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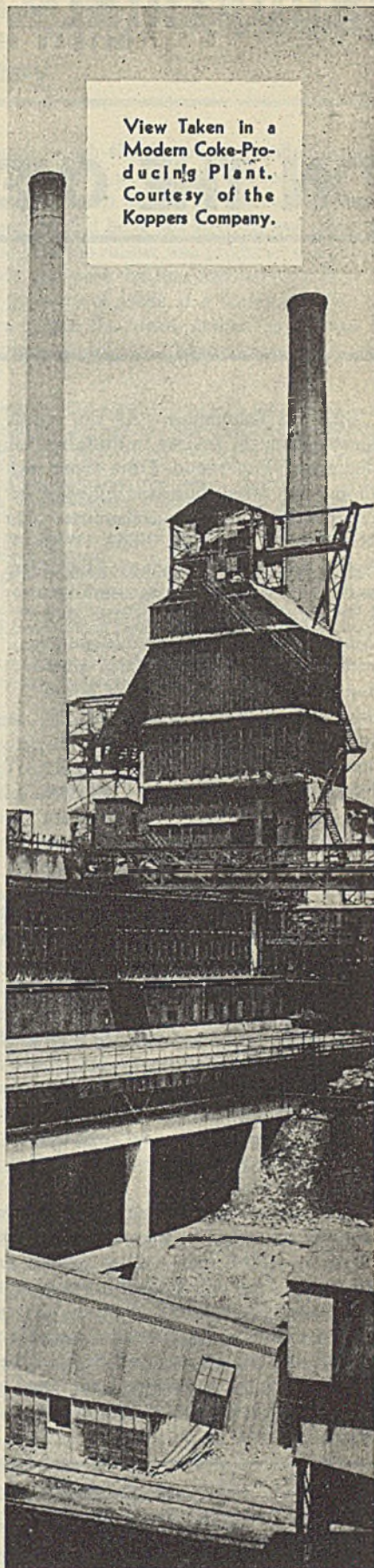
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View Taken in a
Modern Coke-Pro-
ducing Plant.
Courtesy of the
Koppers Company.



INDUSTRIAL AND ENGINEERING CHEMISTRY

REPORTS

ON THE CHEMICAL WORLD TODAY

Economics

Chlorine Economics. At the recent meeting of The Electrochemical Society in Buffalo, Philip B. York of The Champion Paper and Fibre Company revived and reviewed the often discussed question of the economics of chlorine production by consumers. He pointed out that Champion Paper and Fibre, West Virginia Pulp and Paper, the Brown Company, and others operate so-called captive chlorine plants successfully; to justify installation of its own chlorine unit, a mill should demonstrate that it can produce chlorine for, at most, the cost of liquid chlorine delivered to its bleach department. The cost of liquid chlorine delivered is, of course, readily determinable. The cost of chlorine produced in the mill is much more difficult to estimate in advance.

York reports that, when the daily use of chlorine is less than 7 tons, the probabilities are that the installation of such a plant will not be economical. However, he points out that in some instances installation may be justified, especially if the caustic soda produced is self-consumed and replaces purchased caustic. Items such as available power for cell operation, steam for evaporation of cell liquor, available supervision, space for the plant, depreciation, interest on investment, etc., must be thoroughly investigated. On such a small plant (7 tons daily) the supervision, taxes, and depreciation may be so large as to increase the costs to a level higher than that of purchased chlorine.

If more than 7 tons of chlorine are consumed daily, just as much care must be taken with the preliminary studies, especially if the pulp mill is near a producer of liquid chlorine. After all, little equipment is required to make lime bleach from liquid chlorine. Storage space for the bleach would be much smaller because very little bleach would have to be kept on hand. Tank cars of liquid chlorine can be, and have been, used as storage tanks. The shipments of liquid chlorine can be scheduled as required.

The cost of a proposed electrolytic chlorine plant will be in the neighborhood of fifty thousand dollars per ton capacity of chlorine to be produced daily. This figure will vary with the size, location, and equipment of the proposed plant, and with the availability of power, steam, etc. In some mills steam for evaporation and heating and also electricity for the cells and motors may be available. In other mills the installation of new boilers to produce steam and new generators to produce needed power might be required.

Pulp mills consuming chlorine in excess of one tank car per day were advised by York to investigate the possibility of producing their own chlorine. One of the chief factors is the cost of liquefaction which is an unnecessary step in a captive plant. According to the speaker, chlorine requirements of 16 tons or

more per day normally should be sufficient margin to justify installation of a chlorine unit; but all factors involved should be carefully analyzed before a decision is reached. He discussed the various cost factors in the production of chlorine in a captive plant, including raw materials, salt, power, steam, graphite anode consumption, labor, maintenance, supervision, general overhead costs, and investment, as well as additional factors, such as geographical location of the mill with reference to raw materials, caustic markets, and nearness of merchant chlorine producers.

The York paper and others on various phases of chlorine production given at The Electrochemical Society reminds us that the chlorine industry faces a tremendous problem in the postwar era due to the rapid expansion in productive capacity during the war. It is no secret that chlorine producers are researching to find new markets and new materials which will employ chlorine as a raw material. We have been informed on what we believe to be reliable authority that the treatment of water with chlorine in the United States would consume, at best, approximately 50 tons per day.

(Continued on page 8)

Readers will find three new departments introduced in this issue under the authorship of an authority in each field; they will be found in the advertising section: Equipment and Design, by C. O. Brown, page 57; Instrumentation, by Ralph H. Munch, page 63; Plant Management, by Walter von Pechmann, page 69.

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

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

Economics

This is not a large consumption figure when we consider the total productive capacity of chlorine plants in this country. Furthermore, the 1930's witnessed many installations in municipalities so that growth in this direction is not likely to result in further heavy increases in chlorine consumption. Treatment of sewage and industrial wastes, however, is another matter; we are told by the same authority that the ultimate market in this field totals approximately 500 tons of chlorine per day. It must be borne in mind, however, that we are likely to move rather slowly in the introduction of sewage disposal units and industrial wastes disposal plants even though it is admitted that legal pressure will be applied universally, once the war is over.

Currently the consumption of chlorine in both water treatment and sewage disposal, we are reliably informed, runs 40 to 45 thousand tons per year. It is apparent, therefore, that some increase in chlorine consumption is still possible in these two fields. By way of comparison, however, we point out that current consumption of chlorine in the manufacture of carbon tetrachloride totals 100,000 tons, or more than twice the total amount used in water treatment and waste disposal. Introduction of the new organic products popularly known as Silicones is one striking example of the possibility of utilizing chlorine as a raw material. At present we are producing tremendous quantities of hypochlorite, and peacetime uses are being sought eagerly. One possibility is the much wider introduction of hypochlorite into the general consuming field in small package form for use in connection with dish washing. The problem is really two-pronged—finding new uses not only for chlorine but for caustic as well. In many ways, finding new outlets for caustic will be the more difficult phase.

We cannot close this discussion on chlorine without pointing out the astonishing fact that we have not experienced in this country any serious epidemics of diseases which are associated with impure water and unsanitary conditions caused by waste disposal. This achievement is remarkable in view of the vast exchange of population and overcrowded conditions in most of our industrial cities. A bouquet to that small band of municipal engineers who, without fanfare, have guarded the health of America during the war.

Postwar Rubber. Crystalline facts are beginning to settle in the cauldron, once boiling and heartily agitated, that contains our compounded mixture of rubber knowledge. Authorities and dispassionate scientists are issuing clean-cut and well-thought-out statements on all aspects of the rubber problem—and a problem it is, for there are as many international leaves on the rubber tree as there are on the oaks of Dumbarton.

First in our digest of the rubber situation are a few thoughts from a recent address of W. P. Hasselman, Trade Commissioner of the Netherlands Indies. He believes that plantations and other cultivated lands have not been destroyed to any great extent because they are (Continued on page 10)

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

Economics

capital investments which the Japanese intended to enjoy, and attempts at destruction would have met too much native opposition since most rubber estates are native-owned. The Dutch even expect to find large stocks of rubber when they return, for in the past the rubber was produced solely to obtain foreign goods, and since the Japanese cannot make available the former quantity of goods, it is highly probable that the natives have hidden the rubber rather than accept currency that will prove worthless. Concerning postwar rubber supply he said:

While we respect the place which synthetic rubber has gained for itself as a result of the war, we feel that rubber—synthetic and crude—will not be overplentiful during the first few years of peace. The endless stream of war supplies and equipment which is speeding interminably over every highway in Europe, Asia, and Africa will have opened the eyes of even the most conservative to the fact that outside this country it had not been visualized to what extent motor traffic could contribute to economic and social progress.

After the first great rush to resupply . . . rubber, there will undoubtedly be a lessening in the demand, and a time will come for reappraisal of the producing plants for both natural and synthetic rubber. I believe that such an appraisal will be based on sound economy in both cases, and that the sound synthetic plant and the sound natural plant will both survive as prosperous components of the raw rubber industry.

To the delicate question of how rubber will be handled after the war (cartels are an unsolved world-trade stumbling block) he could not answer but remarked that "no single nation will be the arbiter of what are to be the methods of international trade. . . . I should like to point out, however, that for over four hundred years we Dutchmen have been very jealous of our individual rights of free enterprise. To change—if world-wide practices and conditions so demanded—would be at least as great a wrench to us as it would be to the traders of any other nations."

The Rubber Director's office issued a special report on plant investment and production costs in the synthetic program which is the subject of our second digest in this report. Bradley Dewey, in the introduction, makes several noteworthy remarks. In speaking of the economic necessity for rubber, "unused stand-by plants of the complex type required to make synthetic rubber and basic materials, deteriorate rapidly. *Chemists and chemical engineers do not stand still—research discovers improvements constantly which call for changes in plant equipment.*"

In speaking of rubber supply: "I believe that the world demand for rubber after the war will be far greater than the capacity of the world's plantations before the war" (he probably precedes Hasselman in that idea). He mentioned that Buna S will act as a governor and will set a ceiling on the world price for crude rubber. In conclusion he said: "However, I believe the postwar world demand will be so large that there will be need for all the crude rubber present plantations can turn out and also the production of the low-cost producers of the synthetic rubber program—from 400,000 to 600,000 tons. There should be no duties or subsidies or international agreements. This country is today independent for its supplies of rubber of other nations, of the effect of wars between other nations, or the destruction of plantations by plant blights. It must so remain." (Continued on page 14)

The main portion of the report dealt with costs of synthetic rubber, an analysis made by E. R. Gilliland and H. M. Lavender, Jr. For proper analytical study, use must be made of four charts relating costs of butadiene from alcohol, costs from petroleum, costs of styrene, and production costs of GR-S. We think the following, however, to be a fair approximation of the authors' message:

Operating expenses of butadiene alcohol plants, other than those for raw materials, are much less per pound of product than are those for making butadiene from butylenes. At present, plant cost, exclusive of feed stock, amortization, preliminary, and research costs, is 2.21 cents per pound for butadiene from alcohol, 4.63 cents for butadiene from butylenes, 2.52 cents for styrene, and 4.83 cents for the processing of copolymer.

Investment per long ton of synthetic capacity is Buna S \$663, Butyl \$779, and Neoprene GN \$717. Costs per pound of finished rubber under the present program are Neoprene, 24.04 cents per pound, and Butyl, 21.51 cents per pound. Buna S costs yield only to a complicated method of figuring. In the alcohol process, butadiene costs about 40 cents per pound with alcohol selling at 90 cents per gallon as it does now. With industrial alcohol at 15 cents per gallon, butadiene will cost 8.75 cents per pound. Under the butylene dehydrogenation process, cost estimations are hazardous because production has not yet been stabilized, but with 9.5-cent per gallon butylenes and a utilization of 0.65, butadiene costs are 7.6 cents per pound, approximately their present price. If in the postwar butylenes drop to 6 cents per gallon, the same utilization will give butadiene at 6.4 cents per pound.

At present styrene, with ethylene at 6 cents per pound and benzene at 16 cents per gallon, costs 6.6 cents per pound. Future possibility is ethylene at 2-3 cents per pound, benzene at 8-12 cents per pound → styrene at 4-5 cents per pound. Copolymer costs, naturally, are based on styrene and butadiene costs, plus charges involved in plant operation. The authors of the report state that Buna S can now be produced for an "out of pocket cost" of about 12.2 cents per pound. With butadiene from alcohol the present price of Buna S is 37 cents per pound.

On a postwar basis Buna S could cost 10.7 cents per pound or, as the authors state, an out of pocket basis. Even with butadiene made from alcohol at a cost of 9 cents per pound, Buna S would cost 12.1 cents per pound. In all of the costs the authors include only management fees and royalties; additional costs due to selling, profit, interest charges, increased royalties, and market risks may, they feel, increase costs only 2 to 4 cents per pound.

Without much doubt the petroleum process for making butadiene will be the cheaper method, but the advantage is not too heavily overbalanced in its favor that an upset could not occur. If alcohol drops to 12 cents per gallon, a real scramble will develop. If our intent is to keep our synthetic plants in postwar competition with natural rubber (more on this next month), it is not too unreasonable to expect the alcohol process to be kept also. (Continued on page 16)

Sulfuric Acid. Sulfuric acid has always been one of our basic industrial chemicals, so much so that its rate of consumption at one time was suggested as an industrial barometer. But despite its importance and our huge capacity for producing H_2SO_4 (greatest in the world), the present global war has shown that sulfuric production is not enough. We had the same experience in World War I.

Increased pressure for ordnance and munitions production calls for constantly growing sulfuric requirements for smokeless and rocket powder, high-octane gasoline, steel, and high explosives. These are only part of the story. The superphosphate industry counts its use of H_2SO_4 even in normal times by millions of tons, and to meet heavy and rising fertilizer demand for food and fiber crops, phosphate acidulating plants have to take their sulfuric in the form of spent acid from ordnance projects. When we consider that many hundreds of tank cars are required to haul the spent acid alone from powder and ordnance plants and that fertilizer makers are remotely situated from sources of supply, we begin to get some idea of the problem in sulfuric output and transportation which has been thrown into the laps of the war agencies.

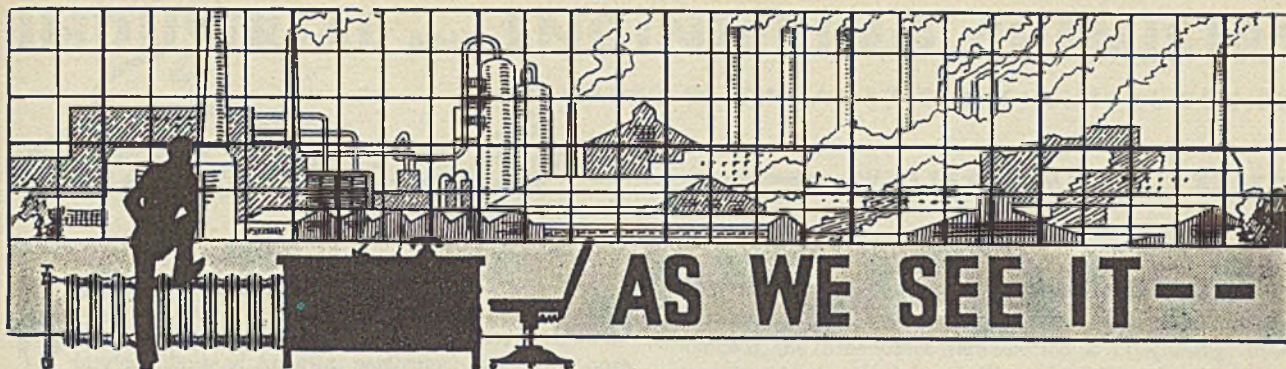
That problem is a real one for War Production Board. The WPB Chemicals Bureau's data show that demands for new and spent acid during 1944 will amount to 10,556,200 short tons, and that the supply during the same period will not exceed 9,650,700 tons, a deficit of 905,500. During the first half of 1945, requirements are estimated at 5,663,600 tons and the supply at 5,251,000 tons, or 412,600 short of needs. Ordnance acid production is not included in the figures, and spent acid from these sources might be counted upon to make up part of the deficit. We will need 400 to 500 tank cars to haul it, however, and here we run into the same problem that faced the industry in 1917-18.

Bernard M. Baruch says that it was much more troublesome to transport the acid at that time than the raw materials which entered into its manufacture, and for that reason the cost of a new acid plant had to be constantly weighed against the importance of having one near an explosives plant.

Superphosphate, chemicals, and petroleum refining, in the order named, at present are taking the greatest quantities of sulfuric acid:

Requirements	Short Tons	
	1944	First half of 1945
Superphosphate	2,852,900	1,558,600
Ammonium sulfate	694,500	361,200
Petroleum refining	1,477,000	890,900
Chemicals	2,188,600	1,130,000
Iron and steel pickling	558,400	291,700
Other metallurgical uses	343,000	174,500
Paint and pigments	767,100	389,600
Explosives other than ordnance	742,600	375,400
Rayon and cellulose film	528,100	289,300
Miscellaneous	404,000	202,400
Total	10,556,200	5,663,600

An interesting side light on this compilation is the allowance made during the first six months of 1945 for continued large tonnages of H_2SO_4 to such basic war manufacturing industries as steel, chemicals, petroleum. As far as petroleum is concerned, (Continued on page 54)



This Month

THIS month, as We see it, an important event in our history is the beginning of three new columns, to be found on pages 57, 63, and 69 of the advertising section. They are written by Charles O. Brown whose subject is Equipment and Design, by Ralph H. Munch, a specialist in Instrumentation, and Walter von Pechmann, on Plant Management. The Editors feel that, with developments coming so fast, it is difficult for chemists and chemical engineers, who are legitimately interested and vitally affected by these subjects though not always conversant with them, to keep up to date except in their own fields of specialization. In an attempt to remedy this situation, we have begun the three columns and created three "colymnists". We recommend them to you.

Water treatment has in recent years become tremendously important. Not only is water softened to save soap costs, but cold calculating chemists have convinced management that prevention of boiler and exchanger scale is a money-saving proposition—leading us to say that the article by Sheen and Woodruff on selective calcium softening is an important paper. Stressing industrial use, the authors show how the seemingly mechanical operation of making airplane motors is quite dependent on proper water. At the huge Wright Aeronautical plant in Cincinnati 14 million gallons of water are treated daily for use in acetylene generation, pickling, plating, cooling, x-ray developing baths, and other processes. By removing only the calcium hardness, savings are made in chemicals cost. Control of the operation is afforded by means of pH; in some instances hardness was reduced 300 parts per million at chemical costs ranging from 1.29 to 2.07 cents per thousand gallons. An installation based on this principle has also been made in a plant treating 120 million gallons per day. It is planned to dewater, thicken, and purify the sludge so that it may be burned to lime.

The handmaiden of the sciences, mathematics, is well represented by three articles in this month's issue as it is applied to chemistry and her offspring, chemical engineering. The first comes from Temple C. Patton, of The Baker Castor Oil Company, on Graphical Methods for Temperature Distribution with Unsteady Heat Flow. Included is a table of methods employed in problems of unsteady heat flow, listing their various advantages, disadvantages, and limitations. Patton states that, although the graphical method is approximate, it is applicable to complex situations incapable of vigorous mathematical solution.

Paper No. 2 in the mathematical category is by Robert Herzog, of the Ethyl Corporation, on Correlations of Critical Constants with Parachors. Herzog derives an equation expressing a relation between the critical temperature and boiling point, involving only two constants. Over 140 compounds have been classified into six groups, and equations have been derived for each group along with measures of the reliability of estimated T_c/T_b values.

The third mathematical baby of our November triplets is by Hugh M. Hulburt, of Hunter College, who studies the correlation between equations of reaction and flow and their application to design. He concludes that, when properly analyzed, data on

flow systems furnish information as reliable as that from static systems.

For a quick roundup as the end of the column approaches: Chemistry has many forces that make $2 + 2 = 5$ (see Synergy in Industrial Chemistry). Alkyd resins have many different fractions, some possessing different characteristics (see Extraction of Alkyd Resins); Lactoprene is a new synthetic rubber and you may read about it in the important articles on acrylic resins in this issue from the Eastern Regional Research Laboratories.

Next Month

THE press juice from waste asparagus butts and trimmings may be used as a microbiological media, and we have a report on the production of bacterial proteinase obtained on asparagus juice. It has been estimated that from 50,000 to 100,000 tons of butts and trimmings are carted away from canneries each year; as can be expected, this entails much expense. Turning this waste into a profit may be possible if the new scheme works out.

Development and performance of three all-metal screen-plate fractionating columns for general laboratory and pilot plant use are reported. The characteristics of six different screens are noted, and performance data will be given along with plate efficiencies on hydrocarbons at total reflux.

When wheat gluten is reacted with chlorosulfonic acid in pyridine, a product forms which, upon neutralization, will absorb one hundred to three hundred times its weight in water. The gel thus formed, according to the author of this article to appear next month, is firm, odorless, tasteless, and nontoxic. Uses suggested are as substitute for scarce natural gums in making therapeutic jellies, ointments, and other pharmaceutical preparations, and as a thickening agent in ice cream. The material has already been used in surgery for the absorption of post-operative drainage.

An improved process for preparing tannin from Western hemlock will be suggested which involves the use of a hydraulic press in preliminary stages. Benefit from this technique is a decreased bleaching time.

Redwood tannin is a depressant for calcite and quartz in the flotation of feldspar as we shall see in another paper on tannin next month.

More data for the petroleum chemists will be forthcoming in an article presenting experimental data on the density of each of a series of paraffin hydrocarbon mixtures of low molecular weight—also analysis of their constitution.

If cable and filter paper is impregnated with liquid paraffin solutions plus a little lauryl sulfonic acid, conductivity of alternating currents is hugely improved. Perhaps in this fact lies the explanation of why certain insulation often acquires, in service, high power factors.

And that's as we see it.

F. S. Van Antwerpen

INDUSTRIAL AND ENGINEERING CHEMISTRY

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Editorials

WALTER J. MURPHY, EDITOR

In Keeping with the Times

ONE cannot visit the chemical, petroleum, and metallurgical plants of America, particularly the newer ones, without being greatly impressed with the increase in the utilization of recording and control devices of one kind or another. Because of the critical shortage of technical manpower during the war period, it is unlikely that we could have performed the production miracles which are now a matter of record if control and recording instruments had not been made available in great quantities. Unquestionably we will see in the postwar era further adoption of automatic devices. Indeed, many of our plants constructed during the war period have been forced to employ a minimum number of such instruments, but this condition is being remedied rapidly.

Even casual inspection of the newer plants indicates not only the trend toward instrumentation, but rather revolutionary new developments in plant equipment and design. One of the favorite topics of discussion today among chemical engineers is speculation on postwar chemical engineering techniques, particularly the introduction of continuous operation replacing batch operation.

Not all the problems that will confront plant managers in the postwar period will be strictly chemical and mechanical. The return of former employees from the Armed Forces, labor relations, improved cost-finding methods, employee incentive plans, simplified production records, plant housekeeping, and plant safety problems, are some of the potential headaches in store for plant managers.

All this is merely an introduction to an announcement that *INDUSTRIAL AND ENGINEERING CHEMISTRY* will include each month, beginning with this issue, three new departments: Equipment and Design, Instrumentation, Plant Management. We have secured an outstanding expert in each of these fields and believe that their contributions will assist materially in the solution of three of the most important phases of postwar production.

The subject of Instruments will be covered by Ralph H. Munch, specialist of the Monsanto Chemical Company, who is in charge of matters concerning automatic recording and control devices in all Monsanto plants. Charles Owen Brown, well-known New York chemical engineering consultant, will discuss over-all problems on equipment and design, and Walter von Pechmann, industrial engineer with fifteen years of production experience and now associated with the Ansco Division of General Aniline and Film Corporation, will comment on various phases of plant operation and management. More detailed biographical sketches of the three contributing editors will be found on advertising pages 58, 63, 69.

The Editors of *INDUSTRIAL AND ENGINEERING CHEMISTRY* over the past several months scrutinized most carefully operations in hundreds of plants located throughout the country and questioned plant managers as to what, in their opinion, this publication could add to its editorial program

that would prove most useful. As a result of these plant inspection trips and frank discussion with plant operating officials, the three topics were selected as a beginning; others may be added in the future. We and the Contributing Editors welcome constructive suggestions and criticisms on how these new services can best be directed to serving our readers.

Controlling German Industry

CONSIDERABLE interest and speculation have developed in Washington and other parts of the country over a news release, under date of October 17, entitled "A Job for the Antitrust Men", written by Herbert J. Seligmann, of the Overseas News Agency.

Seligmann, after giving credit to the Antitrust Division of the U. S. Department of Justice for furnishing the Army Air Force Intelligence Service accurate target information on German and Japanese industry, then goes on to state:

It is now suggested in Washington that the same group which so thoroughly and carefully analyzed the flow of German industry and the bottlenecks of the cartel system, and which knows European industry as well as anyone can in the United States, be sent overseas to deal with the specific problems that control of postwar German industry will pose.

In some quarters in Washington, the Overseas News Agency story is viewed as being inspired and as the opening gun in a campaign by the Antitrust Division to secure dominant representation on any board or boards created to control German industry in the postwar period.

The Overseas News Agency release also states, "It can be said on unimpeachable authority, that the Antitrust Division of the Justice Department, which successfully helped the Army analyze German industry for war purposes, is not being called upon for any of the detailed planning with regard to the future of that industry". In fact, Seligmann, again using the same unimpeachable authority states, "It is doubtful whether any such detailed planning is now going on."

Reverting to the well-known newspaper ambiguity of "informed sources", the Seligmann story continues as follows:

This, say informed sources, is the more absurd inasmuch as the Antitrust Division is virtually the only agency in the United States Government that has had experience in reorganizing industry from the point of view of restoring competitive conditions from monopoly domination.

Continuing, the Overseas News Agency release states:

It is now contended that these same men who know more about the dye, steel, chemical, optical, and electrical industries than some of the high officers in the big corporations, are the ones to send to Europe for the purpose of doing the same kind of job in dismantling the immense German cartels which helped prepare Nazi Germany for World War.

That the members of the staff of the Antitrust Division are better informed on chemical matters or will handle such matters more judiciously than the officials of chemical companies or the outstanding technologists of this country, will be doubted by most capably informed individuals.

In a recent editorial entitled "Planning Postwar Germany", this publication advocated that German industries be directly supervised for many years to come by scientifically trained individuals who will be able to detect and prevent the prostitution of science and industry for war purposes.

We have in this country a number of highly trained chemists, chemical engineers, and technologists in every branch of science, of highest integrity and free of any entangling alliances with industry who are available for the purpose of controlling German industry. It is suggested that men of this caliber be selected, rather than a group consisting largely of politicians, lawyers, and statisticians. Problems to be met and questions to be answered will have technological angles which only scientifically trained minds can properly analyze.

Surplus Property

THE Surplus Property Bill recently passed by Congress has, in the main, throttled the plant disposal program of the Surplus War Property Administration. Under the new law a three-man board appointed by the President has replaced the Surplus War Property Administration. The most general criticism made of the new law is that a three-man committee, so to speak, will not operate so quickly and so effectively as an agency with but one head. Another criticism is the proviso that no property costing over \$5,000,000 can be sold until 30 days after the report has been filed and 30 days after Congress is in session.

Within the next three months the new board must submit to Congress recommendations for handling seven major types of surplus facilities—aluminum, magnesium, synthetic rubber, chemicals, aviation gasoline, iron and steel, and pipe lines. Obviously the chemical industry and industries closely allied to it are concerned with the methods employed to market some \$3,600,000,000 worth of plants in these fields. Somewhere three outstanding individuals with integrity and ability must be found to solve this major problem.

Practice Personal Censorship

THIS publication views with deep concern the growing tendency on the part of some sections of the press, and a few columnists, to publish items purporting to give inside information on matters connected with our war effort. It sounds very smart to hint at these matters, and the authors of such gossip expect to convey the impression that they have special access to highly confidential information, when, in all probability, they are merely repeating some remark they have overheard.

Technologists must recognize that they have a very special responsibility to maintain absolute secrecy on all technical and scientific information. In all military programs of any size it is necessary that many people have access to considerable information of value to the enemy, but it is definitely wrong to assume, because relatively large numbers know or suspect some of the phases of such programs, that it is safe to discuss or even mention them.

Two of the most important angles of all new military developments are suspense and surprise. Idle gossip destroys much of the practical value of secret weapons. Advance information, no matter how meager, may tip off our enemies on

what to expect and permit them to prepare counter measures immediately. Thus not only is the element of surprise destroyed, but thousands of lives may be sacrificed.

Despite the talk of reconversion, demobilization, postwar planning, and Allied victories in Europe and in the Pacific, the war is not yet won and we can assume that it is only when Germany and Japan have capitulated. We still face the possibility of tremendous loss of lives. One heedless remark may mean that the toll of the flower of our manhood may be increased and the war needlessly prolonged.

Those who are actually engaged in secret research work are the least likely to talk about the details. The greatest danger comes from outsiders who speculate on war projects. If each and everyone of us practice personal censorship over our own remarks, our enemies will continue to remain in the dark and, when we are ready to launch new weapons, they will really come as a complete surprise.

U.O.P.—A.C.S.

NATURALLY, considerable interest has been evinced by members of the AMERICAN CHEMICAL SOCIETY and others concerning the status of the offer by the owners of the Universal Oil Products Company to give the company to the AMERICAN CHEMICAL SOCIETY.

Creation of a trust under which the Guaranty Trust Company of New York is trustee of securities of the Universal Oil Products Company in Chicago for the benefit of the AMERICAN CHEMICAL SOCIETY has been announced by Thomas Midgley, Jr., President of the SOCIETY. The trust, known as the Petroleum Research Fund, was set up to administer the gift made by a group of oil companies owning securities in Universal, one of the leading research and development enterprises of the country. The management and operation of Universal Oil Products Company will be under the direction of a board of directors to be appointed by the Guaranty Trust Company of New York as trustee.

The donors are Shell Oil Company, Inc., Standard Oil Company of California, Standard Oil Company (Indiana), Standard Oil Company (New Jersey), The Texas Company, and N. V. de Bataafsche Petroleum Maatschappij. The donor companies made known their proposal to relinquish their holdings of securities of Universal Oil Products Company for the benefit of the SOCIETY at the 108th National Meeting of the SOCIETY in New York on September 13, 1944. At that time they offered to give all their securities of the company to the SOCIETY. The Board of Directors of the SOCIETY accepted the offer in principle and appointed a committee to work out the details. The negotiations culminated in the agreement creating the Petroleum Research Fund with the Guaranty Trust Company as trustee.

The net profit from the Universal Oil Products Company will flow to the AMERICAN CHEMICAL SOCIETY, to be used for purposes of research in the petroleum and natural gas fields. The SOCIETY will have no obligation in so far as the management of Universal Oil Products Company is concerned. The SOCIETY, on the other hand, will have absolute discretion in the matter of selecting the research projects. The SOCIETY can withdraw at any time it feels that it should not act further and it can then disclaim any interest in the trust.

Complete details, including the trust agreement, will appear in *Chemical and Engineering News* for November 10.



Selective Calcium Softening for Industrial Water Supplies

THE many developments in the field of water conditioning have not been overlooked in the pressure of building the many new plants required in the mobilization of this country for war. The results can now be tabulated and the experiences further utilized in the design for reconversion to peacetime industries. A number of the developments in industrial water treatment will also find application in the field of municipal water treatment when construction plans are made in the postwar era.

Only a few years ago (1, 2, 7, 8) the method of softening water by the lime and soda process in a rapid upflow basin with sludge recirculation was considered new. The pressure of the rapid industrial expansion of the last few years has resulted in hundreds of installations. Many war industries are in the Middle West where hard water prevails. In a number of these plants water is required in relatively large amounts for heat exchangers, plating processes, and other uses where hard water is objectionable.

In the usual operation of a lime and soda softening process, past practice has indicated addition of sufficient lime and soda ash to precipitate both the calcium and magnesium. The effluent water may have a residual hardness varying from 35 to 100

p.p.m. as calcium carbonate, depending on its ultimate use. The chemical treatment has been controlled to maintain a slight excess hydrate alkalinity to ensure precipitation of magnesium as well as calcium. Where there is appreciable silica in the water and where it is necessary to maintain a final pH of 9.0 or higher, precipitation of magnesium will be desirable. However, in many industrial processes the magnesium hardness has no objectionable features, and the primary reason for softening is to remove calcium to prevent deposition of calcium carbonate in heat exchange processes and throughout the distribution system. In such plants selective softening for calcium hardness only, allowing the greater part of the magnesium hardness to remain in solution, should prove satisfactory. The primary reason for selective calcium softening is economics. The cost of complete softening varies from 25 to 100% over that for selective calcium softening. Selective calcium softening can be effected by proper control of pH during the process. Plants utilizing this principle have been installed where limitation of treatment with complex phosphate (4) indicated the desirability and necessity of installing a softening plant.

Robert T. Sheen

W. L. & L. D. BETZ, PHILADELPHIA, PA.

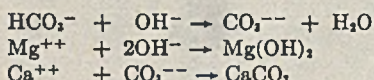
Everett B. Woodruff

WRIGHT AERONAUTICAL CORPORATION, CINCINNATI, OHIO

Many industrial water requirements can be satisfied by softening the raw water to reduce the calcium hardness only and leave the magnesium hardness in solution. This is particularly applicable to process water used for cooling purposes, and where reduction of calcium hardness and alkalinity will establish a balanced water that will not deposit calcium carbonate on heat exchange surfaces with rise in temperature. The chemical cost of reducing calcium hardness is materially less than the cost of reducing both calcium and magnesium hardness. Lime and soda softening for reduction of calcium hardness only can be controlled by pH value of the process, the pH

is normally held between 9.6 and 10.2, and the exact control point is determined for the individual water. The softening process is followed by partial neutralization, either with acid or with scrubbed and purified flue gas to a controlled pH point, designed for a stable water as determined by the Langelier Index or by marble tests, or it may be further stabilized by the application of polyphosphates. Data are presented on results of this treatment at Wright Aeronautical Corporation and other industrial plants. The photo on page 971 shows a laboratory sampling table in the Wright plant, with a meter panel in the background.

The fundamental water softening reactions in a lime and soda process may be expressed ionically as follows:



The quantities of lime and soda ash required to soften any given water supply may be calculated from an analysis by the following formulas; concentrations are expressed in equivalents per million (e.p.m.); lime means either CaO or Ca(OH)₂:

$$\begin{aligned}\text{e.p.m. lime} &= \text{e.p.m. CO}_2 + \text{e.p.m. HCO}_3^- + \\ &\quad \text{e.p.m. Mg}^{++} + \text{e.p.m. (OH)}^- \text{ (excess)} \\ \text{e.p.m. Na}_2\text{CO}_3 &= \text{e.p.m. Ca}^{++} + \text{e.p.m. Mg}^{++} - \\ &\quad \text{e.p.m. HCO}_3^- - \text{e.p.m. CO}_2 + \text{e.p.m. CO}_3^{--} \text{ (excess)} + \\ &\quad \text{e.p.m. (OH)}^- \text{ (excess)}\end{aligned}$$

The excess hydrate in the first reaction is the excess desired in the finished softened water, known to be required to establish the desired pH value for the degree of softening required. The excess carbonate in the second reaction is the excess desired over that required to form calcium carbonate, as the solubility of calcium carbonate is lowered by an excess of carbonate ion.

It is evident from these formulas that to soften under conditions which do not remove the magnesium hardness, in the case of most natural waters, will result in an appreciable reduction of both lime and soda ash requirements. In certain cases it will

eliminate the necessity for using soda ash. The cost of the chemicals required for the partial softening operation in most cases will be reduced from 30 to 80%, depending on the relative amounts of calcium and magnesium hardness present in the water supply.

WRIGHT AERONAUTICAL PLANT

When the water requirements of this plant at Cincinnati were considered, it was necessary to plan for large volumes of cold water for heat exchange because the air for carburetors, engine testing, and gasoline has to be cooled below 75° F. to meet Army specifications. This required water at 60° F. or lower, which was available only from an underground supply. Initial water requirements were estimated to be approximately 5000 gallons per minute. A water treating plant with a capacity of 5500 g.p.m. was installed to take water from six deep wells with a capacity of 1000 g.p.m. each. Water from these wells varied in hardness from 282 to 671 p.p.m. and in iron content from 2.5 to 8.5 p.p.m. (Table I). The average total hardness of the water from these wells is 515 p.p.m., with 171 p.p.m. in the form of magnesium hardness and 344 p.p.m. as calcium hardness. It is most unusual to find such a large variation in the mineral content on well waters located on the same property; the wells are spaced 600 feet apart and draw from the same depth. This variation in hardness was found to continue with use and pumping.

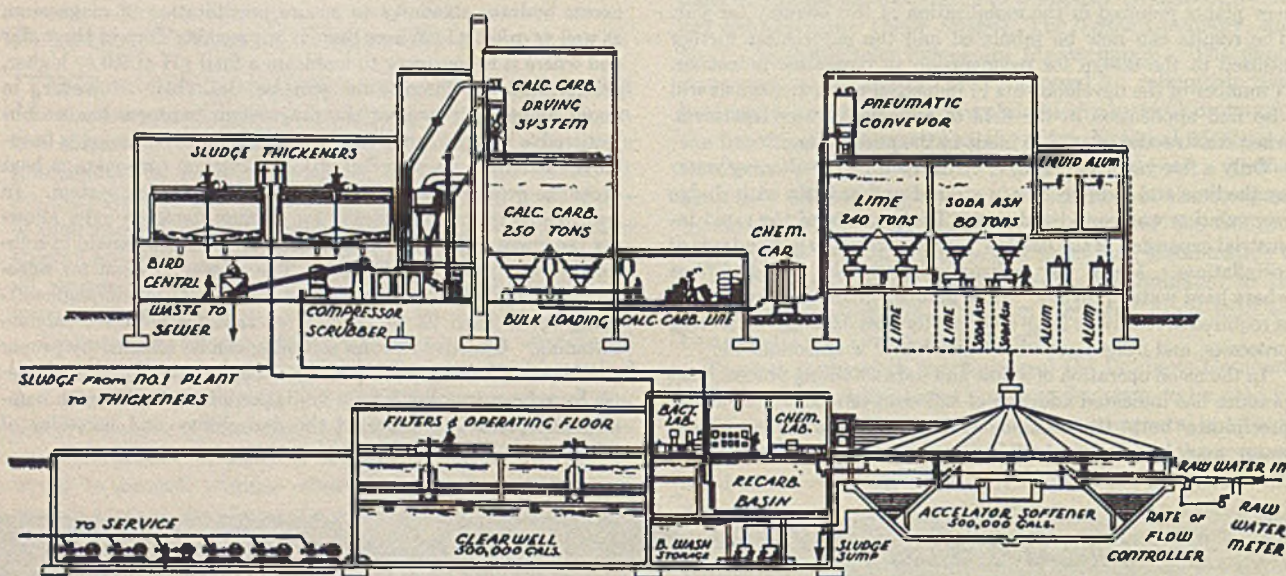


Figure 1. Design of Plant 2, Wright Aeronautical Corporation

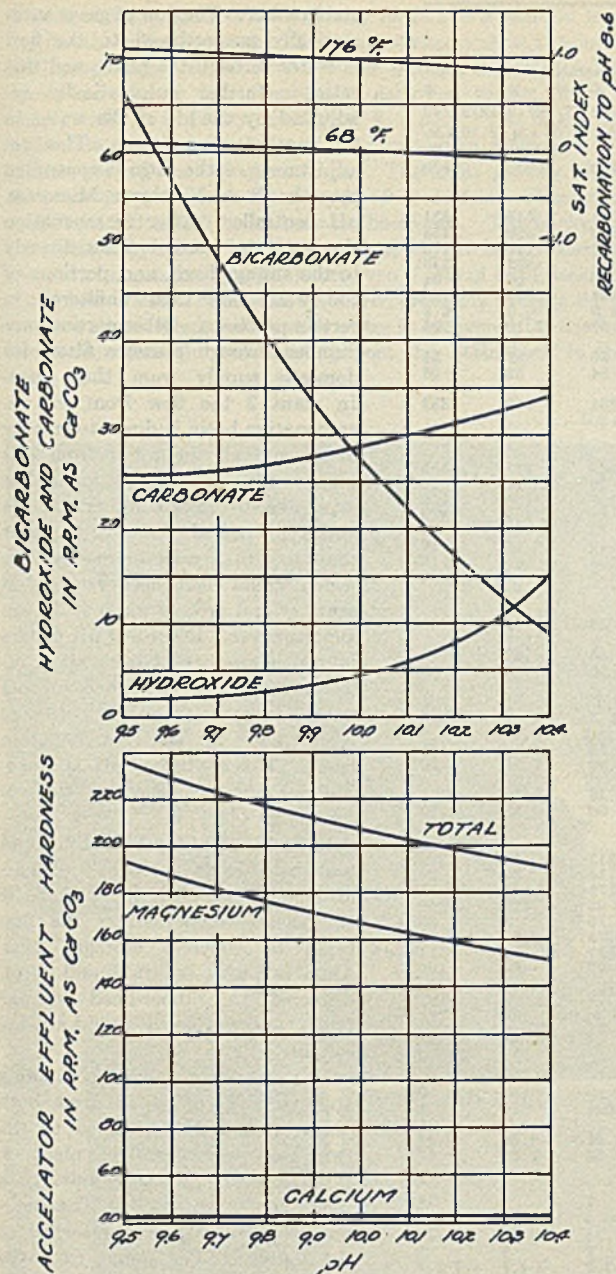


Figure 2. Effect of Varying the pH by Lime Treatment (with Soda Ash Constant) on Alkalinity (above) and Hardness (below)

Before the first treatment plant was completed, the production schedule was revised, and it was decided to expand facilities about 350%. A second water treatment plant was required to handle approximately 9500 g.p.m. or a total of 14,000,000 gallons capacity per day. In the short space of a year, two large water softening plants were placed in service. The second plant was designed to handle the same type of raw water as the first, but as the result of an anticipated failure of the water table in the Mill Creek Valley, a new water project was undertaken by the Federal Government to meet the requirements and to bring a new water supply to the plant from further up the valley. This new supply had a hardness considerably lower than that of the wells on the property, averaging 300 to 370 p.p.m. total hardness, as well as a low iron content. It was estimated that 25% of the output of the plant would be required for domestic consumption

Table I. Analysis of Well Waters

Well No.	1	2	3	4	5	6	Average	Miami Valley
Hardness, p.p.m. as CaCO_3								
Total	670	671	660	438	370	282	515	330
Calcium	454	440	437	312	222	201	344	205
Magnesium	216	231	223	126	148	81	171	125
Total alkalinity, p.p.m. as CaCO_3	383	414	421	319	291	275	350	260
Cl, p.p.m.	70	113	189	15	128	29	87	5
SO_4 , p.p.m.	258	208	188	132	73	118	163	68
Fe, p.p.m.	2.50	8.50	8.05	3.91	4.58	2.6	5.02	0.1
pH	7.08	7.01	6.97	7.34	7.40	7.40	7.20	7.3
CO_2 , p.p.m.	21	25.5	33	12	11	9.2	18.6	26

Table II. Test Series 1

(pH varied by lime; soda ash constant; wells 2, 3, 4, and 6 operating; data taken when conditions were constant)

Test No.	1	2	3	4
Date—Oct., 1942	26-27	28-29	29-31	31 & 11/1
Water flow, gal./min.	2639	2615	2887	2245
Influent water analysis				
Total hardness, p.p.m. as CaCO_3	568	589	570	570
Ca hardness, p.p.m. as CaCO_3	350	357	358	348
Mg hardness, p.p.m. as CaCO_3	218	212	212	222
M or total alk., p.p.m. as CaCO_3	329	324	326	320
Cl, p.p.m.	89	89	83	84
SO_4 , p.p.m.	128	140	135	131
Fe, p.p.m.	5.2	5.5	5.3	5.2
SiO_2 , p.p.m.	12	12	12	12
pH	7.10	7.08	7.10	7.10
CO_2 , p.p.m.				
By titration	33	31	30	31
Graphic detn.	51	52	50	49
Bicarbonate, p.p.m. as CaCO_3				
A.P.H.A. method	329	324	326	320
Graphic detn.	Same as A.P.H.A. at this pH			
Accelerator softener effluent water analysis				
Total hardness, p.p.m. as CaCO_3	229	219	207	200
Ca hardness, p.p.m. as CaCO_3	42	41	43	41
Mg hardness, p.p.m. as CaCO_3	187	178	164	159
M or total alk., p.p.m. as CaCO_3	82	73	61	56
Pht alkalinity, p.p.m. as CaCO_3	26	28	30	33
pH	9.63	9.80	10.03	10.21
Total alk. — Ca hardness	40	32	18	15
2 Pht — total alk.	-30	-17	-1	10
Bicarbonates, p.p.m. as CaCO_3				
A.P.H.A. method	30	17	1	0
Graphic detn.	55	41	27	17
Carbonates, p.p.m. as CaCO_3				
A.P.H.A. method	52	54	60	46
Graphic detn.	26	29	29	31
Hydroxides, p.p.m. as CaCO_3				
A.P.H.A. method	0	0	0	10
Graphic detn.	2.0	3.0	4.8	8.0
pH saturation (Langelier)				
68° F.	8.50	8.55	8.60	8.65
176° F.	7.56	7.61	7.68	7.70
Satn. index with recarbonation to 8.6				
68° F.	+0.10	+0.05	0.00	-0.05
176° F.	+1.04	+0.99	+0.92	+0.90
Chemicals used, lb./1000 gal.				
Lime	2.40	2.57	2.34	2.20
Soda ash	0.87	0.87	0.87	0.87
Alum	0.20	0.20	0.20	0.20
Cost, cents/1000 gal.				
Lime at 0.43 cent/lb.	1.03	1.11	1.01	0.88
Soda ash at 0.8 cent/lb.	0.70	0.70	0.70	0.70
Alum at 1 cent/lb.	0.20	0.20	0.20	0.20
Total	1.93	2.01	1.91	1.76

^a M = methyl orange.

