.0980	1.1539	1.2147	1.2785	...	...	...
45.0	1.0399	1.0930	1.1484	1.2092	1.2726	...	...	...
55.0	1.0347	1.0879	1.1426	1.2033	1.2666	...	...	...
65.2	1.0288	1.0805	1.1361	1.1964	1.2603	1.3968	...	...
75.2	1.0222	1.0742	1.1281	1.1881	1.2513	1.3880	...	...
85.4	1.0296	1.0665	1.1213	1.1811	1.2446	1.3809	...	...
95.0	1.0288	1.0598	1.1206	1.1751	1.2381	...	1.4542	...
106.2	...	...	...	...	...	...	1.4332	1.5014

The curves of Figure 2 were derived from the curves of Figure 1. The upper limits of the isotherms represent the concentrations at saturation as given by Seidell (*7*). According to Badger and France (*1*), aluminum sulfate solution of 44% concentration boils at 105° C.; they state that their boiling point values are accurate to ± 1° C., with results probably low rather than high. In the present work no sign of boiling was observed during the specific gravity determination for a 40% solution at 106° C.

The specific gravities determined in the present work and the values from International Critical Tables (*2*) do not agree with the data from Mellor (*6*).

Figure 2 was used extensively in pilot-plant control work. On the basis of the precision of the temperature measurements, weighings, and chemical analyses (Table I), the accuracy of the data is considered to be within ± 0.25% concentration for pure solutions. The specific gravity of impure solutions, such as those obtained from the reaction between clay or bauxite and sulfuric acid, is influenced by the excess of either alumina or acid in the solution and by the presence of iron and other impurities. According to data from Mellor (*6*), solutions of commercial aluminum sulfate have specific gravities lower than those of pure solutions of the same concentration.

ACKNOWLEDGMENT

Acknowledgment is made to Philip Miller for helpful suggestions in the preparation of this paper.

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Vapor Pressure of Water Adsorbed on Dehydrated Eggs

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Equilibrium pressure of water vapor over spray-dried whole eggs was determined at six temperatures varying from 17.1° to 70° C. and at moisture contents ranging from 0.5 to 5.5%. The results agreed well with similar data on eggs dried from the frozen state and with the less extensive data published by Gane (*6*). The results were analyzed by a graphical method suggested by Othmer (*10*), and from this analysis was derived the isosteric heat of adsorption of water on dried eggs at various moisture levels. The ratio of the isosteric heat to the latent heat of condensation of water vapor increases from 1.1 to 2.1 as the moisture content decreases from 5.5 to 0.5%. It was also shown that the adsorption isotherms can be represented, within certain limits, by the Brunauer, Emmett, and Teller theory (*4*) of adsorption of gases on solids.

KNOWLEDGE of the vapor pressure of water over dehydrated eggs is essential in the design of drying equipment for eggs and in the selection of packaging material for the dry product (*11*). The recent trend in drying toward lower moisture levels has brought about a need for vapor pressure data for eggs that contain less than 2% of water. The data in the literature for this moisture region are meager. Measurements previously obtained in this laboratory (*9*) and by Stuart *et al.* (*14*) were taken at one temperature only. Gane (*6*) measured the equilibrium moisture content at various temperatures and moisture levels, but the vapor pressure data derivable from his data do not adequately cover the region below 2% of water. As Gane points out, his results apply only to the sample of spray-dried eggs used. Vapor pressure may vary with different lots of eggs, as a result of differences in composition or differences in the method of drying or other treatment.

In the present investigation the measurements were extended to the low-moisture region and also repeated at the higher moisture levels, for the purpose of comparing materials prepared in different ways. A sample of dried whole eggs, prepared by drying from the frozen state (lyophilizing), was also included. In the latter method any deteriorative changes are likely to be minimized.

MATERIALS AND METHOD

Spray-dried eggs obtained from a commercial source contained initially about 5% of water. The lyophilized eggs prepared in this laboratory had a moisture content of about 2%. Ten samples of each kind of powder were adjusted to moisture contents covering a range from 0.5 to 5.5%. The samples were adjusted in one of two ways. One method involved addition of a known weight of water to a weighed sample that had been vacuum-dried at room temperature to a moisture level of about 0.2%. The water was evaporated from one vessel and adsorbed from the vapor phase by the powder in another vessel. The transfer was effected in a closed system, in the absence of air. The other method consisted in placing the sample in a vacuum desiccator that served as a constant-humidity chamber. The humidity was controlled by an aqueous sulfuric acid solution of known concentration (*8*). The sample either lost or gained water until equilibrium moisture content had been reached.

The moisture contents of the samples were determined by drying in a vacuum oven at 100° C. for 5 hours at a pressure of 2 to 5 mm. of mercury. This procedure is similar to the A.O.A.C. method (*1*) and is generally used in the industry. (Passage of dry air through the oven, as specified in the A.O.A.C. method, had no appreciable effect on results and was not included.) Vapor pressure measurements are expressed in terms of results obtained by this procedure, although actual water contents are believed to have been somewhat lower. When water contents of a number of samples were determined by drying to constant weight at room temperature (to minimize decomposition) in evacuated desiccators that contained magnesium perchlorate as the desiccant, it was found that the results were about 0.15% lower than those obtained by the vacuum-oven method. If it is as-

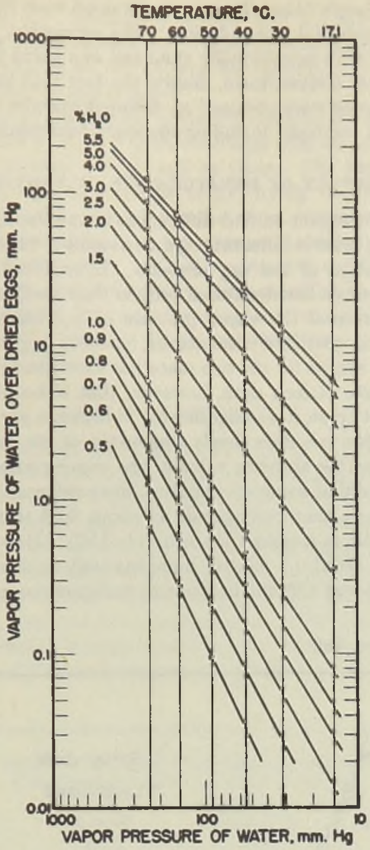

Figure 1. Isosteres of Water Adsorbed on Spray-Dried Egg Powder at Moisture Contents of 0.5 to 5.5%

sumed that the low-temperature drying method yields a more accurate measure of the water content, the present lower moisture limit (0.5%, oven method) for vapor pressure measurements was actually 0.35%. Lindsay and Mansfield (*7*) found nearly the same discrepancy (0.13%) between the results of the A.O.A.C. method and those obtained by drying in high vacuum at 78° C.

A manometric method was used for the determination of vapor pressure. The manometers were U-shaped and contained either oil or mercury. For pressures lower than about 25 mm. of mercury, Octoil (Distillation Products, Inc.) was used as the manometric fluid in an apparatus described by Makower and Myers (*9*). At higher pressures this apparatus could not be used because of condensation of water vapor in the manometer. A modified form was therefore constructed as follows: Mercury was used as the manometric fluid, and the apparatus was modified so that it could be completely immersed in a constant-temperature water bath. Glass-to-glass seals were used in place of ground joints, and stopcocks were eliminated. The modified unit was identical in principle to the one mentioned above. It consisted of a 100-cc. round-bottom flask connected through a small U-trap to a mercury manometer. The two limbs of the manometer were joined across the top (in a Y-joint) to a common tube through which the system could be evacuated. A sample of eggs weighing about 20 grams was introduced into the flask through a side-neck which was then sealed off. The whole unit was evacuated on a high-vacuum pumping system and sealed off near the Y-joint. Two seals were made—one to separate the flask side of the manometer from the reference side, and the other to separate the reference side from the pumping system. During evacuation and sealing, the trap was cooled to −80° C. to prevent the loss of water from the egg sample. The sample itself could not be cooled because it was found to contain adsorbed carbon dioxide, which is difficult to pump off at low temperatures.

The measurement of the pressure was made first at the lowest temperature, 17.1° C., and then at successively higher temperatures, 30°, 40°, 50°, 60°, and 70° C. The pressures in the sealed-off mercury manometers were read with the aid of a cathetometer, with a precision of ±0.05 mm. of mercury. The oil-filled manometers could be read directly with similar precision. Pressure readings were taken for 3 to 4 hours, and it was generally found that the time required to attain equilibrium pressure was approximately 1 hour, which was about the same as the estimated time for the attainment of temperature equilibrium.

During the measurements at 70° C. it was found that the apparent vapor pressure increased with time. The cause of this increase was principally attributable to the evolution of carbon dioxide gas, presumably from some decomposition process.

The identity of the evolved gas was established from the following observations and experiments: (*a*) The gas was uncondensable at dry ice temperature but was condensed at the temperature of liquid oxygen, −183° C. Hence it could not be either oxygen or nitrogen, but it could be carbon dioxide. (*b*) A 300-gram sample of eggs was evacuated on a high vacuum system (oil and diffusion pumps) at room temperature for 3 days and then at 105° C. for 3 hours. This pumping period was intended to remove all the water and adsorbed gases. At the end of this period the gases evolved upon further heating at 105° C. for 4 hours were collected in a liquid air trap. The trap was then warmed with a dry ice bath, and the distilled gas was collected in a second trap cooled with liquid air. The distillate (45 mg.) was then transferred to a gas buret to determine its density, and from this measurement the molecular weight of the gas was calculated to be 44.0 ± 0.2. This is within experimental error, equal to the molecular weight of carbon dioxide. (*c*) The identity of the gas was further confirmed by the well known lime-water test.

The amount of carbon dioxide formed in the Octoil manometers could be determined and corrected for by freezing out the water vapor and measuring the pressure of the residual gas, as explained previously (*9*). This procedure was adopted for measurements at all temperatures merely as a precautionary measure, even though the rate of formation of carbon dioxide below 50° C. was very small. When the sealed mercury manometers were used, similar determination of the evolved gas was not feasible. It is shown later that the error thus introduced becomes appreciable only in the case of the measurements at 70° C.

SPRAY-DRIED AND LYOPHILIZED EGGS

The experimental data at each temperature were smoothed graphically by plotting the measured vapor pressure against the moisture content. From these curves (isotherms) the values of vapor pressure at various chosen values of moisture content were then obtained by graphical interpolation. The results for spray-dried eggs are listed in Table I. Included also are values at low moistures and temperatures, obtained by extrapolation of the linear plots shown in Figure 1. This figure, constructed from data in Table I, shows the variation of vapor pressure with temperature at various chosen values of the moisture content in a graphical form suggested by Othmer (*10*). Vapor pressure of water in equilibrium with the eggs is plotted against the vapor

TABLE I. AQUEOUS VAPOR-PRESSURE OVER SPRAY-DRIED EGGS AT VARIOUS TEMPERATURES AND MOISTURE LEVELS[a]

Moisture Content, %[b]	Vapor Pressure, Mm. of Hg at 0° C.					
	17.1° C.	30° C.	40° C.	50° C.	60° C.	70° C.
0.5	*0.002*	*0.011*	*0.034*	0.1_6	0.2_8	0.6_7
0.6	*0.006*	*0.028*	*0.078*	0.2_1	0.5_5	1.2_5
0.7	*0.014*	*0.057*	*0.15*	0.3_5	0.9_1	2.0_5
0.8	*0.027*	*0.10*	0.2_8	0.6_3	1.4_0	3.1
0.9	*0.046*	*0.17*	0.4_5	0.9_8	2.0_5	4.3
1.0	*0.076*	*0.26*	0.6_2	1.3_2	2.8	5.9
1.5	0.3_6	0.9_2	2.0_8	4.4	8.4	17.5
2.0	0.7_3	1.9_5	3.9	8.2	15.7	31
2.5	1.1_7	3.1_0	6.2	12.7	23	44
3.0	1.7_2	4.5	8.8	17.3	31	59
4.0	3.2	7.8	15.2	27	48	88
5.0	4.9	11.7	21.3	37	64	105
5.5	5.9	13.3	24.2	42	72	125

[a] The italicized values were obtained by graphical extrapolation of the straight-line plots in Figure 1. Other values were taken from smooth curves obtained by plotting logarithm of vapor pressure against moisture content. The deviations of the measured values from the smooth curves are not greater than ±1 in the last significant figure. Where the last figure is subscript, the deviation is ±5 in that decimal place.

[b] Moisture content on wet basis, determined by the vacuum-oven method.

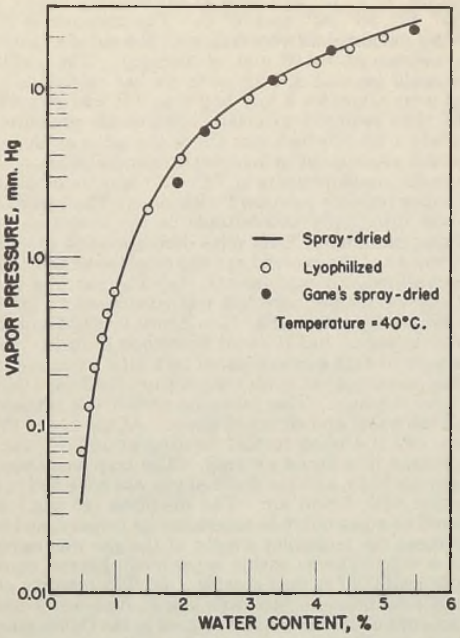

Figure 2. Comparison of Vapor Pressure Results on Spray-Dried with Those on Lyophilized Eggs and with Data of Gane (6) at 40° C.

pressure of pure water at the same temperature on logarithmic coordinates. Linear plots (isosteres) are thus obtained, and the slope of the line is numerically equal to the ratio of the isosteric heat of adsorption of water by eggs to the heat of condensation of water vapor at the same temperature. The deviation of the data points from the straight lines is within the experimental error for all temperatures except 70° C. The values for 70° C., at moisture levels of 1% and higher, appear to be too high by 5 to 10% of the pressure obtained by extrapolation of the straight lines.

The principal cause of this discrepancy was the evolution of carbon dioxide at the high temperature. The presence of this gas did not interfere with the measurements of pressures below 25 mm. of mercury, when the Octoil manometers were used, because the gas was uncondensable at −80° C. and was corrected for in the course of the measurements. In the experiments at higher pressures, when the sealed mercury manometers were used, it was not possible to make the correction. The amount of gas could not have been very great, however, up to 60° C., as judged by the straight-line relation in Figure 1. The lines in Figure 1 are determined principally by the "corrected" values, since they occur in the majority up to 60° C.

The results for lyophilized eggs are not given in detail, since they were nearly identical with those for spray-dried eggs. Figure 2 compares the two sets of results at one temperature, 40° C.; the vapor pressure is plotted against the moisture content. The curve was constructed from the data for spray-dried eggs in Table I. The open circles represent the results for lyophilized eggs. The agreement between the two sets of results is close. The rate of change of vapor pressure with the moisture content becomes very high in the low-moisture region, and the deviations of the points from the curve in this region are to be attributed to the uncertainty in the moisture content (±0.05%) rather than to differences in vapor pressure.

Comparison with Data of Gane. It was of interest to compare the present results with those obtained previously by Gane (*6*) on spray-dried whole egg. The black circles in Figure 2 represent Gane's data. They were obtained from Figure 2 of his paper by graphical interpolation. The agreement with our results at 40° C. is exceptionally close and was found to be equally close at other temperatures, despite the fact that the data from the two sources were obtained on different samples of dried eggs by different methods, including moisture determination.

EFFECT OF DENATURATION OF PROTEIN

One might expect to find differences in the vapor pressure of egg powders dried in different ways, as a result of varying amounts of denaturation of the egg proteins. Lyophilized eggs would probably contain less denatured protein than spray-dried eggs.

Gane compared the vapor pressure of lyophilized egg white with that for completely denatured (cooked) egg white and reported that results for the two materials were nearly alike. It is apparent from Gane's data, however, that although the difference was not great, it was significant; it becomes particularly important at low moisture levels where it is of the same order of magnitude as the absolute value of the vapor pressure. Gane's data indicate that complete denaturation produces an increase in vapor pressure that corresponds to about 0.03 to 0.05 relative humidity unit at moisture levels of 3 to 15%. Barker (*2*) found a change of about 0.1 relative humidity unit on denaturation of crystallizable egg albumin in the same moisture range.

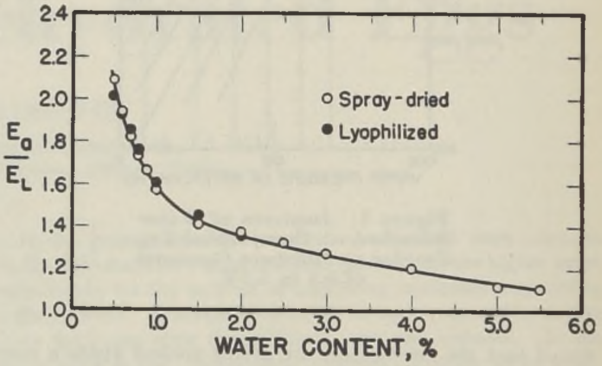

Figure 3. Variation of E_a/E_L (Ratio of Heat of Adsorption of Water on Dried Eggs to Latent Heat of Condensation of Water Vapor) with Water Content

A change of about the same magnitude was observed on heating dried whole eggs, as illustrated in the following experiment: A sample of lyophilized eggs at a moisture level of 0.6% was heated at 70° C. for 20 hours and then at 100° C. for 45 hours. The vapor pressure of the sample (measured at 70° C.) changed from an initial value of 1.0 mm. of mercury to 2.1 mm. at the end of the 70° heating period; at the end of the 100° heating period the pressure increased to 11.6 mm. At the same time the solubility index changed from an initial value of 0.31 to a final value of 0.06 gram of soluble protein per gram of egg. (The solubility index is the amount of soluble protein in 1 gram of egg powder, measured in 0.1 *M* acetate buffer at pH 5.33. Two grams of dried egg powder are placed in a tube containing 100 ml. of the buffer, and the mixture is homogenized by gentle action of a close-fitting rotating rubber plunger. After filtration, the nitrogen content of the filtrate is determined by the Kjeldahl method.) The change in vapor pressure as a result of the heating amounted to 10.6/233 = 0.046 relative humidity unit. (The vapor pressure of pure water at 70° C. is 233 mm. of mercury.)

The rate at which the change occurs is very slow. In the experiment described above, the rate of change amounted to about 0.05 mm. of mercury (or 0.00022 relative humidity unit) per hour at 70° C. Barker (*2*) showed that the rate increases with increasing moisture content. Hence the discrepancies found in our measurements at 70° C. may be accounted for, at least partially, in terms of this change.

The slowness of the change probably explains the agreement of vapor pressure results for lyophilized eggs with those for spray-dried eggs, as measured by us and by Gane. The degree of denaturation that occurred during spray drying was apparently not sufficient to affect appreciably the vapor pressure relations. This fact is important when vapor pressure is used as a measure of the moisture content (*9, 12*). It means that a calibration of vapor pressure *vs.* moisture content, once established, is applicable to samples of dried eggs from various sources. It is assumed that the method of drying does not involve excessively long or drastic heat treatment.

HEAT OF ADSORPTION

The ratio of the heat of adsorption of water by eggs to the heat of condensation of water vapor at the same temperature was calculated from the slope of the isosteres in Figure 1. The results are listed in Table II and shown graphically in Figure 3. The graph also includes the results for lyophilized eggs. The value of the ratio increases slowly from 1.1 at 5.5% water to 1.4 at 1.5% water and then increases very sharply to a value of 2.1 at 0.5% water. Thus, the heat of vaporization of water from eggs that contain 0.5% water is more than twice the heat of vaporization of pure water at the same temperature.

TABLE II. VARIATION IN HEAT OF ADSORPTION WITH MOISTURE CONTENT FOR SPRAY-DRIED EGGS

Moisture Content, %	E_a/E_L*	Moisture Content, %	E_a/E_L*
0.5	2.09	2.0	1.37
0.7	1.82.	3.0	1.27
0.9	1.66	4.0	1.20
1.0	1.57	5.0	1.12
1.5	1.41	5.5	1.11

* E_a is the heat of adsorption of water vapor on eggs; E_L is the heat of condensation of water vapor at the same temperature.

INTERPRETATION IN TERMS OF ADSORPTION THEORY

Most of the water adsorbed by the eggs is presumably taken up by the protein fraction. Shaw (*13*) and Bull (*5*) recently showed that the adsorption of water by proteins is well represented in terms of the adsorption theory of Brunauer, Emmett, and Teller (*4*). It was of interest to apply this theory to the present results on spray-dried eggs.

Figure 4 shows Brunauer-Emmett-Teller plots for three representative isotherms, 30°, 50°, and 70° C., based on the data in Table I. Relative pressure, p/p_o, was plotted as the abscissa and the function $p/a(p_o - p)$ as the ordinate. The symbol p_o represents the water-vapor saturation pressure at the given temperature and p is the aqueous pressure over the eggs at a moisture content of a grams of water per 100 grams of dry eggs. The moisture contents used in this calculation were corrected by subtracting 0.15 from the values listed in Table I. The corrected values were thought to be more accurate, as explained in the section on experimental method. It was found that the data are well represented by straight and nearly parallel lines from the highest measured values at p/p_o equal to about 0.5, down to a certain lower limit that depends on the temperature. The lower limit for p/p_o varied from about 0.05 at 17.1° C. to about 0.12 at 70° C. Bull points out that the value of $p/p_o = 0.5$ is approximately the upper limit of the straight-line relation for many proteins. From the slope and the intercept of the lines it is possible (*4*) to calculate a_1, the number of grams of water adsorbed in the first layer on the surface of 100 grams of dry eggs, and $(E_1 - E_L)$, the difference between the molal heat of adsorption in the first layer and the molal heat of liquefaction of water vapor.

The results of the calculations are shown in Table III. The values of a_1 show a slight decrease with increasing temperature, as might be expected qualitatively from the change of density of water with temperature (*3*). If we assume that all the water in the eggs (at low p/p_o) is adsorbed by proteins alone and assume further that the adsorptive properties of all the proteins are similar to those of egg albumin, we can calculate the percentage of protein in the eggs from the ratio of a_1 for the whole egg to a_1 for egg albumin. From the data of Shaw (*13*), Bull (*5*), and Barker (*2*), the average value of a_1 for egg albumin is 6.0 grams. Values cited by Bull for other proteins are not very different. The average value of a_1 for whole egg (Table III) is 3.5. The ratio of 3.5 to 6.0 yields a value of 58% for the percentage of protein in egg solids. This agrees fairly closely with the value of 51 to 52% usually found by chemical analysis. If any significance is to be attached to the difference between the calculated and the measured value, it would mean that substances other than proteins, such as phospholipides, adsorb a small proportion of the total water.

TABLE III. CONSTANTS CALCULATED ACCORDING TO BRUNAUER-EMMETT-TELLER THEORY

Temp., ° C.	a_1 %	Calories per Mole			
		$E_1 - E_L$	$E_L(6A)$	E_1	E_{a_1} (Isosteric)
17.1	3.7	1630	10,550	12,180	12,820
30	3.6	1590	10,420	12,010	12,720
50	3.5	1460	10,220	11,680	12,570
70	3.3	1260	10,020	11,280	12,550

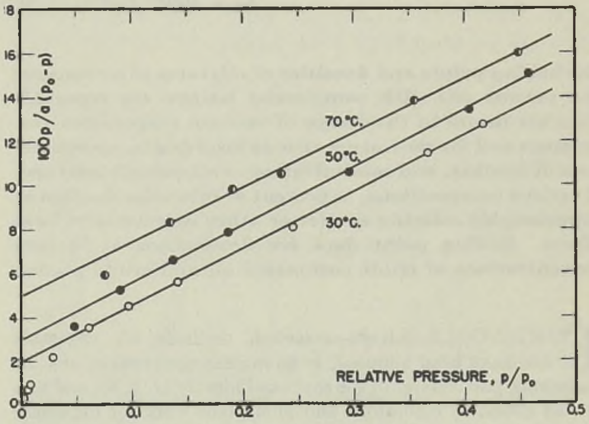

Figure 4. Adsorption of Water Vapor on Dried Eggs Plotted According to Theory of Brunauer, Emmett, and Teller

Table III also gives the values of E_1 that were derived from the calculated values of $(E_1 - E_L)$ and the heat of vaporization of water, E_L. According to the B.E.T. theory, E_1 represents the average heat of adsorption in the first layer, on the less active portion of the surface. Since the heat of adsorption increases with decreasing moisture content, this average value should be greater than the isosteric heat of adsorption E_{a_1} at the moisture content where the formation of the first layer has been completed—namely, at the moisture content corresponding to the value of a_1. Values of E_{a_1} derived from Figure 2 are listed in the last column of Table III.

Comparison with E_1 reveals that E_1 is less than E_{a_1} by 600 to 1200 calories, which is contrary to the supposition stated above. Since this deviation is probably greater than the experimental error in E_{a_1}, it must be assumed that the source of the discrepancy lies in certain simplifying assumptions inherent in the B.E.T. calculations. The discrepancy may be due to the fact that in the theory E_{a_1} is assumed to be equal to E_L, while the experimental results show that E_{a_1} is actually about 25% higher than E_L.