^b Pht = phenolphthalein.

and sanitary purposes by the employees, and the remaining 75% for industrial purposes. Since the original requirements were based on cold water at approximately 58° F., the use of softened well water throughout the plant was deemed the most practical procedure.

The process water requirements include: acetylene generation, pickling, heat treatment, plating, dynamometer and engine testing, paint and baffle shop, gasoline system, air and gas coolers, anodizing and dichromate baths, oil and chip house, boiler house, rotoclones, x-ray developing baths, and miscellaneous heat exchangers. Selective calcium softening was chosen as the method of treatment to give a water that would not cause corrosion or deposit calcium carbonate scale at any point in the system. In addition, it was necessary to assure a sterile water satisfactory for drinking purposes. The general design of the two plants is

Table III. Test Series 2

(pH constant at 10.2, soda ash treatment varied; wells 2, 3, 4, and 6 operating)

Test No.	1	2	3	4	5	6	7
Date	12/14/42	12/16/42	12/17/42	12/18/42	12/19/42	12/20/42	12/21/42
Time	All	All	All	All	All	3:00 A.M. 4:00 P.M.	2:10 A.M. 3:00 P.M.
Water flow, gal./min.	2700	2900	2730	2700	2720	2950	2620
Influent—water analysis							
Total hardness, p.p.m. as CaCO ₃	538	527	521	521	551	547	531
Ca hardness, p.p.m. as CaCO ₃	353	353	353	349	350	350	353
Mg hardness, p.p.m. as CaCO ₃	185	174	168	172	201	197	178
M or total alk., p.p.m. as CaCO ₃	333	332	333	331	331	333	333
Cl, p.p.m.	80	81	80	80	80	80	84
SO ₄ , p.p.m.	120	124	123	120	124	130	128
Fe, p.p.m.	6.0	5.5	5.5	4.5	4.5	6.0	6.2
pH	7.10	7.07	7.08	7.10	7.07	7.10	7.05
CO ₂ , p.p.m.							
By titration	31	28	27	28	30	27	31
Graphic detn.	52	51	50	49	54	52	56
Bicarbonate, p.p.m. as CaCO ₃							
A.P.H.A. method	333	332	333	331	331	333	333
Graphic determination	Same as A.P.H.A. at this pH						
Accelerator effluent-water analysis							
Total hardness, p.p.m. as CaCO ₃	236	220	211	201	204	211	195
Ca hardness, p.p.m. as CaCO ₃	91	76	61	43	35	27	25
Mg hardness, p.p.m. as CaCO ₃	145	144	150	158	169	184	170
M or total alk., p.p.m. as CaCO ₃	42	44	51	71	89	109	135
Pht alkalinity, p.p.m. as CaCO ₃	22	23	26	35	43	51	72
pH	10.17	10.00	10.17	10.15	10.12	10.17	10.19
Total alk. — Ca hardness	-49	-32	-10	28	54	82	110
2 Pht — total alk.	2	2	1	-1	-3	-7	9
Bicarbonates, p.p.m. as CaCO ₃							
A.P.H.A. method	0	0	0	1	3	7	..
Graphic detn.	13	19	16	25	33	39	46
Carbonates, p.p.m. as CaCO ₃							
A.P.H.A. method	40	42	50	70	86	102	126
Graphic detn.	21	20	27	39	50	63	80
Hydroxides, p.p.m. as CaCO ₃							
A.P.H.A. method	2	2	1	0	0	0	9
Graphic detn.	7.3	5.0	7.3	7.0	6.5	7.3	7.5
pH saturation (Langelier)							
68° F.	8.52	8.50	8.47	8.49	8.45	8.42	8.55
176° F.	7.55	7.58	7.60	7.61	7.60	7.61	7.50
Satn. index with recarbonation to 8.6							
68° F.	-0.08	-0.10	-0.13	-0.11	-0.15	-0.18	-0.05
176° F.	1.05	1.02	1.00	0.99	1.00	0.99	1.10
Recarbonation basin effluent-water analysis							
Total hardness, p.p.m. as CaCO ₃	237	220	205	207	212	211	200
Ca hardness, p.p.m. as CaCO ₃	89	76	62	44	36	30	26
Mg hardness, p.p.m. as CaCO ₃	148	144	143	163	176	181	174
M or total alk., p.p.m. as CaCO ₃	44	45	57	73	95	116	140
Pht alkalinity, p.p.m. as CaCO ₃	10	8	9	9	10	13	20
pH	9.00	8.71	8.68	8.71	8.75	8.81	8.88
Total alk. — Ca hardness	-44	-31	-5	29	59	85	114
2 Pht — total alk.	-24	-29	-39	-55	-75	-89	-100
Bicarbonates, p.p.m. as CaCO ₃							
A.P.H.A. method	24	27	39	55	75	87	100
Graphic detn.	39	43	54	69	90	107	130
Carbonates, p.p.m. as CaCO ₃							
A.P.H.A. method	20	16	18	18	20	26	40
Graphic detn.	4	2	3	4	4	7	9
Hydroxides, p.p.m. as CaCO ₃							
A.P.H.A. method	0	0	0	0	0	0	0
Graphic detn.	0.5	0.4	0.4	0.4	0.4	0.4	0.4
pH saturation							
68° F.	8.45	8.51	8.50	8.50	8.52	8.50	8.52
176° F.	7.50	7.60	7.55	7.60	7.52	7.54	7.52
Chemical feeder data							
Lime feeder No.	1	2	2	1	1	1	1
Points on feeder	88.0	87.8	89.1	79.5	80.0	80.7	75.7
Lime, lb./1000 gal.	2.60	2.27	2.39	2.30	2.34	2.35	2.18
Soda feeder No.	..	1	1	1	1	1	1
Points on feeder	0	1-1.0	1-2.1	2-1.5	2-2.2	3-1.7	3-2.2
Soda ash, lb./1000 gal.	0	0.21	0.40	0.60	0.79	1.00	1.20
Alum feeder No.	1	1	1	1	1	1	1
Points on feeder	5	5	5	5	5	5	5
Alum, lb./1000 gal.	0.17	0.17	0.17	0.17	0.17	0.17	0.17
CO ₂ flow, cu. ft./min.	4.5	5.2	5.4	5.7	6.4	6.9	6.5
CO ₂ , %	5.0	5.7	6.5	6.9	8.5	7.8	8.5
Cost, cents/1000 gal.							
Lime at 0.43 cent/lb.	1.12	0.97	1.03	0.99	1.01	1.01	0.94
Soda ash at 0.8 cent/lb.	0	0.17	0.32	0.48	0.63	0.80	0.96
Alum at 1 cent/lb.	0.17	0.17	0.17	0.17	0.17	0.17	0.17
Total	1.29	1.31	1.52	1.64	1.81	1.98	2.07

similar; plant 2 is shown in Figure 1. The raw water flows into an Accelerator softening basin in which lime, soda ash, and alum are mixed with a previously formed sludge. This mixture is circulated and, in turn, mixed with incoming water to produce the softening reaction. The clarified water flows over a weir at the outer rim of this tank into a flume and then to the recarbonation chamber.

At this point scrubbed flue gas generated in a small furnace in the plant is added to the water to lower the pH and deliver a

stable water. The flow of gas is automatically proportioned to the flow of water through the plant, and this ratio is further automatically re-adjusted by the pH of the water in the recarbonation basin. This re-adjustment of the ratio is controlled by a Leeds & Northrup Micromax pH controller. After recarbonation the water in plant 1 flows directly to the storage basin and portions of the water are used unfiltered in certain processes. Other portions are pumped through pressure filters for domestic supply from that plant. In plant 2 the flow from the recarbonation basin is direct to gravity filters and all the water from this plant is filtered. It was found less expensive to install filters for the entire output of this plant rather than to run a dual piping system, which would have been required if sanitary and process water had been kept separate. Recording pH meters in the laboratory at each plant indicate and continuously record pH value of the water in the softening basin and in the recarbonation basin. This control of pH is essential for effective selective calcium softening.

In both plants pebble lime and soda ash are delivered in bulk carload and unloaded by pneumatic equipment which delivers the material to concrete storage bins. Alum is purchased in liquid form, delivered to rubber-lined storage tanks, and fed as a liquid to the softener.

The resulting sludge containing approximately 5% solids from both plants 1 and 2 is pumped to the two Dorr thickeners in plant 2. It is thickened in these units to a solids content of 15%. The overflow clarified water is returned to the softener. The sludge from the thickeners flows in controlled volume to a continuous centrifuge which not only dewateres but also purifies the sludge by reducing the magnesium, iron, and aluminum components and increasing the calcium carbonate content. The sludge cake from the centrifuge contains 65 to 70% solids with 30 to 35% moisture, and is fed to a flash-drying system and dried to a powdered calcium carbonate. The resulting material is ready for the market, and is sold for poultry and livestock feed, plastic filler, board and paper filler, and other uses. The calcium carbonate dewatering and drying system at this plant has a capacity of 2 tons of dry solids per hour. The production of dry calcium carbonate will vary from 20 to 45 tons per day, depending on the hardness and volume of the water being treated.

Lime from the storage bins flows by gravity through dry feeders and continuous slakers to the softening basin. The soda ash

likewise flows by gravity through dry feeders to a solution tank and to the softening basin. The flow of chemicals is automatically proportioned to the flow of water through the plant. The Accelator softener has consistently delivered to the filters a water with a turbidity averaging 3 p.p.m. The filters are anthracite coal and are designed for a maximum filter rate of 3 gallons per square foot per minute. The eight gravity filters are twin-operated; each filter bay is 15 × 30 feet. Filter runs vary from 120 to 200 hours between backwash. The backwash is regulated by loss of head, although filters are backwashed at the end of approximately 200 hours even if loss of head does not reach 6 to 8 feet. Backwash water requirements average 0.3% of the water filtered. Backwash water is recovered by flowing into a storage basin and bleeding from this basin back to the

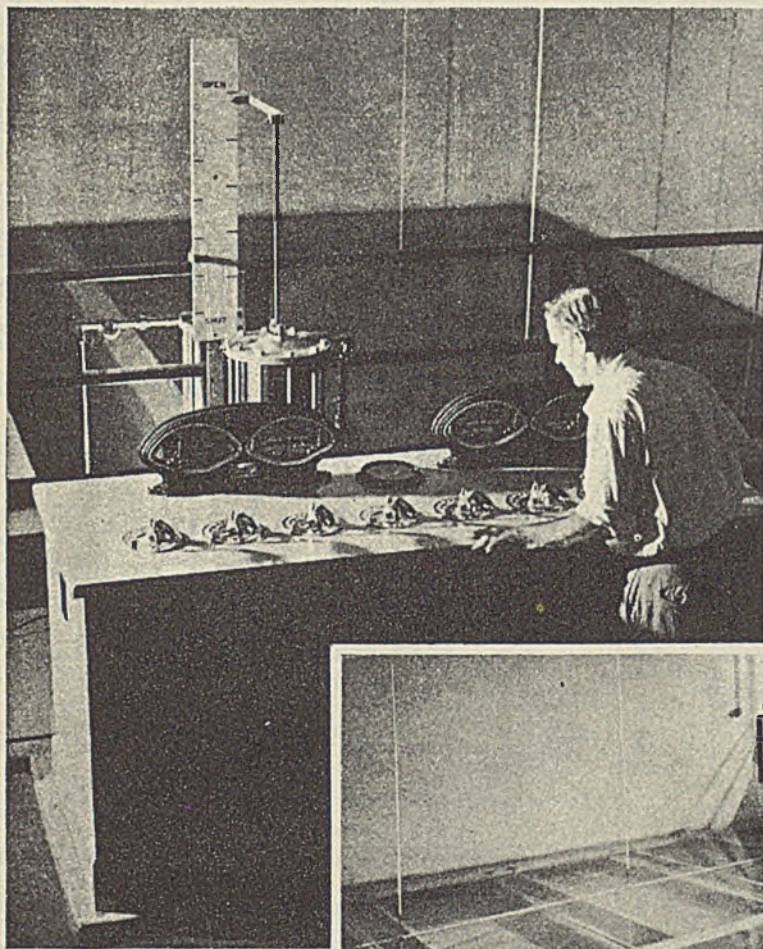
water softener. Continuous tests are made for water quality, both chemical and bacteriological, by the plant operators.

RESULTS OF TEST SERIES

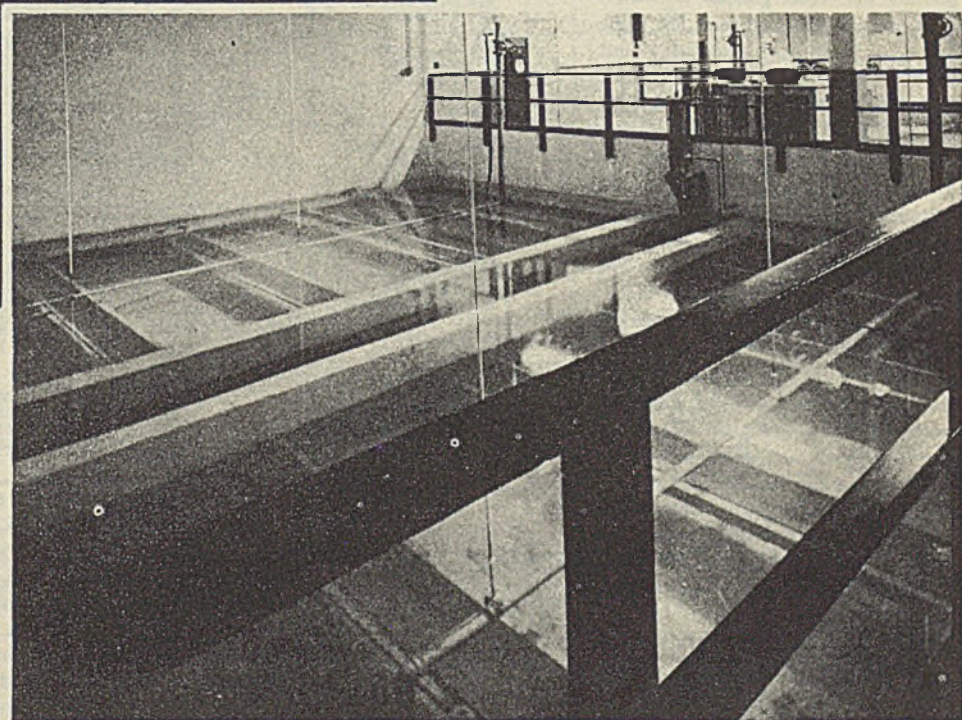
A series of tests were made at plant 1 prior to the time the Miami Valley supply was available, to study the effect of variables on the process of selective calcium softening. These tests were made on a combination of waters from wells on the property. The same combination was operated during all tests and the flow of water was essentially the same in all cases. Plant 1 is equipped with volumetric feeders, and some variation might, therefore, occur in the rate of feed with different apparent densities of the chemicals, particularly lime of different sizing.

During a series an attempt was made to hold all variables constant except one. In test series 1 the soda ash feed was held constant at an arbitrary rate of 0.87 pound per 1000 gallons of water. The pH was varied from 9.63 to 10.21 by changing the lime feed. The quantity of lime feed does not correlate with the pH value, probably because of irregular feeding of the lime, resulting from variation in the size. The setting on the feeder was, however, adjusted to give the desired pH value. The curves in Figure 2 were developed from these data, given complete in Table II.

Two sets of values are given in Table II for the bicarbonates, carbonates, and hydroxides; one set was determined by the A.P.H.A. method which assumes that the titration to the phenolphthalein end point will include all hydroxides plus one half carbonates, and that the methyl orange titration includes hydroxides, carbonates, and bicarbonates. The other set of values (plotted in the upper graph of Figure 2) for the alkalinity is determined from graphs presented by Moore (6). These alkalinities and carbon dioxides are calculated from the



A Filter Operating Table on the Gravity Filters in Water Treatment Plant No. 2 of Wright Aeronautical Corporation is shown in the photograph above; at right is a twin-bay gravity filter in service at Wright Plant No. 2



hydrogen ion concentration and total alkalinity of the water. The original equations used in these calculations were developed by De Martini (3).

The amount of chemicals used during the tests was determined from the feeder setting; the feeder settings as recorded during the tests were converted into pounds of chemicals per 1000 gallons of water by calibration curves.

For any given water there is a pH value which will be in equilibrium with calcium carbonate and will have a tendency neither to dissolve nor to deposit calcium carbonate. Langelier (5) developed a formula for determining the degree of saturation of a given water, which correlates the total dissolved solids, calcium ion concentration, total alkalinity, and temperature at which water is to be used.

Assuming the total dissolved solids of the soft water to be relatively constant at 400 p.p.m., the pH of saturation was determined for temperatures of 68° and 176° F. The saturation index (difference between actual pH and pH of saturation) was determined assuming the water recarbonated to a pH of 8.6. This index shows the tendency of the water to be corrosive or to deposit calcium carbonate.

Test series 2 was run at a pH of approximately 10.2, and the soda ash was varied from 0 to 1.20 pounds per 1000 gallons of water. Test series 3 was run over the same range of soda ash treatment but with a pH of approximately 9.6. Detailed results are given in Tables III and IV. Figure 3A shows that the addition of soda ash lowers the amount of residual calcium in the softened water and that this reduction takes place at both the higher and lower pH values. The reduction is greater at the higher pH. In either case there is a marked tendency for the reduction of calcium per unit of additional soda ash added to decrease with increased soda ash feed. Figure 3D shows the increment cost of calcium reduction in cents per 1000 gallons per 100 p.p.m. of calcium carbonate hardness removed. It will be noted that above 0.5 pound of soda ash per 1000 gallons of water, the cost of further reduction in calcium hardness increases rapidly. Also, this increase in cost of treatment occurs when the calcium is reduced below 40 and 50 p.p.m. at a pH of 10.2.

Magnesium hardness of the water increased as soda ash was added. This is explained by the fact that, in order to hold a constant pH value with increasing carbonate ion concentration it

Table IV. Test Series 3

	(pH constant at 9.6, soda ash treatment varied; wells 2, 3, 4, and 6 operating)						
Test No.	1	2	3	4	5	6	7
Date	12/22/42	12/23/42	12/24/42	12/26/42	12/27/42	12/28/42	12/29/42
Time	5:30 A.M. 12:00 P.M.	All	All	All	All	All	All
Water flow, gal./min.	2680	2780	2590	2740	2785	2890	2960
Influent-water analysis							
Total hardness, p.p.m. as CaCO ₃	524	513	518	506	511	510	516
Ca hardness, p.p.m. as CaCO ₃	348	353	353	347	350	349	344
Mg hardness, p.p.m. as CaCO ₃	176	160	165	159	161	161	172
M or total alk., p.p.m. as CaCO ₃	339	338	333	338	336	333	335
Cl, p.p.m.	80	79	77	80	81	82	77
SO ₄ , p.p.m.	130	132	131	128	126	124	130
Fe, p.p.m.	6.0	5.7	5.5	6.0	5.8	5.5	5.0
pH	7.06	7.10	7.06	7.12	7.08	7.09	7.03
CO ₂ , p.p.m.							
By titration	29	28	27	29	29	31	30
Graphic detn.	58	52	56	53	53	53	60
Bicarbonates, p.p.m. as CaCO ₃							
A.P.H.A. method	339	338	333	338	336	333	335
Graphic detn.Same as A.P.H.A. at this pH.....						
Accelerator effluent-water analysis							
Total hardness, p.p.m. as CaCO ₃	237	227	217	226	227	216	218
Ca hardness, p.p.m. as CaCO ₃	81	72	64	66	52	51	39
Mg hardness, p.p.m. as CaCO ₃	156	155	143	160	175	165	179
M or total alk., p.p.m. as CaCO ₃	52	60	72	81	101	104	133
Pht alkalinity, p.p.m. as CaCO ₃	19	21	23	26	27	33	41
pH	9.70	9.65	9.62	9.60	9.62	9.67	9.73
Total alk. — Ca hardness	-20	-12	8	15	49	53	94
2 Pht — total alk.	-14	-18	-26	-29	-47	-38	-51
Bicarbonates, p.p.m. as CaCO ₃							
A.P.H.A. method	14	18	26	29	47	38	51
Graphic detn.	31	38	48	55	67	67	82
Carbonates, p.p.m. as CaCO ₃							
A.P.H.A. method	38	42	46	52	54	66	82
Graphic detn.	18	19	22	24	29	35	48
Hydroxides, p.p.m. as CaCO ₃							
A.P.H.A. method	0	0	0	0	0	0	0
Graphic detn.	2.5	2.0	2.0	1.8	2.0	2.3	2.7
pH, saturation							
68° F.	8.40	8.40	8.40	8.35	8.30	8.32	8.33
176° F.	7.60	7.48	7.48	7.40	7.38	7.38	7.35
Satn. index with recarbonation to 8.6							
68° F.	-0.20	-0.20	-0.20	-0.25	-0.30	-0.28	-0.27
176° F.	1.10	1.12	1.12	1.20	1.22	1.22	1.25
Recarbonation basin effluent-water analysis							
Total hardness, p.p.m. as CaCO ₃	242	229	218	230	223	213	220
Ca hardness, p.p.m. as CaCO ₃	83	73	67	67	53	50	38
Mg hardness, p.p.m. as CaCO ₃	159	156	151	163	170	163	132
M or total alk., p.p.m. as CaCO ₃	54	65	77	85	106	107	134
Pht alkalinity, p.p.m. as CaCO ₃	7	8	10	10	12	23	81
pH	8.4	8.57	8.61	8.55	8.57	8.31	8.76
Total alk. — Ca hardness	-20	-8	10	18	53	57	96
2 Pht — total alk.	-40	-49	-57	-65	-82	-61	-108
Bicarbonates, p.p.m. as CaCO ₃							
A.P.H.A. method	40	49	57	65	82	61	108
Graphic detn.	54	63	75	83	102	104	130
Carbonates, p.p.m. as CaCO ₃							
A.P.H.A. method	14	16	20	20	24	46	26
Graphic detn.	1	2	2	3	4	2	7
Hydroxides, p.p.m. as CaCO ₃							
A.P.H.A. method	0	0	0	0	0	0	0
Graphic detn.	0	0	0	0	0	0	0
pH, saturation							
68° F.	8.60	8.62	8.70	8.70	8.70	8.70	8.68
176° F.	7.55	7.58	7.61	7.68	7.65	7.63	7.62
Chemical feeder data							
Lime feeder No.	2	2	2	2	2	2	1-14 hr. 2-10 hr.
Points on feeder	77.8	74.3	73.2	74.0	74.5	72.8	67.5 & 71.6
Lime, lb./1000 gal.	2.00	1.90	1.86	1.88	1.90	1.85	1.94
Soda feeder No.	1	1	1	1	1	1	1
Points on feeder	0	1-1.0	1-2.1	2-1.5	2-2.2	3-1.7	3-2.2
Soda ash, lb./1000 gal.	0	0.21	0.40	0.60	0.79	1.00	1.20
Alum feeder No.	1	1	1	1	1	1	1
Points on feeder	5	5	5	5	5	5	5
Alum, lb./1000 gal.	0.17	0.17	0.17	0.17	0.17	0.17	0.17
CO ₂ flow, cu. ft./min.	4.1	3.9	3.8	4.2	4.1	4.3	4.9
CO ₂ , %	5.5	5.3	5.7	5.8	6.4	7.5	9.2
Cost, cents/1000 gal.							
Lime at 0.43 cent/lb.	0.86	0.82	0.80	0.81	0.82	0.80	0.83
Soda ash at 0.8 cent/lb.	0	0.17	0.32	0.48	0.63	0.80	0.96
Alum at 1 cent/lb.	0.17	0.17	0.17	0.17	0.17	0.17	0.17
Total	1.03	1.16	1.29	1.46	1.62	1.77	1.96

was necessary to decrease the lime as the soda ash was added. At the higher soda ash feed there was practically no reduction in magnesium hardness. In the case of the higher pH the decrease over the range of test was 0.2 pound of lime per 1000 gallons of water. This reduction in lime accounts for 40 p.p.m. increase in magnesium hardness. The actual curve shows an increase of 49 p.p.m. in magnesium hardness (Figure 3A). The

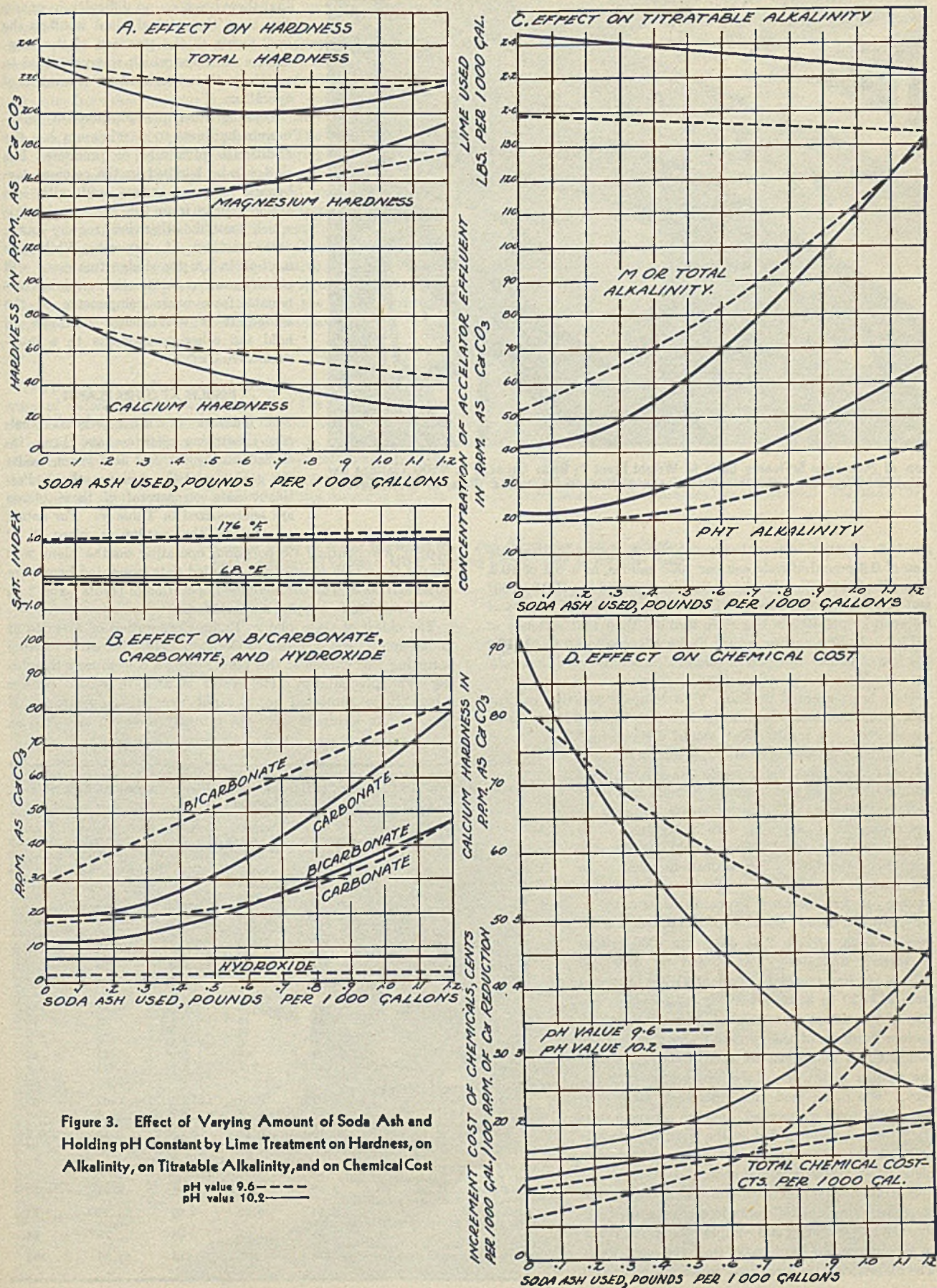
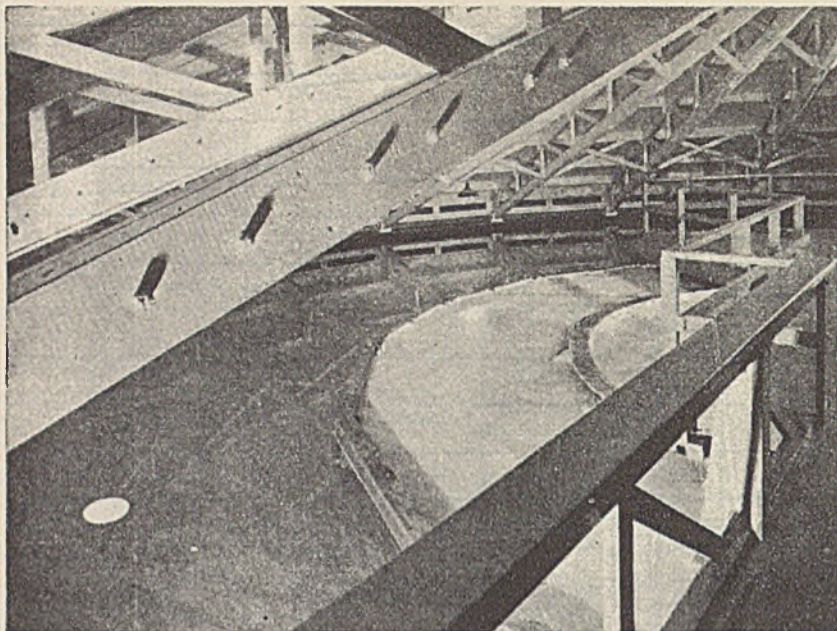


Figure 3. Effect of Varying Amount of Soda Ash and Holding pH Constant by Lime Treatment on Hardness, on Alkalinity, on Titratable Alkalinity, and on Chemical Cost

pH value 9.6—
pH value 10.2—



Top of Accelerator Softening Basin in Wright Plant 2; Basin Capacity Is 9500 Gallons per Minute. Note Circulating Slurry in Center of Basin and Clarified Water in Outer Section

greatest reduction in total hardness is accomplished by the addition of 0.6 pound of soda ash per 1000 gallons, at a pH of 10.2. The pH of saturation for the water recarbonated to pH 8.6 at 68° and 176° F. are compared in Figure 3C. At 176° F. the water softened at pH 10.2 is less scale forming than that softened at pH 9.6. In like manner, at 68° F. the water softened at pH 10.2 has less tendency to dissolve calcium carbonate than that softened at pH 9.6.

Data are presented in Table V to compare selective calcium softening; the results from series 2, test 4, at pH 10.2 are compared with the results that would be obtained by complete softening with lime and soda, and reducing the total hardness to 80 p.p.m. with normal distribution between the calcium and magnesium remaining. With this water softened to the degree indicated and with a residual of 80 p.p.m. total hardness, there would be no appreciable difference in the saturation index or in the tendency to deposit or dissolve calcium carbonate under varying temperature conditions. On the other hand, the cost of treatment has increased from 1.64 to 2.55 cents per 1000 gallons of water; and daily cost, based on 8,000,000 gallons per day (capacity of plant 1) has increased from \$131.20 to \$204.00 per day, or 55.5%. The only disadvantage from the retention of the magnesium hardness of this process water has been the fact that an additional softener was required for the smaller quantities of boiler feed water necessary. The boiler feed amounts to not more than 2% of the total water used, and the separate softener is more than justified by the large difference in cost between selective calcium softening and complete softening by lime and soda.

It is obvious that on the Miami Valley water supply, now in use, the difference in cost between selective calcium softening and complete softening is not so great as on the hard water from the plant wells. The difference is, nevertheless, justified by the fact

that there has been no difficulty in operation since the original plant went on the line, owing to the presence of the magnesium hardness which was permitted to remain in the water under this method of operation.

Holding the precipitation of magnesium hardness to a minimum has the additional advantage of producing less sludge to be handled in the calcium carbonate recovery system and with less actual rejects from this system of solids which would otherwise require some other method of disposal. While the method in use for sludge treatment will classify and separate the calcium carbonate from other components of the sludge, it is nevertheless desirable to hold the other components to a minimum.

RESULTS AT OTHER PLANTS

A number of other selective calcium softening plants have been installed during the last few years, under the guidance of the senior author. Pertinent data on several of these plants are summarized in Table V. For actual comparison the results at plant 1 of

Wright Aeronautical Corporation, operating on the plant well supply (on which most of the detailed data presented here were obtained), as well as the combined operation of plants 1 and 2 on the Miami Valley supply, are included.

The oldest of these plants, Radio Corporation of America at Indianapolis, was installed in October, 1940. Selective calcium softening was chosen at this plant, using a cold-process Spaulding type precipitator. The water is used in record presses where it is subjected to a rapid rise in temperature. If the calcium hardness were not properly removed in this case,

Table V. Results Obtained at Representative Plants Employing Selective Calcium Softening

Company	Wright, plant 1	Wright, plants 1 & 2	R.C.A.	Columbia Steel	Socony- Vacuum
Capacity, gal./day	8,000,000	22,000,000	1,300,000	12,000,000	3,000,000
Date installed	June, '42	June, '43	Oct., '40	Aug., '43	Dec., '43
Raw water source	Plant wells	Hamilton wells	Well	Provo River	Well
Raw water analysis, p.p.m.					
Total hardness, CaCO ₃	521	305	369	256	670
Ca hardness, CaCO ₃	349	203	232	180	450
Mg hardness, CaCO ₃	172	101	137	76	224
Free CO ₂	28	35	27	2	50
Total alk. as CaCO ₃	331	280	352	196	351
pH	7.2	7.3	7.4	8.2	7.4
Treated water analysis, p.p.m.					
Total hardness, CaCO ₃	201	139	164	90	296
Ca hardness, CaCO ₃	43	40	34	38	96
Mg hardness, CaCO ₃	158	99	130	52	200
Free CO ₂	0	0	0	0	0
Total alk. as CaCO ₃	71	69	132	72	48
pH after acid or recarbonation	8.6	8.7	8.0	8.1	8.0
Chemical requirements for selective Ca softening	CaO	CaO	Ca(OH) ₂	CaO	CaO
Lime, lb./M gal.	2.12	1.72	2.3	1.1	2.6
Soda ash, lb./M gal.	0.53	0	0	0.26	0.6
Alum, lb./M gal.	0.17	0.17	0.05	0.15	0.2
Cost, cents/M gal.	1.64	0.91	1.25	1.51	2.84
Cost of complete softening, assuming residual hardness of 80 p.p.m., cents/M gal.	2.55	1.16	2.32	2.62	5.50
Excess cost of complete softening, cents/M gal.	0.91	0.25	1.07	1.11	2.66
Excess cost of complete softening, %	55	27	86	73	94
Excess cost per day based on operation at rated capacity	\$73	\$55	\$13	\$1.33	\$80

deposits would occur in these presses and quickly render them inoperable.

The plant of the Columbia Steel Company, Geneva, Utah, was recently placed in operation to soften all make-up water to a reservoir. The reservoir has a capacity of 800,000,000 gallons, and water from this reservoir is used for all types of cooling processes through the steel mill, with a provision for circulation of as much as 120,000,000 gallons per day. The softening plant is also equipped for thickening and dewatering sludge from the cold process softener, and for purifying the sludge to permit the purified calcium carbonate to be returned to lime. It is ultimately planned to install a lime burning system to handle sludge at this plant of the Columbia Steel Company.

At the plant of Socony-Vacuum Oil Company, St. Louis, Mo., portions of the water following selective calcium softening will be used for process purposes and make-up to a cooling system. Other portions will be further softened by the zeolite process to prepare this supply for boiler feed and other purposes.

CONCLUSIONS

The practical use of pH control to effect selective calcium softening of waters has been demonstrated by the application of the method in a number of commercial installations. This method of control, where calcium softening only is to be considered, offers economy in treatment over complete softening involving the reduction of magnesium hardness. This same method of control could be applied to many municipal water softening installa-

tions to give the same residual hardness as now maintained on the supply and effect economies in treatment. This treatment should, however, be used only in cases where the silica content of the water supply is not sufficiently high to cause difficulty with magnesium silicate scale, and where the pH of the water to be delivered to the distribution system is suitable.

ACKNOWLEDGMENT

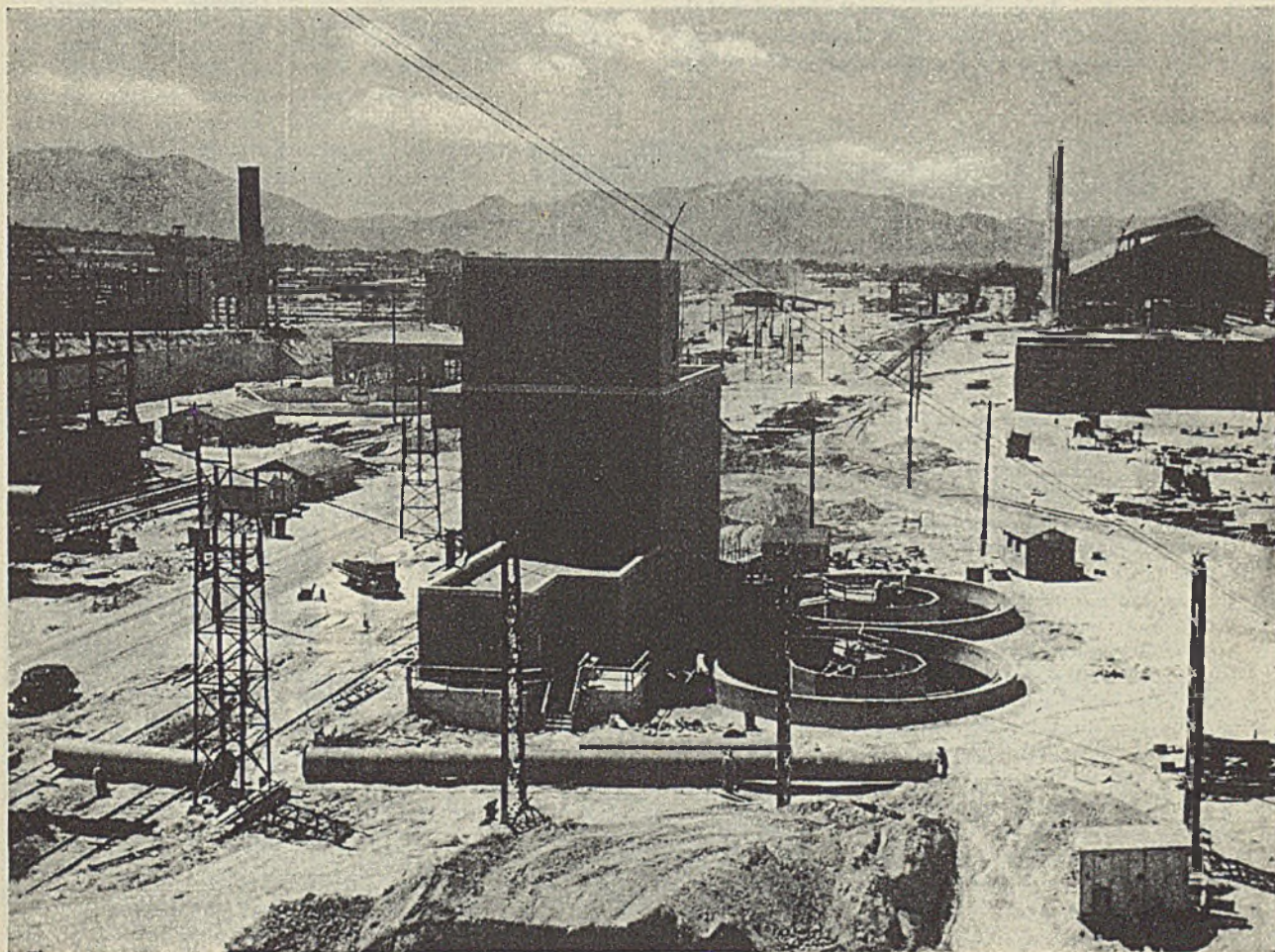
The writers are indebted to H. B. Lammers, C. C. Wylam, and C. Rigas, of Wright Aeronautical Corporation, for assistance in obtaining much of the detailed data presented here. The cooperation of Wright Aeronautical Corporation and W. H. & L. D. Betz is acknowledged in permitting preparation and publication of these data.