ACKNOWLEDGMENT

Acknowledgment is made to Marjory Galvin for assistance with measurements and to T. M. Shaw and F. Stitt for helpful suggestions.

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SOLVENT EXTRACTION OF COTTONSEED AND PEANUT OILS

Boiling Point—Vapor Pressure—Composition Relations for Miscellas of Oils in Hexane

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The boiling points and densities of mixtures of cottonseed and peanut oils with commercial hexane are reported. They are useful in the design of vacuum evaporators and strippers and for control operations involving temperature, time of heating, and concentration of oil-solvent mixtures of various compositions, to prevent or minimize fixation of objectionable coloring matter or other deteriorative heat effects. Boiling point data are determined at various concentrations of crude cottonseed oil and crude peanut oil, over a range of pressures from 160 to 760 mm. absolute in commercial hexane. The reported data should be of value in the further development of the technology of the solvent extraction of vegetable oils. Observations of the effect of agitation in establishing equilibrium conditions of the oil-solvent mixtures are noted. The Raoult law and the Dühring rule cannot be applied for predicting data of the necessary accuracy within the critical operating region.

CONTINUOUS solvent-extraction methods for vegetable oils have been adopted, to an increasing extent in new installations, particularly in the soybean industry (*1, 4, 6*), and to a limited extent in laboratory and pilot-plant work for obtaining tung oil (*5*). Some viscosity and density data on soybean oil-solvent mixtures have been published (*3*). Cottonseed meal or cake has been commercially extracted both in Europe and South America for some time, but the possibility of solvent extraction of oil from cottonseed and peanut meal has received little attention in the United States except during the last few years. Many technical and engineering problems in applying solvent extraction have not been satisfactorily solved. Some of the difficulties are summarized by Olcott (*6*).

Data obtained in the present study are important in determining the maximum safe temperature, time of heating, and vacuum stripping conditions for cottonseed and peanut miscellas of various concentrations without fixation of the objectionable coloring matter and other deteriorative effects which would impair the value of the oil. Boiling point curves are useful in designing engineering equipment for pilot-plant or full-scale operation. Although some work is reported in related fields (*1, 5, 8*), fundamental engineering data are not generally available for the design of vacuum evaporation and stripping apparatus. Experimental data have been published for separating and recovering solvents such as Naphtha E and ethylene dichloride from cottonseed oil (*2*) in which distillation ranges, at atmospheric pressure, of mixtures containing 50% solvent and 50% cottonseed oil, are compared with the distillation ranges of the pure solvents.

In this investigation the boiling points of various mixtures of crude cottonseed and peanut oils in commercial hexane were determined over a range of pressures from 160 to 760 mm. absolute. The hexane was a commercial solvent (Skellysolve B) with the following specifications: gravity at 60° F., 74.4° A.P.I.; boiling range, 140–160° F.; vapor pressure at 100° F. (Reid), 5.1 pounds per square inch; evaporation residue by weight, 0.0016%; color, water-white. Petroleum fractions which have approximately the characteristics of *n*-hexane are widely used and are generally available at low cost. For these reasons a commercial grade of petroleum hexane fraction was chosen for this work.

Refining test data of the crude cottonseed and peanut oils were as follows: (*a*) crude cottonseed oil: free fatty acids (as oleic) 3.5%, specific gravity at 30° C. 0.913, refining loss 12.5%, moisture 0.093%; (*b*) refined cottonseed oil from crude: iodine number 105.5, color 35Y-14.4R, color of bleached oil 35Y-5.5R;

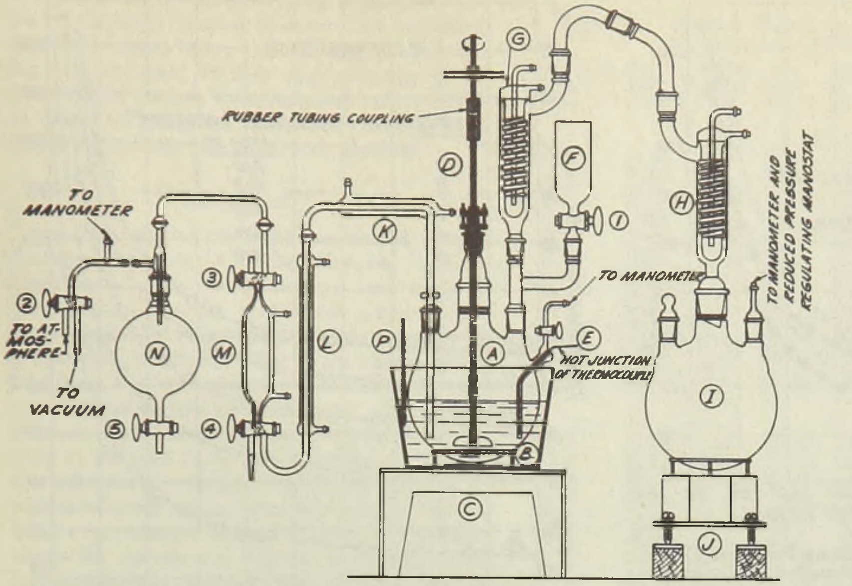

Figure 1. Apparatus for Determination of Boiling Points and Withdrawal of Representative Samples of Oil-Solvent Mixtures at Atmospheric and Reduced Pressures

A. Boiler (5000 ml.)
B. Refined cottonseed oil bath (12 liters)
C. 2500-watt hot plate
D. Stainless steel stirrer
E. Hot junction of thermocouple
F. Feeding vessel (300 ml.)
G. Reflux condenser
H. Distillate condenser
I. Distillate flasks (5000 ml.)
J. Leveling plate
K, L. Precoolers
M. Jacketed sampler (100 ml.)
N. Trap flask (1000 ml.)
P. Bath thermometer

(*c*) crude peanut oil: free fatty acid (as oleic) 0.85%, specific gravity at 30° C. 0.909, refining loss 4.8%, moisture 0.066%; (*d*) refined peanut oil from crude: iodine number 97.9, color 35Y-2.3R, color of bleached oil 2Y-0.5R.

APPARATUS AND PROCEDURE

Figure 1 is a diagram of the apparatus for measuring boiling points and for the withdrawal of cooled representative samples of mixtures under atmospheric and reduced pressures. This assembly was mounted in a laboratory hood, and was suitably supported to ensure easy operation adjustment and alignment.

All glassware was Pyrex, and either standard tapered or spherical ground-glass joints were used to connect the various units. A stainless steel stirrer, *D*, which rotated at 425 r.p.m., uniformly mixed the miscella. White asbestos rope, impregnated with a purified grade of the oil under investigation, was used in the packing gland of the stirrer. Bath *B* was maintained at the desired temperature by an interval time switch (not shown) which controlled the electrical input to hot plate *C*.

Regulation and control of the reduced operating pressure within 0.5 mm. of mercury were obtained with a modified design of a mercury-filled Cartesian manostat (not shown) constructed to bleed air to the system. The manostat and a mercury manometer were located in the vacuum line to distillate flask *I*. Mercury manometers were also installed in the system to indicate the reduced pressures maintained in the sampling and boiler systems. The boiler temperatures were measured with a single-junction thermocouple of standard copper-constantan wire, and the potentiometer had dial graduations in intervals of 5 microvolts.

Water at 4° C. was recirculated to distillate condenser *H*, reflux condenser *G*, jacketed sampler *M*, and finally to precoolers *L* and *K*. Only for the distillation of solvent from mixtures in the boiler was the reflux condenser by-passed.

In each of the ten runs reported, boiling points and samples of fifteen to twenty mixtures of different oil content were taken. An identical set of operations was made for each miscella investigated. Approximately 3000 ml., containing about 15% oil by weight, were poured into the boiler (Figure 1). The stirrer was started, and the manostat adjusted to maintain the desired operating pressure for the run. The bath was heated to approximately 20–25° C. above the boiling temperature of the miscella. The mixture was allowed to boil continuously for 10 minutes, and potentiometer readings were taken each 5 minutes during this interval. If these values agreed within the sensitivity of the potentiometer, the corresponding temperature was recorded as the boiling point.

The next step was the withdrawal of a representative sample of the boiling miscella. Cock 3 was opened to connect the sampler to the trap flask, cock 2 was adjusted to obtain a reduced pressure on the sampling system 40 to 60 mm. lower than the pressure in boiler system, and cock 4 was opened slowly so that miscella flowed steadily from the boiler into the sampling system without flashing of solvent. Miscella was withdrawn until 300 to 600 ml. collected in the trap flask, in order to rinse out the sampling system thoroughly and to reduce the contents of the boiler. Then cock 4 was closed and cocks 3 and 2 were opened quickly to the

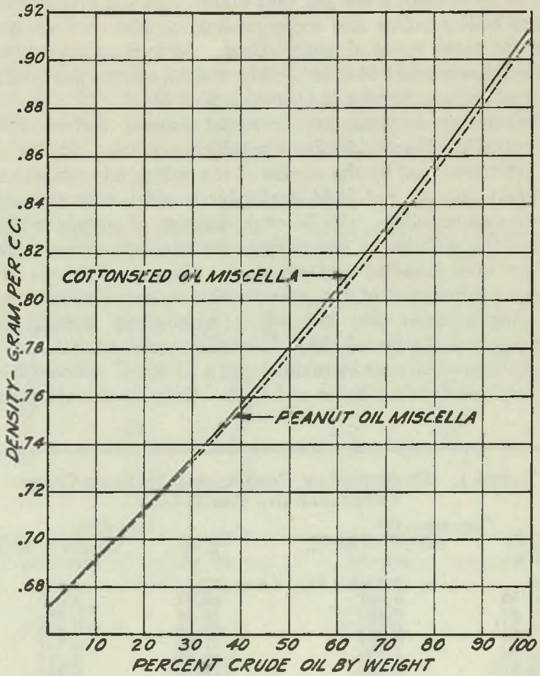

Figure 2. Density-Composition Relation for Miscellas of Crude Cottonseed and Peanut Oils in Commercial Hexane at 30° C.

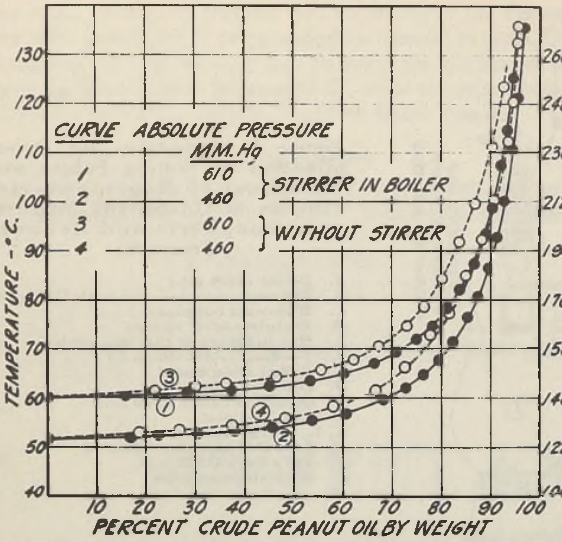

Figure 3. Effect of Agitation on Boiling Point of Commercial Hexane–Crude Peanut Oil Miscellas at Constant Vapor Pressures

atmosphere. This sample was cooled to about 30° C., and by properly opening three-way stopcock 4, appropriate portions were withdrawn for analysis.

A quantity of vegetable oil (300 to 600 ml.) was slowly added to the boiling miscella to increase its oil concentration sufficiently for the next point on the curve. This addition of oil readjusted the volume of oil-solvent mixture to approximately 3000 ml. Then the interval time switch was regulated to raise the bath temperature slightly. When boiling equilibrium for this miscella was established, the same manipulations were repeated as described for the previous point. Thus each succeeding miscella had an oil content a few per cent higher than the previous one. Hence boiling points and corresponding samples were obtained over the entire range of compositions. As soon as the contents of the boiler reached 93 to 95% oil by weight, solvent was distilled from miscella to increase the percentage of oil.

Preliminary investigations revealed several factors which were considered in establishing a suitable procedure: (*a*) Natural agitation produced by the motion of the boiling miscella was not sufficient and did not yield duplicable results; consequently a stirrer was installed. (*b*) To avoid flashing of solvent while a sample was withdrawn, especially at low absolute pressures, precoolers were installed and arranged. The maintainance of a pressure differential of not over 40–60 mm. between boiler and sampling systems also assisted in eliminating flashing. (*c*) Foaming was eliminated throughout the peanut oil and most of the cottonseed oil runs by maintaining a 20–25° C. differential in temperature between boiler and bath. Only for the cottonseed oil runs at the lower operating pressures was it necessary to reduce the temperature differential to 10° C. to minimize and control foaming. Observations indicated that the boiling points were independent of the differential in temperature between bath and boiler for a range of 10° to 30° C. Higher temperature differentials were not investigated. (*d*) Commercial hexane was used in making up the initial miscella for a run, and further addition of this solvent was not required. (*e*) Distillation of solvent for increasing the oil content could not be used for miscella containing less than 92 to 95% oil by weight because the lower-boiling-point components in the commercial hexane distilled off in a higher proportion than the higher-boiling-point fractions; consequently the boiling point of the resulting mixture was

Table I. Densities of Commercial Hexane–Crude Vegetable Oil Miscellas

Cottonseed Oil		Peanut Oil	
% oil by wt.	Density at 30° C., gram/cc.	% oil by wt.	Density at 30° C., gram/cc.
100	0.9116	100	0.9081
91.06	0.883	90.71	0.882
78.84	0.853	79.61	0.852
68.71	0.826	69.38	0.825
58.61	0.801	57.79	0.797
49.33	0.778	49.62	0.777
39.81	0.756	41.33	0.757
29.42	0.733	32.09	0.738
19.80	0.709	19.10	0.710
8.95	0.688	10.24	0.692
0.0	0.6719	0.0	0.6719

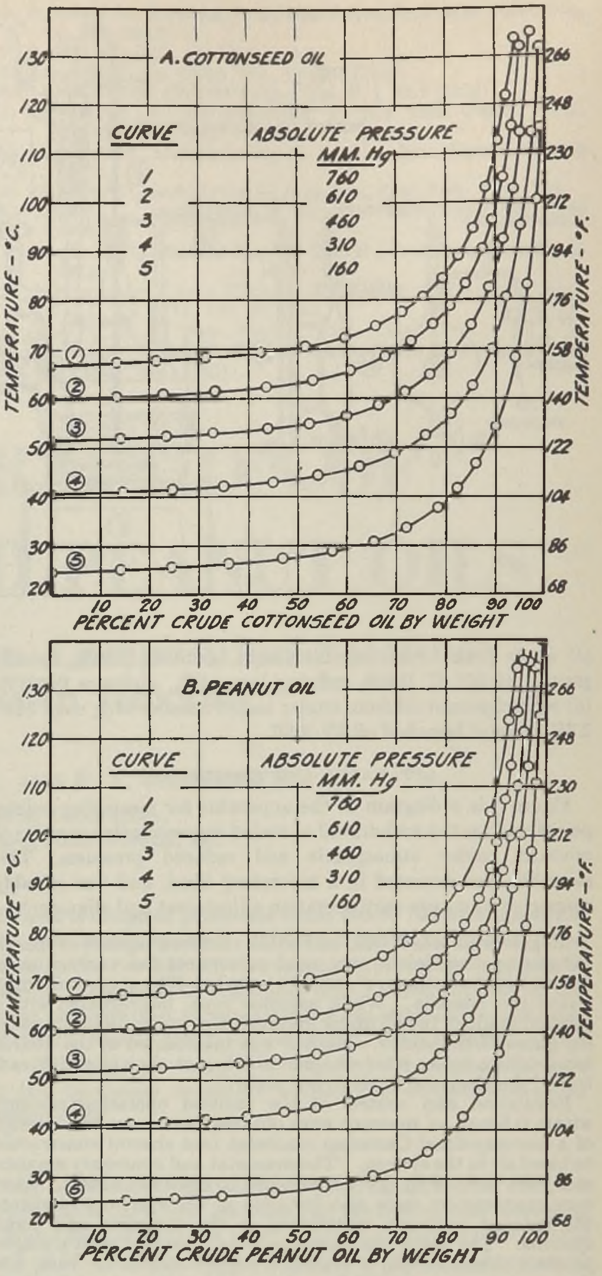

Figure 4. Boiling Point–Composition Curves of Commercial Hexane–Crude Vegetable Oil Miscellas at Constant Vapor Pressures

erroneous. Above 93 to 95% oil, slight fractionation of the small quantity of solvent did not affect the results appreciably. (*f*) Chilling of the cooling and condenser water to approximately 4° C. was required because the commercial hexane boiled at 24° to 66° C. when subjected to reduced pressures ranging from 160 to 760 mm. absolute.

ANALYSES

Densities of the crude oil–commercial hexane mixtures were determined by Westphal balance. Duplicate samples were withdrawn from the sample tube into specially constructed gravity tubes made with standard tapered 24/40 joints to prevent evaporation of solvent. The tubes containing the oil-solvent mixtures were placed in a constant-temperature water bath for 15 minutes, and density determinations were subsequently obtained at 30° C. Prior to the work on boiling points the densities of the mixtures of cottonseed and of peanut oil, each with commercial hexane, were determined at 30° C. by the pycnometer method (Figure 2). Density values for the oils and commercial hexane, determined separately, were checked by the Westphal balance method. The pycnometer and Westphal balance results agreed identically to the fourth decimal place.

Specific gravity determinations by the Westphal balance procedure, converted to percentage oil by weight, were checked analytically by the evaporation method as follows: Samples were withdrawn from sampler *M* (Figure 1) into weighing bottles and evaporated on a steam bath for 1 hour, dried in a vacuum oven at 70° C. for 30 minutes, cooled in desiccators, and subsequently weighed. The statistical differences between the Westphal and evaporation methods for determining the percentage oil by weight are as follows: for peanut oil miscellas the mean difference is 0.395% and the standard deviation of mean difference is ±0.034%; for cottonseed oil miscellas the mean difference is 0.559% and the standard deviation of mean difference is ±0.044%.

Table II. Boiling Points of Commercial Hexane–Vegetable Oil Miscellas at Constant Vapor Pressures

760 Mm. Abs.		610 Mm. Abs.		460 Mm. Abs.		310 Mm. Abs.		160 Mm. Abs.	
% oil by wt.	B.P., ° C.	% oil by wt.	B.P., ° C.	% oil by wt.	B.P., ° C.	% oil by wt.	B.P., ° C.	% oil by wt.	B.P., ° C.
				A. Cottonseed Oil					
13.4	67.35	13.6	60.53	14.3	51.88	14.7	41.08	14.2	25.13
21.4	67.69	22.8	60.81	23.2	52.41	24.7	41.48	24.5	25.64
31.5	68.19	33.3	61.38	32.9	53.04	35.0	42.03	36.1	26.25
42.5	69.16	43.8	62.24	44.0	53.73	45.0	42.86	47.0	27.23
51.6	70.39	53.0	63.49	52.2	54.77	54.2	44.38	57.1	28.81
59.5	72.41	60.5	65.54	59.9	56.28	62.5	46.11	65.4	30.75
65.8	74.75	67.6	68.25	66.4	58.46	69.6	48.62	72.0	33.53
71.0	77.54	72.8	71.41	71.7	61.22	75.8	52.23	78.6	37.74
75.4	80.75	77.2	74.98	76.7	64.63	81.0	56.74	82.5	41.56
79.3	84.49	80.9	78.76	81.0	68.93	85.3	62.58	86.1	46.62
82.5	89.09	84.0	83.39	85.0	74.98	89.1	69.83	90.0	54.07
85.6	94.93	87.2	90.39	88.6	82.62	92.0	80.53	94.0	68.26
88.0	103.30	89.4	96.45	91.5	92.34	95.1	95.15	96.3	83.17
90.5	112.80	91.5	105.11	93.7	102.87	97.5	114.26	98.4	100.52
92.3	121.97	93.3	115.73	95.0	114.47	98.9	131.84	99.3	115.31
94.0	133.88	94.9	132.04	97.2	135.09				
				B. Peanut Oil					
14.5	67.35	15.8	60.40	16.8	51.99	16.0	40.96	15.1	25.27
22.5	67.70	21.6	60.76	22.3	52.34	22.8	41.43	24.9	25.64
32.5	68.37	28.1	61.10	30.5	52.81	31.3	41.91	34.6	26.13
43.0	69.38	37.2	61.56	37.9	53.38	39.6	42.65	45.1	26.98
52.4	70.84	45.0	62.24	45.5	54.08	47.2	43.45	55.4	28.08
60.2	72.87	53.0	63.40	53.7	55.24	53.5	44.39	65.2	30.51
67.2	75.31	60.2	65.08	60.5	56.74	60.1	45.92	72.1	33.05
72.0	78.43	66.2	67.01	68.0	59.84	65.6	47.79	76.1	35.46
77.3	83.17	70.8	69.38	72.6	62.00	70.7	49.67	83.5	42.27
82.5	89.52	74.8	71.85	76.2	64.63	75.0	52.34	86.7	48.03
88.6	104.79	78.0	74.64	79.5	67.58	78.6	55.23	90.3	55.70
92.6	123.63	81.0	78.20	82.4	71.41	81.5	58.92	93.5	66.22
94.2	134.30	83.5	81.85	85.6	76.31	84.3	62.81	95.8	81.52
		86.5	87.12	87.5	80.53	87.2	67.81	97.0	96.66
		88.7	93.42	89.6	86.25	89.2	72.86	98.2	110.70
		90.0	98.81	91.2	92.99	91.3	80.31	98.7	124.56
		91.7	107.33	92.6	99.66	93.2	89.09	99.5	139.96
		93.0	114.26	94.2	110.07	94.9	100.03		
		94.3	125.28	95.6	121.04	96.4	114.17		
		95.5	135.90	96.7	135.50	97.8	134.91		

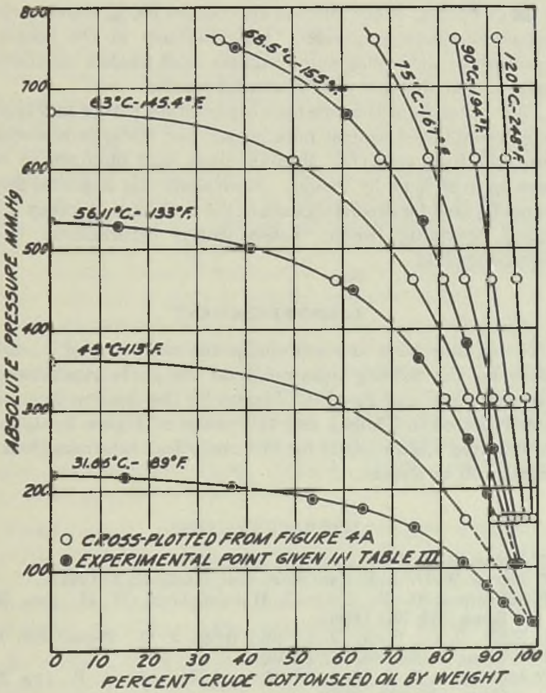

Figure 5. Vapor Pressure–Composition Curves of Commercial Hexane–Crude Cottonseed Oil Miscellas at Constant Boiling Points

DATA

Table I shows experimental results of the measurement of densities by the pycnometer method at 30° C. of the crude cottonseed oil, crude peanut oil, commercial hexane, and mixtures of these oils with the solvent. Figure 2 gives these data on densi-

Table III. Absolute Vapor Pressures of Commercial Hexane–Cottonseed Oil Mixtures at Constant Boiling Points

B.P. = 31.66° C.		B.P. = 56.11° C.		B.P. = 68.50° C.	
Abs. pressure, mm. Hg	% oil by wt.	Abs. pressure, mm. Hg	% oil by wt.	Abs. pressure, mm. Hg	% oi by wt.
219	00.0	530	13.9	749	38.0
216	15.0	500	41.2	667	61.0
203	37.0	448	62.1	534	76.6
187	53.5	362	75.3	379	85.5
174	64.0	260	85.6	249	90.7
150	74.3	192	89.8	103	96.3
107	84.6	102	95.1		
77	89.6	30	99.0		
56	93.0				
32	96.1				

Table IV. Boiling Points of Commercial Hexane at Different Absolute Pressures

Abs. Pressure, Mm. Hg	B.P., ° C.	Abs. Pressure, Mm. Hg	B.P., ° C.
759	66.55	433	49.66
699	64.18	379	46.15
631	60.99	290	38.81
561	57.43	211	31.12
495	53.62	153	23.68

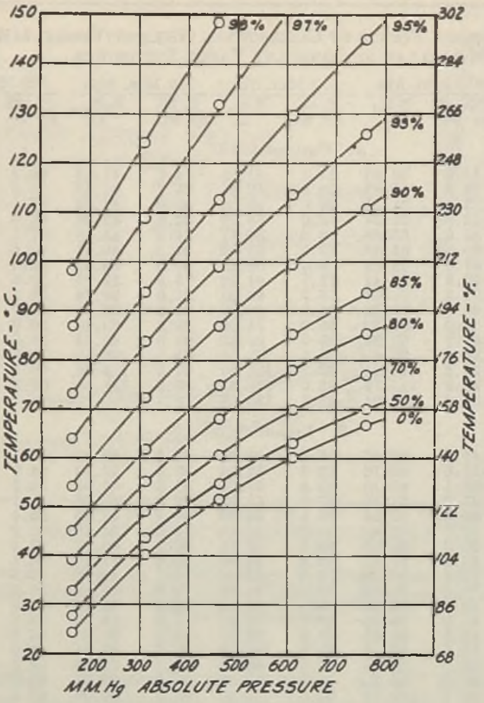

Figure 6. Boiling Point–Vapor Pressure Curves of Commercial Hexane–Crude Cottonseed Oil Miscellas at Constant Compositions (Per Cent Oil by Weight)

ties plotted against composition. The smoothed curves served as satisfactory work charts in this investigation for converting the specific gravities obtained by the Westphal balance procedure to percentage oil by weight.