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PRESENTED before the Division of Water, Sewage, and Sanitation Chemistry at the 107th Meeting of the AMERICAN CHEMICAL SOCIETY, Cleveland, Ohio.

General View of Water Treatment Plant and Accelerators of the Columbia Steel Company at Geneva, Utah, Showing Construction of Softener Basin



Phase Behavior in Systems of Hydrocarbon-Furfural-Water

SYNTHETIC rubber manufacture, as true of most industrial materials, requires numerous steps in a chainlike sequence.

For Buna S and Buna N, primary links are concerned with the formation and isolation of butadiene, and much of this technology cannot be discussed under present war conditions. It is well known, however, that butadiene results from the dehydrogenation of butene or the double dehydrogenation of butane. All present butadiene from petroleum processes lead to a hydrocarbon mixture from which the four-carbon constituents can be fractionated, but the isolation of butadiene is more difficult. The literature shows (13, 14) that this separation can be accomplished by the action of selective solvents, of which furfural is one. On a commercial scale the separation is best carried out in solvent fractionating towers whose design depends upon the behavior of the individual hydrocarbons in admixture with the solvent; hence it is desirable to evaluate certain of the physical properties of these

systems. Some of the work in this connection is reported in the present paper and includes: cloud point data, which indicates whether one or two liquid phases may be expected on the fractionator plates; densities, which were taken as a matter of interest and to aid in fractionator design; and vapor pressures, to permit calculation of activity coefficients which, in turn, allow deviations from ideal solution laws to be calculated.

MATERIALS AND APPARATUS

Furfural was obtained from Quaker Oats Company; the sample was purified by distillation in a forty-plate glass column. Comparison of observed properties with literature values (10) follows:

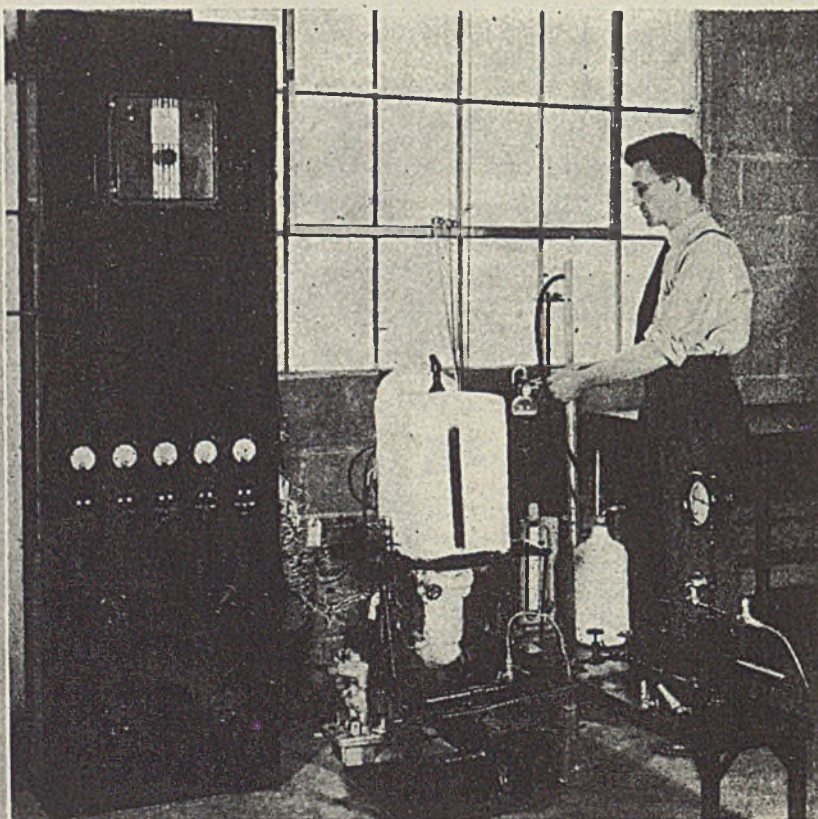
	Literature	Observed
Boiling point at 760 mm. Hg, ° F.	323.1	323.0 ± 0.1
Refractive index, n_D^{20}	1.5261	1.5255
Density at 68° F., grams/cc.	1.1598	1.1565

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Systems of three hydrocarbons with a furfural-water solution are studied with respect to cloud point and to density of cloud point liquid. Isobutane is the least soluble in the 4% water-96% (by weight) furfural mixture, followed by n-butane and 1-butene. Isothermal vapor pressure and density data for the same three systems and for the corresponding butadiene system are taken at four temperatures above the cloud point curves: 250°, 200°, 150° and 100° F. These vapor pressure data permit the calculation of activity coefficients which are presented as plots of γ against x for each system at the four temperatures. It is impossible to correlate the data with the van Laar or similar equations. Experimental vapor pressures for 1-butene and for 1,3-butadiene are given up to 250° F.



n-Butane was obtained from Phillips Petroleum Company and was over 99% pure. Isobutane was secured from Ohio Chemical Company and contained 2.2% *n*-butane. The sample of 1-butene, from the Phillips Petroleum Company, was greater than 99.5% olefinic and contained 99.2% four-carbon hydrocarbons. The 1,3-butadiene also from Phillips Petroleum Company was composed of 1.4% butanes, 0.5% butenes, and 2.1 mole % higher-boiling material which probably was polymer. All hydrocarbons were used without purification, but 0.1 weight % hydroquinone was added to each charge of butadiene as a polymerization inhibitor.

A sketch of the solubility apparatus, which permitted visual inspection of the liquid systems through glass and was similar to that described by Katz and Kurata (6), is presented in Figure 1. The 6.316-cubic-inch equilibrium cell consisted of a 19-T-30 Jerguson sight gage which was suspended in a constant-temperature air bath. The incoming air was heated by electrical resistance wires, and the temperature was controlled by a bimetallic thermoregulator in the air bath. Four temperatures along the length of the sight gage were measured with iron-constantan thermocouples, which were set into the metal gage body about $\frac{1}{8}$ inch, and the incoming air temperature was also measured with a thermocouple. A Leeds & Northrup 0-650° F. potentiometer was used.

The effective volume of the equilibrium chamber could be varied by adding or withdrawing mercury through a $\frac{3}{16}$ inch o.d. $\times \frac{5}{32}$ inch i.d. steel tube. This was done by raising or lowering nitrogen pressure on the mercury reservoir, where the mercury level could be observed in an 11-T-30 Jerguson gage. The volume within the cell was determined by means of a steel scale attached beside the glass of the equilibrium chamber. Pressure on the cell was measured with Bourdon tube gages on the nitrogen phase of the mercury reservoir, with suitable corrections for head of mercury. Two stainless steel Bourdon tube gages were used; one covered the range from 0 to 100 pounds per square inch and the other, from 0 to 600 pounds. The gages were calibrated periodically by a dead-weight gage tester.

Agitation was created within the cell by rocking the air bath and gage through a 90° angle. The steel tube connecting the mercury in the cell to the reservoir was formed into a helix at the center of rotation, which permitted the mercury reservoir and pressure gages to remain stationary at all times.

Figure 1
Simplified Diagram of Equilibrium Cell
and Auxiliaries

- | | |
|----------------------|----------------------|
| A. Thermoregulator | H. Mercury reservoir |
| B. Purge bomb | J. Vent |
| C. Mercury inlet | K. Nitrogen inlet |
| D. Hydrocarbon inlet | L. Pressure gage |
| E. Heating air inlet | M. Equilibrium cell |
| F. Mercury trap | TC. Thermocouples |
| G. Glass charge bomb | V. Vacuum |

Table I. Cloud Point Data for Hydrocarbon-Furfural-Water Systems
(4 weight % water based on furfural + water)

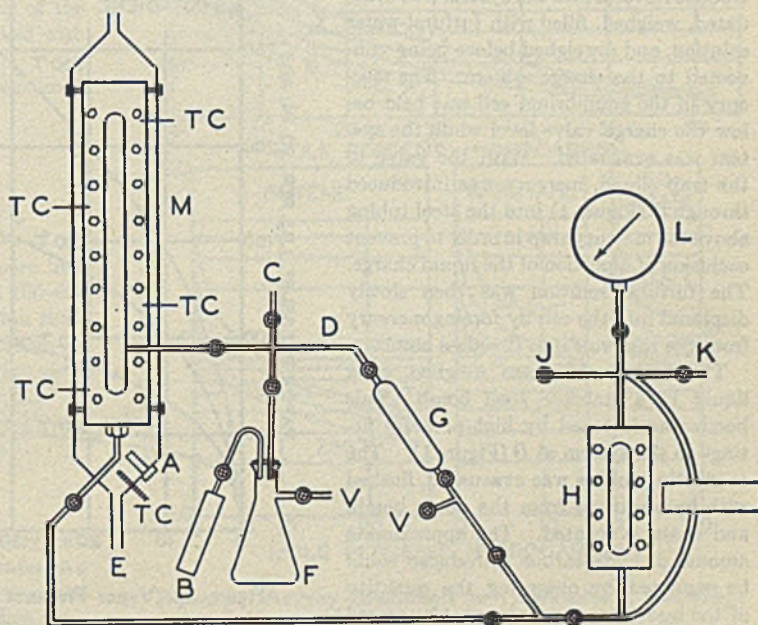
<i>n</i> -Butane			Isobutane			1-Butene		
Wt. % hydrocarbon	Cloud point temp., ° F.	Density at cloud point, g./cc.	Wt. % hydrocarbon	Cloud point temp., ° F.	Density at cloud point, g./cc.	Wt. % hydrocarbon	Cloud point temp., ° F.	Density at cloud point, g./cc.
6.36	88	1.12	4.10	74	1.13	12.12	68	1.06
10.21	137	1.12	10.08	157	1.08	16.56	76	1.02
14.81	180	0.99	16.14	225	0.97	18.88	88	0.99
18.95	213	0.94	20.47	260	0.90	22.57	108	0.96
22.22	230	0.90	24.94	282	0.81	26.03	122	0.94
24.47	242	0.86	31.28	308	0.73	34.17	143	0.84
31.74	269	0.79						

Table II. Vapor Pressures and Liquid Densities in Hydrocarbon-Furfural-Water Systems
(4 weight % water based on furfural + water)

Hydrocarbon		100° F.		150° F.		200° F.		250° F.	
Wt. %	Mole %	V.P. ^a	D. ^b	V.P.	D.	V.P.	D.	V.P.	D.
<i>n</i> -Butane									
1.62	2.27	30	..	39	..	53	..	76	..
2.19	3.06	33	1.13	48	1.10	65	1.07	92	1.04
4.78	6.62	57	1.10	75	1.08	110	1.03	154	1.01
8.42	11.48	110	1.03	157	1.01	211	0.97
10.30	14.02	114	..	180	..	234	..
Isobutane									
0.65	0.91	22	..	29	..	44	..	72	..
1.97	2.76	46	..	66	..	90	..	116	..
3.59	4.99	71	..	102	..	132	..	170	..
1-Butene									
0.69	1.01	19	..	24	..	34	..	59	..
2.00	2.89	27	1.13	38	1.09	53	1.07	80	1.04
3.28	4.72	34	1.10	53	1.08	70	1.04	105	1.02
7.10	10.06	46	1.08	78	1.05	117	1.01	164	0.98
9.47	13.26	49	1.06	91	1.03	153	0.99	197	0.96
16.64	22.59	64	1.00	115	0.97	177	0.93	251	0.90
19.03	25.58	65	0.99	122	0.96	183	0.92	263	0.89
1,3-Butadiene									
0.58	0.88	17	1.15	20	1.07	26	1.04	42	1.01
1.64	2.47	26	1.09	32	1.05	39	1.01	55	1.00
5.83	8.58	38	1.03	55	1.00	79	0.97	116	0.94
11.16	16.00	46	0.99	71	0.96	100	0.93	152	0.90
16.67	23.27	80	0.94	124	0.91	184	0.88
29.12	38.38	98	..	161	..	239	..
38.41	48.60	51	..	100	..	161
49.59	59.86	52	0.78	101	0.71	177	0.71	292	0.68
51.56	61.74	56	0.75	108	0.72	183	0.69

^a Vapor pressure in pounds per square inch absolute.

^b Density in grams per cc.



The upper opening in the Jerguson gage was closed flush with the inner surface so that no unobservable space was present. A $1/16$ -inch i.d. steel tube was provided through the side of the gage at a point about 1.5 inches above the bottom, and extended through the air bath so that its extremity was available for charging

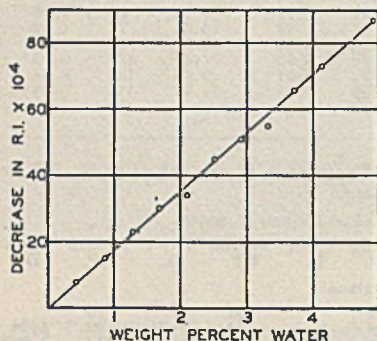


Figure 2. Change of Refractive Index with Composition of Furfural-Water Solution

materials to the equilibrium cell. Since the length was less than 5 inches and since this line was normally below the mercury level, liquid holdup was negligible. After charging, the evacuation and charge lines were disconnected to permit rocking of the apparatus. A standard connection was used for the mercury inlet at the bottom of the gage. Auxiliary equipment included a glass weighing

bomb, a steel weighing bomb, vacuum pump, manometer, purge bomb, and mercury trap.

METHOD OF OPERATION

A furfural-water solution was prepared by adding a definite volume of distilled water from a microburet to a known volume of furfural. Corrections were made for density differences due to temperature in calculating weight per cent from volumetric measurements. As a further check upon the water content, the refractive index of the sample was compared with Figure 2. This curve was experimentally determined by adding water from a microburet to known amounts of furfural and observing the refractive indices. The difference in refractive index was used rather than the absolute value since furfural samples of different age, source, or purity may vary slightly in refractive index and since different operators or refractometers may give slightly different readings.

The 3-cubic-inch glass bomb used to introduce furfural into the system was evacuated, weighed, filled with furfural-water solution, and reweighed before being connected to the charge system. The mercury in the equilibrium cell was held below the charge valve level while the system was evacuated. With the valve to the trap closed, mercury was introduced through *C* (Figure 1) into the steel tubing above the mercury trap in order to prevent occlusion of a portion of the liquid charge. The furfural solution was then slowly displaced into the cell by forcing mercury from the reservoir into the glass bomb.

The hydrocarbon was weighed as a liquid in a stainless steel bomb. This bomb was fastened by high-pressure fittings to the system at *D* (Figure 1). The connecting tubing was evacuated, flushed with hydrocarbon from the purge bomb, and again evacuated. The approximate amount of hydrocarbon introduced could be regulated by observing the quantity of the hydrocarbon phase as it appeared

above the furfural layer within the equilibrium cell. When necessary the charge bomb was heated with hot water to increase the vapor pressure in the charge bomb above the pressure within the system. Substantially all residual hydrocarbon remaining in the connecting tubing after charging was withdrawn to the steel bomb by cooling the lower end of the bomb with liquid nitrogen. The gas charge bomb was allowed to come to room temperature and was dried carefully before weighing.

The cloud point temperature of the hydrocarbon-furfural-water mixture was determined by heating the sample until complete solution occurred and then cooling. As the system was allowed to cool slowly with shaking, an opaque cloud formed at a definite temperature for a particular system and composition (3); below the cloud temperature two liquid phases reappeared. The temperature and volume of the system were recorded at the first visible cloud formation. The mercury level was adjusted so that, at the cloud point, from 0.1 to 0.5 ml. of vapor remained in the chamber. This procedure permitted observing the cloud point at the vapor pressure of the system without appreciably affecting the composition of the liquid. After the cloud point was determined at the original composition, additional hydrocarbon was introduced and another cloud point observed. In this way enough data were obtained so that a composition-cloud point

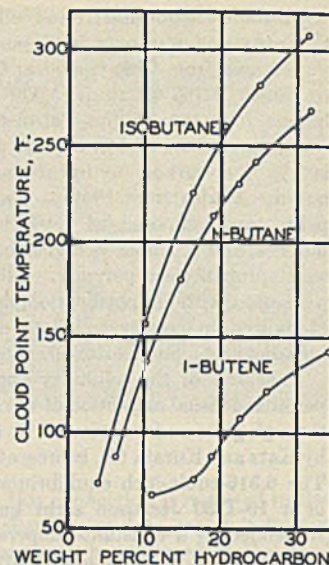


Figure 3. Cloud Points of Three Hydrocarbons in Furfural-Water

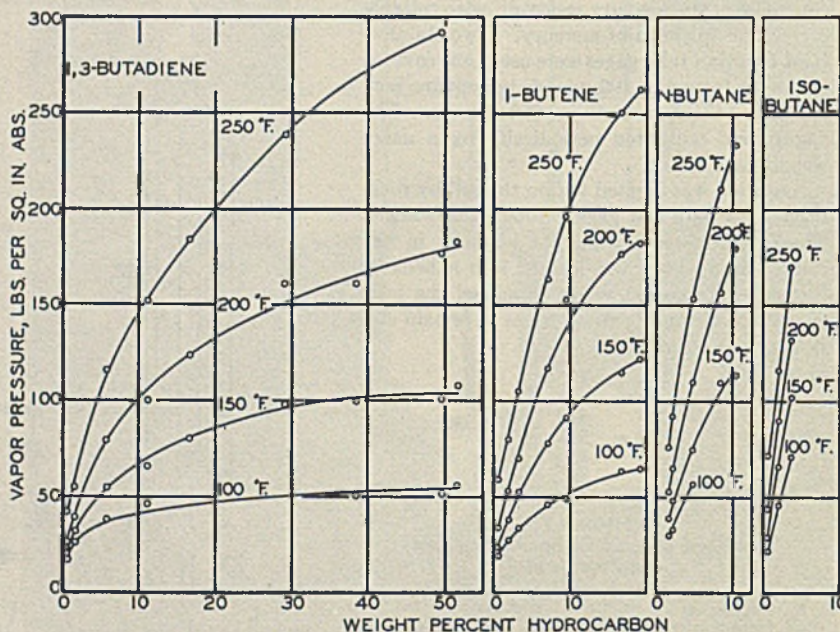


Figure 4. Vapor Pressures in 1,3-Butadiene, 1-Butene, *n*-Butane, and Isobutane Systems with Furfural-Water

curve could be drawn, as well as a composition-density curve for the cloud point liquid.

In order to calculate activity coefficients, isothermal vapor pressures were required over a range of compositions. They were obtained for increasing hydrocarbon concentrations by substantially the same method employed in the cloud point work; however, at each concentration vapor pressures were observed successively at four temperatures: 100°, 150°, 200°, and 250° F.

EXPERIMENTAL DATA

The cloud point curves for *n*-butane, isobutane, and 1-butene in a furfural-water solution of 96 to 4 weight ratio were determined for hydrocarbon concentrations from less than 1 up to 34% by weight, as shown in Figure 3. Vapor pressure data above the cloud point at 250°, 200°, 150°, and 100° F. are plotted for these three systems and for the butadiene system in Figure 4. Liquid densities were determined at each cloud point and each vapor pressure point and are given for butadiene in Figure 5. Table I contains the cloud point data, and Table II gives the isothermal vapor pressures and densities for all systems studied. The same apparatus was used to measure the vapor pressures of 1-butene and 1,3-butadiene from 70° to 250° F., together with liquid densities at the bubble point. The data are given in Table III.

In determining vapor pressures, each composition was allowed to mix overnight at a temperature above the cloud point; it was observed that higher than the true vapor pressures were obtained if sufficient mixing time were not allowed, even though a single phase existed within the equilibrium cell. In other words, hydrocarbon diffusion through furfural-water does not occur at a fast rate, and good mixing is required if equilibrium is to be obtained within a reasonable time. After it was certain that a homogeneous solution of the hydrocarbon in the furfural-water had been established, the vapor pressures were determined at the four desired temperatures without allowing a drop to the cloud point temperature.

The cloud point temperatures obtained were reproducible to 2° F. with correspondingly small uncertainties in the observed vapor pressures and densities. Accuracy of cloud point temperature reading was dependent upon a distinct cloud formation, which was most pronounced in regions of high hydrocarbon content (8). At the higher temperatures, the solution darkened in color noticeably within a few hours although the temperatures were well below those of furfural decomposition. Although similar results have been noted in reports on the thermal stability of furfural (2), this darkening does not affect the accuracy of the results, since in several instances points have been checked with fresh and dark furfural.

The accuracy of the data as read from the smooth curves is considered to be as follows:

Pressure, lb./sq. in.	±3.0
Temperature, ° F.	±0.5
Hydrocarbon concentration, wt. %	±0.02
Density, gram/cc.	±0.02

The pressure gages could be read to ±1 pound per square inch at pressures below 100 pounds and to ±2 pounds in the 100–600 pound range. The calibrations should be accurate within these limits. A temperature differential of 0.5° F. along the Jerguson gage could be detected, and all thermocouples were found to agree with a calibrated mercury-in-glass thermometer within 0.5° F. The volume within the equilibrium cell could be read to ±0.1 ml., and the weight of charge was accurate within 0.01 gram.

ACTIVITY COEFFICIENTS

While the systems investigated here were actually ternary, calculations are greatly simplified by thinking of furfural-water as a single component. The validity of this assumption is discussed below. Raoult's law states that the partial pressure of each com-

Table III. Vapor Pressures and Liquid Densities of 1-Butene and 1,3-Butadiene

Temp., ° F.	Pressure, Lb./Sq. In. Abs.		Density, Grams/Cc.	
	Butene	Butadiene	Butene	Butadiene
89	...	41	...	0.840
89	...	57	...	0.827
92	58
100	65	66	0.578	0.614
110	...	78	...	0.610
112	77	...	0.560	...
120	86	...	0.557	...
141	114
150	128	133	0.535	0.586
151	...	135	...	0.577
200	230	235	...	0.538
250	382	389	...	0.476

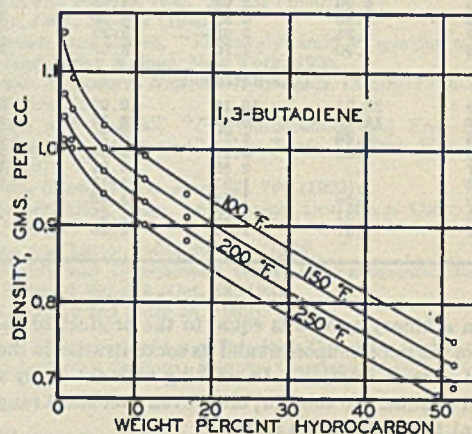


Figure 5. Liquid Densities in 1,3-Butadiene-Furfural-Water System

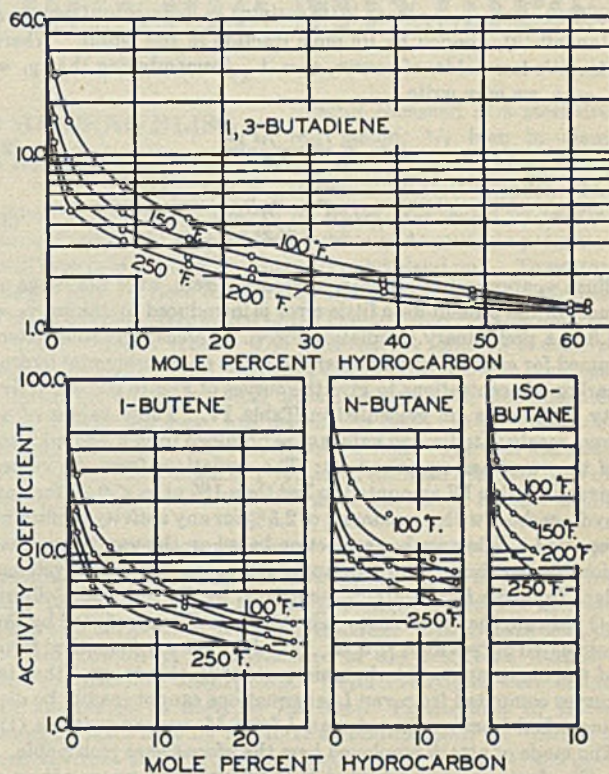


Figure 6. Activity Coefficients for 1,3-Butadiene, 1-Butene, *n*-Butane, and Isobutane Systems with Furfural-Water

Table IV. Calculated Activity Coefficients, Assuming $\gamma_2 = 1.0$

Hydrocarbon, Mole %	Activity Coefficient			
	100° F.	150° F.	200° F.	250° F.
<i>n</i> -Butane				
2.27	25.18	15.91	11.42	9.07
3.06	20.57	...	10.49	8.34
6.62	16.49	10.64	8.39	6.74
11.48	...	9.05	6.98	5.42
14.02	...	7.68	6.59	4.94
Isobutane				
0.91	33.60	21.60	17.55	16.57
2.76	23.32	16.57	12.33	9.28
4.99	19.96	14.25	10.13	7.73
1-Butene				
1.01	28.47	17.72	13.23	13.01
2.89	14.28	9.98	7.49	6.46
4.72	10.98	8.60	6.16	5.35
10.06	6.99	5.98	4.93	4.06
13.26	5.65	5.31	4.92	3.74
22.59	4.34	3.95	3.36	2.83
25.58	3.90	3.70	3.07	2.62
1,3-Butadiene				
0.88	28.75	16.16	10.99	9.69
2.47	15.77	9.42	6.16	4.82
5.58	6.66	4.73	3.77	3.23
16.00	4.33	3.29	2.69	2.32
23.27	...	2.65	2.22	1.96
38.38	...	1.91	1.76	1.56
48.60	1.69	1.64	1.40	...
59.86	1.31	1.26	1.25	1.24
61.74	1.37	1.31	1.25	...

ponent in a binary system is equal to the product of the vapor pressure of the pure component and its concentration in the liquid, expressed as mole fraction. In working with the many systems which fail to adhere to this law, often even over short ranges, it is convenient to use deviation factors

$$\gamma_1 = \frac{Py_1}{P_1x_1}; \quad \gamma_2 = \frac{Py_2}{P_2x_2} \quad (1)$$

which are equivalent to activity coefficients, where the activity coefficient of a component is its activity as defined by Lewis and Randall (9), divided by its mole fraction in the liquid. Where Raoult's law holds, of course, $\gamma = 1$. Remembering that $y_1 = 1 - y_2$, we may write

$$\gamma_1 = \frac{P - \gamma_2 P_2 x_2}{P_1 x_1} \quad (2)$$

$$\gamma_2 = \frac{P - \gamma_1 P_1 x_1}{P_2 x_2} \quad (3)$$

Since γ_2 approaches 1.0 as x_1 approaches zero, over the range of most of the present data little error is introduced by taking $\gamma_2 = 1.0$ in a preliminary calculation for γ_1 . Values were thus determined for each set of data over the range of experimental hydrocarbon concentrations to give the curves of Figure 6. All activity coefficients are presented in Table IV. These values of γ_1 were recalculated, using values of γ_2 obtained from a revised form of the van Laar equations (1): The deviations from the values given in Table IV amounted to less than 1% at $x_1 < 0.25$ for any hydrocarbon, with a maximum of 2.5% for any activity coefficient reported. While such a correction based on the van Laar equation has not been shown to apply for these particular systems, data from the five solutions mentioned by Carlson and Colburn (1) indicate that in all cases γ_2 is satisfactorily reproduced by the calculated curves at $x_1 < 0.25$. Further, the mathematical form of the curve appears to be unimportant in this range; that is, curves computed from van Laar equations cannot readily be distinguished from curves calculated from Margules equations (1). The mode of attack employed here therefore seems reasonable.

The foregoing has assumed that furfural and water act as a single component, which is actually not true. It can be shown, however, that in a ternary system the activity coefficients of two

components which occur in constant ratio can be replaced by a single coefficient according to the following integrated form of the Gibbs-Duhem equation:

$$\frac{\log \gamma_W}{1 + K} + \frac{\log \gamma_F}{1 + 1/K} = \log \gamma_2 + C \quad (4)$$

where K is a constant and equals x_F/x_W . Constant C equals zero where $x_W = 1.0$, since $\gamma_W = \gamma_2 = 1.0$ and $K = 0$, and also where $x_F = 1.0$, since $\gamma_F = \gamma_2 = 1.0$ and $K = \infty$; but this is not necessarily the case in the present example. C (at $K = x_F/x_W$) was calculated for the *n*-butane system from published data (11) to be 0.37 at 200° F. and 0.47 at 100° F. Since these results approximate zero and the calculations are somewhat uncertain, it appears best to take $C = 0$, whereupon γ_2 becomes a weighted average of γ_W and γ_F .

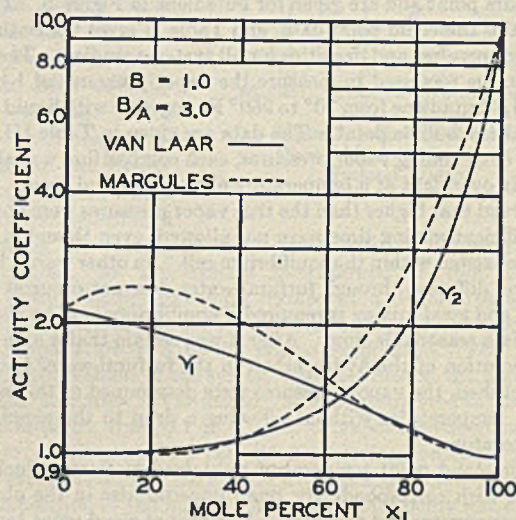


Figure 7. Typical van Laar and Margules Curves

From published liquid-liquid solubility data (4), it is possible to derive van Laar constants A and B and, in turn, the furfural and water activity coefficients at $x_F/x_W = K$, $x_B = 0$. From these values, taking $C = 0$, it is possible to calculate values of γ_2 suitable for use in Equation 2. This procedure was carried out and showed a maximum deviation from the activity coefficients reported in Table IV of 3.4% at 200° F. The deviation is largest at the lowest hydrocarbon concentrations and at the higher temperatures. It was not possible to calculate γ_2 at 250° F. from the solubility data (4) since this temperature is above the critical solution temperature for furfural and water; however, deviations from Table IV would not be expected to be more than 5 or 6%.

The combined effect of the two assumptions made, (a) that γ_2 increases only slightly as x_1 is increased from 0 to 0.25, and (b) that $\gamma_2 = 1.0$ at $x_1 = 0$, is therefore to cause the activity coefficients of Table IV to be not over 5% higher than the true values except at 250° F. At 250° F. a somewhat greater error might occur at the lower concentrations of hydrocarbons. Since the errors from both assumptions are indicated to be small and a completely satisfactory method for correcting is not available from the experimental results, the activity coefficients of Table IV are reported based on the preliminary calculations with $\gamma_2 = 1.0$.

Although the van Laar equations suggest that the initial computation for the experimental activity coefficients is a satisfactory approximation, it is not to be implied that the experimental data fit the van Laar γ_1 equation. In the present work it is evident that the terminal value of γ_2 is substantially greater than the

terminal value of γ_1 , or $B > A$. Typical Margules and van Laar curves are drawn in Figure 7 for the case where $B = 3A$; since the van Laar γ_1 curve is almost a straight line while the experimental data exhibit the sharp curvature shown for butadiene in Figure 6, there seems little hope of reconciling the two, even over short ranges. The Margules equation gives a curve of reverse curvature and, hence, even less applicability.

To permit certain calculations, it may be expedient to assume a pseudo value for B , letting $B < A$. This provides a hydrocarbon γ curve similar to the γ_2 curves of Figure 7; from inspection of Figure 6, it is evident that such a curve could be fitted at least approximately to the experimental data, provided a proper choice of constants were made. It should be clearly understood that Figure 7 is not based on experimental data and has been introduced only to show the type of curves that are obtained from the van Laar or Margules equations.

Vapor pressures from Table III were used for 1-butene and 1,3-butadiene calculations. Isobutane and *n*-butane vapor pressures were taken from the data of Sage and Lacey (12) and Kay (6), respectively. The vapor pressures of the furfural-water mixture were computed from literature values (4, 7), assuming each component to exert a partial pressure equal to the product of its vapor pressure and its mole concentration.

NOMENCLATURE

A, B = arbitrary constants in van Laar and Margules equations, equal to $\log \gamma_1$ at $x_1 = 0$ and $\log \gamma_2$ at $x_2 = 0$, respectively

P = total pressure, lb./sq. in. abs.

P_1, P_2 = vapor pressures of pure components, lb./sq. in. abs.

x = mole fraction in liquid

y = mole fraction in vapor

γ = activity coefficient

Subscripts

1, 2 = components of binary mixture with lower and higher boiling points, respectively; subscript 2 is also used to designate the constant-composition furfural-water mixture

B = any butane hydrocarbon under consideration

F = furfural

W = water

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Compressibilities of Nitrogen-Carbon Dioxide Mixtures

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THE *P-V-T* behavior of gas mixtures is useful to engineers in industry for three principal reasons: considerations of fluid dynamics and heat transfer, calculation of thermodynamic properties, and testing of various proposed "laws" for predicting the properties of mixtures from those of the components. The system nitrogen-carbon dioxide was chosen because the pure materials differ widely, and therefore the system should represent a severe test of the "laws", and because the thermodynamic analyses of proposed cycles for the direct manufacture of dry ice from flue gas (without separation by absorption) would require such data.

The present work includes the determination of the compressibility isotherms for two mixtures of nitrogen and carbon dioxide containing 25.13 and 50.48 mole % carbon dioxide at 25°, 50°, 75°, 100°, and 125° C. at pressures up to 500 atmospheres.

A modified form of Bartlett's constant-volume type of apparatus (2, 3) is illustrated in Figure 1. *C* represents the dividing point between the high-pressure portion to the left and the low-pressure portion to the right. Additional details are given by Haney (7).

INJECTOR. Patterned after the Keyes "volumenometer" (10), the

injector consisted of a steel drill rod piston, $\frac{1}{4}$ inch in diameter and 49 inches long, fitting into an alloy steel cylinder. The

piston, which did not turn in its travel, was sealed by packing made of alternate rings of hard rubber and ceresin-impregnated twill tape held in place by a steel ring and gland nut. To protect the gas mixture from the packing and to diminish the clearance, 5 cc. of mercury were added to the injector after installation.

DEAD WEIGHT GAGE. The construction followed a description by Keyes (9). A U-tube was designed for use with this gage. It consisted of a heavy steel block in which a $\frac{3}{16}$ -inch-diameter well, $3\frac{3}{4}$ inches deep, was drilled. A head was provided containing a dip pipe which fitted into the well. The well was filled with mercury to a depth of $1\frac{1}{4}$ inches, the head attached, and oil forced into the well until all air was displaced. A contact needle

Compressibility factors and residuals are reported for two mixtures of nitrogen and carbon dioxide at 25°, 50°, 75°, 100°, and 125° C. and at pressures up to 500 atmospheres. The mixtures were 25.13 and 50.48 mole % carbon dioxide. These data should be of use to anyone contemplating the direct manufacture of dry ice from carbon-dioxide-rich flue gases without preliminary absorption. Determinations were made in a constant-volume type of apparatus as used by Bartlett. Predictions of these results by the Dalton and Amagat laws and by Bartlett's modification of Dalton's law were tried. Below 200 atmospheres the Dalton law seems best. Between 250 and 400 atmospheres Bartlett's proposal is best, and above 400 atmospheres the Amagat law is superior. All are improved at high temperatures.

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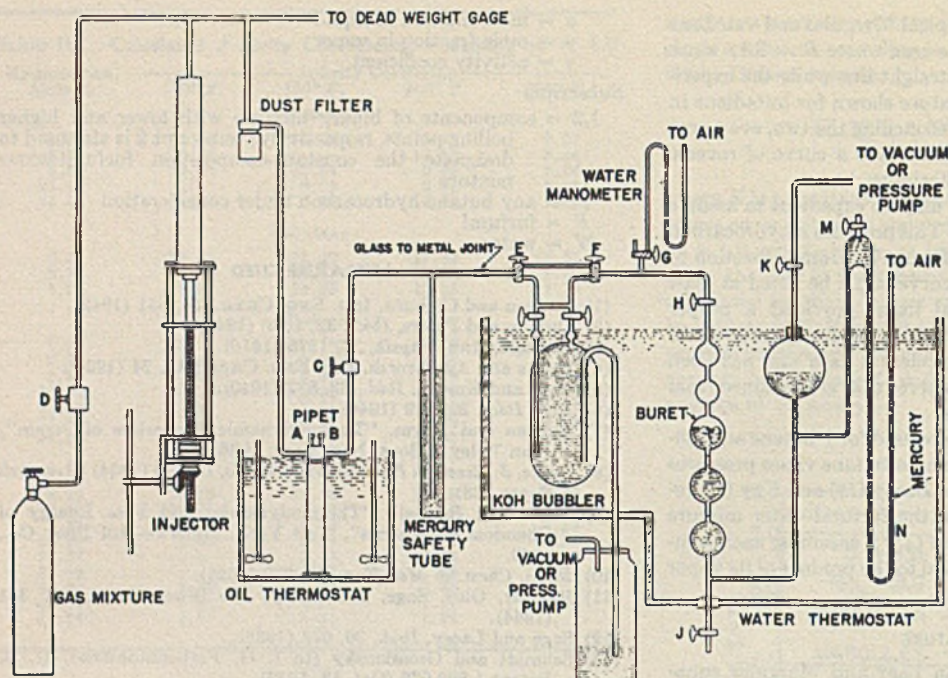


Figure 1. Assembly of Apparatus

was provided in the dip pipe so that the mercury could complete the circuit by which a relay extinguished a small light. The mercury differential in the U-tube was frequently checked, and the uncertainty did not appear to exceed 5 mm. At the balanced condition of measurement with the dead weight gage, the small light flashed on and off as the contact in the U-tube was alternately made and broken by the vibrations of the piston-oscillating system. A vacuum tube circuit described by Heisig and Gernes (8) was employed in the electrical contact circuit of the U-tube. The parts of the weight pan assembly of the piston gage were calibrated by the New Haven Department of Weights and Measures on a W. & L. E. Gurley balance. The weights were adjusted by this department and were accurate to 1 grain.

PIPETTS. Two pipets, differing only in size, were constructed according to a drawing of Bartlett's (2, 3) pipet supplied by the U. S. Department of Agriculture. The pipets were made of 0.9% chromium-0.7% manganese-0.2% vanadium-0.3% carbon steel. The small one (6.16 cc.) had a $\frac{1}{8}$ -inch bore 7 inches deep, and was $2\frac{1}{8}$ inches in outside diameter and $10\frac{1}{2}$ inches long. The large one (22.13 cc.) had a $\frac{1}{2}$ -inch bore $6\frac{1}{4}$ inches deep, and was $2\frac{1}{4}$ inches in outside diameter and $10\frac{1}{4}$ inches long. The bodies were interchangeable so that only one head was required. An iron gasket softened in hydrogen at 1050° C. was used. The valve stems were made of 13% chromium-0.4% carbon-0.4% manganese-0.35% silicon steel and were packed with shredded lead. The tips of the stems were hardened by heating to 970° C. in an electric furnace and quenching in oil at about 140° C. They were then heated at 200° C. for one hour to "draw" some of the hardness. The pipets were immersed in the constant-temperature bath up to the cooling coil of the head. The cooling coil was not necessary in the range of these investigations. The pipets were supported on Celotex blocks to prevent contact with the thermostat shell.

THERMOSTATS. The pipet thermostat was filled with oil, stirred and electrically heated, and controlled to $\pm 0.05^\circ$ C. The buret thermostat (low pressure) was the same except that it was filled with water and controlled to $\pm 0.03^\circ$ C.

ABSORBER. This large glass bulb, similar to those used in gas analyses, had a capacity of $2\frac{1}{2}$ liters and was filled with a solu-

tion of approximately 28% potassium hydroxide. The gas was introduced via a glass tube near the bottom of the vessel and was distributed in fine bubbles through a perforated glass cone.

BURET. Five Pyrex bulbs were joined successively in a vertical line by 8-mm. tubing. Each tube was marked for reading with two loops of fine wire held in place by de Khotinsky cement. A 5-liter reservoir was attached to the lower end of the buret as was also a mercury-in-glass manometer with an etched millimeter scale. A combination vacuum-pressure pump was connected to the top of the reservoir by which the pressure in the reservoir and buret could be controlled.

CALIBRATION

DEAD WEIGHT GAGE PISTONS. The pistons were calibrated against the vapor pressure of carbon dioxide at

the ice point, using Bridgeman's value (4) of 2614.47 cm. of mercury at normal gravity. The carbon dioxide was prepared by two simple distillations of the commercial product, the fore and end cuts being rejected in each case. This carbon dioxide was stored in a steel bulb connected to the piston gage, and the bulb was immersed in a Dewar flask containing shaved ice and distilled water. Repeated determinations after venting gave the same readings, after thermal equilibrium was attained, indicating purity of the carbon dioxide. The constants were found to be 2.3874 atm. per pound for the small piston and 0.59675 for the large one. The latter figure was determined by Molstad (17). The large piston was used up to 200 atm. and the small one above that pressure. Balance on the gage was within 5 grams, which corresponds to about 20 mm. of mercury for the small piston and 5 mm. for the large one.

PIPETTS. The capacities of the pipets were determined from the established compressibilities of nitrogen and hydrogen. The pipet was filled with one of these gases, the pressure and temperature were determined when conditions were steady, and the gas was then expanded and measured. The volume of the pipet was computed from the expression,

$$V_p = \frac{C_a \left(V_b + V_p \frac{P_a}{760} \times \frac{273.16}{T_p} \right)}{P_b}$$

where V_p = pipet volume

V_b = volume of expanded gas in buret corrected to 0° C. and 760 mm.

T_p = temperature of pipet

P_b = high pressure of pipet

P_a = barometric pressure

C_a = Amagat compressibility factor at P_b and T_p

This equation assumes the gas to obey, at barometric pressure, the Charles and Boyle laws but not the ideal gas law (i.e., not $pV = RT$). The compressibility factors for nitrogen were based on those of Michels and co-workers (16, 18). Values at 25° C. were read directly from their data, but values at 30° C. were interpo-

TABLE I. CALCULATED VOLUMES OF PIPETS AT VARIOUS TEMPERATURES AND PRESSURES

Pressure, Atm.	Volume, Cc.		
	25° C.	75° C.	125° C.
Small Pipet			
1	6.1593	6.1694	6.1810
200	6.1807	6.1768	6.1824
500	6.1631	6.1732	6.1848
Large Pipet			
1	22.127	22.163	22.205
50	22.129	22.165	22.207
150	22.133	22.169	22.211

lated on large plots of their data. For hydrogen the data of Bartlett smoothed by Deming and Shupe (6) were used.