Figure 3 illustrates the effect of natural agitation as compared to mechanical agitation upon the boiling point of miscellas. Preliminary investigations showed that reliable data can be obtained only under equilibrium conditions of constant stirring.

Table II*A* gives data for cottonseed oil–solvent mixtures at five absolute pressures. The results were plotted as weight per cent oil (Westphal) against temperature (boiling point), and the smoothed curves are shown in Figure 4*A*. The weight per cent (Westphal) values were used in plotting these curves because they were considered to be more uniformly reliable than the values obtained by the evaporation method; they were performed on larger samples (25 ml. compared with 1 or 2 ml.), could be made more promptly, were subjected to fewer manipulative steps, and yielded smoother curves. Table II*B* gives experimental results for peanut oil–solvent mixtures at five absolute pressures. Smoothed curves (Figure 4*B*) were obtained by plotting the data given in Table II*B*. Boiling point curves for cottonseed and peanut oil mixtures at the same absolute pressure are practically congruent, which indicates similar physical properties for the two miscellas. This similarity shows that the reported data should be applicable to a wide range of oils of similar specifications. The boiling point data should be of value in the further development of the technology of solvent extraction of vegetable oils. Apparently there are no published data on boiling points for miscellas of either cottonseed oil or peanut oil in commercial hexane under reduced pressures; therefore comparisons with other work cannot be made.

Smoothed curves in Figures 5 and 6 present the data of Figure 4*A*, cross-plotted to show constant boiling point and constant composition curves. Curves in Figure 5 required the additional experimental data in Table III.

Table IV gives experimental determinations of the boiling point of the commercial hexane used at different absolute pressures. The vapor-pressure values for 100% solvent plotted in Figures 3 to 6 were interpolated from these determinations.

The data presented in Figures 4*A*, 5, and 6 for cottonseed oil indicate the wide spread in boiling pressures over the range of temperatures from 30° to 120° C. for the pure solvent; as the oil content increases, the spread of boiling pressures decreases and reaches a minimum for 100% oil. Very low absolute pressures are required to boil mixtures with an oil content from 95 to 100% by weight in order to avoid excessive temperatures. At lower temperatures the spread of boiling pressures over the whole range of compositions is small compared to the spread at the higher temperatures. This group of figures is particularly valuable for designing steam stripping equipment and vacuum evaporators.

Figure 6 shows that for miscellas with an oil content from 0 to 50% by weight, there is a small change in the boiling temperature at a given pressure. However, above 50% oil by weight there is a more pronounced temperature rise, and after 85% oil by weight there is a rapid rise in boiling temperature at a given pressure for any increase in oil content. The slope of the curves gradually increases as the percentage of oil in the miscella is increased; for the curves representing 95 to 100% oil, the slope approaches a constant value over the range of pressures investigated. Although no points are given below 160 mm. absolute pressure in Figure 6, it is possible to predict from Figure 5 that, over the entire range of compositions, there is a rapid lowering in boiling temperature with a further reduction of pressure, particularly for the miscellas of higher oil content. The slope of the curves approaches an infinite value as the pressure is further reduced.

Similar curves can be obtained for peanut oil miscellas by cross plotting the data obtained in Figure 4*B*.

The data obtained in this investigation were compared with values calculated from Raoult's law. The agreement between the observed and calculated values is good up to approximately 50% oil by weight. Above 50% the deviations are appreciable; as the oil content of the miscella approaches 100%, the deviations become increasingly greater. Unfortunately in the operating region where the boiling point data are most needed, calculations based on Raoult's law yield erroneous results.

The values from the constant composition curves in Figure 6 were cross-plotted against pure hexane and water in accordance with Dühring's rule (*7*). Straight lines were obtained in both cases up to 80% oil by weight. Here again this empirical device cannot be used for predicting data of the necessary accuracy in the critical operating region; consequently, experimental values must be applied.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of B. Ashby Smith for the refining tests made on the crude vegetable oils; Evald L. Skau and Frank C. Magne for the density determinations reported in Table I and the curves of Figure 2; John D. Guthrie and Claire Leslie for the analytical determinations for per cent oil by weight.

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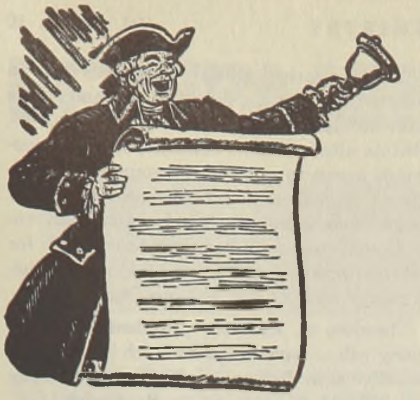

SEPTEMBER'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ September 2. Japan surrenders finally and unconditionally to United States and its allied powers.

¶ September 5. WPB removes import controls from about 40 raw materials and says industrial capacity increased 40% during war but much of it cannot be converted to civilian production.∼∼W. S. Carpenter, Jr., president of du Pont, disclaims any desire for control of atomic bomb developments and protests news broadcast charging United States move to give company control. ∼∼New actions may be instituted under Webb Act against export associations and alkali case is held law's test.∼∼WPB removes all restrictions on production of passenger car, motorcycle, and bicycle tires.∼∼John W. Thomas, chairman Firestone, urges creation of large government-owned stockpile of natural rubber and continuance of broad synthetic rubber research program.∼∼Metalsalts Corp. announces formation of Metal Organics jointly with Edwal Laboratories to produce phenyl mercury metallo-organic compounds[1].∼∼President Truman asks Congress to rescind $3,500,000,000 of its 1946 appropriations not needed by war agencies.∼∼Bernard M. Baruch, adviser to President in mobilization of resources during two wars, urges appointment of a work director and says national job plan is vital to veterans and that one group cannot be protected alone.

¶ September 6. President Truman tells Congress he will make recommendations later on atomic energy plan. Meanwhile Senator Vandenberg in resolution suggests that joint committee of six each from House and Senate be authorized for full and complete study of development and control of atomic bomb. Senator McMahon introduces bill providing that use and application of atomic energy be controlled by Federal Government.∼∼President Truman recommends to Congress creation of single federal agency to correlate and promote developments for federal scientific research and the promotion and support of private research and to provide financial assistance in scholarships and grants for young men and women of proved scientific ability.∼∼H. F. Sinclair, president Sinclair Oil, says Ethiopia has conceded its oil to corporation for a term of 50 years.∼∼Navy reveals that it has virtually completed $20,000,000 double pipeline across Isthmus of Panama.∼∼General Council of League of Nations Union adopts resolution asking United Nations Organization to establish agency to control atomic energy.∼∼Hercules announces Reconstruction Finance Corp. approves company purchase of nitrocellulose plant in Parlin, N. J.

¶ September 7. Alcoa says government-owned aluminum reduction plants will be taken over by RFC Nov. 1.∼∼WPB lifts quota restrictions on glass containers.∼∼Director of War Mobilization and Reconversion Snyder creates interagency policy committee on rubber under chairmanship of William L. Batt.

¶ September 9. Sixty-four members of University of Chicago faculty sign recommendation that United States share secret of atomic bomb with other nations.∼∼R. R. Sayers, director, Bureau of Mines, reveals details of test for presence of uranium. ∼∼WPB says industry advisory committees will be retained "on call" basis until WPB is liquidated.∼∼National Patent Planning Commission submits report to President recommending 8-point guide to new committee.∼∼R. E. Wilson, chairman, and A. W. Peake, president, Standard Oil (Ind.), say construction of new laboratories at Hammond, Ind., has started[2].

¶ September 10. Sewell L. Avery, chairman Montgomery Ward, protests to Secretary Stimson against Army's continued holding of company property.∼∼Charles Adams, chairman, and Charles S. Munson, president, say Air Reduction plans spending $25,000,000 for plant improvements and expansion.

¶ September 11. *National Association of Manufacturers News* says Secretary Wallace's plans to reorganize Department of Commerce have received President Truman's approval and business leaders given a confidential preview are favorably impressed.∼∼ Wm. H. Milton, Jr., manager, plastics division, General Electric, says new plant for manufacture of laminated plastics will be built at Coshocton, Ohio.∼∼WPB lifts controls over delivery and use of wood pulp.

¶ September 13. President Truman in executive order bars disposition of all public lands containing radioactive mineral substances.∼∼Cuban Government makes use of alcohol in gasoline obligatory.∼∼WPB grants manufacturers permission to make any size tire of a single quality standard.∼∼Monsanto's vice president, Francis J. Curtis, says company plans to spend $48,400,000 on 151 construction and expansion projects. ∼∼Arabian American Oil Co., jointly owned by Standard Oil of California and Texas Co., starts operation of its new 50,000-barrel daily capacity oil refinery in Saudi Arabia.∼∼E. J. Thomas, president Goodyear Tire and Rubber, says by year's end company will reach its prewar peak of passenger tire production.

¶ September 14. J. W. Krug, WPB chairman, tells New England Council that survey shows 42 industries expect their production by June 1946 to be 87% above 1939–40 base period. ∼∼WPB assures industries engaged in reconversion that part of Government's 187,000-ton zinc stockpile will be available for civilian production during next six months.∼∼U. S. Group Control Council reveals that I. G. Farben prepared an economic blitz program in 1940 armed as a "trade offensive" against Latin America and excluding key United States exports to Europe.

¶ September 15. Secretary of State James F. Byrnes says Russia has not asked United States to be let in on atomic bomb secret and that he and President Truman have not even discussed possibility of entrusting it to United Nations Organization.

¶ September 16. First trickle of rubber reclaimed from Japs in Malaya goes to England.∼∼Jefferson Chemical will erect large chemical plant at Neches, Texas, for production of intermediate chemicals.∼∼American Cyanamid purchases about 900 acres east of Jefferson site for chemical plant which will utilize some of Jefferson's products.∼∼WPB says U. S. newsprint production

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[1] *Chem. Eng. News*, 23, 1676 (Sept. 25, 1945).

[2] *Ibid.*, 1634 (Sept. 25, 1945).

has fallen 56% in past 20 years.∼∼Alfred P. Sloan Foundation plans projects in economic education to reach masses.

¶ September 17. M. W. Kellogg Co. reveals that more than 5000 new products and procedures are available to industry as result of Government's atomic bomb research.∼∼Attorney General Clark asks Congress to split up Alcoa into a number of competing companies.∼∼Secretary of Interior Ickes says he does not expect American-British oil agreement to provide price or production control.∼∼John S. Knight, editor and publisher Knight newspapers, says he is convinced of necessity of establishing a government department of scientific research.

¶ September 18. President Truman announces that War Labor Board, War Manpower Commission, and U. S. Employment Service have been put under Department of Labor.∼∼F. W. Litchfield, chairman Goodyear, says company has perfected most important development in tire making since the cord tire 30 years ago. New tire is built of rayon, is capable of greatly increased mileage, saves gasoline, and brings into prospect tires that will last longer than usual car ownership by an individual.

¶ September 19. British Military Administration sets up Malayan rubber and produce organization with sole authority to buy rubber in Malaya.∼∼Secretary of Interior Ickes takes steps to reserve Alamogordo air base in New Mexico, where atomic bomb was first tested, as national monument commemorating a "forceful influence toward world peace".

¶ September 20. American Viscose completes expansion plans that will increase its rayon production by about 100,000,000 pounds annually.∼∼Assistant Attorney General Wendell Berge at a Boston conference on employment urges industry to "assume a venturesome lead in promoting peacetime economic activity" and warns that building up international cartels would be fatal to our prosperity.∼∼Congressman Lyle H. Boren, chairman House Newsprint Committee, states committee has recommended that WPB lift all newsprint restrictions effective December 31.∼∼WPB's rubber bureau says Malayan rubber when available and landed in New York will cost about 25.5 cents per pound which is only slightly below cost of synthetic rubber.∼∼Office of War Mobilization and Reconversion rejects WPB recommendation to set up interagency tin committee to alleviate tin shortage.