Determinations for the small pipet were made with nitrogen at 30° C. and 200 or 300 atm., and at 25° and 200 atm., and with hydrogen at 30° C. and 200 atm. in two series. The determinations were then corrected by methods described below to 25° C. and 200 atm. The value was 6.1607 cc. = 0.03% average deviation.

The large pipet was calibrated with nitrogen at 25° C. at 50 and 75 atm. and with hydrogen at 25° C. and 50 atm. The value when corrected to 25° C. and 50 atm. was 22.129 cc. = 0.02% average deviation.

Corrections for the effect of pressure on pipet volumes were computed by Love's formula with the constants used by Bartlett (2). The temperature coefficient of capacity change was obtained from an expression of Keyes, Smith, and Joubert (11) with the constants as used by Bartlett (2). Table I shows the volumes of the pipets at various temperatures and pressures as computed by these methods. More values were listed by Haney (7). Redetermination of volumes at the end of all experiments gave practically perfect agreement, an indication of no contamination by dust or other foreign matter.

BURET. The volumes of the various bulbs were determined by weighing the water discharged from each. The menisci were read at the division points between the bulbs, marked by the two loops of wire previously mentioned. The values for the five bulbs with the average deviations of five determinations at 20.82° C. were 218.60 ± 0.02, 277.67 ± 0.00, 505.24 ± 0.006, 501.23 ± 0.006, 505.22 ± 0.008 cc. The volume from stopcock H (Figure 1) to the top bulb was 0.1 cc.

MATERIALS AND METHODS

NITROGEN. This material was guaranteed by the supplier to contain not more than 0.3% noble gases, principally argon, and 0.2% oxygen. The oxygen was reduced to about 0.05% or less (as shown by Orsat analysis) by slow passage over a bed of copper at 400° C. under tank pressure. For calibration purposes, the nitrogen was dried by passage over barium oxide under pressure. The contact time was many hours.

CARBON DIOXIDE. This material was found to be 99.97% alkali soluble. It was purified by two simple distillations, the fore and end fractions being rejected. Drying was effected by passage over anhydrous calcium chloride.

HYDROGEN. This material, used in calibration only, was purified of oxygen by passage over copper at 300° C. at tank pressure, and dried over barium oxide.

PREPARATION OF MIXTURE. In preparing the 50.48% carbon dioxide mixture, a cylinder containing a known weight of twice-distilled carbon dioxide was placed in an ice bath. Nitrogen was allowed to flow in slowly, passing over copper

at 400° C. and through a drying tube containing silica gel and activated charcoal. The proper amount was determined by weighing. Mixing was accelerated by intermittent heating and periodic rolling of the cylinder for several days. After standing several weeks with no detectable concentration change, it was compressed to a higher storage pressure and dried with anhydrous calcium sulfate. The other mixture was prepared in the same way, except that nitrogen was dried by cooling in dry ice-alcohol and the mixture was not compressed.

ANALYTICAL METHODS. Two ascarite-packed U-tubes were used in the gravimetric method and due precautions were taken with respect to predrying, swelling of absorbent (19), and displacement of gas. The analyses by three different determinations were as follows: 25.15, 25.13, 25.13 and 50.50, 50.47, 50.49 mole % carbon dioxide.

The volumetric method was similar to the usual Orsat analysis, utilizing the low-pressure buret and the potassium hydroxide bubbler (Figure 1). The volume percentage thus determined was converted to mole per cent with the aid of the low-pressure *P-V-T* data of Cawood and Patterson (5) for carbon dioxide, those of Michels, Wouters, and de Boer (16) for nitrogen, and the assumption of Amagat's law at 1 atmosphere. The results were: 25.11, 25.11, 25.09 and 50.47, 50.45, 50.47 mole % carbon dioxide.

The final values were taken by averaging the two sets, giving the volumetric method only half weight because of the assumption of Amagat's law. The values were 25.13 ± 0.02 and 50.48 ± 0.02 mole % carbon dioxide.

PROCEDURE. The procedure was similar to that employed by Bartlett and co-workers (2, 3) except in the expansion of the high-pressure gas from the pipets. After thermal and pressure equilibrium were attained in the pipet, valve *G* (Figure 1) was momentarily opened to equalize the pressure of the low-pressure system with that of the atmosphere. The gas was then expanded slowly by controlling valves *C* and *B* and allowed to flow into the potassium hydroxide bubbler and thence to the buret. When the expansion was almost complete, valve *C* and stopcock *E* were closed

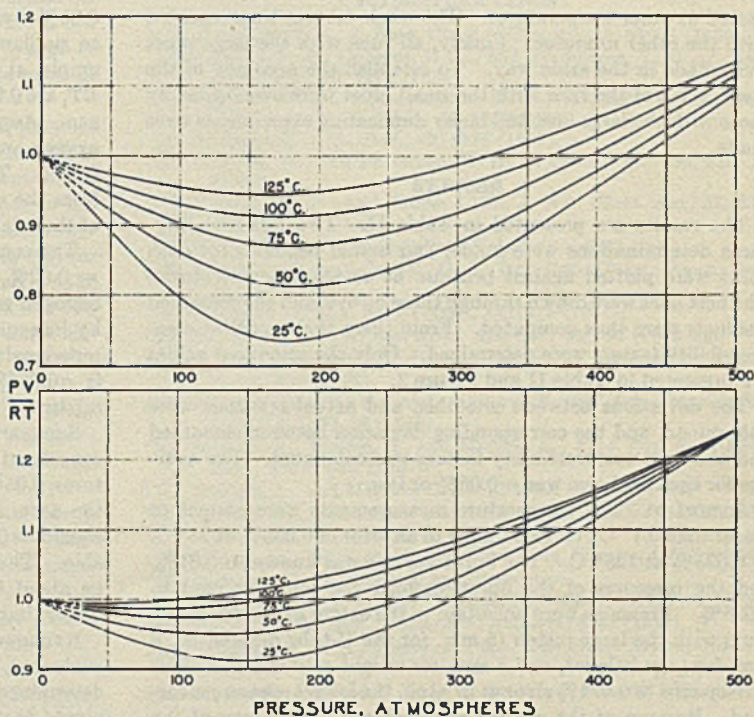


Figure 2. Compressibility Factor, pv/RT , for 50.48 Mole % (above) and 25.13 Mole % (below) Carbon Dioxide Mixtures

TABLE II. SMOOTHED COMPRESSIBILITY FACTORS AND RESIDUALS^a

Pressure, Atm.	25° C. Isotherms		50° C. Isotherms		75° C. Isotherms		100° C. Isotherms		125° C. Isotherms	
	$\frac{RT}{p}$	$\frac{pv}{RT}$	$\frac{RT}{p}$	$\frac{pv}{RT}$	$\frac{RT}{p}$	$\frac{pv}{RT}$	$\frac{RT}{p}$	$\frac{pv}{RT}$	$\frac{RT}{p}$	$\frac{pv}{RT}$
50.48 Mole % Carbon Dioxide										
30	54.60	0.9331	42.34	0.9521	32.79	0.9656	25.88	0.9748	18.85	0.9827
50	53.68	0.8903	41.03	0.9226	31.68	0.9446	24.47	0.9600	18.00	0.9725
75	52.08	0.8403	39.32	0.8888	30.10	0.9210	22.85	0.9440	16.79	0.9615
100	49.80	0.7964	37.30	0.8593	28.22	0.9012	21.17	0.9309	15.31	0.9530
125	46.51	0.7624	34.80	0.8360	26.06	0.8860	19.31	0.9212	13.73	0.9475
150	42.21	0.7413	31.81	0.8201	23.57	0.8762	17.42	0.9147	12.10	0.9444
175	37.19	0.7340	28.32	0.8131	20.87	0.8722	15.34	0.9123	10.38	0.9444
200	31.77	0.7403	24.51	0.8151	18.20	0.8726	13.10	0.9143	8.58	0.9475
225	26.83	0.7533	20.88	0.8228	15.54	0.8776	10.78	0.9208	6.71	0.9538
250	22.36	0.7715	17.40	0.8360	12.90	0.8871	8.68	0.9291	4.98	0.9619
300	14.12	0.8269	11.15	0.8738	7.87	0.9174	4.60	0.9549	1.66	0.9848
350	7.84	0.8875	5.71	0.9246	3.43	0.9580	1.05	0.9880	1.40	1.0150
400	2.87	0.9531	1.41	0.9787	-0.28	1.0039	-2.04	1.0267	-4.12	1.0504
450	-1.11	1.0204	2.18	1.0370	-3.48	1.0548	-5.01	1.0736	-6.67	1.0919
500	-4.31	1.0881	-5.31	1.1001	-6.40	1.1120	-7.42	1.1212	-8.58	1.1313
25.13 Mole % Carbon Dioxide										
30	24.83	0.9696	17.24	0.9805	12.02	0.9874	7.71	0.9925	4.07	0.9963
50	23.28	0.9524	16.04	0.9698	10.63	0.9814	6.45	0.9895	2.84	0.9957
75	21.24	0.9349	14.40	0.9593	9.27	0.9757	4.90	0.9880	1.40	0.9968
100	19.04	0.9222	12.54	0.9527	7.60	0.9734	3.41	0.9889	0.00	1.0000
125	16.68	0.9149	10.68	0.9497	5.88	0.9743	1.94	0.9921	-1.32	1.0051
150	14.15	0.9132	8.71	0.9507	4.16	0.9782	0.50	0.9975	-2.60	1.0119
175	11.55	0.9174	6.64	0.9562	2.40	0.9853	-0.93	1.0053	-3.80	1.0204
200	8.94	0.9269	4.61	0.9652	0.69	0.9952	-2.37	1.0155	-5.02	1.0307
225	6.43	0.9409	2.52	0.9786	-0.90	1.0071	-3.69	1.0271	-6.15	1.0424
250	4.08	0.9583	0.59	0.9944	-2.38	1.0208	-5.01	1.0409	-7.22	1.0553
300	-0.09	1.0011	-2.83	1.0320	-5.24	1.0550	-7.33	1.0718	-9.24	1.0848
350	-3.82	1.0546	-5.77	1.0762	-7.67	1.0940	-9.43	1.1078	-11.05	1.1183
400	-6.97	1.1140	-8.40	1.1267	-9.90	1.1386	-11.39	1.1488	-12.70	1.1555
450	-9.47	1.1742	-10.80	1.1833	-11.89	1.1872	-13.11	1.1927	-14.24	1.1961
500	-11.61	1.2372	-12.59	1.2373	-13.62	1.2383	-14.67	1.2379	-15.51	1.2374

^a p = pressure, atm.; v = specific volume, cc. per gram mole; T = temperature, ° K.; R = gas constant, (cc.)(atm.)/(gram mole)(° K.).

and the gas was forced from the bubbler to the buret. The remainder of the gas in the pipet was expanded directly to the buret. The gas was then passed four to six times from buret to bubbler and back for complete removal of carbon dioxide. The potassium hydroxide solution was returned to its original level, and the residual nitrogen in the buret measured at pressures slightly above and below atmospheric. Thermal equilibrium was quickly attained, and no difference could be observed between readings made 10 minutes and 24 hours after expansion.

Runs were made at one constant temperature for a series of pressures with one mixture in the small pipet. They were repeated at other temperatures. The whole set was then repeated with the other mixtures. Finally, all runs with the large pipet were made in the same way. To establish the accuracy of the work, some of the runs with the small pipet were overlapped by those with the large one, and many duplicating experiments were made.

RESULTS

The results are presented in Table II. Two hundred fifty-three determinations were made, and actual residuals for each point were plotted against pressure at constant temperatures. The best lines were drawn through these by eye, and the smoothed residuals were thus computed. From them the smoothed compressibility factors were determined. Only the smoothed values are presented in Table II and Figure 2.

The deviations between smoothed and actual residuals were determined, and the corresponding deviation between smoothed and observed compressibility factors was computed. The average for each isotherm was $\pm 0.05\%$ or less.

ACCURACY. The temperature measurements were correct to better than 0.1°C ., corresponding to an error of 0.033% at 25°C . or 0.025% at 125°C . The buret volume was known to 0.01% , and the pressures of the buret-confined gas could be read to 0.026% . Pressures were uncertain to the extent of 15 mm. maximum with the large piston (5 mm. for the U-tube differential, 5 mm. for gage balance, and 5 mm. for weight calibration). This corresponds to 0.074% error at 27 atm., the lowest pressure measured. Because of the greater gage balance uncertainty of the smaller piston, the error is perhaps as great as 30 mm. or 0.024% at 225 atm., the lowest pressure measured with the small piston.

These figures indicate an error of 0.10 to 0.16% in the P - V - T measurements, but it is felt that such estimates are high because of the method of calibrating pipet volumes. Since they were calibrated with an accuracy of 0.03% by measuring the amounts of nitrogen or hydrogen contained, errors of temperature, volume, and pressure outlined above should be included. It is therefore felt that 0.05% is a reasonable estimate of errors contributed by measurements of pressure, volume, and temperature.

The only known impurities in the mixtures were argon and oxygen. The former should have been less than 0.3% of the nitrogen by the manufacturer's analysis and the latter less than 0.05% by the authors' analysis. Since these components are so similar to nitrogen, the error introduced is small. For example, at 100°C . and 100 atm. the compressibility factors, pv/RT , are 0.9978 for argon, 0.9998 for oxygen, and 1.0333 for nitrogen. Assuming an average value of 0.9988 for the argon and oxygen and 0.3% total impurities, the error would be less than 0.02% . The error thus introduced in the residual (as distinct from the compressibility factor) is considerably greater because of the relative magnitudes involved and may approximate 0.3% .

The compositions of the mixtures were reported as being $25.13 \pm 0.02\%$ and $50.48 \pm 0.02\%$ carbon dioxide. Since only the nitrogen was measured in the P - V - T work, the error introduced by inaccuracy of these figures is equal to the error of the computed moles of total mixture per mole of nitrogen measured. This is $\pm 0.03\%$ for the 25.13% mixture and $\pm 0.04\%$ for the 50.48% mixture.

Summarizing, the accuracy of the P - V - T measurements was considered to be 0.05% and that of the composition of the mixtures, 0.05% . If errors introduced through impurities are 0.02% , the accuracy of any one observation of compressibility factor should be 0.12% . A maximum deviation of 0.25% seems reasonable. The accuracy for any one observation of the residual would be about 0.4% . The smoothed data are probably somewhat better, but no greater accuracy is claimed.

REPRODUCIBILITY. The precision of the experiments can be evaluated, since the compressibilities of the two mixtures were determined at almost identical pressures with the two different pipets in tests several weeks or months apart. The average deviation of eight such duplicating determinations with the 25.13% mixture was $\pm 0.04\%$ and that of nine with the 50.48%

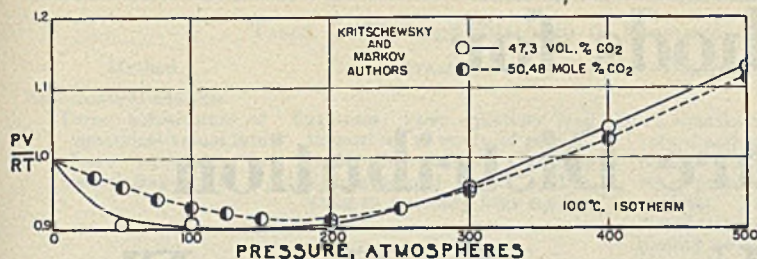


Figure 3. Comparison of Authors' Compressibility Factors, pv/RT , with Those of Kritschewsky and Markov at 100° C.

mixture was 0.05%. A number of points were run in duplicate throughout the whole range of temperatures above 225 atm. with the small pipet alone. Average deviations of eighteen such tests were 0.04% for the lean carbon dioxide mixture and 0.06% for the rich carbon dioxide mixture.

COMPARISON WITH PREDICTED VALUES. For these comparisons the compressibility factors of Michels and collaborators for carbon dioxide (13, 14, 15) and for nitrogen (16, 18) were used. Temperature interpolation and conversion from Amagat compressibility factors to pv/RT were accomplished by a method suggested by Michels *et al.* (15).

Amagat's law predicted volumes which were in every case lower than the measured volumes, averaging 2.8% low in twenty six cases for the 25.13% carbon dioxide mixture and 4.4% low in twenty seven cases for the 50.48% mixture. The greatest deviation was 17.1% at 50° C. and 100 atm. with the 50.48% carbon dioxide mixture. In general, the pressure at which the greatest difference occurs was a function of the particular temperature. At high pressures the agreement was fairly good.

Dalton's law predicted pressures which were lower than the observed values at high pressures but higher at low pressures. It could be applied to all mixtures at all temperatures except with the 50.48% mixture at 25° C. and above 175 atm. Under such conditions the pressure of carbon dioxide in the mixture becomes greater than its pure vapor pressure. The Dalton law value was 30.3% low at 50° C. and 500 atm. and 3.2% high at 50° C. and 50 atm. Agreement was, in general, quite good at low pressures.

Bartlett's modification of Dalton's law (i.e., the total pressure of a gas mixture is the sum of the products of the mole fraction of each component and the pressure which that component would exert at the temperature and the molecular concentration of the mixture) was tried. Predicted pressures were in all cases lower than the measured values, the average difference being 3% for the 50.48% carbon dioxide mixture and 2% for the other. Like Dalton's law, its error was far greater at high pressures. In general, however, it is better than Dalton's law. The worst discrepancy was 9.4% at 50° C. and 400 atm. with the 50.48% carbon dioxide mixture.

Summarizing, at pressures below 200 atm. Dalton's law seems best. In the intermediate region from 250 to 400 atm. Bartlett's law seems best, and above 400 atm. Amagat's law is indicated. At high temperatures all are improved.

PHASE SEPARATION. Pressure-composition curves for nitrogen-carbon dioxide mixtures were given qualitatively by Abdulaev (1). At 25° C. he indicated that the maximum pressure at which liquid can exist was 121 atm., but the composition was not given. Although the present work may have been very near a phase separation region, no evidence of any condensed phase was observed.

COMPARISON WITH OTHER DATA. After this work was finished, Kritschewsky and Markov (12) reported data at 0°, 50°, 100°, 150°, and 200° C. from 50 to 500 atmospheres on the same system. Their compositions were quite near the present ones—i.e., 24.2%

and 47.3% carbon dioxide. For comparison, their data at 100° C. with the approximately equimolar mixture are compared with those of the present work in Figure 3. Their values are lower than the present ones below 250 atm. and higher above 250 atm., the average discrepancy being 1.1%. They also worked with hydrogen-nitrogen and their result was 1.1% lower at 100° C. and 50 atm. than that of Wiebe and Gaddy (21) with a similar mixture. Their hydrogen-carbon-dioxide result was 1.5% lower at 50° C. and 50 atm. than that of Verschaffelt (20) at 32° C. and 50 atm. with approximately the same mixture. They made no mention of correcting their pipet volume for temperature and pressure changes, and appar-

ently deviations of the gases from ideality at 1 atm. were not considered. The mixtures were confined over oil in the experiments of Kritschewsky and Markov, and the solubility of carbon dioxide in oil, which could change during the course of a series of experiments as the pressure was reduced, could affect their results. At high pressures an appreciable quantity of carbon dioxide could have been dissolved in the oil which would then escape as the pressure was reduced. This would explain high results at high pressures and low ones at low pressures, compared to the present results.

UTILITY OF DATA. From these data the effect of pressure could be calculated on enthalpy and entropy of mixtures of the compositions here used. These values in conjunction with the thermal and thermodynamic properties of the pure components, should permit the analyses of cycles for the direct manufacture of dry ice from carbon dioxide-rich flue gases (such as might be produced in cement or lime kilns) and the calculation of yields, energy requirements, etc.

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BASED on a dissertation submitted by R. E. D. Haney to the Yale School of Engineering in partial fulfillment of the requirements for the degree of doctor of engineering.

Graphical Methods for Temperature Distribution with Unsteady Heat Flow

The field of usefulness of the graphical method in solving unsteady-state heat conduction problems is outlined by briefly comparing the graphical method with several alternate procedures. Methods which extend the graphical type of solution to cover temperature distributions through a composite wall, a cylinder, and a sphere are presented. Each procedure is fully illustrated by a representative problem, and an approximate theoretical derivation is submitted for each of the three cases discussed. The manner in which a situation is treated, where some quantity takes on variable values, is also indicated.

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HEAT flow through a conducting material is unsteady or transient when the temperature at any given point in the material changes with time. Conditions of unsteady heat conduction are often encountered in engineering work—for example, in the molding and extruding of plastics, thermal processing of food, control of temperature in massive concrete structures, heat treatment of metals, annealing of glass, vulcanization of rubber, flow of heat through walls, etc. Hence, not infrequently the engineer is confronted with the problem of computing the temperature distribution within a material as a function of time.

Several methods are available, and each has advantages as well as disadvantages and limitations. These methods are usually limited in application to some simple geometrical shape such as a plane slab, a cylinder, a sphere, a box-shaped figure, etc. However, most shapes can be considered as approximating one or more of these simple forms. Table I lists several of the methods employed in solving problems of unsteady heat conduction.

This article deals exclusively with the graphical method of obtaining temperature distributions. It extends the methods already in use to include several new situations which have not been discussed before in the manner presented here. Credit for the establishment of the graphical method is usually given to Schmidt (19) although the discussion of a paper by Emmons (3) brought out that priority for the method should be assigned to L. Binder.

Although the graphical method is approximate, it circumvents many of the difficulties imposed by the purely mathematical approach. For example, it is readily applicable to more or less complex situations which cannot be simply resolved by a rigorous mathematical analysis. Essentially, the graphical method consists in replacing the differential equation by an equation of finite differences. In keeping with this idea, the method will be presented in terms of algebra and finite increments of change.

UNITS

The rate of heat diffusion through a solid conducting material depends on the factors of temperature difference, time, and

the thermal conductivity, specific heat, and density of the conducting material. In working with heat conduction problems, it is necessary that these factors be expressed in a set of consistent units.

Unless stated otherwise, the units used here are given in Table II. The diffusivity of a material is defined by the equation,

$$a = k/(c\rho)$$

The rate of heat transfer through a unit cross section of area is assumed to follow the basic heat transfer equation,

$$q = k(\Delta t / \Delta x)$$

TEMPERATURE DISTRIBUTION ACROSS BOUNDARY OF COMPOSITE WALL

Schmidt (19) and Sherwood and Reed (20) outlined graphical methods for obtaining the temperature distribution across the boundary interface of a composite wall. Both methods, however, are rather involved. A third method, considerably simpler, is given here which requires the use of only a single auxiliary construction line.

All three procedures require the time period $\Delta\theta$ to be the same for both of the materials making up the composite wall. Let primes be used to identify the quantities referring to one side of the composite wall:

$$\Delta\theta = \Delta\theta' = \frac{(\Delta x)^2}{2a} = \frac{(\Delta x')^2}{2a'} \text{ or } \Delta x' = \Delta x \sqrt{\frac{a'}{a}}$$

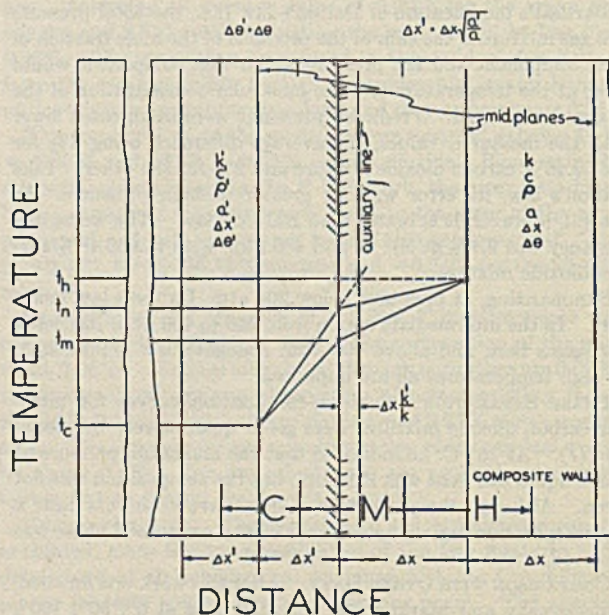


Figure 1. Method for Obtaining Temperature Distribution across a Composite Wall Interface

TABLE I. METHODS EMPLOYED IN PROBLEMS OF UNSTEADY HEAT CONDUCTION

Method	Advantages	Disadvantages and Limitations	References
Mathematical analysis			
Direct substitution of numerical values into basic equations in calculating results	Exactness; basic equations lend themselves to study of generalized interrelations existing among several factors contributing to unsteady heat conduction	Basic equations in general are highly involved and require extensive computation work in getting results. Complexity of problem may defy mathematical analysis. Function of initial temp. distribution required. In general, limited to one material and constant k , c , and h	(2, 8, 12, 18)
Numerical results evaluated by prepared charts and tables	Quite exact; results quickly obtained	Limited to coverage of charts and tables extant in literature. Considerable work necessary to obtain sufficient points for over-all temp. distribution	(1, 6, 13, 14, 18, 22)
Numerical procedure: approximate solution obtained by using a network of temperature points covering the region being investigated	Good approx. results can be rapidly obtained. Method widely applicable, especially to right-angled shapes. Gives over-all temp. distribution	Approx. solution, although precision of method is probably better than data available for problem. Cylindrical and spherical shapes call for somewhat more involved procedure than right-angled shapes	(3)
Graphical procedure: approximate solution obtained through line constructions	Good approx. results can be quickly obtained. Applicable to complex temp. distributions (two materials). Gives in visual form the over-all temp. distribution prevailing at any time. Allowances for change in ambient fluid temp. and in k , c , and h can be incorporated in procedure	Approx. solution, although accuracy of method is probably better than data available for problem. Construction work requires care and is somewhat tedious	(4, 5, 7, 9, 11, 16, 17, 19, 20, 21)
Analogical procedures			
Electrical analogy	Accuracy of method probably as good as data used in setting up and adjusting controls of apparatus. Adaptable to wide variety of problems, especially to periodic temp. fluctuations over long periods	Expensive and elaborate equipment required. Training necessary to master technique of setting up apparatus and operating controls. Limitation of use is largely matter of skill with which operator can adjust controls to simulate unsteady-state conditions	(15)
Hydraulic analogy	Fair accuracy	Considerable equipment required. Many inherent faults and imperfections in proposed apparatus appear to limit method to rough and approx. results	(10)

This means that the lamina thickness Δx and $\Delta x'$ are interdependent. Hence in selecting a thickness value for Δx , it must be borne in mind that this selection arbitrarily fixes $\Delta x'$ for the other side. A judicious choice can usually be made which gives convenient lamina thickness values for both sides.

In the proposed new method, lamina half sections of thickness $\Delta x/2$ and $\Delta x'/2$ are laid off to either side of the interface boundary to give a mixed but full lamina section altogether. The interface surface is considered as the midplane of this composite lamina section. To the side of the interface having the larger Δx , an auxiliary construction line is drawn parallel to the boundary line and at a distance $\Delta x (k'/k)$ from it, or at a distance $\Delta x' (k/k')$ if $\Delta x'$ is larger than Δx (Figure 1).

In proceeding with the graphical process, temperature steps or temperature increments through the walls to either side of the interface boundary are obtained by standard graphical procedures as described by previous writers (9, 19, 20, 21).

Briefly, the graphical procedure for obtaining successive temperature distributions through a homogeneous solid as a function of time consists in progressively connecting alternate temperature values, as plotted on the midplane lines of the several laminae sections into which the solid is conveniently divided, by straight lines. The intersection of each connecting straight line with the intervening midplane which it crosses gives the desired new temperature value for the intervening midplane. By proceeding across the solid in some regular manner and by dealing with three adjacent midplanes at a time, a series of temperature increments or jumps are obtained and, when interconnected, result in a new temperature distribution. A succeeding distribution is obtained

by building on a previously completed distribution. The time interval elapsing between successive distributions is given by the relation $\Delta \theta = (\Delta x)^2/2a$, an expression which involves the lamina thickness value and the diffusivity of the solid under consideration.

To provide for the heat flow contribution of a fluid at a solid-fluid interface, a point corresponding to the temperature of the fluid is located at a distance (k/h) beyond the surface of the solid (a pole center). Any subsequent graphical construction which gives the temperature distribution is then made to tie in with this pole center point. If the value of half the lamina thickness ($\Delta x/2$) is less than (k/h) , a fictive midplane is also to be drawn at a distance $(\Delta x/2)$ outside of the solid-fluid interface to aid in the graphical construction. This is a purely mechanical device to aid

TABLE II. CONSISTENT UNITS

Quantity	Symbol	Units
Diffusivity	a	Sq. ft./hr.
Specific heat	c	B.t.u./(lb.) ($^{\circ}$ F.)
Surface conductance	h	B.t.u./(sq. ft.) (hr.) ($^{\circ}$ F.)
Thermal conductivity	k	B.t.u./(ft.) (hr.) ($^{\circ}$ F.)
Rate of heat transfer	q	B.t.u./hr.
Total heat transferred	Q	B.t.u.
Radius	r	Ft.
Temperature	t	$^{\circ}$ F.
Thickness	x	Ft.
Time	θ	Hr.
Density	ρ	Lb./cu. ft.
Difference or increment	Δ

in closely approximating the temperature distribution actually occurring. For details of these graphical procedures reference should be made to the sources already noted.

The temperature jumps for the interface midplane, however, are obtained by considering the auxiliary line as one of the adjacent midplanes and using it in conjunction with the midplane to the other side of the interface boundary to obtain a temperature increment. At all times the temperature of the auxiliary line assumes the temperature value of the midplane it replaces. In Figure 1 the method is shown in detail; t_c , t_m , and t_h give initial temperatures, t_m being that of the interface midplane. To obtain a new value for the midplane temperature $\Delta\theta$ time units later, temperature t_h is projected horizontally to intersect the auxiliary line. A straight line connecting t_c with this point of intersection cuts the interface midplane to give t_m , the new temperature value required. The following problem gives an illustrative application of the method.

PROBLEM I. A 13.5-inch firebrick wall (9.00-inch firebrick, 4.50-inch insulating brick), initially at a uniform temperature of 100° F., is subjected to a furnace temperature of 2900° F. for 12 hours. Assuming the values tabulated below, determine the approximate temperature distribution through the wall at the end of this 12-hour period:

Wall Material	k	ρ	c	a	h
Firebrick	1.02	125	0.26	0.0314	20.0
Insulating brick	0.103	30	0.23	0.0149	5.0

By successive trials it is found that a division of the 0.75-foot firebrick wall into 3.5 laminae results in a division of the 0.375-

foot insulating brick wall into 2.5 laminae. Using these values, the $\Delta\theta$ time period for either side of the wall is approximately 0.74 hour:

Wall Material	Thickness, Ft.	No. of Laminae	Δx	Δz
Firebrick	0.75	3.5	0.214	0.73
Insulating brick	0.375	2.5	0.150	0.75

The graphical solution to the problem is given in Figure 2. The temperature distribution at the end of the 12-hour period is given at the end of the $(12/0.74 =)$ 16th $\Delta\theta$ time period.

DERIVATION OF COMPOSITE WALL RELATION

Consider the three laminae C , M , and H in Figure 1. During a relatively short time period $\Delta\theta$, the heat which flows into the composite lamina M (from H) per unit of area is:

$$Q_{in} = k(t_h - t_m) \frac{\Delta\theta}{\Delta x}$$

During the same time period the heat which flows out of lamina M (into C) is:

$$Q_{out} = k'(t_m - t_c) \frac{\Delta\theta'}{\Delta x'}$$

If $\Delta\theta'$ is made equal to $\Delta\theta$, the net gain of heat by lamina M becomes:

$$Q_{gain} = Q_{in} - Q_{out} =$$

$$\frac{\Delta\theta k}{\Delta x} \left[t_h - t_m \left(1 + \frac{k' \Delta x}{k \Delta x'} \right) + t_c \left(\frac{k' \Delta x}{k \Delta x'} \right) \right]$$

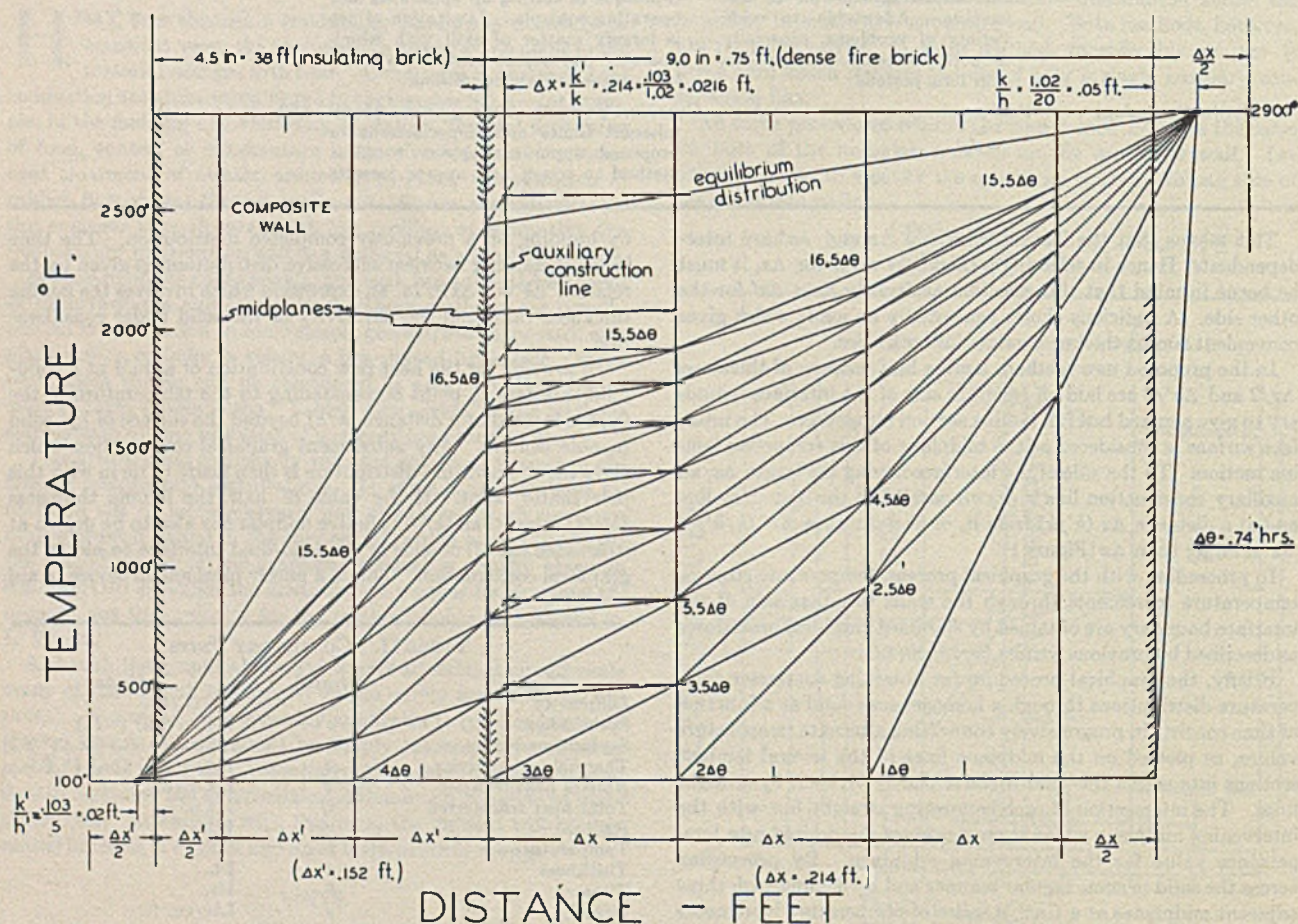


Figure 2. Temperature Distribution across a Composite Brick Wall

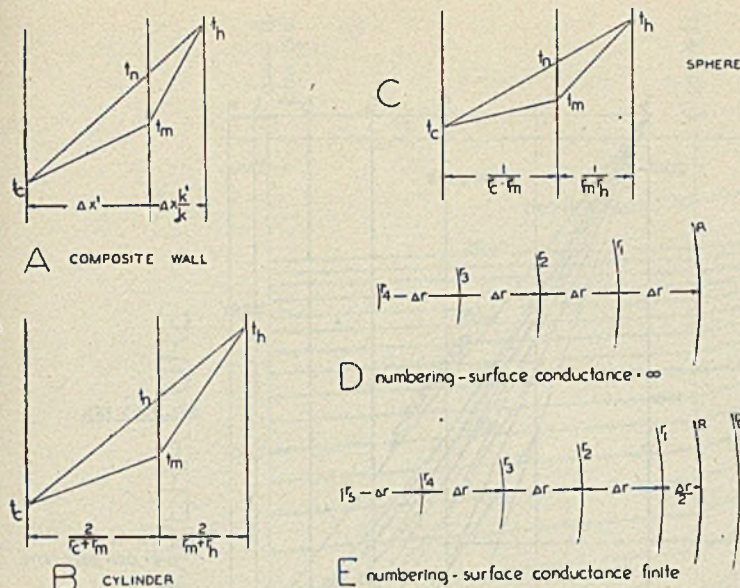


Figure 3. Modified Spacing Arrangements to Be Used in Obtaining Temperature Distributions

This heat which is gained by lamina M goes to increase its average temperature from t_m to t_n ; hence the heat absorbed by the lamina (per unit of area) is:

$$Q_{\text{gain}} = (t_n - t_m) \left[\frac{\rho' c' \Delta x'}{2} + \frac{\rho c \Delta x}{2} \right]$$

Equating these two expressions for the heat gain, solving for $(t_n - t_m)$, and arbitrarily setting

$$\Delta \theta = \frac{(\Delta x)^2}{2a} \text{ and } \Delta \theta' = \Delta \theta = \frac{(\Delta x')^2}{2a'}$$

it is possible to obtain the following expression for t_n :

$$t_n = \frac{1}{\left(1 + \frac{k' \Delta x}{k \Delta x'}\right)} \left[t_h - t_m \left(1 + \frac{k' \Delta x}{k \Delta x'}\right) + t_c \frac{k' \Delta x}{k \Delta x'} \right] + t_m$$

At first glance it would appear that t_n in this expression could not be easily obtained by graphical means. However, a graphical solution can be simply obtained (Figure 3A). If the distance between midplanes C and M is made equal to $\Delta x'$, and the distance between midplanes M and H is made equal to Δx (k'/k), a straight line connecting t_h and t_c on midplanes H and C , respectively, automatically cuts midplane M at a point corresponding to a value of t_n , the temperature of the midplane M at the end of $\Delta \theta$ time units in accordance with the requirements of the equation.

TEMPERATURE DISTRIBUTION THROUGH A CYLINDER

Trinks (21) outlines a graphical procedure for obtaining the temperature distribution across a solid cylinder. The method assumes the cylinder to be made up of a series of concentric cylindrical shells fitted inside of each other, each of thickness Δr . The temperature at the midradius of any shell is taken as a measure of the average temperature of the shell, and a plot of these midshell temperatures against their radial distances gives the temperature distribution across the cylinder.

The method of obtaining increments of temperature change for given increments of change in time is similar to the method for the plane slab or wall, and as before, time interval $\Delta \theta$ is re-

lated to Δr by the equation $\Delta \theta = (\Delta r)^2 / 2a$. However, in laying off the midshell distances, it is necessary to modify the distance Δr between the midradii of adjacent shells.

One spacing schedule for modifying the mid-radius separation distances when the surface conductance is involved is given in column A, Table III, where R is the outside radius of the cylinder and r_0, r_1, r_2 , etc., are the midshell radii, the numbering starting from the outside (Figure 3E). If the surface conductance is infinite—i.e., if the surface and ambient fluid temperatures are always the same—the spacing schedule in column B of Table III is suggested (Figure 3D).

As done in the case of the plane wall situation, the temperature distribution across a solid-fluid boundary is accomplished by locating a pole center at a distance k/h beyond the surface of the cylinder and at a temperature corresponding to the temperature of the ambient fluid. An illustrative problem is given to demonstrate the method.

PROBLEM II. A steam pipe (1.25-inch nominal diameter) is covered with cork insulation 1.4 inches thick. The inside of the pipe is suddenly raised from 88° to 211° F. by admitting steam. Assuming an initial pipe and insulation temperature of 88° F. and neglecting the thermal capacity of the pipe, determine the temperature distribution through the insulation at the end of 12 minutes.

Material	k	c	ρ	a	h
Cork insulation	0.025	0.485	8.15	0.00633	3.9

A solution is given in Figure 4. The cork insulation is divided into 5½ concentric shells, giving a Δr value of 0.0212 foot and a $\Delta \theta$ time period of 0.0355 hour. The schedule outlined in column A of Table III was followed. The temperature distribution at the end of 12 minutes is nearly the distribution given at the end of the 3.5th $\Delta \theta$ time period.

Actual measurements have been made on this particular setup. The graphical solution gives values which are about 5° F. higher on the average than the measured values. This is probably due to the fact that the thermal capacity of the steel pipe was neglected in the graphical procedure and hence a temperature lag at the inner surface of the cork insulation was not taken into account.

DERIVATION OF CYLINDER RELATION

Consider the three concentric shells H , M , and C in Figure 5, each of thickness Δr and having midradius temperatures of t_h , t_m , and t_c at midshell radii of r_h , r_m , and r_c , respectively. During a relatively short time period $\Delta \theta$, the heat which flows into shell M (from H) per foot of linear length is:

$$Q_{in} = \frac{(t_h - t_m) k \cdot \Delta \theta \cdot 2\pi \left(r_m + \frac{\Delta r}{2}\right)}{\Delta r}$$

TABLE III. SPACING SCHEDULES FOR CYLINDERS

Radii Involved	Modified Spacing Separation	
	A, finite surface conductance	B, infinite surface conductance
R and r_0	$\Delta r/2$	Δr
R and r_1	$\Delta r/2$	Δr
	Let $Y = 2 \Delta r \cdot R$	Let $X = (R + r_1) \Delta r$
r_1 and r_2	$Y/(r_1 + r_2)$	$X/(r_1 + r_2)$
r_2 and r_3	$Y/(r_2 + r_3)$	$X/(r_2 + r_3)$
r_3 and r_4	$Y/(r_3 + r_4)$	$X/(r_3 + r_4)$
	(etc.)	

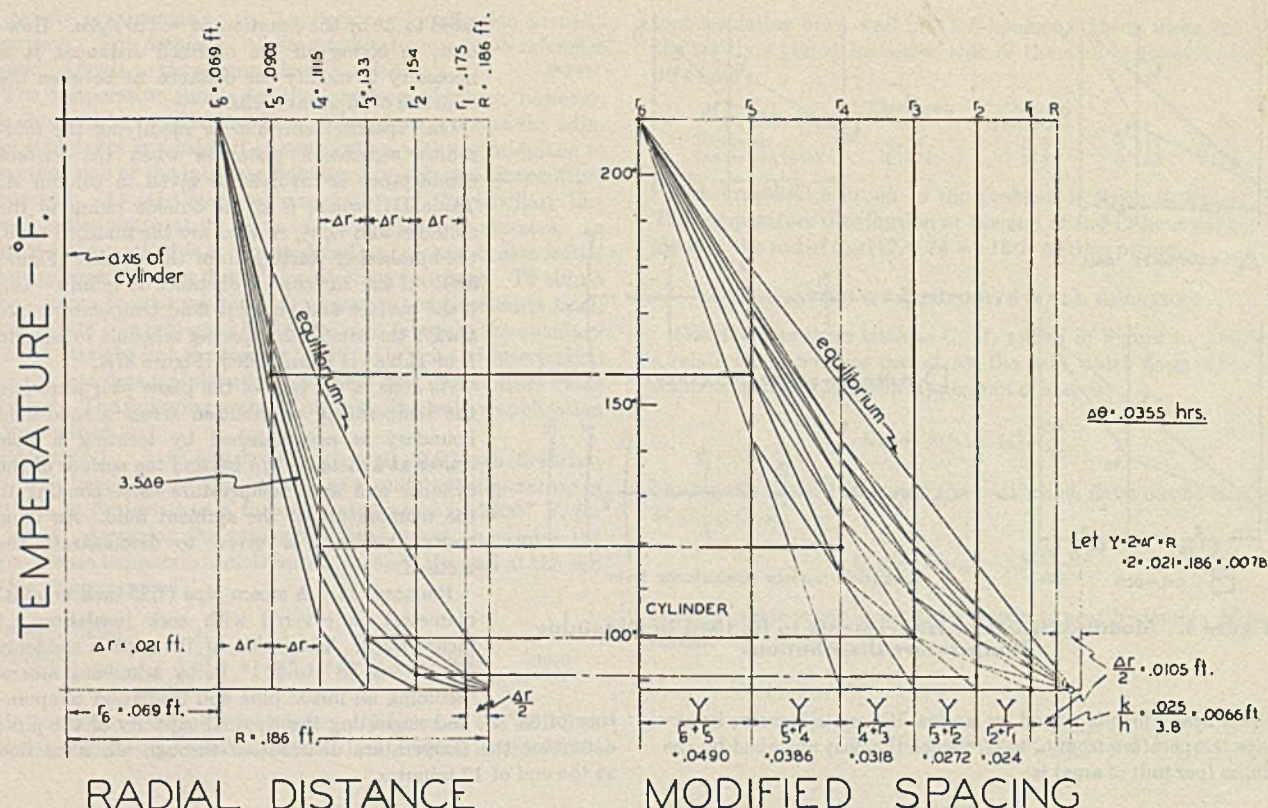


Figure 4. Temperature Distribution across a Cylindrical Pipe Cover

During this same time period the heat which flows out of shell M (into C) is:

$$Q_{out} = \frac{(t_m - t_c) k \cdot \Delta\theta \cdot 2\pi \left(r_m - \frac{\Delta r}{2}\right)}{\Delta r}$$

The net gain of heat by shell M is then $Q_{in} - Q_{out}$. This heat gain goes to increase the average shell temperature from t_m to t_n , and hence the heat absorbed by shell M is

$$Q_{gain} = (t_n - t_m) (2\pi r_m \Delta r \rho c)$$

Equating these two expressions for the heat gain, arbitrarily setting $\Delta\theta = (\Delta r)^2/2a$, and solving for t_n ,

$$t_n = \frac{t_h + t_c}{2} + (t_h - t_c) \frac{\Delta r}{4r_m}$$

which can be rearranged to give

$$t_n = \frac{t_h \left(\frac{1}{r - \frac{\Delta r}{2}} \right) + t_c \left(\frac{1}{r + \frac{\Delta r}{2}} \right)}{\left(\frac{2r}{r^2 - \frac{\Delta r^2}{4}} \right)}$$

This equation is in suitable form so that t_n can be graphically obtained, for if the distance between the midradii of C and M is made equal to $2/(r_c + r_m)$ and the distance between the midradii of M and H is made equal to $2/(r_m + r_h)$, a straight line connecting t_c and t_h on C and H , respectively, will automatically cut the midradius line of M at a point corresponding to t_n , the temperature of shell M at the end of $\Delta\theta$ time units as demanded by the equation (Figure 3B). In the actual working out of a problem it is advisable to multiply the spacing distances by some constant

factor as suggested in the schedules of Table III for convenience in the graphical plotting.

TEMPERATURE DISTRIBUTION THROUGH A SPHERE

The graphical method proposed for obtaining this temperature distribution assumes the sphere to be made up of a series of con-

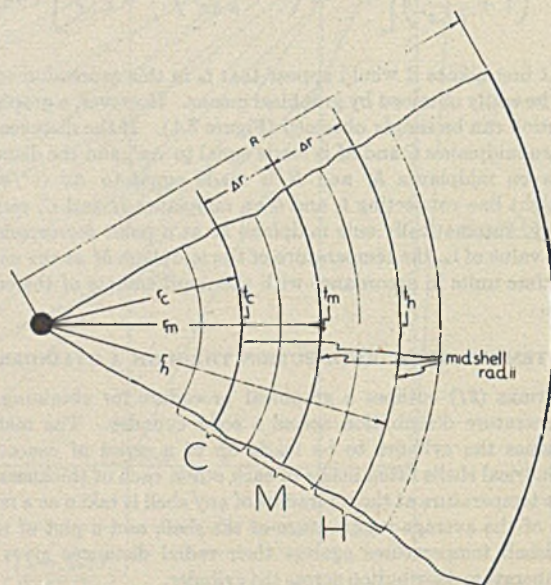


Figure 5. Assumed Cross Section of Cylinder or Sphere

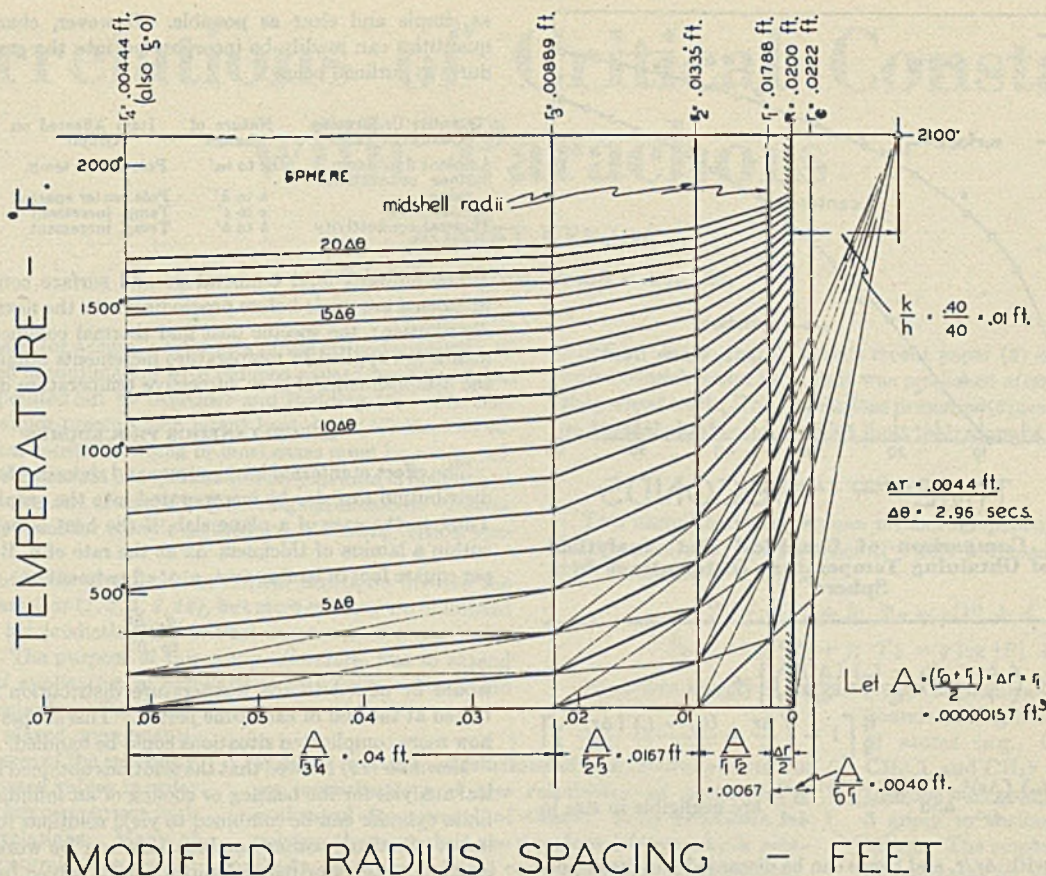


Figure 6. Temperature Distribution across a Ceramic Ball

centric spherical shells fitted inside of each other, each of thickness Δr . The temperature at the midshell radius of any shell is taken as a measure of the average temperature of the shell, and a plot of these midshell temperatures against their radial distances gives the temperature distribution through the sphere.

The method of obtaining increments of temperature change with time is similar to the procedures outlined previously. The time interval $\Delta\theta$ is related to Δr by the equation $\Delta\theta = (\Delta r)^2/2a$; as in the case of the cylinder, it is necessary to modify the spacing between the midshell radii of adjacent shells.

A spacing schedule for modifying the midradii separation distances when the surface conductance is involved is given in column A, Table IV, where R is the outside radius of the sphere and r_0, r_1, r_2 , etc., are the midshell radii, the numbering starting from the outside (Figure 3E). The schedule in column A was used in working out problem III. A simpler and probably as satisfactory a schedule is given in column B. If the surface conductance is infinite, the spacing schedule of column C is suggested.

PROBLEM III. A 0.48-inch diameter refractory ceramic ball, initially at 100° F., is placed in a 2100° F. gas stream. Assuming a surface conductance value of 40, determine the temperature at the surface and at the center of the ball during the first minute of time.

Material	k	c	ρ	a	h
Ceramic ball	0.40	0.25	133	0.0120	40

A solution to this problem is given in Figure 6. Starting from the outside, the ball is divided into four concentric shells, each having a thickness Δr of 0.0045 foot. The effect of the spherical core at the center of the ball can be neglected as it comprises less than 0.2% of the ball volume. The temperature at the center of the spherical ball will be essentially the temperature of the inner-

most shell. The $\Delta\theta$ period, given by $(\Delta r)^2/2a$, is 2.96 seconds. The schedule outlined in column A of Table IV was followed. The temperature distribution during the first minute of heating is given by the first 20 $\Delta\theta$ time increments of change. The temperatures at the surface and center of the ceramic ball at the end of 1 minute are 1920° and 1700° F., respectively. Figure 7 shows the closeness with which the values obtained by the graphical method check the equivalent values obtained by a Gurney-Lurie chart.

DERIVATION OF SPHERE RELATION

Consider the three concentric spherical shells H , M , and C in Figure 5, having thickness Δr and temperatures of t_h , t_m , and t_c at the midshell radius distances r_h , r_m , and r_c , respectively. During a relatively short time interval $\Delta\theta$, the heat which flows into shell M (from H) is:

$$Q_{in} = \frac{k(t_h - t_m) 4\pi (r + \frac{1}{2}\Delta r)^2 \Delta\theta}{\Delta r}$$

During this same time period the heat which flows out of shell M (into C) is:

$$Q_{out} = \frac{k(t_m - t_c) 4\pi (r - \frac{1}{2}\Delta r)^2 \Delta\theta}{\Delta r}$$

The net gain is $(Q_{in} - Q_{out})$ which goes to increase the average temperature of shell M from t_m to t_n . Hence the heat gain by shell M is:

$$Q_{gain} = (t_n - t_m) (\rho \cdot c \cdot 4\pi r^2 \cdot \Delta r)$$

By equating these two expressions for the heat gain and arbitrarily setting $\Delta\theta = (\Delta r)^2/2a$, it is possible to obtain the following expression for t_n :

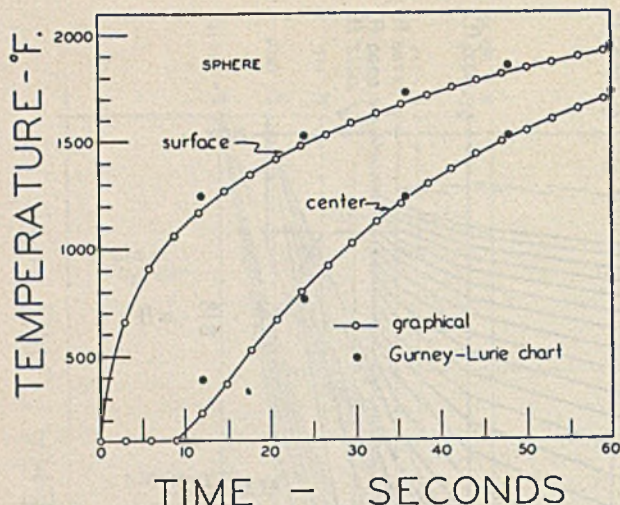


Figure 7. Comparison of Graphical and Analytical Methods of Obtaining Temperature Distributions in a Sphere

$$t_n = \frac{t_h}{2} \left[1 + \left(\frac{\Delta r}{r} + \frac{(t_h - t_m)(\Delta r)^2}{t_h 4r^2} \right) \right] + \frac{t_c}{2} \left[1 - \left(\frac{\Delta r}{r} + \frac{(t_m - t_c)(\Delta r)^2}{t_c 4r^2} \right) \right]$$

Both $\frac{(t_h - t_m)(\Delta r)^2}{t_h 4r^2}$ and $\frac{(t_m - t_c)(\Delta r)^2}{t_c 4r^2}$ are negligible in size in

comparison with $\Delta r/r$, and hence can be discarded and make possible the following relation for t_n :

$$t_n = \frac{\frac{t_h}{r_c r_m} + \frac{t_c}{r_h r_m}}{\frac{2}{r_h r_c}}$$

In this equation t_n can be graphically obtained as follows: Mid-shell temperatures t_h , t_m , and t_c are plotted against a modified spacing arrangement as shown in Figure 3C; t_n is obtained by connecting t_h and t_c by a straight line.

The effect of the core at the center of the sphere can be neglected, the temperature at the center being essentially the same as that of the shell next to the center. In the actual working out of a problem, it is advisable to multiply the spacing distances by some suitable constant factor as suggested in the schedules of Table IV for convenience in graphical plotting.

PROCEDURE WHEN k , h , c , AND t_m VARY

The values for k , h , c , and t_m in the illustrative problems have all been purposely assumed constant to make the basic procedures

TABLE IV. SPACING SCHEDULES FOR SPHERES

Radial Involved	Modified Spacing Separation		
	Finite surface conductance		Infinite surface conductance
R and r_1	Col. A	Col. B	Col. C
R and r_2	$\Delta r/2$	$\Delta r/2$	Δr
	$\frac{\Delta r}{2} \left(\frac{r_1}{r_2} \right)$	$\Delta r/2$
	Let $A = \frac{(r_2 + r_1)r_1}{2} \Delta r$	Let $B = r_2 r_1 \Delta r$	Let $C = R r_1 \Delta r$
r_2 and r_1	$A/r_2 r_1$	$B/r_2 r_1$
r_1 and r_2	$A/r_1 r_2$	$B/r_1 r_2$	$C/r_1 r_2$
r_1 and r_1	$A/r_1 r_1$	$B/r_1 r_1$	$C/r_1 r_1$
	(etc.)		

as simple and clear as possible. However, changes in these quantities can readily be incorporated into the graphical procedures as outlined below:

Quantity Undergoing Change in Value	Nature of Change	Item Affected on Graph	Nature of Adjustment
Ambient fluid temp.	t_m to t_m'	Pole center temp.	t_m to t_m'
Surface conductance value	h to h'	Pole center spacing	k/h to k/h'
Specific heat	c to c'	Temp. increment	Δt to $\Delta t(c/c')$
Thermal conductivity	k to k'	Temp. increment	Δt to $\Delta t(k'/k)$

The ambient fluid temperature and surface conductance adjustments are made before proceeding with the next temperature distribution; the specific heat and thermal conductivity adjustments are applied to temperature increments obtained following the establishment of each successive temperature distribution.

MISCELLANEOUS PROCEDURES

The effect of internal heat sources and sinks on the temperature distribution can also be incorporated into the graphical solution. Thus, in the case of a plane slab, if the heat is being generated within a lamina of thickness Δx at the rate of q , B.t.u. per hour per square foot of lamina area, a Δt adjustment of

$$\Delta t = \frac{q_s}{c_p} \frac{\Delta \theta}{\Delta x}$$

would be added to the temperature distribution normally obtained at the end of each time period. This simple case suggests how more complicated situations could be handled.

Newman (12) showed that the solutions obtained by mathematical analysis for the heating or cooling of an infinite slab and infinite cylinder can be combined to yield solutions for a finite cylinder. Similarly other combinations can be worked out. For example, a brick or parallelepiped can be solved by a consideration of three pairs of infinite parallel planes intersecting at right angles. The method of combining results obtained mathematically can be applied with equal validity to the combining of results obtained graphically.

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Correlations of Critical Constants with Parachors

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THE need for accurate estimates of the critical constants, to be used in conjunction with reduced equations of state, has been pointed out by Meissner and Redding (8). The correlation of vapor pressure and latent heat data (10) likewise involves critical constants which in most cases must be estimated. In general, the amount of experimental critical data is insufficient to meet the demand of useful engineering applications. Hence, there is a real need for reliable methods of estimating critical constants.

Several methods of estimating critical constants involve the use of the parachor (1, 2, 4, 8, 12), but most of them are of limited application for predicting the critical constants of a particular substance. The purpose of this study, therefore, was to extend the range of application of correlations between parachors and critical constants. Particular emphasis is placed upon quantitative measures of the reliability of the estimated values in order to provide a fair comparison with existing correlations. Many of the existing correlations are not discussed in this paper, since Meissner and Redding (8) have already analyzed them suc-

cinctly. Gamson and Watson's recent paper (9) is not given detailed consideration because it was published after completion of the present work. The correlations presented (5) are based entirely on normal paraffin data, which limit their scope of application.

CRITICAL TEMPERATURE

Two useful relations between critical temperature T_c , normal boiling point T_B , and parachor $[P]$ were proposed by Lewis (6, 7). These are of the type:

$$T_c = a[P] + b; T_B = c[P] + d \quad (1)$$

$$T_c = e \log [P] + f; T_B = g \log [P] + h \quad (2)$$

Equations 1 apply to various groups of chemically similar compounds having the same number of atoms (e.g., CH_4 , CH_3I , CH_3Br , CH_3Cl , and CH_3F might constitute one such group); Equations 2 apply to various homologous series. The constants $a \dots h$ are different for each particular group and each particular homologous series. The use of these correlations is limited to com-

Various existing correlations of the critical constants are examined, and the reliability of estimate is evaluated for several of them. Four relations involving the parachor are developed from which relatively accurate critical constants can be estimated, using the normal boiling points and calculated parachors as auxiliary data. Statistical measures of the reliability of the estimated constants are presented.

TABLE I. CRITICAL TEMPERATURE

Equation No.	Groups of Compounds Covered by Equation ^a		Equations Derived by Least Squares ^a	n^b	$(T_c/T_B)_m$	Reliability ^c	
	Organic	Inorganic				Absolute (2S) ^d	Relative, %
3A	Satd. & unsatd. hydrocarbons (acyclic and unsubstituted)	Paraffinic analogs, such as silicanes	$T_c/T_B = 2.501 - 0.4176 \log [P]$ Range: 1.29-1.70	20	1.529	0.034	2.2
3B	Aromatics & cyclics (substituted & unsubstituted)	$T_c/T_B = 2.640 - 0.4634 \log [P]$ Range: 1.38-1.65	28	1.510	0.082	5.4
3C	Substituted aliphatics containing halogen* & S as functional groups	Inorganic halogen compounds	$T_c/T_B = 2.602 - 0.4449 \log [P]$ Range: 1.37-1.78	26	1.607	0.075	4.7
3D	Aliphatic esters, ethers, acetals, oxides*	Some inorganic oxides & O compounds such as SO_2 , O_3 , H_2O	$T_c/T_B = 2.544 - 0.4429 \log [P]$ Range: 1.35-1.64	38	1.467	0.036	2.5
3E	Aliphatic ketones, aldehydes, carboxylic acids, & N compounds	Some inorganic N compounds such as N_2 , N_2O , N_2O_4	$T_c/T_B = 2.301 - 0.3548 \log [P]$ Range: 1.41-1.69	23	1.515	0.067	4.4
3F	Aliphatic alcohols & anhydrides	Inorganic "anhydrides" such as CO_2 , H_2	$T_c/T_B = 1.783 - 0.1479 \log [P]$ Range: 1.41-1.52	14	1.441	0.033	2.3

* Equations are based almost entirely on organic compounds, for which good values of the parachor can be calculated from atomic and structural constants. Inorganic compounds to which equations were found to apply are indicated. For compounds falling in two or more groups, as chloroacetic acid 3C and 3E, the average of values obtained by using equations for each group is recommended. Compounds not covered by any of listed groups can be handled by the principle of chemical similarity. Reliability of estimate for such compounds is indeterminate and probably poorer than tabulated values. Indicated ranges are for experimental (T_c/T_B) values used in establishing equations.

^b n = No. of experimental (T_c/T_B) values used in determining equation.

^c Relative reliability (per cent) of an estimated value of (T_c/T_B) is defined as: $100 \times 2S/(T_c/T_B)$, which is a measure of the percentage deviation of the value from the least squares line which will not be exceeded in about 95% of cases. $(T_c/T_B)_m$, the mean of experimental values, has been tabulated and used to calculate a reliability for the equation. This procedure was followed to give a common basis for comparison of the reliabilities of the equations. The total range of (T_c/T_B) values covered by the data used in establishing these equations is 1.29 to 1.78. Calculated values which fall outside of this range will have poorer reliabilities than are determined by the defining equation above.

^d $S = \left[\frac{\sum (T_c/T_B \text{ calcd.} - T_c/T_B \text{ exptl.})^2}{n - 2} \right]^{1/2}$; and $2S$ is a measure of accuracy to be expected in about 95% of cases.

* All fluoromethanes and moderately substituted fluoroethanes (as $\text{C}_2\text{H}_4\text{F}_2$) can be estimated with greater accuracy from Equation 3D. Equation 3C gives results which are about 10% high. Highly substituted fluoroethanes (as $\text{C}_2\text{Cl}_4\text{F}_2$) are handled with Equation 3C.

TABLE II. PARACHOR CORRELATION OF MUMFORD AND PHILLIPS (9)

ATOMIC AND STRUCTURAL CONSTANTS									
CH ₂	40.0	O	20	Triple bond				38	
C	9.2	S	50	Double bond				19	
H ^a	15.4	Se	63	Single bond (duplet); semi-polar double bond				0	
F	25.5	B	21.5						
Cl	55	Si	31	Singlet linkage				-9.5	
Br	69	Be	42						
I	90	Al	55						
N	17.5	Cr	58	3-membered ring				12.5	
P	40.5	Tl	62	4-membered ring				6	
As	54	Sn	64.5	5-membered ring				3	
Sb	68	Hg	69	6-membered ring				0.8	
		Bi	80	7-membered ring				-4	
STRAIN CONSTANTS ^b									
+3	0	-3	-6	-9	-12	-15			
Carbonyl in ring	RCH ₂ R RCH ₂ X RCHO RCOR	RCHX ₂ R ₂ CHX R ₂ CHR RCOOH RCOOR RCOCI RCONH ₂ ROCOOR ROCOCl	RCX ₂ R ₂ CX R ₂ CR CICOCl -C(COOEt) ₂	CX ₂ R ₂ C CCl ₂					
		R ₂ SOOR R ₂ SOOR	CISOCI RSO ₂ Cl RSO ₂ R ROSO ₂ R ROSO ₂ OR	SCl ₂ SO ₂ Cl ₂	SOCl ₂	SCl ₂			
	RNH ₂ NOR NOOR	R ₂ NH NOCl NO ₂ R NO ₂ OR Asides R ₂ SeO R ₂ SeOOH	R ₂ NCl NO ₂ Cl PX ₂ R ₂ P PO(OR) ₂ ClSeOCl BX ₂ AsX ₂ SbX ₂	NOCl ₂	NCl ₂	POCl ₂ SiX ₂ SnX ₂ CrO ₂ Cl	PCH ₃ SbCl ₃		

EXAMPLES OF USE OF TABLE II

Triethylamine, (C₂H₅)₃N:

6 CH ₂ groups	= 6 × 40.0 = 240.0
3 H's attached to C's	= 3 × 15.4 = 46.2
1 N	= 1 × 17.5 = 17.5

Strain constant	303.7
(Corrected) parachor	297.7
Experimental parachor	297.8

m-Xylene, C₆H₄(CH₃)₂:

8 C's	= 8 × 9.2 = 73.6
10 H's attached to C's	= 10 × 15.4 = 154.0
3 double bonds	= 3 × 19 = 57.0
1 6-membered ring	= 1 × 0.8 = 0.8

(Corrected) parachor	285.4
Experimental parachor	285.1

NOTE. Table II does not appear in its entirety in any readily available text or handbook. A portion is reproduced in Gilman's "Organic Chemistry, An Advanced Treatise", but the strain constants are not even mentioned although they were used in calculating some of the parachors. This error has been called to the attention of Gilman and Leermakers by George Calingaert and G. W. Thomson, of Ethyl Corporation.

^a Value of hydrogen in combination with other elements:

C	15.4	S	15.4	Cl	12.8
N	12.5	O	10.0	Br	16.4

^b R = hydrocarbon radical; X = negative group, Cl, CN, COOR, OR, etc.; for X = Br, multiply strain constant by 1.5.

pounds which belong to groups or series for which sufficient data are available to determine the constants.

Equations can be derived from relations 1 and 2 to estimate T_c/T_B from $[P]$ or $\log [P]$, respectively, for such groups and series. The following simpler equation

$$T_c/T_B = a - b \log [P] \quad (3)$$

was found, however, to be of more general application since it required the classification of over 140 compounds into only six groups, as shown in Table I. The six groups of compounds (3A to 3F) are described in Table I together with the derived equations and measures of the reliability of estimated T_c/T_B values.

Parachors as used throughout this paper were calculated from the atomic, structural, and strain constants of Mumford and Phillips (9) shown in Table II, unless otherwise noted. For some of the "simple" molecules (CO, O₂, N₂, etc.), where calculated parachors differ appreciably from measured values, the measured

values were used. For compounds not covered by Mumford and Phillips constants, such as those of germanium, measured values or the atomic constants given by Sugden (12) or Lewis (7) were used. Examples of the use of Mumford and Phillips constants are given in Table II.

Comparison of the equations given in Table I with the Lewis Equations 1 and 2 shows that a considerable extension in range of application has been effected. The six equations are applicable to many times that number of homologous series, chemically similar groups, and miscellaneous compounds, most of which were outside the scope of Lewis' relations because of the paucity of experimental critical data. However, it must be emphasized that the correlation presented is subject to the inherent limitations of any empirical relation.

Returning to Equations 1 and 2, the parachor can be eliminated from each pair of equations to give a relation of the form:

$$T_c = kT_B + j \quad (4)$$

Two of the empirical equations proposed by Meissner and Redding (8) have this form and can be readily tested. The method of least squares was used to obtain the best possible constants for the equations as applied to the particular data available, with the results shown in Equations 5 and 6. The constants so derived differ from those of Meissner and Redding, since these authors based their equations only on the critical data for hydrocarbons, thus assuming that the behavior of the hydrocarbons was representative of all compounds. This assumption is open to some question, and while experimental critical data are available for relatively few compounds besides the hydrocarbons, it appeared desirable to consider all available data in calculating the constants in Equations 5 and 6. For thirty-one compounds boiling below 235° K.:

$$T_c = 1.725T_B - 5.7 \quad (5)$$

Reliability of $T_c = 12.8\%$

For ninety-three compounds (halogen- and sulfur-free), other than aromatics and naphthenes, boiling above 235° K.:

$$T_c = 1.112T_B + 131.8 \quad (6)$$

Reliability of $T_c = 5.4\%$

Although the stated T_B limit of these equations is 235° K., the value selected by Meissner and Redding, they actually intersect at 225° K. There is a similar discrepancy in Meissner and Redding's own equations which, however, is well within their limits of accuracy.

The reliabilities in Table I show that the correlations proposed in this paper are considerably better than those for Equation 5 and slightly better than those for Equation 6. From the definition presented in note (c) to Table I, the "reliabilities" reported here are a measure of the maximum deviation, the average deviation being only about 40% as great in each case. The reason for adopting this more stringent definition of reliability is the paucity and doubtful value of much of the available critical data. The equations proposed by Meissner and Redding for aromatics and naphthenes boiling above 235° K. and for halogen and sulfur compounds boiling above 235° K. are more complicated and were not tested. Since the groupings used by Meissner and Redding are, in general, different from those used in this paper, estimates of T_c can be independently checked by the two methods.

CRITICAL VOLUME

Several relations between the critical volume, V_c , and parachor have been proposed. The simplest is due to Sugden (12):

$$V_c = [P]/0.78 \quad (7)$$

and is based on his theoretical interpretation of the parachor. The value of the "constant" (0.78), however, has been found to vary by as much as $\pm 30\%$. A purely empirical relation, having

a higher degree of accuracy, was proposed by Meissner and Redding:

$$V_c = (0.377[P] + 11.0)^{2/4} \quad (8)$$

A quantitative measure of the reliability of this equation was not given by the authors.

A dimensional analysis of the parachor (11) results in the equation:

$$[P] = KV_c^{2/3}T_c^{1/4} \quad (9)$$

This relation, with $K = 0.41$, was first proposed by Ferguson (1), who subsequently (2) offered the following empirical relation which is not consistent with dimensional analysis:

$$[P] = kV_c^{2/3}T_c^{1/4} \quad (10)$$

Lautie (5) arrived at the equations

$$[P] = 0.681V_c^{2/3}T_c^{1/4} \quad (11)$$

$$[P] = 0.316V_cp_c^{1/4} \quad (12)$$

by combining several theoretical and empirical equations which apply strictly only to normal liquids.

Since Equation 10 appears to have the most rational basis of all the proposed relations, it was first selected for further investigation. Rewriting Equation 10 in the form

$$V_c = K[P]^{1.2}/T_c^{0.3} \quad (13)$$

and empirically separating the available data into two groups, the following results were obtained:

1. For compounds having the functional groups $-\text{C}=\text{O}$, $-\text{C}\equiv\text{N}$, $-\text{COOH}$ and $-\text{OH}$, and one to three additional non-functional carbons:

$$V_c = 3.34[P]^{1.2}/T_c^{0.3} \quad (13A)$$

Reliability = 10.0%

2. For all other compounds:

$$V_c = 2.92[P]^{1.2}/T_c^{0.3} \quad (13B)$$

Reliability = 6.5%

Reliabilities were determined statistically as in Table I.

The reliability of the values of V_c estimated from Equations 13A and 13B is relatively high, and is not influenced appreciably by the accuracy of the T_c values used (e.g., an error of 5% in T_c will introduce an error of less than 2% in V_c).

Lautie's relation, Equation 12, was also studied further; rewriting it in the form

$$V_c = C[P]/p_c^{0.25} \quad (14)$$

and empirically separating the available data in three groups, the following results were obtained.

1. For aliphatic organic compounds containing two or less carbons in addition to the functional atom or group (e.g., CH_4 , $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{COOH}$), and all other compounds having $T_c < 450^\circ\text{K}$:

$$V_c = 3.58[P]/p_c^{0.25} \quad (14A)$$

Reliability = 8.1%

2. For aliphatic organic compounds containing three or four carbons in addition to the functional atom or group, and all other compounds having T_c between 450 and 600°K :

$$V_c = 3.31[P]/p_c^{0.25} \quad (14B)$$

Reliability = 5.2%

3. For aliphatic organic compounds containing more than four carbons in addition to the functional atom or group, and all other compounds having $T_c > 600^\circ\text{K}$. (excluding H_2O):

$$V_c = 3.19[P]/p_c^{0.25} \quad (14C)$$

Reliability = 7.5%

The reliability of V_c values estimated from Equations 14A, 14B, and 14C is about the same as that of estimates made from Equations 13A and 13B. The latter equations are more useful because experimental values of T_c are more numerous than experimental values of p_c , and T_c can be estimated much more accurately than p_c . When appropriate data are available, relations 14A, 14B, and 14C can be of service by offering an independent check on values of V_c estimated from 13A and 13B.

In order to make a quantitative comparison between the equations developed above and those of Sugden and of Meissner and Redding, the available data were fitted by the method of least squares to equations of the types proposed by these authors. Assuming Sugden's relation to have the form $V_c = A[P] + B$, it was found that

$$V_c = 1.447[P] - 20.09 \quad (15)$$

Reliability = 18.1%

Similarly, assuming that Meissner and Redding's relation had the form $V_c = (D[P] + E)^{1.25}$, it was found that

$$V_c = (0.3591[P] + 14.00)^{1.25} \quad (16)$$

Reliability = 15.7%

The constants in Equation 16 differ from those in Meissner and Redding's paper since the latter were based only on hydrocarbon data.

Inspection of the above results shows that the correlations developed in this paper (Equations 13 and 14) are more reliable than those of the type proposed by Sugden or Meissner and Redding, based on the data available at present. They also show that Meissner and Redding's correlation (Equation 16) is not appreciably more accurate than the simpler modified Sugden relation (Equation 15). Further investigation of equations of the type:

$$V_c = (F[P] + G)^n \quad (17)$$

where n varies from 1.0 to 1.25, indicated that the reliability of this type of correlation is not very sensitive to the value of n used.

CRITICAL PRESSURE

The estimation of critical pressures, p_c , is generally made by means of equations which include T_c and V_c . Meissner and Redding proposed:

$$p_c = 20.8T_c/(V_c - 8) \quad (18)$$

Wohl (13, 14) proposed:

$$p_c = 21.8T_c/V_c \quad (19)$$

The reliability of estimate is usually poorer than for T_c or V_c alone. Equation 12, involving the parachor and V_c , was proposed by Lautie and has been developed in this paper as a method for estimating V_c . Rearranging Equation 12 into the form

$$P_c = (C[P]/V_c)^4 \quad (20)$$

gives a relation for estimating p_c (the empirical groupings and values of C are the same as for Equations 14A, 14B, and 14C). The reliability of estimate for p_c is relatively poor (about 20 to 30%) because of the fourth power involved. This reliability is of the same order as that obtained by other generalized methods for estimating p_c , and the relation is useful because of its broad scope.

In an attempt to obtain a more reliable relation for estimating p_c , the following line of attack was tried.

In general (11): $\log p/p_c = m - nT_c/T$
 At the normal boiling point: $p = 1$, and $T = T_b$
 Therefore $-\log p_c = m - nT_c/T_b$
 Combining with Equation 3: $\log p_c = -m + n(a - b \log [P])$
 Or $\log p_c = a' - b' \log [P]$ (21)

TABLE III. CRITICAL PRESSURE

Equation No.	Groups of Compounds Covered by Equation ^a	Equations Derived by Least Squares ^a	n^b	(Log p_c) _m	Reliability ^c	
					Absolute (2S) ^b	Relative, %
21A	Satd. & unsatd. hydrocarbons (acyclic, unsubstituted), excluding methane	Log $p_c = 3.0477 - 0.6528 \log [P]$ Range: 1.140-1.792	18	1.503	0.035	8.4
21B	Aromatics and cyclics, excluding biphenyls & condensed ring systems	Log $p_c = 3.8584 - 0.9215 \log [P]$ Range: 1.453-1.782	25	1.622	0.100	26
21C	Aliphatic amines, esters, halogen, & S compounds (excluding CH ₃ F and CS ₂); inorganic halogen & S compounds (excluding F ₂), and NH ₃	Log $p_c = 3.4271 - 0.7829 \log [P]$ Range: 1.477-2.047	45	1.664	0.070	18
21D	Aliphatic acids, alcohols, & anhydrides	Log $p_c = 2.9929 - 0.5718 \log [P]$ Range: 1.681-1.896	8	1.746	0.036	8.6
21E	Aliphatic ethers & ketones	Log $p_c = 3.3777 - 0.7810 \log [P]$ Range: 1.507-1.716	5	1.617	0.024	5.7
21F	Aliphatic nitriles, HCN	Log $p_c = 2.6387 - 0.4627 \log [P]$ Range: 1.508-1.679	4	1.594	0.006	1.4

^a Application of these equations to compounds not specifically covered in listed groups is accompanied by a decreased reliability of estimate (exact magnitude not predictable).

^b S and n have same significance as in Table I; (log p_c)_m is similar to (T_c/T_B)_m.

^c Reliabilities for p_c were calculated from values of 2S and (log p_c)_m. Since the plus and minus deviations were unequal (in transposing from logarithms to natural numbers), the larger deviation was used to give a more conservative estimate of reliability. The tabulated values were calculated from the expression:

$$100 \times [(\text{antilog } [2S + (\log p_c)_m] / \text{antilog } [(\log p_c)_m]) - 1]$$

An analysis of data for over a hundred compounds showed that Equation 21 could be successfully fitted to six groups of compounds. The equations obtained (21A to 21F), together with statistical measures of the reliability of estimate, are shown in Table III.

It is readily apparent that the scope of Equations 21A to 21F is more limited than the scope of Equations 3A to 3F, and that the reliability of estimate is generally poorer. This result is not unexpected, since Equation 21 combines several rough approximations. It is also evident that the reliability of estimate is

highest for the most limited groups. Therefore, the best results should be obtained when a single homologous series or group of chemically similar compounds is fitted by Equation 21. Where sufficient data are available, this procedure is recommended, but owing to the limited data on p_c , the less accurate general relations have greater application.

To make a quantitative comparison, the p_c relations proposed by Meissner and Redding and by Wohl were re-examined. Fitting the data for eighty-nine compounds by least squares to Wohl's equation gave:

$$p_c = 21.75T_c/V_c \quad (22)$$

$$\text{Reliability} = 18.1\%$$

Similarly, Meissner and Redding's equation gave:

$$p_c = 20.8T_c/(V_c - 8.00) \quad (23)$$

$$\text{Reliability} = 19.1\%$$

Except in the case of the paraffin hydrocarbons, relation 23 proposed by Meissner and Redding affords, on the average, no improvement over the simpler relation 22 of Wohl. As compared to Equation 21, inspection of the reliabilities shown in Table III shows that Wohl's relation is less reliable than five of the six proposed equations. Wohl's relation, however, has greater scope than Equations 21A to 21F, and hence will prove valuable for application to substances not included in the specific groups listed in Table III. It should be emphasized that Wohl's relation will probably give poorer reliabilities than are indicated above when experimental values of V_c and T_c are not available and it is necessary to use estimated values.

TABLE IV. TEST OF PROPOSED RELATIONS

Substance	[P] ^a	T _B	T _c				V _c				p _c			
			Exptl.	Estd. ^b	% deviation ^b		Exptl.	Estd. ^c	% deviation		Exptl.	Estd. ^d	% deviation	
Bromine	132.1*	332	575	550	-4.3		135.4	154	+14		72.8	77.6	+6.6	
Carbon dioxide	78.1*	195	304	293	-3.6		94.2	99.2	+5.3		72.8	77.6	+6.6	
Chlorine	107*	239	417	406	-2.6		123.7	131	+5.9		76.1	68.9*	-9.5	
Cyanogen	129.4	253	401	393	-2.0		166	166	0		59	60.6	+2.7	
Dichlorofluoromethane	160.1	282	452	458	+1.3		197.2	205	+4.0		51.0	50.4*	-1.2	
2,2-Dimethylpentane	311	352	521	514	-1.3			28.4	26.3*	-7.4	
Ethylamine	137.9	290	457	447	-2.2		181.6	173	-4.7		
Ethylbenzene	285	409	619	614	-0.8			38.1	39.5*	+3.7	
Ethylene dichloride	190	357	561	567	+1.1		236.2	236	-0.1		53	44.3*	-16	
Ethyl fluoride	120.9	238	375	386	+2.9		...	154	...		49.62	62.6	+26	
Germanium tetrachloride	257	356	550	545	-0.9			38	34.7*	-8.7	
Heptadecane	711	576	749	755	+0.8		1095	1057	-3.5		14.4	15.4*	+6.9	
Hydrogen	33.7*	20.3	33.1	31.6	-4.5		65.0	70.5	+8.5		12.80	11.9	-7.0	
Isobutylene	179	267	418	417	-0.2		239.7	241	+0.5		39.48	37.8*	-4.3	
Naphthalene	31.1	491	752	729	-3.1		408	397	-2.7		40	35.2	-12	
Nitrous oxide	81.1*	184	310	299	-3.5		97.9	103	+5.2		71.7	77.7	+8.4	
1-Pentyne	207	313	493	480	-2.6		
Phosgene	152.2	281	455	444*	-2.4		190	195	+2.6		56.0	52.3*	-6.6	
Silicon tetrahydride (silicane)	92.6	161	270	270	0		...	125	...		48	50.5	+5.2	
Water	32.2*	373	647	665	+2.8		57.6	55.2	-4.2		218.2	^	...	

^a Calculated from values shown in Table II unless otherwise noted.

^b Calculated from Equations 3A to 3F: % deviation = 100 X (estd. - exptl.)/exptl.

^c Calculated from Equations 13A and 13B, using estimated T_c values.

^d Calculated from Equation 20, using experimental V_c values where available, or 21A to 21F.

^e Experimental parachors.

^f Calculated from atomic and structural constants of Lewis and of Sugden.

^g Average of Equations 3C and 3E.

^h Correlations do not apply.

ⁱ Indicates that Equations 21A to 21F were used.

TEST OF PROPOSED RELATIONS

To provide an independent check of the proposed equations, they were applied to several compounds for which critical data were available but which had not been used in establishing the equations. The results are given in Table IV. Deviations of the calculated constants from the experimental values are in excellent agreement with the reliabilities of estimate determined from statistical considerations. In view of the essentially empirical nature of the proposed relations, the substantiation afforded by this test provides some measure of confidence in their utility.

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NOMENCLATURE

[P] = parachor
 T_c = critical temperature, ° K.
 T_B = boiling point, ° K.
 V_c = critical volume, cc./mole
 p = pressure, atmospheres
 p_c = critical pressure, atmospheres
 $A, B, C, \dots K; a, b, c, \dots k$ = constants
 S = standard error of estimate

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Hydrolysis of Starch by Sulfurous Acid

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STARCH may be hydrolyzed by enzymes and inorganic and organic acids. The use of enzymes, as in malt, is objectionable because of the simultaneous introduction of bacterial contamination and the necessity for a secondary conversion of the residual dextrans, which requires considerable time. Hydrolysis of starch to glucose by the usual acids must be followed by neutralization and the subsequent production of large amounts of salts. If starch could be hydrolyzed by sulfurous or carbonic acid (formed by the solution of sulfur dioxide or carbon dioxide in the aqueous suspension of starch or amylaceous materials), then at the end of the reaction the gas might be removed from the solution by a release of pressure and little or no neutralization would be necessary. The high temperature and low pH of the conversion would provide conditions for complete sterility of the mash which would be favorable to continuous alcoholic fermentation. Here the problem was to determine the optimum conditions whereby sulfurous acid could be used for the hydrolysis, and the experiments reported were exploratory in nature.