¶ September 21. West Coast receives first shipment of rubber from overseas since Pearl Harbor.∼∼Robert W. Hutchins, chancellor, University of Chicago, says university has established an institute to apply discoveries of atomic research to such problems as cancer, heredity, and aging.∼∼General Leslie R. Groves, officer in charge of atomic bomb development, urges complete U. S. control of secret at least for next few years.

¶ September 22. General James B. Newman, Jr., head War Department Atomic Bomb Mission, says no sign of radioactivity was found in Nagasaki by 17 allied scientists and doctors now in Japan completing observations of effect of second atomic bomb.

¶ September 23. President Truman says he will take full responsibility for future development of atomic bombs and atomic energy and denies Secretary Wallace had recommended at Friday's Cabinet meeting that bomb secrets be turned over to Soviet Union.∼∼Senator Bridges calls on President Truman to end war agencies immediately.∼∼Davison Chemical plans big plant modernization program, Chester F. Hockley, president, says.∼∼Standard Oil of California announces through its president, H. D. Collier, construction program totaling more than $20,000,000.∼∼Chemicals Bureau, WPB, says chemical output rose 90% in war and that it directed allocation of approximately 10 billion dollars worth of chemicals.∼∼Plan to solicit substantial amounts from western industries by end of year to establish $5,000,000 Pacific Research Foundation to promote West's economic and scientific future laid before Chairmen of Commissions on Inter-State Co-operation of Western States.

¶ September 24. Representative Arends introduces bill in House to create committee of scientists, industrialists, and others to study and recommend defenses against atomic bomb.∼∼United States and Britain after six days' deliberation sign document providing for equal access to world's oil resources and calling for world agreement on international oil questions. Pact would create commission of six members, three from each government.∼∼Executive Committee of American Association for United Nations advocates formulation of terms by U. S. for sharing secrets of atomic energy with United Nations Organization.

¶ September 25. Theodore C. Klumpp, president Winthrop Chemical, says company will construct new research laboratories costing more than $2,000,000 at Rensselaer, N. Y.∼∼Hercules Powder announces $1,250,000 addition to its Brunswick, Ga., naval stores plant.∼∼Attorney General Clark, following luncheon of the Commerce and Industry Association of New York, says Department of Justice plans to proceed with 27 cases involving alleged antitrust law violations.∼∼Surplus Property Administration says Reynolds Metals has offered to lease four government aluminum plants now operated by Alcoa.∼∼Authoritative reports from British circles in Washington say shortage of labor is only bar to producing Malayan rubber.∼∼Department of Interior urges careful conservation in use of many commercial minerals.∼∼General Eisenhower says five war production plants in U. S. zone of occupation in Germany will be dismantled immediately and turned over to United Nations as part payment of German reparations.

¶ September 26. Surplus Property Board advocates sale of aluminum plants owned by Government to competitors of Aluminum Co. of America.∼∼National Engineers Committee of Engineers Joint Council makes public detailed plan for industrial control of Germany by eliminating or controlling critical war potential elements in German industry.∼∼General Electric announces plans for first flying laboratory for experimentation in jet propulsion, gas turbines, and all types of aerial innovations.∼∼WPB says its Rubber Bureau has streamlined its rubber control order to conform with rubber conservation needs of reconversion period.∼∼Hercules discloses work in production of VT-Fuse which automatically detonates a projectile when it reaches correct proximity of target.∼∼U. S. Department of Agriculture eases controls for linseed oil.∼∼George W. Dolan, president Mathieson Alkali, says a new plant which will double sodium chlorite output is being added to Niagara Falls production facilities.∼∼Chemical Unit, Department of Commerce, urges greatest sales promotion activity by manufacturers and exporters to increase this country's share of total world trade in chemicals.

¶ September 27. Former President Hoover, in statement to North American Newspaper Alliance, says United States and Great Britain should keep atom bomb secret.∼∼Almost unanimous Congressional opposition to disclosure of atomic bomb secret is shown in answers to telegrams of inquiry.∼∼Zay Jeffries, vice president General Electric, says Chemical Engineering Division will be established as part of G. E.'s Chemical Department, Oct. 1.∼∼U. S. Senate unanimously approves and sends to House resolution to set up joint committee to study development, control, and use of atomic energy.

¶ September 28. President Truman, by proclamation, asserts exclusive rights of U. S. to all mineral resources in the 759,600 square miles of "Continental Shelf" running to an off-shore depth of 600 feet from U. S. mainland.

¶ September 29. Standard Oil (Ind.) says work on largest construction program ever undertaken at its refinery in Sugar Creek, Mo., has begun.

¶ September 30. WPB bids farewell to its Controlled Materials Plan governing distribution of steel, copper, and aluminum, and retains simplified priorities rating system for few materials in critically short supply.

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EQUIPMENT AND DESIGN

Technical opportunities and bargains are available in the many new methods and products developed during wartime.

Discussed by Charles Owen Brown

EVERYONE joins this writer in a feeling of grateful relief that the war is over. Scientific and practical efforts have won a war and established peace for the second time in one generation. Even more, our gross scientific assets have shortened the duration of tragic years, reduced the cost in lives, and alleviated the huge financial burden. Those who have seen the waste of war may be slow to believe this. The strength of Japan was unbelievably overrated, but the waste could have been greater.

To understand our postwar opportunities we must look at the results of technical progress during the last three and a half years. There are two aspects of interest to every scientist or layman: We want to know first about new methods used and about the new products made. A more difficult phase—what should be done with the new plants and facilities available—will be discussed in this column next month.

Arming for war was undertaken by commerce and industry. Administrative judgment came from the Commander-in-Chief and the War Department. How much our war needs expanded our productive capacity can only be estimated, since the record is not definite or accurate. The last year unaffected by the war was 1939, and in 1943 the "gross national product" had risen 175% over 1939 to 155 billion dollars; 47 to 49% of this amount was spent directly for war activities. The only hope in this record is that these successful developments can be preserved and devoted to help expand and support a better economy. But most of the enlargement and advances made were in materials needed directly for war. Civilian progress was not only stopped but deliberately set back (for example, the ordered shortening of the tails on men's shirts). The war accelerated the rate at which improvements were finished; but since almost all were military, these developments must be carefully screened to find those helpful in civil life.

Technical and practical improvements in methods were directed more to saving time than to saving labor, more to improving accuracy and quality. In this way wastefulness of time and material was cut. Production was increased but waste decreased. This type of process improvement always can be used at full face value.

The last three years have seen the birth of many new products. Many of them are better known to the readers of this article than to the writer, but several should be mentioned briefly as a measure of the rate of scientific advancement. In 1942 a few scientists had imperfect knowledge of the processes for synthetic rubber, but synthetic rubber was in tires and at the front in 1944 backed up by an annual production of over 950,000 tons. Equally amazing is the vast scale of production of 100-octane gasoline. Plastics developed so rapidly that the results are difficult to describe. It should be noted that recent uses have frequently replaced steel, a field almost untouched by plastics formerly. Finished products of steel and nonferrous metals are now often made with certain essential parts of plastics—the handwheel on valves and light bomber turrets, for example. The binders for file papers and bayonets for training purposes have been made entirely of plastics. Ten years of normal progress in plywood have been crowded into the last three; plywood flows to a heavier and broader market than do plastics; for example, it is made into complete houses, boats, and bomber planes. Methods have also changed, for now finished articles are made from the plies and adhesive resins direct without first forming a board Curved objects such as plane wing tips and elevator assemblies are put into a strong rubber bag which is then placed in a metal pressure chamber with one small opening at a neutral point in the bag, passing through the chamber wall to atmosphere. When pressure is applied to the chamber, the air is expelled from the inside of the rubber bag and an even pressure is exerted all over the object. Magnesium was a production problem as complicated as rubber, but in two and one-half years the 1939 production of 3,980,000 pounds grew to 500,000,000 pounds of this metal, which is stronger than aluminum and 35% lighter. The history of magnesium production, however, has not been entirely happy; the oldest process has now proved to be the cheapest and the best.

Methods of assembly of large objects such as bomber planes, cargo boats, and blast furnaces were radically changed. Perhaps as much as one-quarter of the whole has been completed in four different places, moved to the assembly line or the ways, and then put together and finished. A steel company, forced to replace a blast furnace, built the new furnace near by; when it was completed, the old one was shut down and demolished, the new one moved into the same place, and the connections to the auxiliary equipment were then completed. Ninety-six days of full production by the old furnace were saved by this carefully planned engineering. The main electrical wiring for a large plane was done by painting the wiring diagram on a long table; the wires were placed in proper position on pegs and bound together for strength, and the bundle was given protective coatings and a cover. It could then be placed quickly in the body of the plane as a rugged unit.

Packard decided to redraw the two thousand left-handed British designs of the Rolls-Royce Company; this was completed without impairing top performance of the wartime tested-in-line Merlin engine. Surgical instruments were often used to remove foreign matter from complicated oil ducts. Wind tunnels to prove the fast-changing types of planes grew to 700 feet in length, and wind velocities of 600 miles per hour were created by a 40,000 horsepower motor; an additional 3600-horsepower motor and refrigerating compressor lowered the air temperature to −67° F., although the larger part of the temperature

(Continued on page 94)

drop was obtained by changing static pressure into velocity, which expands the air and lowers its temperature. Liquid carbon dioxide is used as a source of energy in planes to operate auxiliaries when the main power source has been damaged; about 30,050 foot-pounds of energy are available per pound of gas.

Two newcomers have appeared in the inorganic list, sulfamic acid and ammonium sulfamate. Ethyl alcohol is produced by fermenting the wood sugars in waste sulfite liquors, and glycerol has been produced by fermentation and also synthetically from a cracked gasoline fraction. Tricalcium phosphate, substantially citrate soluble, is now made on a large scale by a one-step blast furnace process using a catalyst, even though the temperature is about 1600° C. Ethyl mercaptan injected in the ventilating air to mines warns miners more promptly than any sound alarm yet used. A new "ballast" in fluorescent lighting fixtures saved 23,750 pounds of copper, 81,000 pounds of steel, 325 pounds of aluminum, and 303 kilowatt-hours in the lighting system of one airplane plant. The iron penny was unsuccessful, but the Administration permitted several million pounds of mint silver to be leased for use in heavy-amperage bus bars, on the condition that it should all be returned. By better hardening and heat-tempering methods, the cement industry in 1944 saved 5860 tons of steel grinding slugs per year.

The dingy foundry also deserves recognition. Good ship propellers have been cast in permanent cement, not sand cores, and wooden core boxes are now protected from sand abrasion with a sprayed metal coating. Some of the most important munitions were made of "N.E." steels, in which the alloying elements were reduced to meet the national emergency. Copper tube ends have been sealed in less than one second by revolving the tube at high speed against a steel die; friction heat anneals the copper, melts and centrifugally casts the end closed. The degree of fineness of metal powders, once determined by the amount which settled in three to seven hours in glycerol, is now determined in a few minutes; a beam of light is passed through an air-borne suspension while the current is measured from an electric eye energized by the light pickup passing through the metal powder suspension. A new x-ray was produced for the first time from the 100,000,000-volt discharge created by electron acceleration. Blood plasma, Freon insecticide bombs, fresh water from sea water plants, maps mounted on thin steel sheets which hold small magnet markers without marring the map surface, 108,000-kilowatt hydroelectric generators—all are typical of new processes and products now available.

Statistical analysis is widely used in sampling materials which are produced by the million, and also to interpret the results of inspections and the control of rejections. A new professional society of men devoting their talents to this type of work may become permanent.

Let us not forget, however, that the last three years have not shown a net gain on balance. The entropy of the United States has decreased at a rapid increment rate. We have exhausted our best iron ores, Michigan copper is nearer a memory, petroleum reserves have been lowered, and our forest supplies are most seriously depleted. Basic costs are at a much higher level. Next month's article will deal with a wise and logical program for disposing of these facilities.

Current Developments in INSTRUMENTATION

Wire-type strain gages and their applications to pressure measurements.

Discussed by Ralph H. Munch

The bonded wire-type strain gage is a device which has made an important contribution to the war effort. Nevertheless, many scientific workers have not yet become acquainted with it. A strain gage is a device which measures changes in the dimensions of a body when it is subjected to stress. A bonded wire-type strain gage consists of a resistance element of alloy wire, approximately 0.001 inch in diameter, arranged in the form of one or more hairpin loops cemented between two layers of thin paper. Heavy terminals are provided to which leads may be attached. In use, the gage is cemented to the part in which the strain is to be measured with the long sides of the hairpin loops parallel to the direction in which stress is applied. The nominal resistance of the commercial gages is 120 ohms. When the part being tested is stretched or compressed by the forces applied to it, the fine wire of the gage cemented to it is also stretched or compressed; resistance changes result which are proportional to the dimensional changes. For a type A_1 gage, a strain of 0.001 inch per inch produces a resistance change of about 0.25 ohm. With suitable resistance-measuring equipment, it is possible to measure strains ranging from a few up to several thousand microinches per inch. Changes in gage temperature also produce changes in gage resistance. To eliminate the effect of temperature, a second gage identical with the strain gage is mounted near it on a similar piece of material which is not subject to stress. The strain gage and compensator form adjacent arms of a Wheatstone bridge, so that temperature changes produce no change in bridge balance. The bridge balance is affected only by strain in the part under stress.