Some research has been reported on the hydrolysis of starch by sulfurous acid. In 1814 Bouriart (3) stated that sulfurous acid could be substituted for sulfuric acid as a catalyst for the hydrolysis of starch. Berge (2) in 1897 reported the effect of the treatment of starch with sulfur dioxide. He found that dextrans could be produced on a commercial scale by the treatment of dry potatoes with sulfur dioxide at 135° to 140° C. Using solutions of potato starch, Berge noted that slight saccharification occurred with the use of sulfurous acid at temperatures lower than 45° C., but with increasing temperatures a greater degree

of hydrolysis took place. The optimum conditions for the sulfurous acid conversion of starch were reported to be 25 parts of amylaceous material in 75 parts of water containing 3 to 6% sulfurous acid at 135° to 140° C. and a pressure of nearly 6 atmospheres. Under these conditions the starch was completely converted to glucose in approximately one hour.

HYDROLYSIS EXPERIMENTS

Hydrolyses were carried out on pure starch suspensions, corn slurries, and wheat slurries, and were run in sealed Pyrex tubes. Glass tubes were used because metal tubes could not be obtained within a reasonable time. The aqueous starch suspension or grain slurry was introduced into the tubes along with sufficient sulfur dioxide in the form of a standard aqueous solution to give the desired starch and sulfur dioxide concentrations in a volume approximately four sevenths of the total volume of the tube.

To determine the concentration of sulfur dioxide in the liquid phase at elevated temperatures, partial pressures of sulfur dioxide over aqueous solutions of the gas were taken from International Critical Tables (4) and were extrapolated to 170° C., the

maximum temperature used in any of the hydrolyses. The distribution constant for the gas between the liquid and gaseous phases could then be calculated for any temperature between 100° and 170° C. Assuming that this constant held for all concentrations of sulfur dioxide used in the tests, the percentage of the gas in the liquid phase could be determined. This procedure is subject to error, but no better method was available. The sulfur dioxide concentrations reported below are the corrected concentrations.

The hydrolysis of starch has been studied in the presence of sulfurous acid. Time, temperature, and concentration of sulfur dioxide were varied, and nearly complete conversion to glucose was obtained in 15 minutes at 165° C. in the presence of 0.2 to 0.4% sulfur dioxide. Extension of this method of hydrolysis to corn mash showed that the most satisfactory conditions were a 2% concentration of sulfur dioxide at 160° C. for 15 minutes. For wheat mash the most satisfactory conditions appear to be a 2% concentration of sulfur dioxide at 165° to 170° C. for 10 minutes. The sulfur dioxide may be removed and the resulting mash fermented to produce alcohol in good yields.

TABLE I. GLUCOSE RECOVERY FROM HYDROLYSIS OF STARCH AS A FUNCTION OF TIME, TEMPERATURE, AND SULFUR DIOXIDE CONCENTRATION

Time, Min.	100° C.			135° C.			155° C.			165° C.			
	0.1% SO ₂	0.2%	0.4%	0.2% SO ₂	0.4%	0.6%	0.2% SO ₂	0.4%	0.8%	0.2% SO ₂	0.4%	0.8%	1.0%
10	52.5	70.8	88.1	90.5	92.2	92.7	90.0
15	85	91.9	100	100	98	99.5	..
30	17.1	30.6	40.6	100.0	87.5	90.4	..	83.5	..	98.8
60	1.2	1.6	2.6	65.2
120	48.9	89.5	100
180	3.6	4.2	4.5
300	4.4	4.7	5.5

TABLE II. GLUCOSE RECOVERY FROM HYDROLYSIS OF CORN MASH AS A FUNCTION OF TIME, TEMPERATURE, AND SULFUR DIOXIDE CONCENTRATION

Time, Min.	160° C.			165° C.			170° C.			
	1.0% SO ₂	1.5%	2.0%	1.0% SO ₂	1.5%	2.0%	1.0% SO ₂	1.5%	2.0%	2.5%
5	41.2	49.6	58.9	59.5	72.8	87.3
10	55.2	58.9	71.2	84.5	89.5	91.0	78.2	82.3	85.4	..
15	70.8	81.9	94.0	74.7	78.8	79.9

concentration of the catalyst, but the degree of sugar degradation also increases with these variables and a point must be found where the most desirable balance is reached between sugar formation and destruction.

PURE STARCH

For the reactions run at 100° C., the tubes were held in a boiling water bath for the designated time and the tubes held at higher temperatures were placed in an autoclave in which a steam pressure of 98 pounds per square inch could be obtained. The tubes in the autoclave were heated to the maximum temperatures in 1 to 2 minutes, but cooling had to be gradual to avoid rupture of the tubes. Tables I, II, and III report the times for which the tubes were held at the designated temperatures; the reduction of temperature to 100° C. required up to 15 minutes for the samples kept at 165° to 170° C. Since it was found that the rate of reaction decreased rapidly with decreasing temperature, the error introduced was probably not significant.

The extent of hydrolysis was determined by analyzing the hydrolyzates for reducing material by the method of Stiles, Peterson, and Fred (6), and the reducing material was calculated as glucose. The fraction of glucose recovered was determined from the ratio of glucose found to glucose theoretically available from the starch. In the experiments where corn or wheat was used, the theoretical yield of glucose was based upon the starch content of the grain, as determined polarimetrically. The starch was solubilized by shaking 2 grams of sample with 90 ml. of 5.7 *N* hydrochloric acid for 10 minutes at 33° C. The suspension was clarified with 10 ml. of 16% stannous chloride dissolved in 5.7 *N* hydrochloric acid. After filtration the clear filtrate was examined polarimetrically, and the starch content of the original sample was calculated on the basis of a specific rotation of 200 for starch. Previous to the sugar determinations, the hydrolyzates were aerated or boiled to remove most of the sulfur dioxide, and the remaining small amount was removed by adding a dilute iodine solution, the slight excess of iodine being removed by thiosulfate.

The problem of obtaining the optimum hydrolysis of starch to glucose involves finding those conditions under which there is a maximum conversion of starch to glucose and a minimum degree of glucose destruction. The rate of starch hydrolysis increases with an increase in the time or temperature of the reaction or the

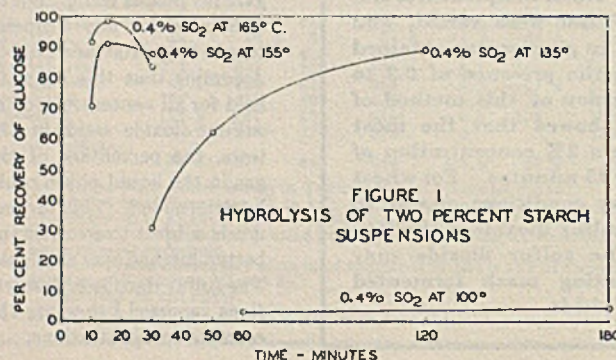
It was desirable to determine the effects of temperature, time, and acid concentration upon the hydrolysis of pure starch prior to working with corn and wheat. Experiments were carried out with 2% boiled suspensions of Argo cornstarch at 100°, 135°, 155°, and 165° C. The results of these preliminary experiments cannot be correlated exactly with the results of experiments carried out with corn and wheat, but they served as an indication of the effect of the variables upon the recovery of glucose. The data for these experiments are given in Table I and some characteristic curves are shown in Figure 1. The recovery of glucose for a given time at 100° C. increased only slightly with an increase in concentration of sulfur dioxide in the suspension. At 100° the saccharification of starch was slight for periods up to 5 hours, and even for times up to 10 hours the maximum recovery of reducing material was equivalent to an approximate glucose yield of only 25%. However, as the temperature was raised above 100° C., the rate of reaction increased considerably for a given sulfur dioxide concentration. Thus, only 2 hours at 135° and 15 minutes at 155° C. were required for complete conversion of the starch in a 2% solution when the sulfur dioxide concentration was 0.6 to 0.8%.

Under such conditions as 0.4% sulfur dioxide at 165° for 15 minutes, at 0.8% at 155° C. for 30 minutes, and at greater concentrations of sulfur dioxide or longer periods of time at the respective temperatures, glucose broke down, as indicated by the dark brown color produced in the solution; this led to a low recovery of glucose. The effect of this caramelization is shown graphically in Figure 1 where the recovery of glucose at 155° and 165° C. rises sharply to a maximum for 16 minutes and then decreases for longer times of reaction. For conditions less severe than 15 minutes at 165° C. the recovery of glucose increased with an increase in catalyst concentration until approximately 100% was recovered. In the absence of sulfur dioxide the recovery of reducing material from a 2% starch solution heated for 15 minutes at 165° C. corresponded to a yield of 0.5% of the theoretical.

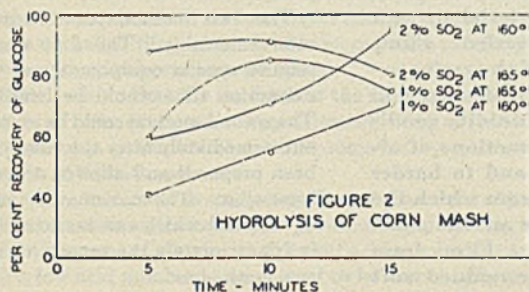
The optimum conditions for the hydrolysis of the starch in a 2% solution appear to be 0.2 to 0.4% sulfur dioxide in the solution and 15-minute heating at 165° C.

CORN

After the work with pure starch, it was desired to find those conditions which would be practical for the conversion of grain mashes with sulfur dioxide. Preliminary experiments showed that grain mash could be cooked and converted in one operation; therefore, only uncooked slurries of ground corn were used. In the sealed tubes after the addition of the sulfur dioxide solution, the concentration of mash was 25 to 27 gallons per bushel, corresponding to a starch suspension of approximately 16%. From the known starch content of the grain and the amount of grain used, the theoretical yield of glucose could be determined. On this basis the yield of glucose in the hydrolysis could be calculated after the reducing material in the hydrolyzate was known.



Experiments with corn were run at 160°, 165°, and 170° C. with sulfur dioxide concentrations of 1, 1.5, and 2%. The lower limits of temperatures and catalyst concentration were determined by the yields of reducing material under the various conditions. Thus, nothing was to be gained by using conditions which would give poor yields. The upper limits of temperature and acid concentration were determined by the fragility of the glass tubes, the maximum temperature obtainable in the autoclave, and the degree of caramelization of the hydrolyzates. Because the tubes containing 2.5% sulfur dioxide were ruptured at 165° C., no data are given for such concentrations of catalyst. Since a practical method for continuous hydrolysis was being sought, no hydrolyses were run for times greater than 15 minutes. The data for the experiments with corn are given in Table II, and some representative curves are shown in Figure 2.



The most satisfactory conditions found in these experiments for the conversion of corn mash appear to be 2% sulfur dioxide in the mash and 15-minute heating at 160° C. That these conditions were satisfactory from a practical viewpoint was checked by running several samples of corn; the values for recovery of glucose were: 95.0, 86.1, 85.0, 95.1, 88.0, 95.1, and 89.5%.

Glucose caramelized in the reactions run under the most severe conditions; Figure 2 shows the effect of this sugar degradation on yield. An increase in temperature of 5° C. seems to increase the rate of glucose destruction considerably, enough to offset the increased rate of starch hydrolysis. It is apparent in comparing the yield of glucose after 15 minutes at 160° C. in the presence of 2% sulfur dioxide with the yield after 10 minutes at 165° C. in the presence of the same amount of catalyst that the increase in temperature corresponds approximately to the decrease in time.

The shape of the curves in Figures 1 and 2 may have been affected by experimental conditions. That is, the yields from the reactions might have been somewhat different if other conditions had been used. In particular, more rapid cooling after the reaction and means of agitation during the reaction might have affected the results somewhat. But from the shape of the curves it seems likely that in further work critical ranges of all the variables may give a maximum yield of sugar. It may be possible to limit the variables more than was done here.

Preliminary alcoholic fermentations were run on some of the converted corn mash by the method of Stark, Adams, Scalf, and Kolachov (5); 4.9 proof gallons of alcohol per bushel of grain were obtained. This is equivalent to a yield of 85.8% of theoretical. It cannot be considered a good indication of the yield of alcohol from grain converted by sulfurous acid, but it proves that the mash can be fermented, and in this case the yield compares favorably with the yield of alcohol from malt-hydrolyzed mash. The sulfur dioxide can be removed by heat and vacuum to such an extent that it is undoubtedly no longer toxic to yeast. Other investigators have reported (7) that in the fermentation of molasses a sulfur dioxide content up to 0.35% by weight has little influence on the yield of alcohol, and a content of 0.1% influences the fermentation slightly but only at the beginning. In the experiments it was possible to reduce the content of sulfur dioxide below 0.05% without difficulty.

Sulfur determinations were run by the A.O.A.C. method (1)

on the original corn and on dried mash, obtained by evaporating to dryness a portion of a hydrolyzate. It was found that the ratio of sulfur in the dried mash to that in the original corn was 2.9 to 1. It is unlikely that under any circumstances could more sulfur remain in the mash than was found here, and therefore the amount probably represents an upper limit. Nothing is known about the form of the sulfur in the mash, but it is unlikely that this sulfur could be carried over into an alcoholic distillate after fermentation of the mash.

WHEAT

A few experiments were run on cooked distillery wheat mash, but cooking prior to hydrolysis with sulfurous acid was not found to be necessary, and after this only slurries of ground wheat in sulfur dioxide solutions were used. The concentration of starch again corresponded to approximately 16%. Reactions were run at 160°, 165°, and 170° C. For times of 5, 10, and 15 minutes with sulfur dioxide concentrations of 1 through 2.5%. The data are given in Table III. Again the choice of what conditions were to be used was determined by the fact that a practical method of continuous hydrolysis was being sought, by the extent of reaction under the first conditions tried, and by the nature of the equipment. It was possible to run a few experiments with sulfur dioxide concentrations as high as 2.5%.

In the work with wheat, as in that with corn, the most satisfactory concentration of sulfur dioxide was found to be 2%. Table III shows that in two cases increasing the sulfur dioxide concentration from 2 to 2.5% caused a decrease in sugar recovery because of glucose destruction. With wheat the other most satisfactory conditions from a practical standpoint appear to be a 10-minute reaction period at 165° to 170° C. These conditions were checked by hydrolyzing several samples of wheat, and the following values were obtained for the recovery of glucose: 93.3, 94.0, 89.0, 90.4, and 95%.

TABLE III. GLUCOSE RECOVERY FROM HYDROLYSIS OF WHEAT MASH AS A FUNCTION OF TIME, TEMPERATURE, AND SULFUR DIOXIDE CONCENTRATION

% SO ₂ Concn.	160° C., 15 Min.	165° C., 10 Min.	170° C.	
			5 Min.	10 Min.
1.0	62.9	62.0	60.0	80.5
1.5	63.9	89.0	75.0	85.0
2.0		96.0	85.1	98.0
2.5	72.2	93.1	84.2	..

It seems probable that the hydrolysis of grain starch by sulfurous acid can be adopted as a continuous process, and it is believed that the sulfur dioxide can be recovered from the converted mash and recycled. Further work is being carried out on this hydrolysis process.

CONCLUSIONS

Experiments on pure starch, corn, and wheat have shown the feasibility of using sulfur dioxide as a catalyst. From 2% starch suspensions, a maximum recovery of glucose of practically 100% has been obtained. Corn can be cooked and converted in one step in the presence of 2% sulfur dioxide to yield as much as 95% glucose; a like yield can be obtained from wheat. The sulfur dioxide can be removed from the hydrolyzate, and the resulting mash can be fermented to alcohol with a resultant yield which compares favorably with that from mash converted with malt.

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EXTRACTION of ALKYD RESINS

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THE separation of polymeric materials into fractions possessing different characteristics has been the subject of many investigations in the resin field. Such separations have been carried out in many ways and, depending on the nature of the polymer, by either chemical or physical means. Such separation procedures have been applied to alkyd resins, but information on the operating conditions, results, and significance of such work has not been made available nor is it complete.

Ellis (1) treated alkyd resins with solvents such as kerosene, gasoline, and ethyl alcohol, and extracted slow-drying portions of the resins. Alkyd resins were extracted according to another patent (2) by dissolving them in methyl or ethyl alcohol with heating and then cooling or adding a precipitant to the solution. Sandig (7) dissolved alkyds in one to three times their weight of an alcoholic solvent with heating, and then cooled them until two layers were obtained; the lower layer contained the more desirable product. Glazener and Wolf (3) introduced an acetone solution of an alkyd into ethyl alcohol and distilled the acetone, during which operation the resin separated into fractions. Hall, McBurney, and Nollau (4) extracted alkyds with butyl alcohol or dissolved them in toluene and added mineral spirits to precipitate the desirable fractions.

The purpose of undertaking the work reported here was to apply extraction procedures to various types of alkyd resins and to determine the physical and chemical characteristics of the fractions obtained.

EXTRACTION METHODS

Two methods have been found satisfactory for extraction of certain types of alkyd resins. In the first an alcohol was used as the extractant in a liquid-liquid type continuous extractor. A Kjeldahl flask fitted with a side arm near the top of the neck was the extraction chamber. A stirrer extending to the bottom of the Kjeldahl flask was run at a speed that would permit the alkyd being extracted to be mixed well with the solvent, but not allow any insoluble portion to be carried over with the extractant. The extraction chamber was kept at a temperature just below the boiling point of the solvent. This maintained the resin in a fluid state, promoted more efficient extraction, and prevented violent ebullition which would carry over insoluble portions of resins. The extract-containing alcohol was run from the side arm into a receiver from which the alcohol was continuously distilled and recycled through a glass tube leading to the bottom of the extraction chamber.

The second method was to dissolve the resin in a solvent with heating and then allow the solution to cool; a fraction of the

The problem of extracting alkyd resins with lower monohydric alcohols was investigated. Factors such as method of preparation, degree of polymerization, excess hydroxyl and carboxyl groups, oil length, fatty acid modifiers, and substitution of other polyhydric alcohols for glycerol in the resins were studied to find the amounts of extractable material present when such conditions were varied. Films were prepared from fractions of the resins extracted, by both baking and air-drying, and were stored under controlled humidity conditions. The alcohol-insoluble fractions of alkyd resins dried more rapidly and to harder films than the original alkyds from which the fractions were obtained. None of the films showed any signs of brittleness. Films from the alcohol-soluble fractions remained soft and tacky. Analyses of fractions showed that alkyds are probably mixtures of resins of various oil lengths and that the shorter oil length portions comprise the unextractable material. Methods of utilizing the extractable portions of alkyd resins were found. The improvement in the properties of extracted alkyds may in the future promote commercial utilization of such processes.

resin then precipitated, and the supernatant solution containing the resin extract was decanted. The amount of resin extracted in this manner can be varied by the amount of alcohol used and/or by the number of times this procedure is repeated.

The two methods can be used interchangeably. The first would require special equipment and the extraction time would be lengthy. The second method could be carried out immediately after the resin had been prepared and allowed to cool somewhat. The maximum amount of material which can be extracted is approximately the same with the two methods.

CHOICE OF SOLVENT. Extractions carried out in a liquid-liquid extractor (method 1) must be run at a temperature high enough to keep the resin fluid, in order to permit thorough mixing with the solvent. A good solvent for such an extraction would therefore be one in which the extractable material is soluble at such extraction temperatures and residual material is insoluble at the same temperature. Of

the solvents tested, methanol and ethanol were the only ones which seemed of value in this type of extraction. A temperature of 60° C. was suitable with these extractants.

The ideal solvent for an extraction in which the whole resin is dissolved in hot solution and then cooled to precipitate a part of the resin (method 2) is one in which the extractable material is soluble, the residual material is insoluble in the cold, and the whole resin is soluble hot. The solvents which were most satisfactory in this type of procedure were propanol, isopropanol, and butanol. The solvents tested for use in the extractions included: polyhydric alcohols, esters, nitroparaffins, chlorinated hydrocarbons, ethers, various hydrocarbon fractions, alcohols, and naphthas. Of these the above mentioned lower alcohols seemed most suitable.

Solvents in which the entire resin is soluble might be used in a modification of method 2 if the desirable portion could be precipitated by the addition of a precipitating agent. This phase of the problem was not investigated thoroughly.

RESULTS OF EXTRACTIONS

The amount of the resin to extract in order to obtain the best films from the residue most economically depends to a great extent upon the oil length of the resin, the completeness of the reaction in the resin kettle, and the excess of hydroxyl or carboxyl groups present in the finished product. Therefore this amount will vary with the resin to be extracted.

The effects on the film-forming properties of a resin from which various amounts have been extracted is evident in Table I. This resin was a 40% soybean-modified alkyd prepared to contain 5%

excess glycerol on the entire weight of the finished batch. The resin was prepared by heating together soybean acids, phthalic anhydride, and glycerol, in the required amounts, to 180° C. in one hour, to 235° in the next hour, and holding at 235° until the acid number was below 15, at which time the resin was poured. The acid number of the resin was 13, and the hydroxyl number corrected for the acid number (as determined by a modified acetic anhydride-pyridine method) was 113.5. Converted to glycerol, this would be equivalent to 6.2% free glycerol.

Films of this resin and the residues from extraction were cast in duplicate from xylene solutions with a Bird film applicator on glass plates. These films were baked at 155° C. for one hour and then stored in cabinets at the indicated humidity for 24 hours, after which time the hardness of the films was tested with a Sward hardness rocker. The thickness of the films was taken by cutting a 0.5-cm. square out of the film and measuring the thickness all around this square with an Ames thickness gage, model 100. All results on baked films given in this report were obtained in the above manner unless otherwise stated.

Table I shows that the hardness of the films increases with the amount of resin extracted. Approximately 50% of the resin was the maximum amount that could be removed by continuous extraction with methanol.

An effort was made to study the effect of the extent of polymerization of a resin on the extraction procedure by preparing batches of the same type of alkyd with different acid numbers. An alkyd with a low acid number was assumed to be more highly polymerized than the same type with a higher acid number. Thus a 40% soybean alkyd with 5% excess glycerol having an acid number of 13 contained approximately 50% extractable material; the same alkyd with an acid number of 25 contained approximately 96% extractable material. Therefore, it is evident that a low acid number is one essential in keeping the extractable material at a minimum.

The effect of the extent of unsaturation of the fatty acid modifiers on the amount of extractable material in a resin was studied by preparing 40% oil-modified alkyls containing 5% excess glycerol based on the weight of the finished batch. The acid mixtures used, the acid and hydroxyl numbers of these alkyls, and the amounts of extractable material present are given in Table II.

These figures show that no important effects of unsaturation of the fatty acid modifiers could be noticed on the amount of extractable matter which the various resins contained. Small effects would probably not be noticed because of slight differences in the acid and hydroxyl numbers of the resins.

The effect of excess hydroxyl groups on the amount of extractable material in a resin is shown by the experiments summarized in Table III. Three 40% soybean alkyls were prepared, calculated to contain 5, 10, and 15% excess glycerol based on the weight of the finished product. Another 40% soybean alkyd was prepared, calculated to contain stoichiometric amounts of reactants, and finally a 40% soybean alkyd was prepared containing

5% less glycerol than the theoretical amount. All of these resins were extracted under similar conditions.

Results in Table III indicate that reduction in the excess of glycerol used in preparation of a resin down to stoichiometric amounts reduces the amount of extractable material present in the finished product; reducing the glycerol below the amount necessary to esterify the acid components of the reaction does not have a continuing effect on lowering the amount of extractable material. Film tests on these alkyls and residues are given in Table IV. The figures show that, no matter what amount of extractable material is present in the original alkyd or what amount of glycerol is used, the characteristics of films cast from the residues are comparable if the maximum amount of extractables is removed.

The effect of oil length of an alkyd resin on the extraction procedure was studied by preparing alkyls of 35, 40, 45, 50 and 55% oil length, all containing 5% excess glycerol on the basis of weight of the finished resin. These alkyls were extracted and the results are shown in Table V. They indicate that increasing the oil length of an alkyd results in an increase in amount of extractable material present. Film tests on the original and residual materials from this series are given in Table VI. They show that, no matter what amount of extractable material is present in the original alkyd or what oil length alkyd is being extracted, the residues obtained when the maximum amount of extractable is removed are roughly comparable.

Other polyhydric materials were substituted for part of the glycerol in the preparation of 40% soybean-modified alkyls with 5% excess glycerol. These preparations included substitution of 10 and 20% of the glycerol with equivalent amounts of pentaerythritol and also with equivalent amounts of diethylene glycol. The resins were extracted, and results are shown in

TABLE II. EFFECT OF UNSATURATION OF FATTY ACID MODIFIERS

Fatty Acid Modifier	Acid No.	Hydroxyl No. Cor. for Acid No.	Hydroxyl No. as % Glycerol	% Extractable Material
Linseed oil acids	15.0	115.9	6.3	48.9
Soybean oil acids	13.0	113.5	6.2	49.5
Oleic acid, U.S.P.	15.6	115.0	6.3	42.0
Neo-Fat 23 ^a	20.0	105.4	5.8	41.9
Neo-Fat 19 ^b	33.2	99.3	5.4	45.2

^a 30% oleic, 56% linoleic, 10% linolenic, 4% saturated.

^b 90% unsaturated C₂₀ acids with 3 and 4 double bonds; balance mainly oleic and linoleic.

TABLE III. EFFECT OF EXCESS HYDROXYL GROUPS

40% Soybean Alkyd	Acid No.	Hydroxyl No. Cor. for Acid No.	Hydroxyl No. as % Glycerol	% Extractable Material
15% excess glycerol	3.3	263.1	14.3	100
10% excess glycerol	4.3	171.0	8.3	73.5
5% excess glycerol	13.0	113.5	6.2	49.5
0% excess glycerol	35.1	64.7	3.5	36.7
5% less glycerol than theory	48.0	53.9	2.9	51.2

TABLE I. FILM-FORMING PROPERTIES OF EXTRACTED RESINS

40% Soybean Alkyd, 5% Excess Glycerol	Approx. Relative Humidity, %	Sward Hardness	Thickness, Mils
Original material	0	22	1.2
	50	14	1.2
	100	6	1.2
22% extracted	0	36	1.1
	50	24	1.1
	100	17	1.1
36% extracted	0	44	1.0
	50	44	1.0
	100	31	1.0
49.5% extracted	0	50	1.2
	50	50	1.2
	100	39	1.2

TABLE IV. FILM TESTS

40% Soybean Alkyd	Approx. Relative Hum., %	Original		% Extracted	Residue	
		Sward hardness	Thickness, mils		Sward hardness	Thickness, mils
10% excess glycerol	0	16	1.6	73.5	46	1.4
	50	10	1.4		39	1.6
	100	6	1.4		24	1.7
5% excess glycerol	0	22	1.2	49.5	50	1.2
	50	14	1.2		50	1.2
	100	6	1.2		39	1.2
0% excess glycerol	0	23	1.2	36.7	52	1.2
	50	19	1.1		40	1.2
	100	13	1.2		33	1.2
5% less glycerol than theory	0	28	1.2	51.2	52	1.4
	50	24	1.2		50	1.3
	100	18	1.2		40	1.4

TABLE V. EFFECT OF OIL LENGTH

Alkyd Resin with 5% Excess Glycerol	Acid No.	Hydroxyl No. Cor. for Acid No.	Hydroxyl No. as % Glycerol	% Extractable Material
35% soybean	23.9	116.9	6.3	41.0
40% soybean	13.0	113.5	6.2	49.5
45% soybean	12.4	100.6	5.5	60.5
50% soybean	9.0	102.6	5.6	73.6
55% soybean	11.3	100.7	5.5	90.5

TABLE VI. FILM TESTS

Alkyd Resin with 5% Excess Glycerol	Approx. Relative Hum., %	Original		% Ex- tracted	Residue	
		Sward hard- ness	Thick- ness, mils		Sward hard- ness	Thick- ness, mils
35% soybean	0	32	1.2	41.0	61	0.9
	50	25	1.2		55	0.9
	100	17	1.2		44	1.0
40% soybean	0	22	1.2	49.5	50	1.2
	50	14	1.2		50	1.2
	100	6	1.2		39	1.2
45% soybean	0	16	1.3	60.5	45	1.2
	50	10	1.4		38	1.2
	100	8	1.4		24	1.3
50% soybean	0	4	1.6	73.6	56	1.1
	50	4	1.6		44	1.2
	100	4	1.6		40	1.2

TABLE VII. EFFECT OF GLYCEROL SUBSTITUTION

40% Soybean Alkyd, 5% Excess Glycerol	Acid No.	Hydroxyl No. Cor. for Acid No.	Hydroxyl No. as % Glycerol	% Ex- tractable Material
Unmodified	13.0	113.5	6.2	49.5
10% of glycerol substituted with pentaerythritol	21.8	112.9	6.1	45.7
20% of glycerol substituted with pentaerythritol	36.8	94.2	5.1	53.5
10% of glycerol substituted with diethylene glycol	10.73	98.4	5.3	48
20% of glycerol substituted with diethylene glycol	9.38	104.7	5.7	> 80

TABLE VIII. FILM TESTS

40% Soybean Alkyd, 5% Excess Glycerol	Approx. Relative Hum., %	Original		% Ex- tracted	Residue	
		Sward hard- ness	Thick- ness, mils		Sward hard- ness	Thick- ness, mils
Unmodified	0	22	1.2	49.5	50	1.2
	50	14	1.2		50	1.2
	100	6	1.2		39	1.2
10% of glycerol sub- stituted with pen- taerythritol	0	28	1.3	45.7	55	1.3
	50	18	1.3		45	1.3
	100	11	1.2		32	1.3
20% of glycerol sub- stituted with pen- taerythritol	0	28	1.2	53.5	55	1.3
	50	24	1.3		44	1.3
	100	22	1.3		33	1.4
10% of glycerol sub- stituted with di- ethylene glycol	0	8	1.2	48	43	1.2
	50	4	1.3		32	1.2
	100	2	1.4		22	1.2

TABLE IX. WATER RESISTANCE OF FILMS

Resin No.	40% Soybean Alkyd	Immersion at Room Temp.		Re- cov- ery Time, Hr.	Immer- sion at 100° C. for 1/2 Hr.	Re- cov- ery Time, Hr.
		18.5 hr.	66 hr.			
1	5% excess glycerol	OK	OK	..	OK	..
2	Alkyd 1, 29.8% extd.	OK	OK	..	OK	..
3	No excess glycerol	OK	OK	..	OK	..
4	Alkyd 3, 26% extd.	OK	OK	..	OK	..
5	10% excess glycerol	Blushed	Blushed	1 1/2	Blushed	1
6	Alkyd 5, 73.5% extd.	OK	OK	..	OK	..
7	5% excess glycerol	OK	OK	..	OK	..
8	Alkyd 7, 41% extd.	OK	OK	..	OK	..
9	5% excess glycerol; 10% of glycerol re- placed by diethyl- ene glycol	Very slight blush	Blushed	1	OK	..
10	Alkyd 9, 48% extd.	OK	OK	..	OK	..
11	5% excess glycerol; 10% of glycerol re- placed with penta- erythritol	OK	Slight blush	1	OK	..
12	Alkyd 11, 45.7% extd.	OK	OK	..	OK	..

Table VII They indicate that adding about 20% of a polyhydric alcohol containing less than three hydroxyl groups tends to increase the amount of extractable material in the finished product. The effect of substituting pentaerythritol for part of the glycerol was complicated by the fact that it was necessary to have a high acid number in these resins to prevent gelation. The film tests on the original alkyds and residual materials are given in Table VIII.

WRINKLING, WATER RESISTANCE, AND BRITTLINESS

An observation of interest was made when the materials worked with were baked with driers. Wrinkling of the films occurred in all cases where the original alkyds were used, but the unextractable portions of alkyds under the same conditions showed no wrinkling. This can possibly be explained on the basis of difference in composition of the materials as shown in Table XI.

Resistance of the various alkyd films to water vapor has been illustrated by the film tests run at different humidities. Resistance to liquid water of some of the materials was also tested. This was done by baking films on glass plates for one hour at 155° C. and, after cooling, immersing these films to half their length in distilled water at room temperature for 66 hours. Another set was tested by boiling in distilled water for 30 minutes. Any blushing in the films was noted along with the time necessary for blushed films to recover. The results are given in Table IX.

Films of the same types tested for liquid water resistance were also tested for brittleness. This was done by casting the materials on tin sheets and baking at 155° C. for 1 hour. After these films had cooled, they were bent double within 2 seconds over a 1/8-inch mandrel. The films were examined at the bend with an 8X magnifying glass. None of the films showed any signs of brittleness.

AIR-DRY TESTS ON EXTRACTS AND RESIDUES

Tests have so far been given only on baked films. It has been shown how these films have been improved by extracting the alkyd used in making them. Similar improvement has also been noted on air-drying tests of the residues from extraction procedures, and improvements are equally remarkable in these tests.

Some air-dry tests are given in Table X. The method used in casting these films was the same as described previously. The films were allowed to dry initially at room temperature (about 25° C.) and at room humidity (approximately 50%). Dust-free time was determined by drawing a thread from a piece of cheesecloth slowly across the surface of the film. If the string moved smoothly, the film was considered dust-free; if the string moved jerkily, the film was not dust-free. Tack-free time was determined by placing a strip of paper on the film, rubbing the paper into contact with the film surface, and then pulling off the paper. If there was any audible evidence of adhesion when the two surfaces were separated, the film was not considered tack-free. The films were then placed in relative humidity cabinets, and the Sward hardness and thickness readings were recorded after the indicated interval. The driers were added as the naphthenates (Nuodex) on the basis of the solids in the resin solutions.

CHARACTERISTICS OF EXTRACTS AND RESIDUES

The extracts obtained from alkyds by these procedures are soft, gummy materials of about the consistency of molasses. They are poor film formers and are difficult or impossible to gel by heat alone.

The physical properties of the residues cannot be completely defined. The residues of alkyds which have been completely extracted cannot be completely freed of the alcohol used in the extraction without causing the residues to gel. The only residues obtained free of solvent were those from alkyds which had been

TABLE X. RESULTS OF AIR-DRY TESTS

Resin No.	Composition of Alkyd	Driers	Dust-free Time	Tack-free Time	Approx. Rel. Hum., %	Sward Hardness	Thickness, Mils
A	40% linseed, 5% excess glycerol	0.65% Pb 0.05% Mn 0.02% Co	30 min.	2 hr.	0 50 100	8 ^a 5 ^a 4 ^a	1.2 1.3 1.2
B	Alkyd A, 47% extd.	0.65% Pb 0.05% Mn 0.02% Co	35 min.	45 min.	0 50 100	23 ^a 16 ^a 8 ^a	1.4 1.4 1.4
C	40% soybean, 5% less glycerol than theory	0.65% Pb 0.05% Mn 0.02% Co	1 hr.	3 1/2 hr.	0 50 100	6 ^a 6 ^a 2 ^a	1.3 1.3 1.3
D	Alkyd C, 51.2% extd.	0.65% Pb 0.05% Mn 0.02% Co	15 min.	25 min.	0 50 100	26 ^a 23 ^a 12 ^a	1.5 1.8 1.6
E	40% soybean, 5% excess glycerol; 10% of glycerol replaced with diethylene glycol	0.65% Pb 0.05% Mn 0.02% Co	2 1/2 hr.	5 1/4 hr.	0 50 100	2 ^b 2 ^b 2 ^b	1.4 1.3 1.4
F	Alkyd E, 48% extd.	0.65% Pb 0.05% Mn 0.02% Co	20 min.	25 min.	0 50 100	21 ^b 17 ^b 13 ^b	0.9 1.0 0.9
G	40% soybean, 5% excess glycerol; 20% of glycerol replaced with pentaerythritol	0.65% Pb 0.05% Mn 0.02% Co	30 min.	5 1/2 hr.	0 50 100	14 ^a 14 ^a 10 ^c	1.4 1.3 1.4
H	Alkyd G, 53.5% extd.	0.65% Pb 0.05% Mn 0.02% Co	25 min.	35 min.	0 50 100	30 ^a 28 ^a 24 ^a	1.4 1.4 1.4

^a 48 hours after casting.^b 24 hours after casting.^c 72 hours after casting.

incompletely extracted. The residues were similar in appearance to the original alkyds except that they were usually somewhat harder. When extract and residue from an alkyd were recombined in the proportions present in the original, films from the mixture were comparable to those from the parent resin.

Analysis of an original 40% soybean alkyd and the extract and residue obtained from it illustrates the chemical characteristics of these materials. The alkyd was prepared by heating all the reactants (glycerol, soybean acids, and phthalic anhydride) together until an acid number of 14.4 was obtained. Thirty-five per cent of this resin was extracted with isopropanol according to method 2. This was not a complete extraction. The method of analysis for phthalic acid and fatty acids was that of Kappelmeier (5). The water-soluble portion from that procedure was analyzed for glycerol by the periodate method (6). The results are summarized in Table XI along with values for the amounts of these ingredients in the original resin which were calculated from the amounts used in making the resin.

Extracts and residues of two other 40% soybean oil alkyds with 5% excess glycerol were analyzed. One of them was prepared by heating glycerol and part of the phthalic anhydride to a low acid number. The fatty acids were then added, and the acid number was again brought to a low value. The rest of the phthalic anhydride was added, and the acid number was brought to its final value. The other alkyd was prepared, following commercial practice, by alcoholysis of soybean oil and subsequent treatment with phthalic anhydride and glycerol. The results of the analysis of these alkyds and their fractions were similar to those shown in Table XI.

TABLE XI. ANALYSIS OF RESIN, EXTRACT, AND RESIDUE

Material	Acid No.	Hydroxyl No. Cor. for Acid No.	% Phthalic Acid		% Fatty Acid		% Glycerol	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
40% soybean alkyd, 5% excess glycerol	14.4	108.5	49.5	48.3	36.4	36.3	27.3	26.6
Ext. (35% of original)	22.0	125.1	..	36.3	..	47.1	..	24.9
Residue (65% of original)	10.3 (estd.)	98.0 (estd.)	..	54.4	..	29.6	..	27.4

The alcohol-soluble parts of the resins contain higher percentages of fatty acids than either the original resins or the residues; the phthalic acid content of the extracts is lower than that of the original resins or of the residues. This probably accounts for the fact that the extracts are such soft, gummy materials; more important, it gives some insight into the question of why there is an extract at all.

In the case of the resin described in Table XI, the residue corresponds to a 32% oil length alkyd with 4.7% excess glycerol; the extract corresponds to a 52% oil length alkyd with 5.6% excess glycerol. Therefore, in effect this alkyd consists of two fractions, one of 32% oil length and one of 52% oil length. It was previously pointed out that alkyds of long oil length are largely or completely extractable, and what is accomplished therefore in extracting an alkyd is the removal of high oil length portions which form during preparation even of a short or medium oil length resin. Any means by which the even distribution of fatty acids throughout all component parts of the resin could be promoted would, therefore, be a method of producing better and more uniform alkyds, at least for film formation and probably for other uses.

A 45% linseed alkyd with 20% excess glycerol was extracted (43.2%), and molecular weights were run on the original alkyd and the extract by the cryoscopic method in benzene. One cannot place much dependence on this method when applied to resins. However, our results showed a molecular weight for the original resin of 3194 and for the extract of 976. These figures give some indication that, in addition to the extract being different in composition from the rest of the alkyd, it is lower in molecular weight.

DISCUSSION

The extraction of an alkyd resin is a process that could readily be carried out on an industrial scale. The residual material obtained in such a process has greatly improved film-forming properties, and it is believed more uniform products could be obtained by such a procedure. An important problem in connection with the extraction of alkyds would be the disposition of the extract. This could properly be the subject of another paper, but a few preliminary experiments will be mentioned to illustrate means of utilizing the extract.

Knowing the composition of the extract, we have added original reactants in amounts necessary to change the proportions to those of a chosen type of alkyd. Heating such a mixture as in ordinary resin formation gave a resin similar to one made in the classical manner. There is some advantage in heating the extract with glycerol alone before adding acids. The action in this case seems to be similar to that in cases where glycerol and triglycerol are heated together before acids are added; i.e., the glycerol reacts with the esters, forming hydroxylated compounds which can undergo esterification with added acids. Using this procedure a 40% soybean alkyd with 5% excess glycerol was extracted, and the extract was used to prepare another 40% soybean alkyd with 5% excess glycerol. This alkyd was then extracted. Films from the alkyd prepared from the extract were equivalent to those of the original alkyd. The residue from the extraction of the alkyd prepared from the extract was also equivalent to the residue obtained from extraction of the original alkyd. In this manner it should be possible to carry out the extraction again and again, each time using the extract obtained in preparation of

new alkyds. If this were done, there would be no accumulation of extract and thus no problem of its disposal.

Extracts have been heated alone for many hours at resin-forming temperatures without undergoing gelation or appreciable change in viscosity. When heated with phthalic anhydride, however, they have been found to react with ultimate formation of a gel.

The similarity in composition of extracts and alkyds indicates the probable usefulness of extracts as plasticizers in products now plasticized with straight alkyds.

SUMMARY

The process of extracting alkyd resins with certain aliphatic alcohols has been reinvestigated. Film-forming alkyds have been separated by this procedure into two fractions; one forms superior films, and the other as such has little or no usefulness in this respect. By analysis of fractions obtained from typical alkyds, information has been obtained on the composition of alkyd resins.

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Preparation of Viscous Phenolic Resins

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SINCE phenol-formaldehyde resins were first introduced, many methods have been studied for their utilization with drying oils. A successful method (1) has been the condensation of heat-reactive phenolic resins with rosin. This condensate is usually esterified with glycerol to form a hard resin which can be dispersed in drying oils. The literature on these resins, consisting chiefly of patents, is surprisingly small when their commercial importance is considered.

This study was made to determine if better resins could be produced. It was felt that the less active drying oils could be used to better advantage with more highly polymerized resins. Since the viscosity in solution is accepted as a measure of molecular size, the condensates were evaluated in these terms. Conditions for formation of highly viscous condensates of the reactive phenolic resins with rosin were investigated. Commercial heat-reactive resins, resins from para-substituted phenols, and resins from mixtures of phenols having two and three positions which could condense with formaldehyde, were condensed with rosin and the condensates evaluated.

CONDENSATES FROM COMMERCIAL RESINS

Six typical "heat-reactive" phenolic resins were used in this study. The condensates were formed by gradually adding the

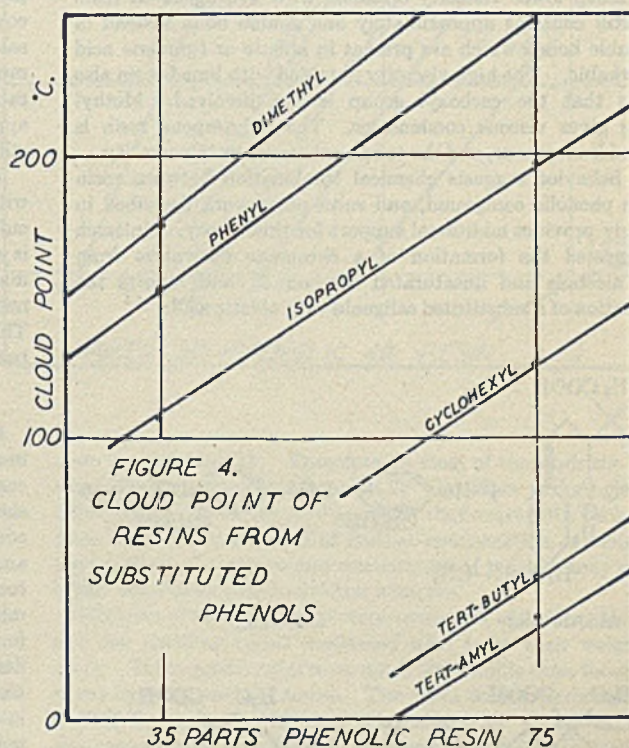
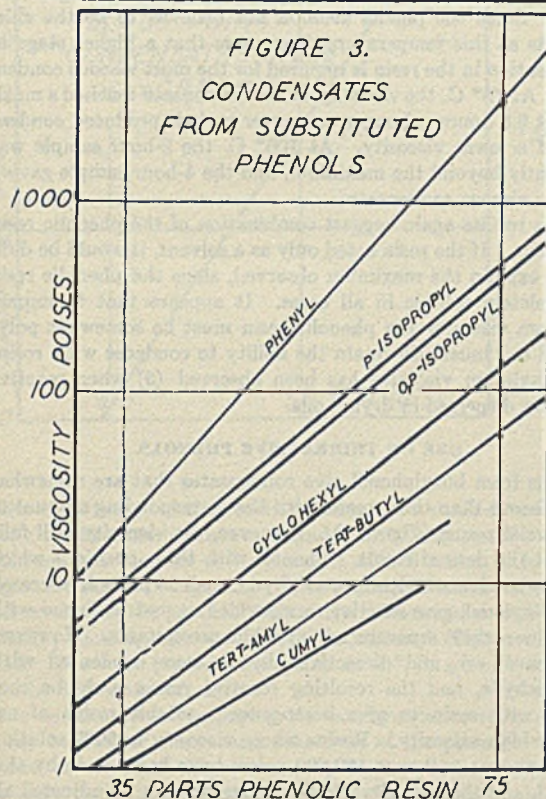
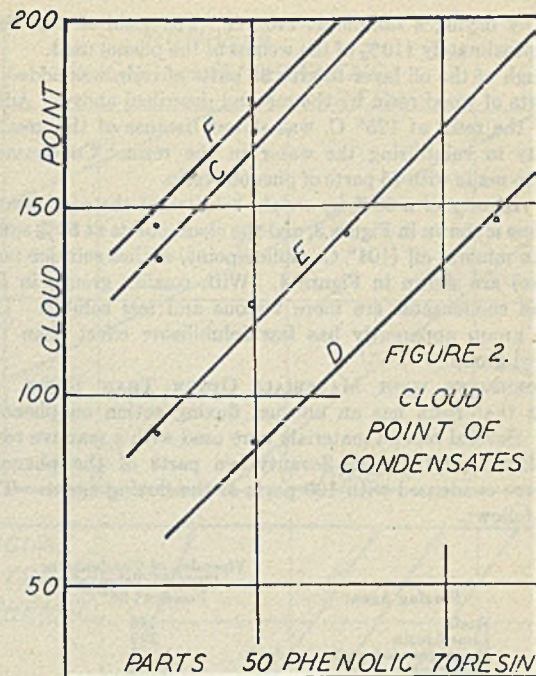
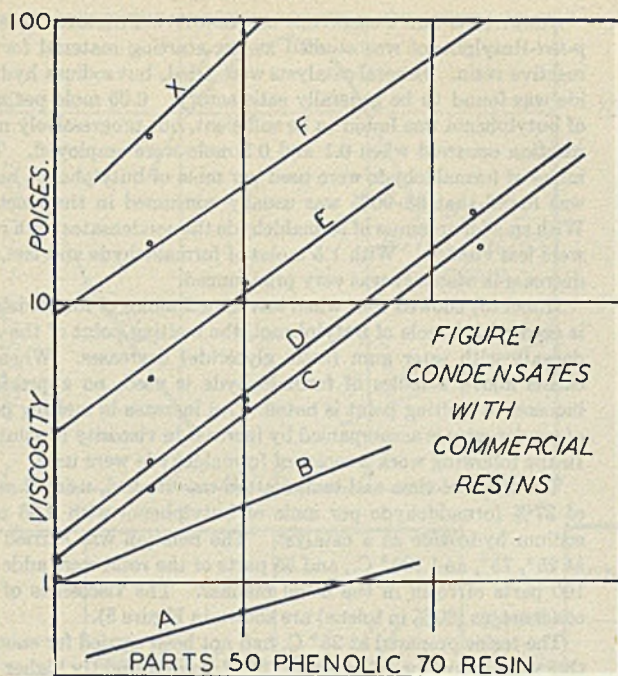
phenolic resin to the molten WW wood rosin at 125° C. with vigorous mechanical agitation. After all the resin had been added, the temperature was raised to 250° C. in about 60 minutes. The batch was then poured and, on cooling, the viscosity at 60% solids in toluene was determined in Gardner-Holdt tubes (2) at 25° C. The cloud point (5) was determined at 50% resin concentration by weight in a highly paraffinic mineral oil (137° C. aniline point, critical solution temperature).

The results obtained with the six resins, designated as A to F, are shown in Figure 1, where the viscosity is plotted against varying amounts of phenolic resin per 100 parts of rosin. The X curve refers to an experimental resin made from *tert*-butylphenol and formaldehyde. Only with the experimental resin (X) were condensates approaching 100-poise viscosity obtained. The cloud points of the condensates are shown in Figure 2. They increase with the amount of phenolic resin. The more viscous resins give the higher cloud point and less soluble resins. Some of the resins (A and B) giving low-viscosity condensates did not cloud at 20° C.

It will be noted (Figure 2) that resin C gives condensates that are nearly as high in cloud point and hence as insoluble as resin F. However, resin C gives much less viscous condensates than resin F (Figure 1). The viscosity generally is dependent on the

Viscous resins may be prepared by condensing heat-reactive phenolic resins with rosin or rosin derivatives. A relatively large proportion of the commercially available phenolic resins of this type is required to produce viscous condensates. Somewhat more viscous products may be obtained by using low-stage reaction products of formaldehyde and para-substituted phenols with an alkaline catalyst. However, to form highly viscous condensates with a moderate proportion of phenolic resin, a mixture of phenols with two and three positions available

for reaction with formaldehyde is used as the starting material for the reactive resin. Condensation products of such resins from mixtures containing 25 to 67 mole % trireactive phenol have been prepared. The viscosity of the condensate with rosin increases with the amount of trireactive component. These highly viscous condensates cannot be esterified with glycerol since gelation occurs before the reaction proceeds very far. They can be dispersed in drying oils and be subsequently esterified with glycerol.



length of the molecules, whereas solubility is influenced not only by the size of the polymer but also by the type of groups attached to the phenolic molecule.

CONDENSATES FROM SUBSTITUTED PHENOLS

Since the commercial resins had been found to vary considerably in behavior, resins from several substituted phenols were prepared. Condensation of a large number of substituted phenols with formaldehyde (8) has shown that heat-reactive resins

are formed when the condensation is carried out in alkaline media. Reactive resins were made by condensing 1 mole of the phenol with 2 moles of 37% formaldehyde for 6.5 hours at 70° C. using enough 10% sodium hydroxide solution to dissolve the substituted phenol. One half mole of sodium hydroxide was required in the case of phenylphenol, much less with the others. At the end of the heating period, the batch was cooled to room temperature and made definitely acid (pH 4) with dilute acetic acid. The oil layer which settled out was separated. This still contained water and a resin content of 60-80% which was deter-

mined by drying a sample at 110° C. The yield of dry resin was approximately 110% of the weight of the phenol used.

Enough of the oil layer to give 35 parts of resin was added to 100 parts of wood rosin by the method described above. Addition of the resin at 125° C. was slower because of the greater difficulty in volatilizing the water in the resin. Condensates were also made with 75 parts of phenolic resin.

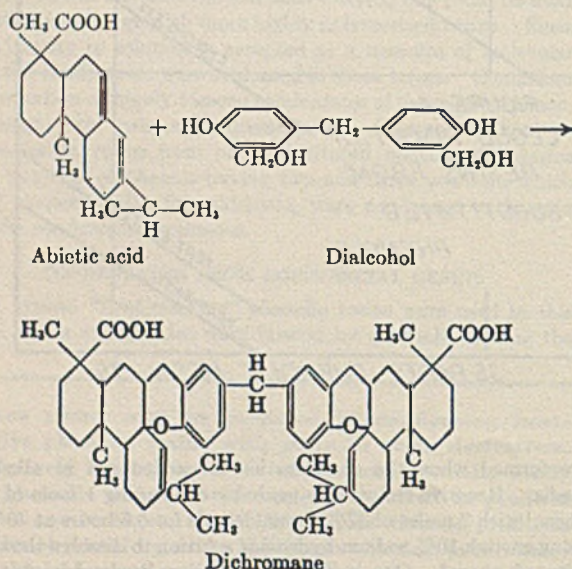
The viscosity of a 60% by weight solution of the condensates in toluene is shown in Figure 3, and the cloud points at 50% solids in white mineral oil (104° C. aniline-point, critical solution temperature) are shown in Figure 4. With smaller groups in the ring the condensates are more viscous and less soluble. The phenyl group apparently has less solubilizing effect than the isopropyl group.

CONDENSATES WITH MATERIALS OTHER THAN ROSIN. It appears that rosin has an unusual fluxing action on phenolic resins. Several related materials were used with a reactive resin made from butylphenol. Seventy-five parts of the phenolic resin were condensed with 100 parts of the fluxing agent. The results follow:

Fluxing Agent	Viscosity of Condensates (60% in Toluene), Poises at 25° C.
Rosin	143
Limed rosin	129
Hydrogenated rosin	3
Polyterpene resin	6

The much lower viscosity obtained with hydrogenated rosin which still contains approximately one double bond instead of two double bonds which are present in abietic or *l*-pimeric acid is remarkable. The high viscosity obtained with limed rosin also suggests that the carboxyl group is not involved. Methyl abietate gives viscous condensates. The polyterpene resin is produced from pinene, and the condensates are low in viscosity.

This behavior suggests chemical combination between rosin and the phenolic compound, and subsequent work described in this study provides additional support for this theory. Hultsch (4) suggested the formation of a chromane derivative from phenol alcohols and unsaturated compounds, and reports the condensation of a substituted saligenin with abietic acid:



While the saligenin-type materials may condense with rosin, it appears that the phenolic resin must be further polymerized to give highly viscous condensates, as will be shown below.

CONDITIONS FOR FORMATION OF REACTIVE PHENOLIC RESINS. *p*-tert-Butylphenol was studied as the starting material for the reactive resin. Several catalysts were tried, but sodium hydroxide was found to be generally satisfactory; 0.05 mole per mole of butylphenol was found to be sufficient, but progressively more reaction occurred when 0.1 and 0.2 mole were employed. Two moles of formaldehyde were used per mole of butylphenol, and it was found that 85–90% was usually consumed in the reaction. With smaller amounts of formaldehyde the condensates with rosin were less viscous. With 1.5 moles of formaldehyde and less, the decrease in viscosity was very pronounced.

Honel (3) showed that when less than 2 moles of formaldehyde is used with 1 mole of butylphenol, the melting point of the condensate with ester gum (rosin glyceride) decreases. When an excess above 2 moles of formaldehyde is used, no appreciable increase in melting point is noted. An increase in melting point of condensates is accompanied by increase in viscosity in solution. In the following work 2 moles of formaldehyde were used.

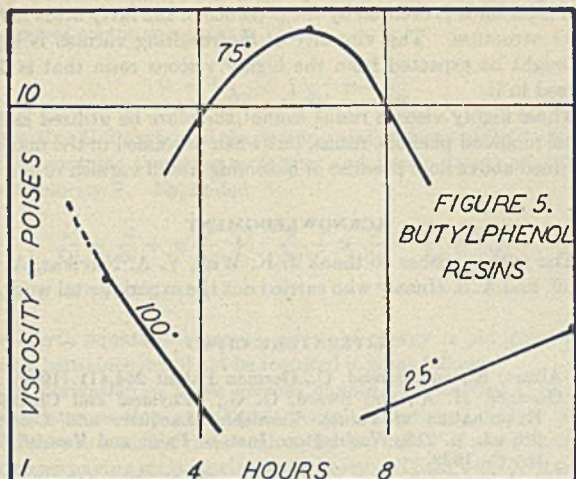
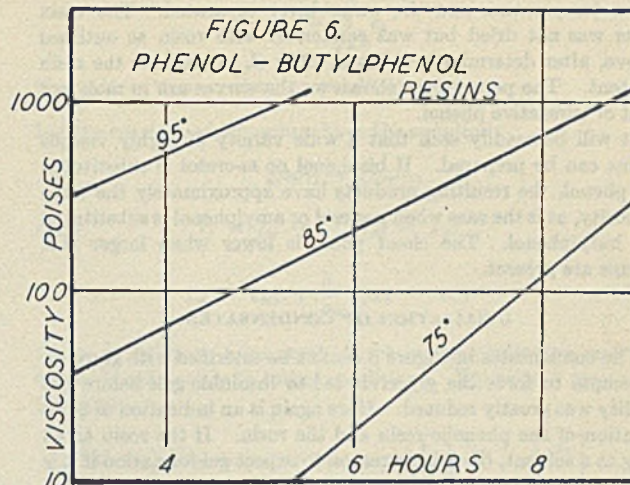
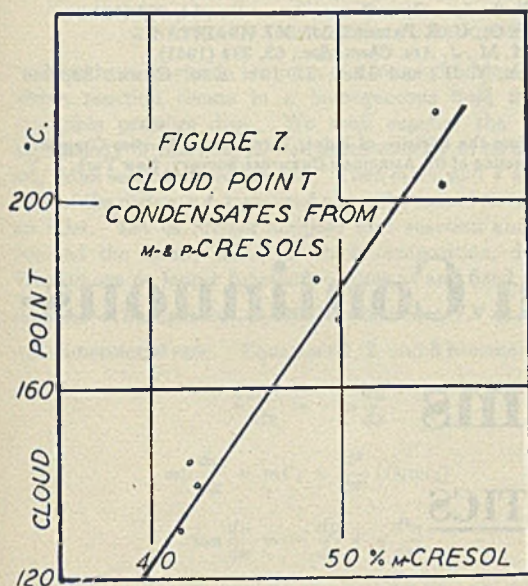
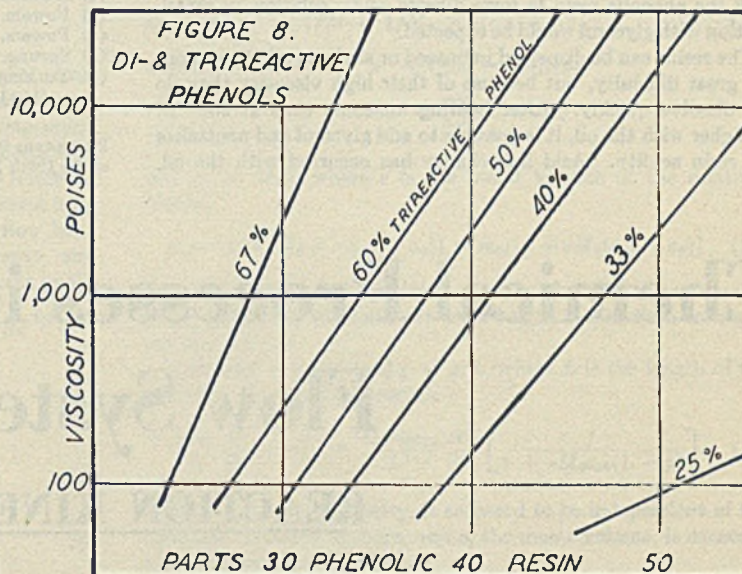
The effect of time and temperature was studied, using 2 moles of 37% formaldehyde per mole of butylphenol with 0.05 mole sodium hydroxide as a catalyst. The reaction was carried out at 25°, 75°, and 100° C., and 35 parts of the resin were added to 100 parts of rosin in the usual manner. The viscosities of the condensates (60% in toluene) are shown in Figure 5).

The resins prepared at 25° C. had not been carried far enough. One sample run for 50 hours at 25° C. gave a slightly higher viscosity. Since the phenol alcohols are believed to be the chief products at this temperature, it appears that a higher stage of condensation in the resin is required for the most viscous condensates. At 75° C. the viscosity of the condensate reached a maximum at 6.5 hours. Longer or shorter periods produced condensates of a lower viscosity. At 100° C. the 2-hour sample was apparently beyond the maximum, and the 4-hour sample gave a still less viscous condensate.

These results again suggest combination of the phenolic resin with rosin. If the rosin acted only as a solvent, it would be difficult to explain the maximum observed, since the phenolic resin is completely soluble in all cases. It appears that to impart maximum viscosity the phenolic resin must be somewhat polymerized but must still retain the ability to condense with rosin. This maximum viscosity has been observed (3) when reactive resins are dispersed in drying oils.

USE OF TRIREACTIVE PHENOLS

Resins from butylphenol give condensates that are somewhat more viscous than those made with the corresponding amount of commercial resins (Figure 1). However, the viscosity still falls short of the desired result. Phenols with three positions which could be condensed with formaldehyde, such as phenol, *m*-cresol, and 3,5-xyleneol, give reactive resins which cannot be fluxed with rosin since they separate as infusible precipitates. However, mixtures of tri- and direactive phenols were condensed with formaldehyde, and the resulting reactive resins could be condensed with rosin to give homogeneous soluble resins of extremely high viscosity. Resins whose viscosity in 60% solution in toluene was well over 100,000 poises have been made by this method, and the viscosity of the condensate can be adjusted almost at will. The catalyst, the ratio of formaldehyde to phenol, and the extent of the reaction all have a definite effect on the phenolic resin produced. The percentage of trireactive phenol used is of even greater influence, and the content of such phenols must be accurately known to determine the type of resin that will be formed. If phenols with but one reactive position are present, such as 2,4-xyleneol, the activity of the resin is greatly reduced. In this study only direactive (*p*-cresol and butylphenol) and tri-reactive (*m*-cresol and phenol) materials were used. Bisphenol was also studied and found to behave like a trireactive phenol, since it may be regarded as the first product in forming a resin from phenol.

FIGURE 5.
BUTYLPHENOL
RESINSFIGURE 6.
PHENOL - BUTYLPHENOL
RESINSFIGURE 7.
CLOUD POINT
CONDENSATES FROM
M- & P-CRESOLSFIGURE 8.
DI- & TRIREACTIVE
PHENOLS

The conditions for the reactive resins were studied, and the results of the time-temperature study for a mixture of 1 mole of phenol and 3 moles of butylphenol with 8 moles of formaldehyde are shown in Figure 6. Fifty parts of reactive resin were condensed with 100 parts of rosin. No evidence of a maximum viscosity, such as was noted with butylphenol (Figure 5) was found. The resin heated for 6 hours at 95° C. gelled before it could be dispersed in rosin.

The conditions for preparing the condensates were modified slightly because of the greater reactivity of the phenolic resins. Because of the much higher viscosity of the condensates, resin was added to rosin at about 90° C., and the temperature gradually raised to remove the water which was present with the resin. After the water was evolved the temperature was raised, and at about 180° C. a further evolution of water and formaldehyde was accompanied with a sudden increase in viscosity. Vigorous stirring was essential throughout the condensation. The temperature was then raised rapidly to 250° C. where the condensate was fluid, except in the case of the most viscous condensates which barely flowed at that temperature.

While condensates of considerably higher viscosity are obtained if the reaction between phenol and formaldehyde is carried well along, it has been found that less advanced resins are more readily separated from water, and their condensation with

rosin is much simpler. Therefore, in most of the work the resin was made by cooking for 6 hours at 75° C. Since various phenols differ greatly (?) in the rate at which they react with formaldehyde and also in the rate of further condensation, a more extensive study of the time and temperature of reaction may reveal better conditions with individual mixtures.

Mixtures of *m*- and *p*-cresol were condensed with formaldehyde and the resulting resins condensed with twice their weight of rosin. These condensates were much less soluble than those prepared from commercial resins. The cloud point was determined at 70% concentration in white mineral oil (104° C., critical solution temperature in aniline). The results are shown in Figure 7. These condensates are much less soluble than the commercial modified phenolic resins, and they are also much more viscous. It will be noted that the cloud point increases as the content of the trireactive phenol is increased.

Many combinations of di- and trireactive phenols were condensed with formaldehyde, and the resulting resins were condensed with various amounts of rosin. Figure 8 summarizes the viscosities of the (60% in toluene) condensates of a large number of such resins with rosin. These resins were made from mixtures of phenol and butylphenol (2 moles of formaldehyde, 1 mole of the blend of phenols, 0.05 mole of sodium hydroxide) and condensed for 6 hours at 75° C. The resin was acidified at

room temperature and the water layer separated. The resin layer was not dried but was condensed with rosin as outlined above, after determining solids at 110° C. to estimate the resin content. The percentages shown on the curves are in mole per cent of trireactive phenol.

It will be readily seen that a wide variety of highly viscous resins can be prepared. If bisphenol or *m*-cresol is substituted for phenol, the resulting products have approximately the same viscosity, as is the case when *p*-cresol or amylphenol is substituted for butylphenol. The cloud point is lower when larger side groups are present.

UTILIZATION OF CONDENSATES

The condensates in Figure 8 cannot be esterified with glycerol. Attempts to form the glyceride led to insoluble gels before the acidity was greatly reduced. Here again is an indication of combination of the phenolic resin and the rosin. If the rosin acted only as a solvent, there is no reason to expect gel formation if it is converted to an ester. However, if the rosin acids are combined with the phenolic resin to form dibasic acids, gelation on esterification with glycerol would be expected.

The resins can be dispersed in linseed or soybean oil (6) without too great difficulty, but because of their high viscosity they do not dissolve quickly. After heating for some time at 250° C. or higher with the oil, it is possible to add glycerol and neutralize the resin acidity. Acid interchange has occurred with the oil,

and gelation is prevented by the presence of the fatty acids in the ester structure. The viscosity of the resulting varnish is high, as might be expected from the highly viscous resin that is dispersed in it.

These highly viscous resins cannot therefore be utilized as the usual modified phenolic resins, but when processed in the manner outlined above hold promise of becoming useful varnish resins.

ACKNOWLEDGMENT

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Chemical Processes in Continuous-Flow Systems

REACTION KINETICS

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General equations governing reacting, flowing mixtures are presented and applied to the discussion of homogeneous reactions. Dimensional analysis based on these equations gives a simple and direct means of correlating empirical rate data and of determining activation energies and specific reaction rates. Equations and charts showing dependence of yield on process variables are given for simple reaction mechanisms.

THE growing importance of industrial processes whose success depends upon adequate control of reaction rate emphasizes the need for a rational analysis of factors which relate yields to equipment size and reaction conditions. Such an analysis is the key to the translation of laboratory bench experiments into pilot plant design, no less than that of pilot plant to full scale units. Nevertheless, there is but scant discussion in the literature of the general principles of this analysis (4, 9, 11). The purpose of the present paper is to summarize the basic features of the kinetics of reactions in flow systems and to point out some of the implications for design.

Straightforward analysis results in the derivation of four equations which govern a homogeneous, reacting, flowing mixture (5). These four equations embody in appropriate symbolism

the fundamental laws of conservation. The first states that no matter is created or destroyed within the system. The second states that the rate of appearance of each kind of substance within a given small region moving with the mean velocity of flow is equal to the rate at which it is formed by chemical reaction plus the rate at which it diffuses into the region. The third law states the conservation of momentum for the fluid as a whole: The rate of change of momentum density in a region is equal to the force density in the same region. The fourth is the law of conservation of energy for the system as a whole. Explicitly, these equations take the forms:

$$\frac{Dm}{Dt} = -m\nabla \cdot \mathbf{V} \quad (1)$$

$$m \frac{Dc_k}{Dt} = m\Gamma_k + \nabla \cdot D_k \nabla mc_k \quad (2)$$

$$m \frac{DV}{Dt} = \nabla \cdot \mathcal{P} \quad (3)$$

- where m = mean density of mixture, grams cm^{-3}
 \mathbf{V} = mean (vector) velocity of the mixture, cm. sec^{-1}
 c_k = concentration of k th component of mixture in moles per unit weight of mixture, moles gram^{-1}
 Γ_k = rate of production of k th component of mixture, $\text{moles gram}^{-1} \text{sec}^{-1}$
 t = time, sec.
 \mathcal{P} = pressure tensor, composed of components of viscous stresses and hydrostatic pressure, gram cm. sec^{-2}
 D_k = diffusivity of k th component in fluid mixture, $\text{cm}^2 \text{sec}^{-1}$

Vector notation has been used for brevity. The operator ∇ has the formal vector components,

$$\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z}$$

Derivative D/Dt refers to changes in a unit volume of fluid which always contains the same molecules and hence moves with the mean velocity V . Expanded:

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u \frac{\partial}{\partial x} + v \frac{\partial}{\partial y} + w \frac{\partial}{\partial z} = \frac{\partial}{\partial t} + V \cdot \nabla$$

where $V = iu + jv + kw$

The fourth equation for conservation of energy is not given explicitly here since it will not be required in what follows.

The derivation of these general equations is carried through in the later section on "Fundamental Equations". It is proposed first to examine their content by the study of some important cases having mathematical simplicity. These will serve as a guide for more complex situations.

KINETICS IN A CYLINDRICAL REACTOR

Consider a reactor in the form of a long cylindrical tube within which reaction occurs in a homogeneous fluid flowing with negligible pressure drop. We shall suppose the composition and density of this fluid as well as its velocity to be uniform over any cross section of the reactor. Then c_k , m , and V are functions only of the distance x , measured along the axis of the reactor from its inlet. Let us further suppose that reaction and flow have reached the steady state in which composition, density, and velocity are no longer functions of time at any fixed point in the reactor. The operator D/Dt then becomes $V \cdot \nabla$ or $u \frac{\partial}{\partial x}$ for the one-dimensional case. Equations 1, 2, and 3 become:

$$u \frac{dm}{dx} = -m \frac{du}{dx} \quad (4)$$

$$mu \frac{dc_k}{dx} = m\Gamma_k + \frac{d^2}{dx^2} (D_k mc_k) \quad (5)$$

$$mu \frac{du}{dx} = -\frac{dp}{dx} + \eta \frac{d^2 u}{dx^2} \quad (6)$$

where u = x component of mean velocity V
 η = coefficient of viscosity of mixture

Equation 4 can be integrated immediately to give

$$mu = G$$

where G = a constant, the mass velocity (gram cm.⁻² sec.⁻¹)

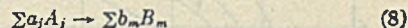
In this simple case the constancy of mass velocity is evident without writing differential equations. Equation 1 is simply the generalization of this to less self-evident cases. When integrated, Equation 6 gives the flow pattern in the reactor. As is well known, this integration is feasible only in a few extremely simple cases. However, if the flow pattern is known empirically or can be assumed, Equation 5 can be integrated in many cases where Equation 6 cannot. We have supposed a uniform velocity throughout any cross section of the reactor and no pressure drop in the tube. It will be recalled that the flow pattern defined by Equation 6 and the boundary conditions is a function only of the dimensionless group, $Re = dm u / \eta$, the Reynolds number, in which d refers to the diameter of the cylinder. Thus the same flow pattern can be reproduced in different sized tubes by altering velocity u so as to maintain Re at a constant value.

Let us now examine Equation 5 to determine the dimensionless groups in terms of which its solution may be expressed. It will be necessary to express density m in terms of the concentration per unit weight, c_k . This is readily done by the relation

$$\frac{1}{M} = \sum_{k=0}^N c_k \quad (7)$$

where M = mean molecular weight of mixture

Let the reaction which occurs have the equation:



$$\text{then} \quad c_j = c_{j0} - \frac{a_j}{a_\alpha} (c_{\alpha 0} - c_\alpha) \quad (9)$$

$$c_m = c_{m0} + \frac{b_m}{a_\alpha} (c_{\alpha 0} - c_\alpha) \quad (10)$$

where c_α refers to a reactant A_α chosen for reference, and the subscript zero refers to initial conditions. Equation 7 may now be written:

$$1/M = \sum_{j,m} (c_{j0} + c_{m0}) + (c_{\alpha 0} - c_\alpha) \left[\frac{\sum b_m - \sum a_j}{a_\alpha} \right] \quad (11)$$

$$\text{or} \quad 1/M = 1/M_0 + v(c_{\alpha 0} - c_\alpha) \quad (12)$$

where $v = (\sum b_m - \sum a_j) / a_\alpha$

$$1/M_0 = \sum_{j,m} (c_{j0} + c_{m0})$$

But $m = M/v$, where v is the molar volume of the mixture. Hence,

$$m = 1/v [1/M_0 + v(c_{\alpha 0} - c_\alpha)] = m_0 / [1 + vM_0(c_{\alpha 0} - c_\alpha)] \quad (13)$$

It is the simplicity of this expression that justifies the expression of concentration in moles per unit weight rather than in moles per unit volume.

Now let $f = c_\alpha / c_{\alpha 0}$ and $\zeta = x/L$, where L is the length of the reactor. Equation 5 becomes:

$$\frac{Gc_{\alpha 0}}{L} \frac{df}{d\zeta} = m\Gamma_\alpha + \frac{D_\alpha m_0 c_{\alpha 0}}{L^2} \frac{d^2}{d\zeta^2} \left[\frac{f}{1 + vM_0 c_{\alpha 0} (1 - f)} \right] \quad (14)$$

in which D_α , the diffusivity, is assumed to be independent of the composition of the mixture, and v , the molar volume, is constant since the pressure is constant.

It is now necessary to make some assumption concerning the reaction velocity, $m\Gamma_\alpha$. A simple illustrative example will be to suppose

$$m\Gamma_\alpha = -k_n (mc_\alpha)^n \quad (15)$$

That is, A_α disappears by an n th order reaction involving no other components of the mixture. Using Equation 13,

$$m\Gamma_\alpha = -k_n \left(\frac{M_0 c_{\alpha 0}}{v} \right)^n \frac{f^n}{[1 + vM_0 c_{\alpha 0} (1 - f)]^n} \quad (16)$$

The term $M_0 c_{\alpha 0}$ represents the mole fraction of A_α in the feed mixture. Thus Equations 14 and 16 include the possible presence of inert components in the feed mixture. Equation 14 becomes:

$$\frac{Gv}{M_0 L} \frac{df}{d\zeta} = -k_n \left(\frac{M_0 c_{\alpha 0}}{v} \right)^{n-1} \left[\frac{f}{1 + vM_0 c_{\alpha 0} (1 - f)} \right]^n + \frac{D_\alpha}{L^2} \frac{d^2}{d\zeta^2} \left[\frac{f}{1 + vM_0 c_{\alpha 0} (1 - f)} \right] \quad (17)$$

The controlling ratios are seen to be

$$\begin{aligned} S &= Gv/M_0 L = G/m_0 L \\ t_{D/2} &= D_\alpha/L^2 \\ \gamma_n &= k_n (M_0 c_{\alpha 0}/v)^{n-1} \end{aligned}$$

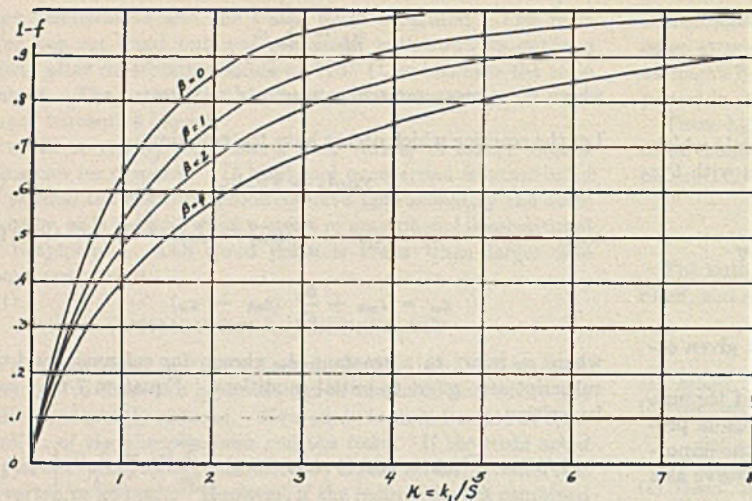


Figure 1. Yield of Product ($1-f$) vs. Time-Temperature Parameter
First-order kinetics, diffusion negligible. $\kappa = k_1/S$; $\beta = \gamma M_0 C_{A0}$

The ratio S has the dimensions sec.^{-1} and is the familiar space velocity (vol./vol./sec.) used in engineering. The factor $t_D/2$ has dimensions sec.^{-1} and is best understood in terms of Einstein's diffusion law,

$$t_D = L^2/2D$$

which gives the time required for a molecule to diffuse a distance L . The third factor gives the dependence on feed composition ($M_0 C_{A0}$), total pressure (RT/v), and specific reaction rate (k_n).

Thus, in general, two ratios, γ_n/S and t_D/S , must be kept constant if constant yields are to be maintained. This fact contains the key to rational design of pilot plants and full-scale units from data on other units. The situation is inherently more complicated than when only the flow pattern is to be considered, since here there are two dimensionless ratios instead of only one. Since the diffusivity, D_a , is generally small, whereas L is large in comparison, the last term of Equation 17 is of little importance in most practical cases. When this is true, Equation 17 states that the yield will depend solely upon the space velocity and feed composition at constant temperature and pressure, since k_n and v are functions of temperature and pressure only.

All this is well known. However, it should be pointed out that the space velocity considered here is that of the feed. Its reciprocal, the apparent contact time, is less than the actual contact time for all constant-pressure reactions in which the total number of moles increase ($\nu > 0$). In these cases it is difficult to calculate a contact time exactly. However, Equation 17 states that even then yields depend

only on the space velocity of the feed. Thus runs on the same reaction may be properly compared at equal-feed space velocities, regardless of the extent of reaction. The form of the functional dependence of yield upon space velocity will vary with the value of ν and will differ from that for the corresponding nonflow reaction system. This form can be found by integrating Equation 17 when the kinetic order is known, or empirically from a series of experiments in which the space velocity is varied.

Thus, when diffusional effects are negligible, one series of experiments at various space velocities and constant temperature would enable one to plot $f(\gamma_n/S)$. Similarly, a series of experiments at constant space velocity and different temperatures would give $f(\gamma/S_0)$. Since the ratio γ/S alone controls the yield, it is obvious that time and temperature are compensating factors. When the function $f(\gamma/S)$ is known theoretically or empirically, it becomes possible to predict just what adjustments in feed rate or equipment size must be made to compensate for a change in operating temperature. The criterion is that yields will be maintained when γ/S is restored to its initial value. Thus a great deal of data can be organized for predictive purposes even though the analytical formulation is difficult.

This presupposes that γ can be calculated for each case, which requires a knowledge of the rate constant k_n as well as the mechanism of the reaction. Occasionally these can be obtained from nonflow experiments. For the static case Equation 4 reduces simply to $dc_k/dt = m\Gamma_k$.

Equation 14 may be considered to give the transition from static to flow conditions when the reaction mechanism is the same in both cases. More often, however, only flow data will be available and the mechanism must be deduced from the data. The procedure will then be to plot contour lines of $S(\gamma)$ for constant values of f . Since γ/S is a constant for each of these lines,

$$\gamma/S = \kappa = k_n \left(\frac{M_0 C_0}{v} \right)^{n-1} \frac{m_0 L}{G} \quad (18)$$

Hence, if $k_n = A_n \exp. (-E/RT)$,

$$\ln [\kappa/A_n (M_0 C_0)^{n-1}] - (n-1) \ln v + \ln S = -E/RT$$

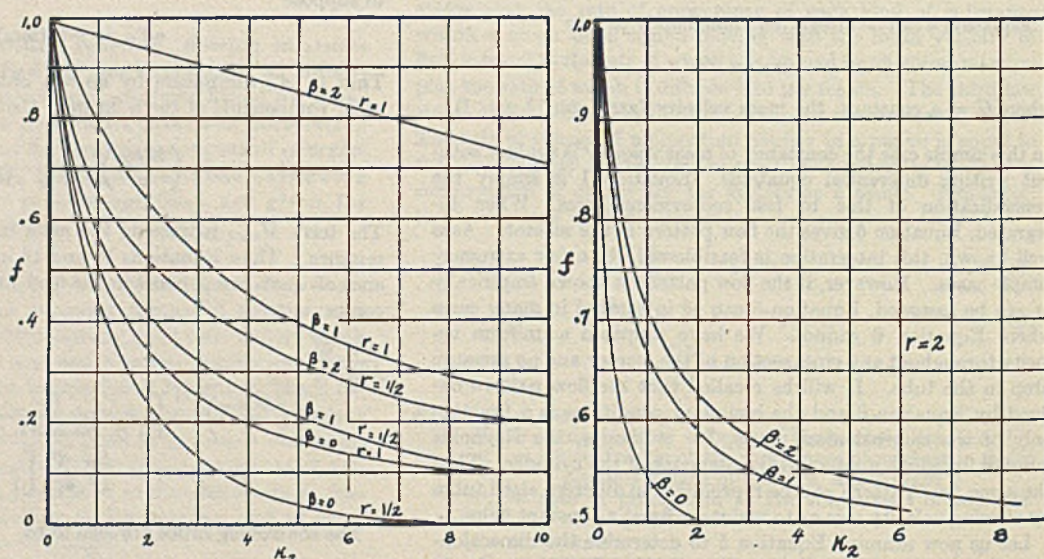


Figure 2. Fraction of Reactant A_2 Remaining (f) vs. Time-Temperature Parameter
Second-order kinetics, diffusion negligible. $\kappa_2 = k_2 M_0 C_{A0}^2/S$; $\beta = \gamma M_0 C_{A0}$; $r = C_{A0}/C_{B0}$

Thus at constant molar volume v and constant feed composition, a plot of space velocity S , required at each temperature to maintain constant yield, as a function of $1/T$ gives a straight line whose slope is proportional to the activation energy, regardless of the reaction order. Having determined E , a plot of $\ln v$ against $1/T$, holding S constant, yields another straight line of slope $E/R(n-1)$. Since E is known, n can be determined.

The remarkably simple connection between space velocity of feed and temperature at constant yield holds for a wide variety of reaction mechanisms. A little calculation will show that the relation holds whenever the kinetics can be expressed in terms of only one over-all rate constant. For reactions involving more than one kind of molecule, the order n is the sum of the exponents in

$$m\Gamma_\alpha = k_n(m c_\alpha)^p(m c_\beta)^q(\dots)(m c_\omega)^r$$

$$n = p + q + \dots + r$$

Thus the flow system would appear to afford a means of determining activation energies much more directly than the static system.

Absolute rate constants, moreover, are no more difficult to calculate. The value of γ/S must now be determined experimentally by comparison of theoretical and actual yields as a function of γ/SA_n for various values of A_n .

FIRST-ORDER REACTIONS. As an example we shall integrate Equation 17 for $n = 1$ when diffusion is negligible:

$$S \frac{df}{d\xi} = - \frac{\gamma f}{1 + \beta(1-f)} \quad (19)$$

where $\gamma = k_1$ and $\beta = \nu M_{0c_0}$, the mole per cent increase when reaction has gone to completion. Equation 19 is readily integrated to give:

$$\beta(1-f) + (1+\beta) \ln f = -\gamma/S = -\kappa \quad (20)$$

Figure 1 is a graph of this relation for several values of β . For any given experimental conditions, κ/A can be found from Equation 18 after E and n are determined, and κ can be obtained by substituting the known yield in Equation 20. Thus A_1 is readily found and, hence, the specific rate constant.

SECOND-ORDER REACTIONS. Second-order reactions are treated as easily when diffusion may be neglected:

$$m\Gamma_\alpha = -k_2(m c_\alpha)(m c_\beta)$$

so that Equation 19 is replaced by

$$S \frac{df}{d\xi} = -k_2 m_{0c_0} \beta_0 \frac{f[1-r(1-f)]}{[1+\beta(1-f)]^2}$$

where $r = a_\beta c_{\alpha 0}/a_\alpha c_{\beta 0}$, and the chemical equation is Equation 8. Writing $\gamma_2 = k_2 M_{0c_0} \beta_0/v$ and $\gamma_2/S = \kappa_2$,

$$-\kappa_2 = \int_1^f \frac{f[1-r(1-f)]}{[1+\beta(1-f)]^2} df \quad (21)$$

The ratio κ_2 has the same form as Equation 18 so that the dimensional analysis and conclusions given there hold for this case as well. Equation 21 may be integrated to give, for $r \neq 1$,

$$-\kappa_2 = \frac{(1+\beta)^2}{1-r} \ln f - \frac{(r+\beta)^2}{(1-r)r^2} \ln [1-r(1-f)] - \frac{\beta^2(1-f)}{r} \quad (22)$$

When $r = 1$,

$$\kappa_2 = (1+\beta)^2 \frac{(1-f)}{f} (1+\beta^2 f) + 2\beta(1+\beta) \ln f \quad (23)$$

When $\beta = 0$, there is no increase in the total number of moles flowing and these two equations reduce to their static analogs, respectively:

$$-\kappa_2 = \frac{1}{1-r} \ln \frac{f}{1-r(1-f)} \quad (22A)$$

$$\kappa_2 = (1-f)/f \quad (23A)$$

In this case the actual contact time is $1/S$. The case $r = 1$ is identical with the case of a second-order reaction involving only one component.

Figure 2 shows plots of Equations 22 and 23 for various values of r and β . It should be noted that f refers to the fraction of component A_α remaining. Hence, when r is greater than unity, all of A_β will be used up before A_α is gone. Hence f will have a lower limit below which it cannot fall. This value, of course, is zero when $r \leq 1$ and A_β is no longer the limiting component in the reaction.

LIQUID PHASE. The preceding analysis is equally valid for gas, liquid, or mixed phase reaction, provided the actual values are used for v , the molar volume of the mixture. When a large amount of diluent is present, the mole fraction of reference component A_α is very small. Hence, from Equation 13, $m = m_0$ to a sufficient approximation. The appropriate formulas in this case are those for which $\beta = \nu M_{0c_0} = 0$. When the molar volume varies significantly with composition, one must usually resort to numerical integration of the differential equations.

Nonisothermal reactions can be treated in the same way if the actual temperature at each point in the reactor is known:

$$\kappa_n = \int_0^1 \frac{1}{S} \frac{A_n (M_{0c_0})^{n-1}}{[RT(\xi)]^{n-1}} \frac{p^{n-1} e^{-E/RT(\xi)}}{d\xi}$$

When $T(\xi)$ is known, κ_n can be found by a numerical integration.