Strain gages of this type have given invaluable information to designers of aircraft, ships, turbines, locomotives, gunbarrels, and other types of equipment subject to stress. Accurate data on the stress encountered during operation in parts of structures such as these make possible the use of small safety factors This decreases the weight and cost of the structure and, in many cases, makes possible improved performance. Recently these gages have come into use in industrial applications where they serve to measure any variable which can be made to produce a strain within their range. Measurements of weight and pressure are two of the most important of these variables. The wire-type strain gage is used in such applications because it furnishes a convenient means of converting the variable to be measured into a quantity which can be indicated and recorded electrically. In the June issue (advertising section page 82) an electrical pressure transmitter made by Statham Laboratories was described. This instrument, which was suitable for low pressures, used an unbonded strain gage to convert the mechanical deformation of a bellows or diaphragm into an electrical output.

The Foxboro Company (Foxboro, Mass.) recently completed development of a line of strain-gage type, pressure-sensitive cells for measuring high pressures. These cells are constructed on a steel plug base which is threaded or provided with other suitable means for connecting it to the vessel or pipe in which pressure is to be measured. Mounted on this plug and connected to the threaded end through a drilled passage is an elastic tubular element. The fluid pressure being measured is applied to the inside of this tube and causes it to expand. The design is such that the tube operates well within its elastic limit. Mounted on the outside of the tube is the wire-type strain gage which converts the expansion of the tube into a corresponding change in electrical resistance. The plug also carries elements to provide temperature compensation, calibration resistors, and a protective housing. Figure 1 is a photograph of the pressure-sensitive cell, along with the cable used to connect it to the measuring instrument.

(*Continued on page 100*)

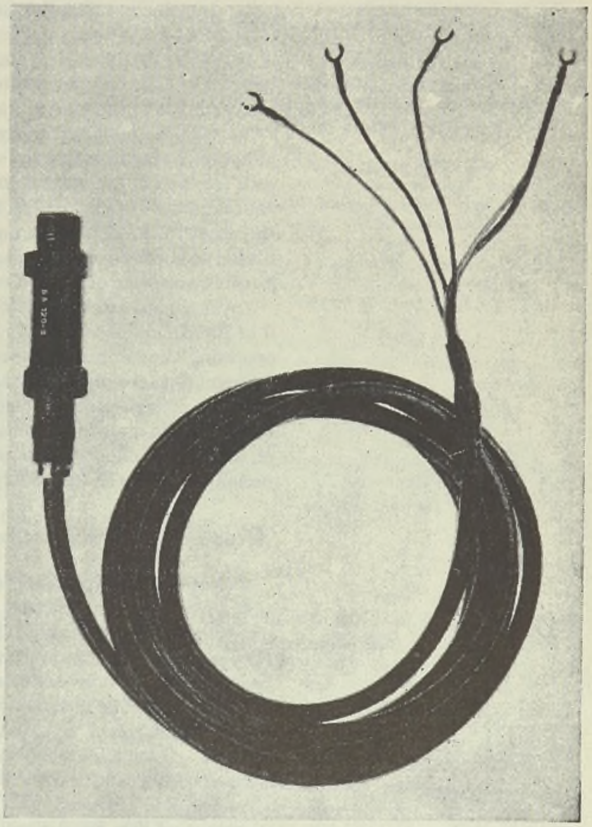

Figure 1. Foxboro Strain-Gage Pressure-Sensitive Cell

Instrumentation

The measuring instrument used with these cells can be any type of indicating or recording equipment suitable for determining small changes of resistance with high accuracy. Foxboro Dynalog recorders are especially suitable for this purpose because the measuring range needed is similar to that used for general strain-gage work. These instruments are suited for measuring either static or slowly changing pressures. Rapidly changing pressures can be indicated on the screen of a cathode ray oscilloscope.

Advantages of Equipment

1. It can be used where pressure pulsation or flutter makes mechanical instruments unsatisfactory because of rapid wear or inaccurate readings. The only part subject to the effect of pressure pulsations is the elastic tube. Since there is no system of gears or links, there is no wear.
2. The equipment is safer and cheaper for high-pressure applications. The measuring cell is mounted on the pressure vessel and connected to the indicating or recording instrument by electrical cable. The instrument board, therefore, does not carry any high-pressure connections, and long runs of tubing to the board are eliminated. Problems of sedimentation or freezing of liquids in these lines are not encountered.
3. Since the pressure measurement is transmitted from the sensitive cell to the instrument electrically, the response is almost instantaneous. The distance between cell and instrument can be as much as 500 feet with no change in measuring speed or accuracy.
4. Multipoint measuring using a single indicating or recording instrument and a selector switch is possible.
5. No auxiliary electric power supply is needed at the measuring point. The only connection to the sensitive cell is the cable connecting it to the measuring instrument.
6. Cells in standard ranges are interchangeable. They are adjusted during manufacture so that the electrical outputs of the cells for each of the various pressure ranges are the same. Thus the instrument can be used on different ranges merely by changing the chart to the new range and substituting a pressure cell calibrated to correspond. No electrical changes are needed with the possible exception of zero adjustment.
7. Standard ranges are 0 to 500, 0 to 1000, 0 to 2000, 0 to 5000, 0 to 10,000, and 0 to 20,000 pounds per square inch. Maximum operating temperature of the cells is 200° F.

Pressure gages of this kind should have many applications in the field of high-pressure technology. Catalytic hydrogenation and synthetic ammonia plants should find them useful. Because of their small physical size and low volume, they should be especially valuable in laboratory work involving high pressures.

Manufacturers Publications

Fisher & Porter Company (Hatboro, Pa.) recently announced that a new edition of "Theory of the Rotameter" is now ready for distribution. It covers the history and technical development of flowmeters of the variable-area type, and explains how the patented Ultra-Stablvis Rotameter overcomes the effects of viscosity and density in flow rate measurement. The accuracy of Rotameters is compared with that of other types of flow-measuring devices. Complete technical and engineering data, together with diagrams and illustrations, are given in this comparison. Chemists and engineers who are interested in a good technical discussion of flow measurement will find this an interesting book.

Current Developments in
WASTE UTILIZATION

There are three methods of disposing of wastes—all have attendant problems.

Discussed by Harold R. Murdock

Disposal is not synonymous with pollution. Pollution is a condition created by improper disposal. Industry can dispose of its useless products either upon land, into the air, or in streams. When a plant disposes of its refuse prudently, only the management of that factory is concerned, but when the surroundings are polluted with such wastes and the rights of others are affected, management cannot escape liability, and the matter falls outside of its jurisdiction. The plant can then be called upon by the authorities to abate the nuisance.

Disposal on Land

Dumps are convenient places for disposal when the substance is an inert solid which will not produce a malodorous condition. Such wastes must also not leach from the dumps into near-by streams or underground waters. Barren lands or depressions in the ground serve admirably for such disposal. Tailings from mining operations, ashes from power plants, and solid residues from smelters, steel mills, ceramic, and chemical operations are examples of residues that can be placed upon the land. Often it is prudent to store solid waste out of doors, or in the case of liquids to store them in reservoirs or tanks and then await an economical use for the material. The wisdom of such practice depends upon the probabilities of a practical solution of the waste problem. The judgment of the technical staff and the confidence of management in its chemists constitute the important yardstick.

In the manufacture of acetylene from calcium carbide, huge piles of the calcium hydroxide sludge which discharges from the reactors have been accumulated out of doors. In many localities these sludges have found profitable applications; other acetylene plants are alert to possible uses for them. Synthetic phenol plants produce enormous amounts of waste sodium sulfite. Some operators have dried and stored this material in anticipation of an eventually profitable market. After the first World War, vast dumps of niter cake had accumulated from the production of nitric acid for war plants. These deposits were later purchased by the kraft pulp industry and used as a substitute for salt cake. Many such examples can be found where management is resourceful in attempting to use its waste materials.

An example of confidence in the ultimate utilization of a by-product chemical occurred in the acetone industry during the first World War. The Allies were unprepared to fill their requirements for acetone. Someone in the British Admiralty remembered that a Manchester professor, Chaim Weizmann, had obtained acetone while experimenting with unusual bacteria in the fermentation of corn. Weizmann's bacteria did not produce ethyl alcohol as did the better known types of bacteria. Weizmann was searching for a source of butyl alcohol to make butadiene for synthetic rubber. (It is interesting that this work of Weizmann was twenty years before the Germans announced Buna rubber.) But the Allies wanted acetone. Now they had a method based on the abundant raw material corn, but the process yielded twice as much butyl alcohol as it did acetone. Several plants were constructed quickly in the United States. What was to be done with the butyl alcohol? Someone in authority had confidence in the chemists who told him that butyl alcohol could become a profitable by-product. Instead of burning the alcohol under boilers, which would have been convenient, large numbers of storage tanks were erected and tremendous quantities of butyl alcohol were accumulated. Many thought the plan foolhardy. Soon the publicity of this adventure reached the ears of chemists who were working vigorously to find a quick-drying lacquer for coating the canvas on airplane wings. With such a finish the production of airplanes could be stepped up materially. The butyl alcohol was found to be superior to existing solvents. From this cheap war surplus material came the first modern quick-drying cellulose lacquer, which was so effectively used later in automobile finishes.

Disposal into the Air

When waste materials of an organic nature cannot be thrown onto dumps without creating a nuisance, they are best burned under boilers or in an incinerator. The burning of great quantities of petroleum sludges by the refineries is a good example. Most refineries burn this refuse in open pits, but some of the larger operators have found it worth while to cotnsruct specially designed steam generators which utilize these high-sulfur hydrocarbon sludges as fuel.

The huge piles of sawdust produced by every sawmill continue to be a problem. Ten per cent of the forests becomes sawdust before it becomes lumber. The furniture industry wastes 25% of its purchased lumber in the form of sawdust. Usually this waste is burned in open piles or in large operations under boilers for fuel. Technology is beginning to find answers to the problem. With the tremendous demand for ethyl alcohol to meet the synthetic rubber program of the war, chemists have shown that alcohol can be produced economically from sawdust. America's first full-size plant is now in production in Oregon. A yield of 50 to 55 gallons of ethyl alcohol per ton of sawdust is reported, and another product (lignin), which amounts to 25–30% of the weight of the original sawdust, has become a problem for utilization. Without a use for lignin, the economics of the process is questionable for postwar operations.

Spent gases from industry are usually purged directly into the air. Sometimes they create nuisances because they are either corrosive, malodorous, or laden with fumes or small dust particles which are too small to settle out readily in the standard-type dust collectors. Such gases can be corrected before release to the atmosphere. In the case of corrosive gases they can be scrubbed with water or alkaline solutions. Malodorous gases can be processed satisfactorily, but they usually do not yield a sufficient amount of the odorous substance to pay for the treatment. Necessity for correcting odor nuisances has to be found in the intangible benefit of good will in the community for the plant making the objectional odor. High-voltage electrical precipitators are used to recover finely divided dust particles from gases. Unfortunately such installations have to be designed on the gas volume and not the dust loading, which makes the economics marginal in most cases. Installations on power-plant stack gases and also on the smelter stacks in the reclamation of pulp mill liquors have proved effective and advisable in communities where dust and odors were troublesome.

Disposal into Streams

A river is an efficient chemical and biological factory, since it purifies itself constantly. Oxygen dissolved in the surface waters is the purifying chemical. The bacteria within the water are the activating agent. At 20° C. and sea level, the solubility of oxygen in fresh water is 9.2 parts per million. When organic matter is present in the stream from natural or external causes, the bacteria normally present in the water use the oxygen to digest the complex organic substances into simpler chemicals which are not injurious to fish and vegetable life. As the river moves along its course, it continually takes on more oxygen to replace that consumed by this digestive process. Most streams can regenerate themselves within a few miles of flow; but when organic matter such as sewage or

(Continued on page 106)

industrial waste empties into the water, such a burden is added to the natural process that the oxygen content is lowered to, perhaps, 50% of normal, and a foul, putrid water condition is created.

In the early industrial period of our country, industries were small and the volume of process residues thrown into the streams were relatively low in respect to capacity to absorb the added burden. Stream pollution was a rare situation. Now, however, huge plants place such an excessive load on the stream that the waters are seriously polluted in many places during its flow. Therefore the large enterprises have become the chief source of trouble.

Public and industrial water supplies, fishing, recreation, agriculture, power development projects, and navigation are all concerned in an equitable division of rights in the use of water from a stream. On the other hand, it must always be kept in mind that industry is a vital part of our economy. It must be given an opportunity to continue. Until technological processes for utilization of the material are found or, failing that, a process for treating the waste to make it more receptive to the individual characteristic of the stream, it is advisable that an existing plant use the stream as the final disposal medium for liquid wastes from municipality as well as industry.

The elimination of industrial wastes from the streams of this country is such an important problem from the standpoint of health, conservation, and public welfare that many states are taking legal steps to abate the nuisance. The subject is complicated, and many industries are alert to the need for finding a practical and economical answer. The types of wastes are many, but some basic unit processes for correcting the trouble already exist. These will be discussed in future articles.

A convenient method for classifying the quality of surface waters and describing their condition has been proposed. Such a technique would serve as a means of describing streams during a survey and is not designed to indicate the desired quality of the waters. Four groups are proposed, and additional standards for the first three are given in Table I.

CLASS 1. Waters suitable for public water supplies with minimum treatment such as chlorination or disinfection and possibly filtration to remove turbidity. These are preferred for swimming and recreational sites.

CLASS 2. This type can be treated by normal filter plant operation to produce satisfactory water supplies. This is the normal classification of streams that receive surface runoff and distant pollution. They may be acceptable for swimming if the number of bacteria of the coliform group is low. They are suitable for healthy fish life.

CLASS 3. These waters can be treated by advanced methods. They are not desirable as sources of public water supply because of taste-producing substances and low factor of bacterial safety. They are not considered safe for swimming and are not desirable for other recreational uses. They will support fish and other aquatic life, but the most desirable types of fish may be absent.

CLASS 4. Waters of this type are unsuitable for public or industrial supplies. They are not fit for swimming and will not support desirable aquatic life.

TABLE I. STANDARDS FOR WATERS OF CLASSES 1, 2, AND 3

STREAM CONDITIONS	CLASS 1	CLASS 2	CLASS 3
Appearance (oil, floating solids, scum, or debris except from natural sources)	None	None	Moderate, localized
Color, p.p.m.	20 (desirable)	Amount of color and turbidity which can be removed with normal equipment by standard practices	Amount of color and turbidity which can be removed economically by advanced methods
Turbidity, p.p.m.	10 (desirable)		
5-day B.O.D., p.p.m.			
Monthly average	1.0	2.0	4.0
Maximum observation	2.0	4.0	6.0
Dissolved oxygen, p.p.m.			
Monthly average	Above 7.0[a]	6.5	5.5
Minimum observation	7.0[a]	5.0	4.0
Coliform group, monthly geometric av. most probable No. per ml.			
Swimming	0.5	10	Not approved
Water supply	0.5	50	200
pH	6.5–8.6	6.5–8.6	5.0–9.5

[a] Upper layers of stratified lakes and pools.

Current Developments in
PLANT MANAGEMENT

> To convert our plants quickly and efficiently, it is essential to adhere to principles of sound business practice.

Discussed by Walter von Pechmann

Despite the strenuous efforts made by government agencies and private enterprise to be prepared for the resumption of civilian production soon after V-J day, many manufacturers have experienced difficulties in getting started. This condition can rarely be attributed to improper planning; most frequently it is brought about where reconversion measures cannot be put in effect because of certain circumstances over which the manufacturer has little or no control. In this event there is the choice of either waiting until conditions become more favorable or drastically revising the entire reconversion program. It is therefore not uncommon to find reconversion projects stalled or measures taken which are contrary to sound business practice. The purpose of this article is to discuss some of the reconversion problems with which we are confronted today and to suggest ways and means of overcoming some of the difficulties.

It might be advisable to point to the fallacy of the belief that only one of the choices mentioned can be selected for putting an entire reconversion program into effect. Individual factors making up the program can be analyzed, and decisions made as to whether to accept loss of time or the departure from the original layout. Anticipated changes, however, should be scrutinized to determine if they will cause only temporary inconvenience and involve expenditures at one time, or increase the cost of manufacturing in the future, and possibly violate established company policies.

Time is often wasted in deciding on the methods which should be employed when changes have to be made, because matters pro and con are intermittedly discussed which confuse the issue. Furthermore, the people consulted are frequently ill-prepared to give intelligent answers to the questions raised because no time is given them to accumulate the statistical information necessary for rendering sound judgment. Decisions, therefore, are too often based on the greatest number of objections raised instead of on their relative importance. To gain a clear picture of the issues involved when the change of a reconversion layout must be decided on, it is recommended that questionnaires be filled out by the person who is in need of a decision from management (Figure 1). Depending on the value management attaches to obtaining detailed information on the changes which take place during the reconversion period, such a record can be condensed or enlarged. For instance, the printing shown under 5 in Figure 1 can be grouped according to the organizational setup of a plant, subdividing production, purchasing, accounting, sales, personnel, research, etc. The circulation of this paper among the departments involved can solve at least one of the many reconversion problems—how to coordinate the efforts of the various sections of a plant into a unified reconversion program. In large organizations it has been found advantageous to appoint a reconversion director in the capacity of an assistant production manager whose main function is to see that the elimination of a bottleneck in one department will not cause difficulties in another.

Attention is called to other advantages of the record shown in Figure 1. The tabulation of similar reasons given for actual or anticipated holdups enables management to spot quickly the weak points of a reconversion program. For instance, if inadequate storage facilities are predominant, an investigation may reveal that the engineer responsible for floor layout was never correctly informed as to where inventories might accumulate in the new manufacturing process. Other proposed layouts of storage facilities can then be rechecked and changed if necessary.

Disadvantages in proposed changes as reported on the record can also be tabulated. This has two advantages: First, management can take preventive action on difficulties expected to arise out of authorizing measures which do not comply with the standards prevailing in the plant. For example, if the measures approved may cause mix-ups in production, the prevailing methods of identifying the goods in process can be improved to such an extent that the possibility of such errors becomes almost nonexistent. Second, management can prevent those undesirable but necessary measures which have to be approved occasionally from assuming plant-wide proportions. For example, if bottlenecks can be eliminated only by the addition of labor, management can limit the number of employees hired to overcome temporary difficulties to a certain percentage of the requirements originally anticipated.

Lack of experience is one of the most common causes of difficulty during the reconversion period. This applies especially to plants where new products are scheduled to be manufactured. Experience can be gained only in time, yet time is the factor which must be reduced in order to start quickly. Therefore it is often better to employ a highly paid specialist to overcome an obstacle than to attempt to solve all current problems with personnel untrained in the intimate phases of future production. It is also recommended that a check be made to determine if research facilities are unnecessarily overburdened with assignments which could be handled by an experienced foreman.

Most reconversion layouts were made during the war. This necessitated the assumption of postwar conditions which did not always materialize. Furthermore, wartime restrictions on the publication of important developments made it impossible to incorporate many improvements made during the last few years. To re-establish civilian production on an efficient and competitive basis, the original product and manufacturing specifications should be rechecked. In an effort to start at the earliest possible date, many manufacturers pay little or no attention to this phase. Since it is impossible to conduct extensive investigations now, it is recommended that management make available to production all information on new developments in materials and latest types of equipment. This will make it possible to incorporate at least some of the new inventions which will be accepted as a standard in our industry within the next few years.

Many flaws in reconversion setups originate from exaggerated sales forecasts and excessive provisions for future plant expansions. Some of the reasons for this are: No time, money, or facilities were available at the time of planning to conduct intelligent product research; "to play safe", the most ideal conditions were assumed. Sales forecasts and provisions for future plant expansion were purposely overstated for prestige (to satisfy stockholders, accounts, employees, etc.). Space needed for future plant expansion was calculated by simply deducting from the total plant area future production requirements.

The manufacturer who freely admits that his reconversion preparations need improvement is sure to take the necessary steps to overcome shortcomings. Unfortunately, the dangerous attitude is displayed by many executives that the original plan has to be carried out, regardless of consequences, since the great number of changes which would have to be made to start production on an efficient basis would undoubtedly reflect on their ability to plan properly. This attitude can result only in disappointment. Leaders in industry must be flexible enough to adjust their decisions according to prevailing conditions, and should not hesitate to admit the need for changes if this will bring about improvements. Attention was called in the August issue (advt. sect., page 91) to the importance of adjusting manufacturing facilities to either centralized or decentralized production control. This phase has not been given sufficient consideration in many layouts and should receive special attention.

In the April issue of the *Service Bulletin*, published by the Policy Holders Service Bureau, Group Division, Metropolitan Life Insurance Company, Leonard J. Smith described a procedure for the orientation of supervisors in plant operating functions. This article stressed the importance of making supervision familiar with all the aspects of future plant operations. Few foremen in a plant know of the company's future operations or reconversion programs. The fact that employees have once been told in general terms and rosy colors what management intends to do can hardly satisfy the foreman who *(Continued on page 112)*

Plant Management

has to answer daily questions raised by employees who become increasingly "layoff conscious". Orientation courses not only keep supervision informed of the present status of reconversion, but also teach that successful reconversion depends to a great degree on all departments working together harmoniously.

It is suggested that a discussion on current reconversion problems follow each meeting. This is a simple and efficient means to make the foreman appreciate the problems of his associates. Furthermore, when improvements made in one section of the plant are brought to light, interest is stimulated for general acceptance where feasible.

TO: FROM: DATE:
CC:

Re: Reconversion Project No.______
Title__________ __________

1. This is to inform you that the above numbered reconversion project $\frac{\text{has been}}{\text{will be}}$ temporarily held up for reasons as follows:

2. It is estimated that this project will be behind schedule:

________days ________months
________weeks ________until further action is taken.

3. I have taken the following actions:

4. I recommend that management take the following action:

5. This recommendation will or may (check):

☐ Eliminate this bottleneck without any disadvantages.
☐ Lower quality of the product. ☐ Call for the revision of product specifications.
☐ Increase the cost of manufacture.
☐ Require additional labor.
☐ Require special training of employees.
☐ Increase the number of tests for quality control.
☐ Require new testing methods.
☐ Call for the revision of layout and/or flow of production
☐ Constitute a manufacturing hazard.
☐ Call for the revision of operating standards.
☐ Cause "mix-ups".
☐ Make the standardization of equipment $\frac{\text{difficult}}{\text{impossible}}$.
☐ Require new source of energy.
☐ Be opposed by employees.
☐ Other reasons (explain):

SIGNATURE:__________________

Write your remarks on plain sheet of paper in the event not sufficient space is available. Give number.

Figure 1

Last-Minute Flashes

FROM THE EDITOR'S DESK

THE chemical industry slipped in its safety record for 1944. Statistics show that frequency of accidents was up over the previous year; as compared with other industries, the chemical field dropped to eleventh place from seventh.

★ Salvage of tin cans by the public during the past three years added some 6000 tons to the scrap pile.

★ Bethlehem Steel Company is planning huge expansion of its bar production facilities. The bars made will be used in automotive applications.

★ Less than 20% of our original deposits of silver and lead is still unmined.

★ Penicillin, sprayed as an aerosol, is being found effective by the doctors in combating respiratory diseases such as sinusitis.

★ Australia prospected and found deposits of uranium ore which have come in for considerable development.

★ Canada may obtain considerable relief from the spruce budworm, a serious economic pest to the forests, through the use of DDT sprayed from airplanes.

★ Tsetse flies, infecting agents in sleeping sickness, are killed by DDT and may be effective in ridding Africa of this scourge.

★ Over four million dollars were appropriated last year by the National Foundation for Infantile Paralysis as an aid to scientific investigation and research on this disease.

★ During the war the state of Texas alone added more than five thousand producing oil wells to its total.

★ The corn crop for this year will be one of the largest ever, according to estimates of the U.S. Department of Agriculture.

★ New rotenone plantations are beginning in Brazil.

★ Uranium deposits on public lands have caused certain tracts to be withdrawn from sale.

★ Retreating Germans were prevented from damaging the electrochemical plants at Rjukan, Norway, and the plants are now said to be in production.

★ Disposal of immense stores of auto parts is the first major disposal task tackled by the Government.

★ New cobalt mines and recovery units are reported in operation in the Belgian Congo.

★ New waste problems have been created by the synthetic rubber industry, and processing difficulties are being experienced at disposal and water plants.

★ Tin is in short supply, but the processing kinks learned by our mechanical industries during the war will stand them in good stead during the temporary reconversion shortage.

★ The oil refineries at Balikpapan have been so badly damaged by bombings that production cannot be reached for well over a year.

★ The gas generators that were put on many of the motor cars in Brazil during the war may remain for some time, for it has been decided to continue the Gasogenio organization in force.