AXIAL DIFFUSION IN ONE-DIMENSIONAL CASE

We have assumed hitherto that, for most cases, diffusion parallel to the direction of mass flow would be negligible. It remains to show for what range of controllable variables this will be true.

For the one-dimensional case, Equation 17 may be rewritten:

$$\lambda(1+\beta) \frac{d^2 f}{d\xi^2} + \frac{2\lambda\beta(1+\beta)}{1+\beta-\beta f} \left(\frac{df}{d\xi} \right)^2 - (1+\beta-\beta f)^2 \frac{df}{d\xi} - \kappa_n f^n (1+\beta-\beta f)^{n-2} = 0 \quad (24)$$

$$\begin{aligned} \text{where } \kappa_n &= (k_n/S)(M_{0c_0}/v)^{n-1} \\ \lambda &= D/L^2 S \\ \beta &= \nu M_{0c_0} \end{aligned}$$

Since it is a second-degree reaction, Equation 24 will require two boundary conditions to specify its solutions uniquely. One of these is given by $f(0) = 1$, which states that there is no decomposition of the feed before it enters the reactor. A second condition can be obtained by considering conditions at the exit of the reactor. We shall suppose that there is an abrupt decrease in the diameter of the reactor where it joins the outlet tube. This will cause the fluid to be sharply accelerated as it enters the outlet. We shall suppose this region of acceleration to be infinitely thin, so that there will be a discontinuity in the mass velocity G at the reactor outlet. This idealization is no more serious than the assumption of uniform velocity in every cross section.

If A_1 and A_2 are the cross-sectional areas of the reactor and outlet, respectively, conservation of matter at the outlet requires that

$$G_1 A_1 c_j - D A_1 \frac{d m c_j}{d x} = G_2 A_2 c_j - D A_2 \frac{d m c_j}{d x} \quad (25)$$

for each component j in the fluid. But at constant pressure the total number of moles per cc. in the fluid is constant. That is, $\Sigma m c_j = 1/v = p/RT$ everywhere in the reactor and outlet. Summing Equation 25 for all components gives $G_1 A_1 = G_2 A_2$ and hence $d(m c_j)/dx = 0$ at the exit of the tube. Similar conditions do not prevail in the interior of the reactor, since the amount of reaction going on is just sufficient to maintain the

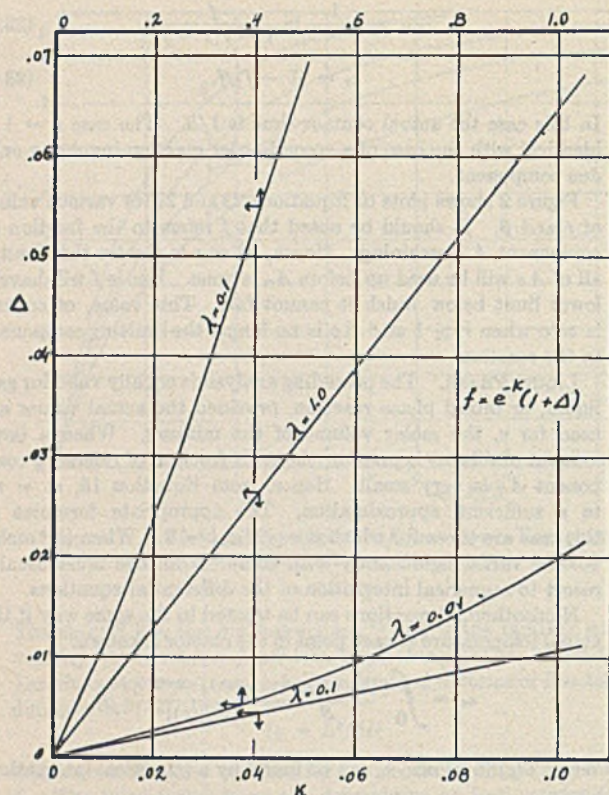


Figure 3. Effect on Yield of Diffusion in Direction of Flow First-order kinetics. $f = e^{-κ}$ when $λ = 0$ (diffusion negligible) $κ = k_1/S$; $λ = D/L^2S$

steady-state concentration gradient. At the exit, however, where reaction ceases, no concentration gradient can exist in the steady state.

Summarizing, the appropriate boundary conditions for Equation 24 are

$$f(0) = 1; f'(1) = 0 \quad (26)$$

The integration of Equation 24 is difficult since it is not linear in the differential operator. This obstacle vanishes however for those reactions in which there is no change in the total number of moles flowing. In this case $β = 0$, and for a first-order reaction,

$$\frac{d^2f}{dx^2} - \frac{1}{λ} \frac{df}{dx} - \frac{κ}{λ} f = 0 \quad (27)$$

$$\begin{aligned} f(0) &= 1 & κ &= k_1/S \\ f'(1) &= 0 & λ &= D/S L^2 \end{aligned}$$

This linear differential equation with constant coefficients is readily integrated under the given boundary conditions to give

$$f(1) = α e^{1/2λ} / [\sinh α/2λ + α \cosh α/2λ] \quad (28)$$

where $α = +\sqrt{1 + 4κλ}$

When diffusional effects are small, $G \gg D$, and hence $κλ \ll 1$. The square roots can then be expanded so that Equation 28 gives

$$f(1) = e^{-κ} \left[\frac{1 + 2κλ}{1 + κλ(1 + e^{-(1/λ + κ)})} \right] \quad (29)$$

correct to the first power of $κλ$. For $λ = 0$, this becomes just $f(1) = \exp(-k_1\tau)$, where $\tau = 1/S$ is, in this case, the actual as well as apparent contact time. The factor

$$\Phi = (1 + 2κλ)/(1 + κλ) = 1 + \Delta$$

serves to estimate the effect of a small diffusivity on the conversion. We see that diffusion shortens the contact time and leaves more unreacted material in the outlet gas than when it is negligible. Figure 3 is a plot of Δ for several values of $κ$ and $λ$. It shows that yields may be reduced by only 1% when $κλ = 10^{-2}$. This represents close to a maximum value in practice. For example, if $k_1 = 10^{13} \exp.(-18,000/RT)$, $T = 162^\circ \text{C.}$, $D = 10^{-2} \text{ cm}^2 \text{ sec}^{-1}$, $L = 100 \text{ cm.}$, and $S = 1$, we find $κλ = k_1 D/S^2 L^2 = 10^{-2}$. If $κλ$ is less than 10^{-2} , the effect of diffusion is negligible ($< 0.1\%$). Thus the diffusion of reactant in the direction of flow will modify the expected yield only for very low space velocities or for relatively fast reactions where steep concentration gradients are set up.

This numerical example made use of a diffusivity for laminar flow. When, as is the usual practical case, the flow is turbulent, the effective diffusivity varies with the mean velocity and is of the order of 10–100, approximately 10^3 times as great as in the laminar case. But this high turbulent diffusivity is reached only at high space velocities. Hence the parameter $λ$ is small even in the turbulent region. This may be seen by expressing it in terms of the Reynolds number, $Re = Gd/\eta$, where d is the hydraulic radius and η the viscosity of the fluid. Remembering that $S = G/m_0 L$, $S = \eta Re/m_0 L D$ and

$$λ = m_0 D d / \eta Re L$$

For gases η/m_0 , the kinematic viscosity, is of the order of unity. The ratio d/L is small by the conditions of our problem. Since turbulence sets in at $Re = 2000$, the ratio D/Re is never greater than 10^{-2} . Thus $λ$ falls well below the value (10^{-2}) at which diffusion becomes a significant mode of mass transport.

When reaction results in an increase in the total number of moles of fluid, $β$ is no longer zero and the preceding integration is not applicable. Qualitatively it is clear that the concentration gradient will be steeper in this case, since the reactant is being diluted by products as well as decomposed. Therefore one would expect a somewhat more rapid diffusion. However, since $β$ rarely exceeds 3 or 4, this effect should not be large. Actual integration of Equation 24 can be carried out only by successive approximations, but it is improbable that the criterion for importance of diffusion will be much modified.

FUNDAMENTAL EQUATIONS

Consider an infinitesimal element of volume in a fluid into and out of which there is mass transport by flow and diffusion and within which chemical reaction is occurring. Let the concentration of the k th component of the fluid be c_k moles per gram of fluid mixture, let its molecular weight be M_k , and let its velocity be V_k . Let m be the density of the fluid mixture in grams per cc. Then the total rate of transport of material across unit area of the y, z plane is

$$\sum_{k=1}^N m M_k c_k (V_k)_x = m (V)_x \quad (30)$$

This equation serves to define the x component of the average velocity, V . The factor $M_k c_k$ is the weight fraction of the k th component in the mixture. The diffusion velocity, U_k , is now defined by

$$U_k = V_k - V \quad (31)$$

By Fick's law of diffusion,

$$-m c_k U_k = D_k \nabla m c_k \quad (32)$$

where D_k is the coefficient of diffusion ($\text{cm}^2\text{sec}^{-1}$) of the k th component in the mixture and ∇ is the operator of the gradient. The negative sign appears because the gradient has the direction of increasing concentration whereas the diffusion velocity has the direction of decreasing concentration.

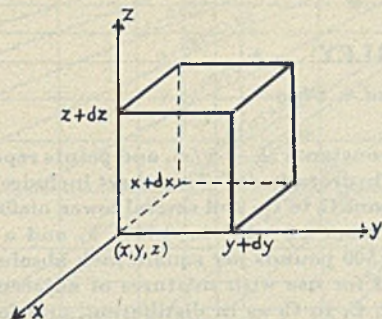


Figure 4

The equation of mass component change is easily derived. Consider a cubical volume element of dimensions dx , dy , and dz having one corner at the point x , y , z . Consider flow parallel to the x axis. For the k th component, we have $-mc_k(V_k)_x dy dz$ ($\text{gram cm}^{-2}\text{sec}^{-1}$) flowing out through the rear face (Figure 4).

At the front face the concentration is $mc_k + \frac{\partial mc_k}{\partial x} dx$ and the flow into the volume element through the front face is:

$$- \left[mc_k + \frac{\partial mc_k}{\partial x} \right] \left[(V_k)_x + \frac{\partial (V_k)_x}{\partial x} dx \right] dy dz$$

Hence the net accumulation per second in the volume element is:

$$- \frac{\partial}{\partial x} (mc_k(V_k)_x) dx dy dz$$

Repeating the reasoning for the other two pairs of faces and summing, we have for the total rate of accumulation by mass transport into the volume element:

$$-\nabla \cdot mc_k \mathbf{V}_k dx dy dz$$

Now let the rate at which component k is formed by chemical reaction within the volume element be Γ_k moles $\text{gram}^{-1}\text{sec}^{-1}$. The total rate of accumulation of k by all processes is given by

$$\frac{\partial mc_k}{\partial t} = m\Gamma_k - \nabla \cdot mc_k \mathbf{V}_k \quad (33)$$

By similar reasoning we obtain the usual equation of continuity for the fluid mixture:

$$\frac{\partial m}{\partial t} = -\nabla \cdot m\mathbf{V} \quad (34)$$

That this equation is consistent with the definition of \mathbf{V} in Equation 30 is shown by Eckart (5). Equation 31 may now be substituted into Equation 33 giving

$$m \frac{\partial c_k}{\partial t} + c_k \frac{\partial m}{\partial t} = m\Gamma_k + \nabla \cdot D_k \nabla mc_k - c_k \nabla \cdot m\mathbf{V} - m\mathbf{V} \cdot \nabla c_k$$

by Fick's law. But the second term on the left equals the third term on the right by Equation 34, so that

$$m \left[\frac{\partial c_k}{\partial t} + \mathbf{V} \cdot \nabla c_k \right] = m\Gamma_k + \nabla \cdot D_k \nabla mc_k \quad (35)$$

The term in brackets on the left is the total derivative of c_k , the derivative following the motion of the volume element. Hence

Equation 35 states that the rate of accumulation of the k th component in the moving volume element is equal to the sum of the rate of its chemical production and the rate at which it diffuses into the volume element.

For the derivation of hydrodynamic Equation 3, reference should be made to any standard treatise on hydrodynamics.

HISTORICAL

So far as is known, the general hydrodynamic equations for reacting fluids have not been applied previously in the discussion of reaction kinetics in flow systems. Several special cases have been worked out as needed in past investigations. Among these may be mentioned work by Bodenstein and Wolgast (3), Benton (2), Förster and Geib (6), Hougen and Watson (7), Thiele (10), and Wenner (11). The excellent qualitative discussion by Damköhler (4) does not develop the practical formulation. The general hydrodynamic equations are given for reacting fluids by Bateman (1) and Eckart (5), but without any discussion of their significance for the sort of problem we have considered. The interesting work of Rashevsky (8) on diffusion, metabolism, and stability of cells is developed independently from the same principles. Many empirical formulations of "time-temperature factors" in flow systems owe their success to the degree to which they approximate the factors derived in this theoretical treatment. Nonisothermal systems are treated rigorously by Wilhelm, Johnson, and Acton (12), who derive fundamental equations.

CONCLUSIONS

It is evident that, when properly analyzed, data on flow systems furnish kinetic information fully as reliable as that from static experiments. The foregoing analysis is applicable rigorously only for homogeneous reactions in long tubes. It will fail if the mechanism of reaction changes with the pattern or velocity of flow, as may be the case when surface reactions control the rate. If adsorption reaches equilibrium, it will still be possible to express the reaction velocity as a function of the bulk phase concentrations through the adsorption isotherm. At fast flow rates, however, diffusion radially to the reactor or catalyst surface will be rate controlling. In this case the previous analysis must be revised.

ACKNOWLEDGMENT

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Correlation of Vapor-Liquid Equilibria Data for Hydrocarbons

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Empirically it has been found that, for the *n*-paraffin hydrocarbons from propane through *n*-octane, the vapor fugacity f_v is a single function of total pressure at conditions of constant liquid fugacity. It was known previously that, for a given substance, liquid fugacity f_L is a single function of temperature. By employing these two relations, values derived from the experimental vapor-liquid equilibria data of Katz and Hachmuth (4) have been correlated. The correlation is presented in the form of an alignment chart with scales for temperature, pressure, and

equilibrium constants ($K = y/x$), and points representing various light hydrocarbons. This chart includes *n*-paraffin hydrocarbons C_1 to C_{14} and several lower olefins over a temperature range of -10° to $+700^\circ$ F. and a pressure range of 1 to 500 pounds per square inch absolute. It is recommended for use with mixtures of adjacent hydrocarbons—e.g., C_1 to C_4 as in distillation, and for lighter components absorbed in heavier. Other incidental uses are in estimation of vapor pressures and extrapolation of vapor-liquid equilibria data.

VAPOR-liquid equilibria data are used in designing equipment for distillation, condensation, or absorption operations. The correlation presented here should be useful when it is desired to extend the range of meager vapor-liquid equilibria data or to approximate unknown vapor-liquid equilibria data from such other properties as may be known—e.g., vapor pressure data.

Vapor-liquid equilibria data are usually expressed in the form of equilibrium constants. These constants may be determined experimentally as follows: A liquid hydrocarbon mixture is brought to equilibrium with its vapor at a definite temperature and pressure. The equilibrium constant, K , of a given substance is then found by analyzing vapor and liquid and dividing the mole fraction in the vapor, y , by the mole fraction in the liquid, x .

Among the first to measure equilibrium constants ($K = y/x$) were Souders, Selheimer, and Brown (14). More recently Katz and Hachmuth (4) measured equilibrium constants for mixtures of natural gas and mid-continent crude. They prepared charts of equilibrium constants for methane through "heptanes and heavier" on which the temperature range is -30° to $+270^\circ$ F. and the pressure range is 5 to 3000 pounds per square inch absolute. Brown and White (1), working with a naphtha and distillate furnace oil, determined equilibrium constants through the relatively large temperature range 0° to 1000° F. (approximate) and pressure range 10 to 1000 pounds per square inch absolute (approximate). Standing and Katz (15) made similar measurements on mixtures of natural gas and crude oil in which pressures up to 8200 pounds per square inch were used. The thermodynamic properties of systems such as propane-*n*-pentane were evaluated by Sage, Lacey, and colleagues (11). As a result of their work, the vapor-liquid equilibria relations of many relatively simple systems have been fixed.

Vink *et al.* (17) and Kirkbride and Bertetti (6) studied the effect of solvent

on equilibrium "constants". The correlation presented here depends on data obtained with mid-continent crude as the solvent or base.

CALCULATION OF EQUILIBRIUM CONSTANTS

The preceding paragraphs refer to equilibrium constants experimentally determined by analysis of liquid and vapor in equilibrium. These constants may also be determined approximately by calculation from the fugacity. The fugacity concept is described by Lewis and Randall (7). The development from the equilibrium constant expressed in terms of mole fractions to that in terms of fugacities will be briefly reviewed since fugacity is used in the correlation to be presented here.

Raoult's law may be combined with Dalton's law in the form.

$$p_a = Py_a = P^o_a x_a \quad (1)$$

where p_a = partial pressure of component a over a mixture in vapor-liquid equilibrium

P = total pressure

P^o_a = vapor pressure of pure component a at temperature of mixture

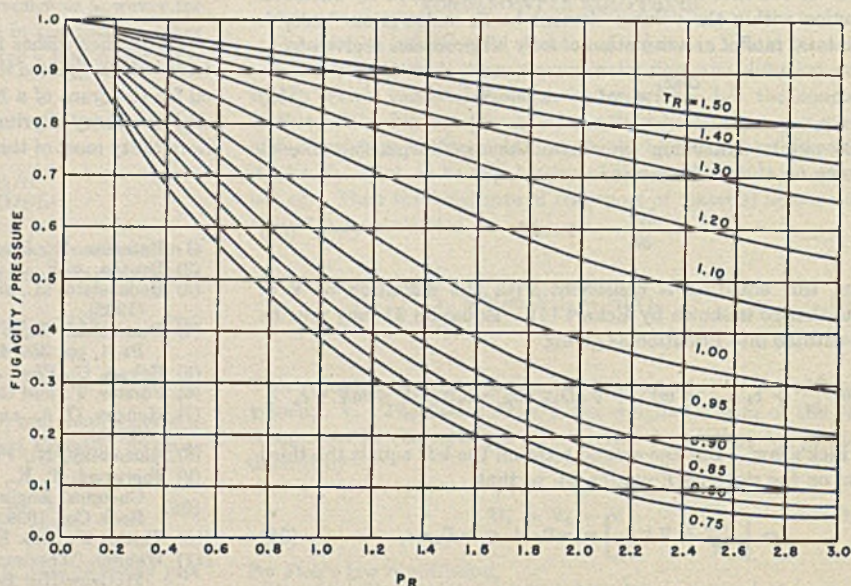


Figure 1. Fugacities of Hydrocarbons Plotted on a Reduced Basis

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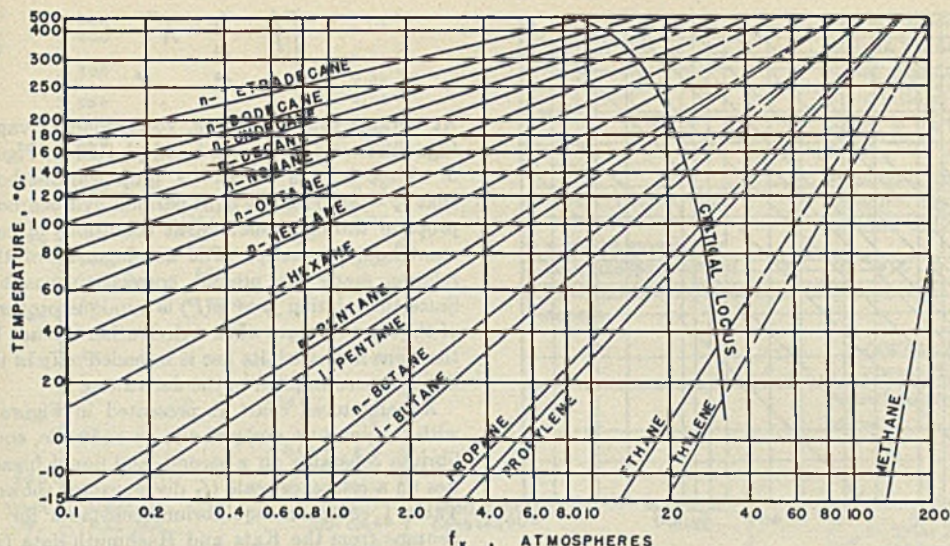


Figure 2. Fugacities of Liquid Hydrocarbons

Since $Py_0 = P^0x_0$

then $y_0/x_0 = P_0^0/P$

$$\text{or } K_a = P^0/P \quad (2)$$

in regions of relatively low pressure when the Raoult and Dalton laws apply. At higher pressures the simplicity of Equation 2 may be kept by using the modification:

$$K = f_x/f_y \quad (3)$$

where f_x = fugacity of a pure liquid component under its own
vapor pressure at temperature of system
 f_v = fugacity of a pure component in vapor at temperature
and total pressure of system

f_v = fugacity of a pure component in vapor at temperature and total pressure of system

A liquid fugacity f_x is sometimes called a "corrected" vapor pressure; and a vapor fugacity is sometimes called a "corrected" total pressure although, as Weber (18) indicates, it is probably better to state that fugacity approaches pressure as pressure approaches zero.

Fugacities of hydrocarbons to be used as indicated above can be obtained by graphical integration of equations involving compressibility data. These data have been determined experimentally from the P - V - T relations of the hydrocarbons. Lewis and Kay (8) correlated fugacity data for light hydrocarbons as shown in Figure 1. From this figure vapor fugacity f_v of Equation 3 may be obtained. From data included in Figure 1, Kay (5) prepared a plot (Figure 2) similar to a Cox chart (2) from which liquid fugacity f_L of Equation 3 may be obtained. [It is interesting to note that the liquid fugacities could be arranged on an Othmer type of plot (9), using a substance such as n -pentane for reference. The slope of the resulting straight line for a given hydrocarbon would then be equal to the ratio of the heats of evaporation of that hydrocarbon and n -pentane.] For illustration, the equilibrium constant for n -pentane at 5 atmospheres absolute pressure and 200° F. may be calculated by the use of Figures 1 and 2. The critical temperature T_c of n -pentane is 470.3° K., the critical pressure P_c is 32.8 atmospheres:

$$\frac{T}{T_c} = T_R = \frac{366.4}{470.3} = 0.778 \quad (4)$$

$$\frac{P}{P_c} = P_R = \frac{5.0}{32.8} = 0.1526 \quad (5)$$

From Figure 1, $f_v/P = 0.88$:
 $f_v = 0.88 \times 5 = 4.40$ atm.
 From Figure 2, at 200° F
 (93.3° C.) $f_z = 4.27$ atm.

$$K = \frac{f_z}{f_y} = \frac{4.27}{4.40} = 0.97 \quad (\text{h})$$

Equilibrium constants for methane through octane, calculated according to the above procedure by Taylor and Parker (16), are tabulated by Sherwood (12). Before proceeding with the present correlation which

makes use of the fugacity, four previous correlations will be mentioned.

CORRELATION

By the use of *n*-pentane as a reference substance, Shiah (13) gathered the vapor-liquid equilibria data for the light hydrocarbons on a single chart. Gilliland and Scheeline (3) recently presented a correlation of minimum values of equilibrium constants for the less volatile components occurring in various binary systems. Brown and White (1) made a plot similar to Gilliland's Figure 10 (3) which includes data for additional binary mixtures and for complex mixtures. In another cor-

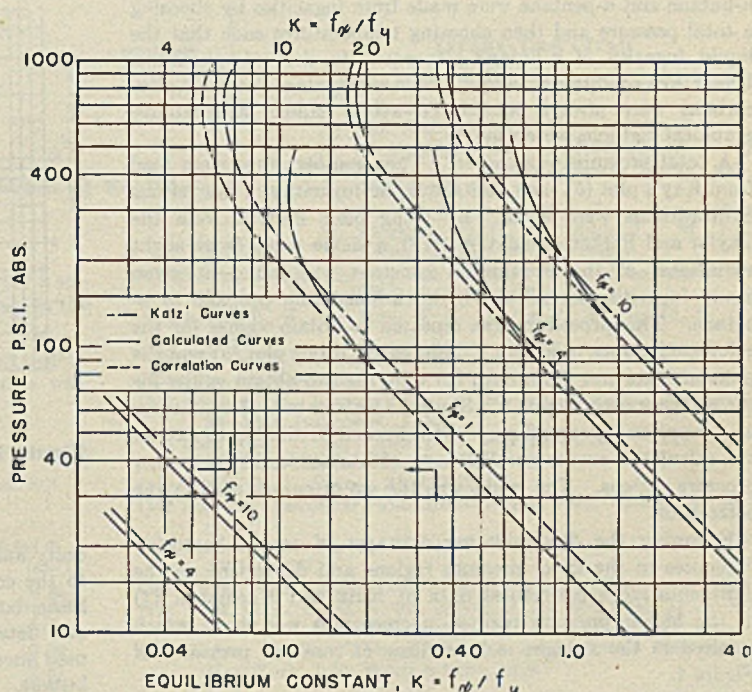


Figure 3. Equilibrium Constant Data Plotted in Terms of Liquid Fugacity and Total Pressure

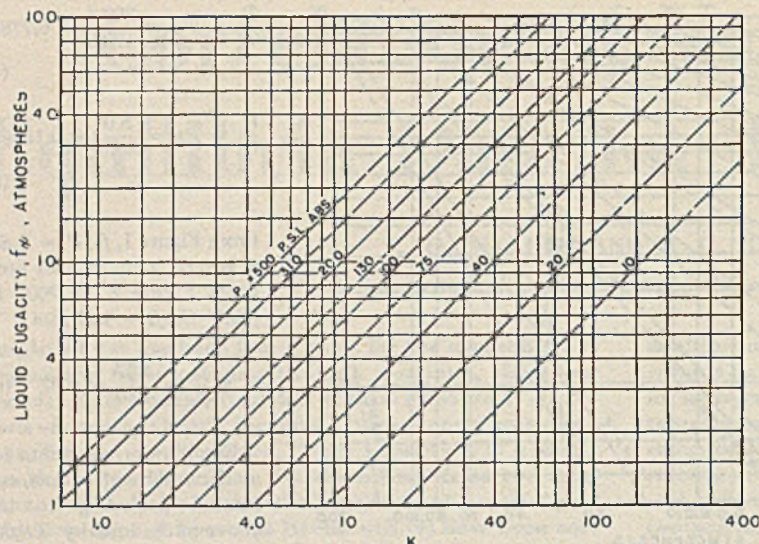


Figure 4. Liquid Fugacity vs. Equilibrium Constant at Various Pressures

relation made by Othmer (10), calculated equilibrium constants are correlated by vapor-pressure data of a reference substance.

It will be recalled that liquid fugacity f_z is sometimes likened to a corrected vapor pressure and that vapor fugacity f_v is sometimes likened to a corrected total pressure. From Figure 2 it is evident that temperature fixes the liquid fugacity of a given hydrocarbon. It was found empirically that total pressure fixes, with satisfactory approximation, the vapor fugacity for a given hydrocarbon for pressures up to about 500 pounds per square inch absolute at conditions of constant liquid fugacity. Thus, if temperature and total pressure are known, the former fixes the numerator in $K = f_z/f_v$, and the latter fixes the denominator. The manner in which it was found that $f_v = \phi(P)$ follows:

Some preliminary calculations of equilibrium constants for *n*-butane and *n*-pentane were made from fugacities by choosing a total pressure and then choosing temperatures such that the liquid fugacity of *n*-butane was equal to that of *n*-pentane. Under such conditions the equilibrium constants of the two hydrocarbons were always equal. To avoid tedious calculations, graphical methods were used.

A total pressure was chosen. Then temperatures were read from Kay's plot (5) such that the liquid fugacities of the various hydrocarbons were equal. By using plots derived from the Taylor and Parker calculations (16), a single value (with slight variations) of the equilibrium constant was found at given liquid fugacities for all the hydrocarbons from propane to *n*-octane. This procedure was repeated to obtain values for the calculated curves of Figure 3. Similarly, Kay's plot (5) and the plots of Katz and Hachmuth (4) were used to obtain values for the Katz curves of Figure 3. Since the Katz data are for mixtures of normal and isoparaffins, it was deemed justifiable to extend the calculated curves parallel to the Katz curves in the higher pressure regions. The result was the set of curves used in the correlation.

Following the determination of a set of curves based on fugacities in the lower pressure regions and dependent on the representative experimental data of Katz and Hachmuth (4) in the higher pressure regions, a cross plot was made which resulted in the straight isobars (lines of constant pressure) of Figure 4.

The ratio of liquid fugacity to equilibrium constant at points along a given isobar was found to give a single value of vapor fugacity:

$$\left[\frac{f_z}{K} = \frac{f_z}{f_v} = f_v \right]_P \quad (7)$$

At various total pressures, corresponding vapor fugacities were determined and plotted on Figure 5. Thus it was shown by graphical methods that $f_v = \phi(P)$ for the light paraffin hydrocarbons propane through *n*-octane at conditions of constant liquid fugacity. The development of this relation made the present correlation possible. Since the relation $f_v = \phi(P)$ is a unique property of the fugacity data when a derivation is made by the steps indicated, its use is intended only in the limited sense implied in the derivation.

An alignment chart is presented in Figure 6 with temperature and pressure on one scale, equilibrium constants on a second, and liquid fugacities on a reference scale (f_z divisions not shown). Table I compares equilibrium constants for *n*-pentane from the Katz and Hachmuth data (4), the calculated data (16), and the present correlation. The alignment chart values agree with the calculated data at pressures up to 80 pounds per square inch absolute with the exception of methane, ethylene, and ethane. The points for *n*-C₈ through *n*-C₁₄ are based solely on calculated data.

USES

The alignment chart condenses the equilibrium constant data from the correlation curves of Figures 3 and 4. The chart has several incidental uses, a few of which follow. Estimation of vapor pressures is possible by aligning temperature and the point for a substance, and determining at what pressure the equilibrium constant is equal to unity. Estimation of boiling points is possible by aligning pressure with an equilibrium constant equal to

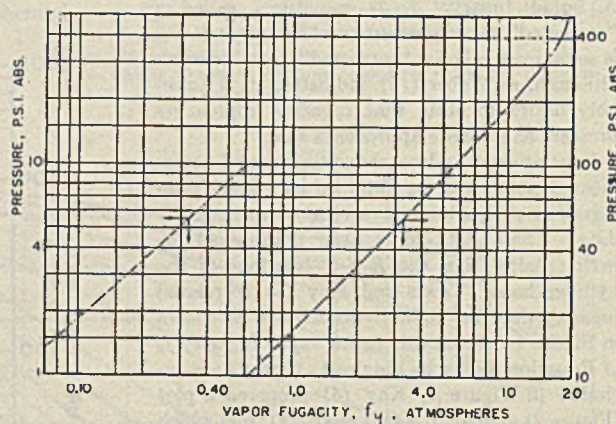


Figure 5. Equilibrium Constant vs. Vapor Fugacity at Conditions of Constant Liquid Fugacity

unity and running an index through the point for a substance to the corresponding temperature. Meager vapor-liquid equilibria data may be extended by plotting the few data available and determining their point locus. This procedure has been used successfully on such systems as hydrogen chloride and *n*-butane. The point locus for such a system does not fall on the straight line connecting the *n*-paraffin hydrocarbons, illustrating the fact that the equilibrium constant for a given substance at a given temperature and the total pressure varies from one solvent

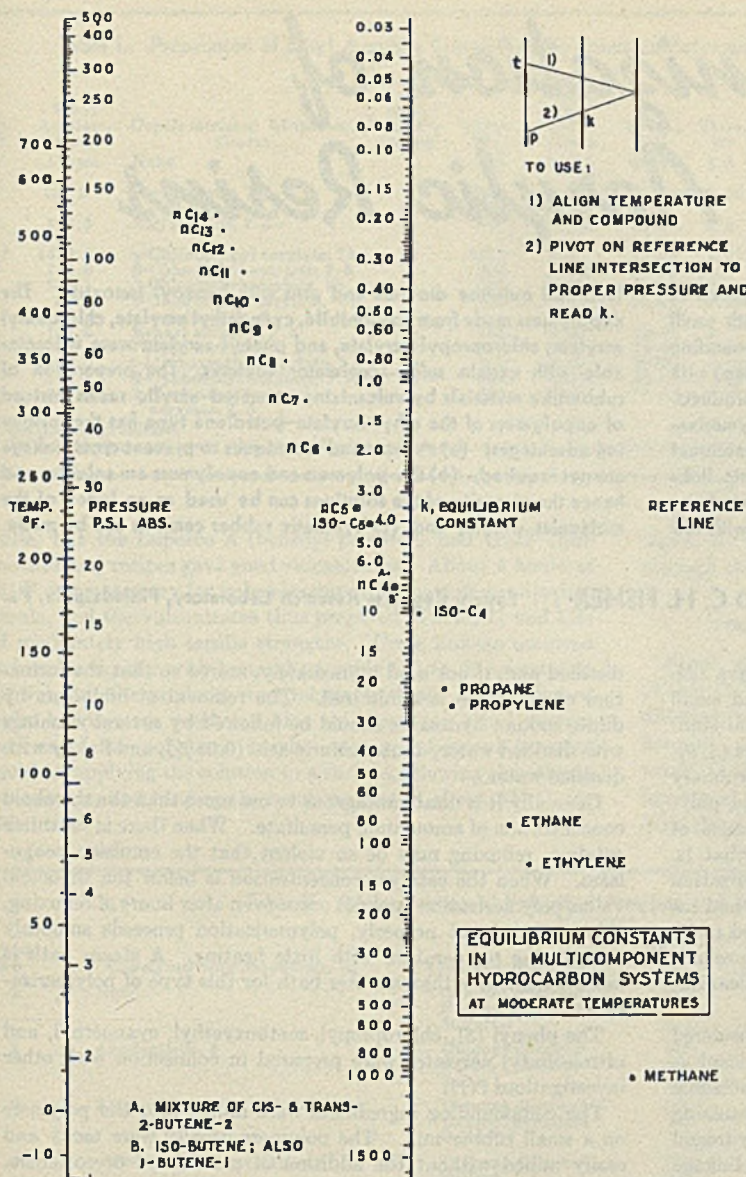


Figure 6. Alignment Chart Presenting Correlation of Equilibrium Constants

to another. This variation is not great, fortunately, from a solvent such as a gas oil to one such as a mid-continent crude in the case of light hydrocarbon solutes.

It is to be hoped that further experimentation on vapor-liquid equilibria of multicomponent hydrocarbon systems will,

TABLE I. COMPARISON OF EQUILIBRIUM VAPORIZATION CONSTANTS

Temp., ° F.	Pressure, Lb./Sq. In. Abs.	K for Pentane, Katz (4)	Calcd. K (16) n-C ₄	Calcd. K (16) Iso-C ₄	Correlated K n-C ₄	Correlated K Iso-C ₄
50	14.7	0.51	1.05	1.33	0.39	0.58
100	14.7	1.27	4.32	5.32	1.08	1.44
200	14.7	4.83			4.6	5.5
50	100	0.0835	0.193	0.240	0.062	0.09
100	100	0.204	0.732	0.875	0.17	0.23
200	100	0.75			0.725	0.90
50	200	0.047	0.113	0.161	0.0345	0.05
100	200	0.113	0.467	0.560	0.094	0.128
200	200	0.40			0.40	0.49

perhaps with the aid of a correlating method such as the one here presented, allow more universal correlation for engineering purposes of the relations governing these systems. Correlation is particularly desirable at higher pressures—500 to 10,000 pounds per square inch absolute—where for a given temperature and pressure the nature of the system involved appears to be an important variable.

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NOMENCLATURE

P = total pressure, lb./sq. in. abs. or atm.
 P^o = vapor pressure, lb./sq. in. abs.
 P_c = critical pressure, atm.
 T = absolute temperature, ° K.
 T_c = critical temperature, ° K.
 f = fugacity
 P_R = reduced pressure
 T_R = reduced temperature
 y = mole fraction of a component in vapor of hydrocarbon mixture in vapor-liquid equilibrium
 x = mole fraction of a component in liquid of hydrocarbon mixture in vapor-liquid equilibrium
 K = equilibrium constant (y/x)
 p = partial pressure of a component over a mixture in vapor-liquid equilibrium

Subscripts

y = vapor
 x = liquid
 a = component a of a mixture in vapor-liquid equilibrium.

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Vulcanization of Saturated Acrylic Resins

Rubberlike materials, designated as Lactoprene, were prepared in earlier investigations by copolymerizing ethyl acrylate with small proportions of butadiene, isoprene, or allyl maleate, compounding the resulting copolymers (assumed to have olefinic unsaturation) with sulfur and accelerators, and then curing the compounded products. Since it was difficult to prevent cross linkage during polymerization of mixtures containing butadiene and other polyfunctional monomers, vulcanization of acrylic resins not having olefinic linkages was attempted. Polyethyl acrylate and various saturated copolymers of ethyl acrylate were vulcanized satisfactorily with red

lead and quinone dioxime and also with benzoyl peroxide. The copolymers made from acrylonitrile, cyanoethyl acrylate, chloroethyl acrylate, chloropropyl acrylate, and phenyl acrylate were vulcanizable with certain sulfur-accelerator mixtures. The preparation of rubberlike materials by vulcanizing saturated acrylic resins instead of copolymers of the ethyl acrylate-butadiene type has the following advantages: (a) Agents and techniques to prevent cross linkage are not required, (b) the polymers and copolymers are soluble, and hence the viscosity of the solutions can be used as an index of the molecular weight, and (c) synthetic rubber cements can be made.

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THE vulcanization of copolymers (presumed to have olefinic unsaturation) made from alkyl acrylates and small proportions of butadiene, isoprene, allyl maleate, and similar polyfunctional monomers are described in other papers (4, 9). Although the vulcanizates prepared in this manner were rubbery and seemed suitable as rubber replacements in some fields, polyfunctional monomers were generally objectionable because of their tendency to create cross linkages prematurely—that is, during polymerization. After a study of the copolymerization of ethyl acrylate with many polyfunctional compounds had indicated that cross linkage (or effects ordinarily attributed to it) nearly always occurs when this method is used to produce unsaturated copolymers, it was decided to attempt the vulcanization of saturated acrylic resins.

Although olefinic unsaturation has generally been considered necessary for vulcanization (10), it seemed likely that vulcanization could be effected through some combination of a nonolefinic functional group (ester, cyano, halogen, etc.) and a vulcanizing agent. Acrylic resins contain ester groups and one hydrogen alpha to the carboxyl group that might enter into cross linkage or vulcanization reactions. Acrylic resins containing other functional groups were prepared by copolymerizing ethyl acrylate with small proportions of acrylonitrile, β -cyanoethyl acrylate, γ -chloropropyl acrylate, and similar monomers. Vulcanization of these copolymers was attempted with various recipes including benzoyl peroxide and reinforcing agents, sulfur and organic accelerators, *p*-quinone dioxime and red lead, *p*-dinitrobenzene and litharge (13), sulfur and litharge, and Polyac (14). The results of this study and certain properties of vulcanizates prepared from saturated acrylic resins are given in the present paper.

The polymerizations were carried out as before (4, 9) in round-bottom, three-neck, Pyrex flasks fitted with a thermometer well, reflux condenser, and water-sealed stirrer (ground-glass joints). Steam was passed through the emulsion to distill monomer or volatile impurities, and then coagulation was effected by the addition of a dilute solution of sodium chloride. The polymers were washed with water on a small washing mill and air-dried.

The acrylic esters were emulsion-polymerized more successfully when proper consideration was given to purity of the monomer and the threshold or minimum catalyst concentration required for polymerization. The threshold catalyst concentration was related to the temperature, and only small amounts of catalyst (ammonium persulfate) were needed under refluxing conditions (approximately 82° C.). The monomers should be freshly

distilled and, if not used immediately, stored so that the formation of peroxides is minimized. The removal of inhibitors by dilute sodium hydroxide should be followed by several washings with distilled water, dilute sulfuric acid (0.01%), and finally with distilled water.

Generally it is disadvantageous to use more than the threshold concentration of ammonium persulfate. When there is too much catalyst, refluxing may be so violent that the emulsion coagulates. When the catalyst concentration is below the threshold value, polymerization may not occur even after hours of refluxing. When carried out properly, polymerization proceeds smoothly at refluxing temperature with little heating. A steam bath is more satisfactory than a water bath for this type of polymerization.

The phenyl (3), chloropropyl, methoxyethyl, cyanoethyl, and nitroisobutyl acrylates were prepared in connection with other investigations (11).

The compounding ingredients were milled into the polymers on a small rubber mill. The polymers usually were tacky and easily milled without the addition of plasticizers or softeners. Benzoyl peroxide (Luperco A) was so active as a vulcanizing agent that it was difficult to prevent scorching on the mill, even when the peroxide was incorporated last.

The compounded mixtures were cured in stainless-steel sandwich molds having the dimensions 4 × 4 × 0.032 inch or 6 × 6 × 0.075 inch. Cellophane sheets were used in the smaller mold. These were apparently detrimental, since in some instances the tensile strengths were lower.

Unlike the copolymers (4, 9) prepared with monomers having two or more olefinic linkages, most of the copolymers of the present work were soluble in organic solvents before vulcanization. The viscosities of solutions containing about 0.05 gram of polymer per 100 ml. of toluene were determined at 25° C. (constant-temperature bath) with modified Ostwald tubes. The natural logarithm of the relative viscosity divided by the concentration—that is, $(\ln \eta/c)$ —was used as an index of the average molecular weight of the polymers (6). It was shown experimentally that the values for $(\ln \eta/c)$ were approximately the same when *c* was 0.05 or extrapolated to 0.

VULCANIZATION OF POLYETHYL ACRYLATE

Polyethyl acrylate, prepared as shown in Table I, was compounded by several different recipes and molded at 298° F. (Table II). The sulfur-Captax-Tuads combination gave unsatisfactory

Table I. Preparation of Ethyl Acrylate Copolymers by Emulsion Polymerization

Expt. No.	Ethyl Acrylate, Grams	Copolymerizing Monomer, Grams	Tergitol Penetrant No. 4 ^a , Grams	Water, Ml.	Ammonium Sulfate, Gram	Temp., °C.	Time, Hr.	Yield, %	$\ln \eta_r$
1	150 ml.	None	4	300	0.025	80-92	1.5	87.5	3.82
2	142.5	Acrylonitrile, 7.5	4	250	0.02	78-92	4.25	88.5	3.96
3	142.5	Acrylonitrile, 7.5	4	300	0.045	78-91	4.5	90.5	3.52
4 ^b	1470.0	γ -Chloropropyl acrylate, 7.5	28	3200	0.02	81-90	1.25	...	3.91
5	142.5	β -Chloroethyl acrylate, 7.5	4	300	0.015	78-92	1.5	90	5.27
6	135	β -Chloroethyl acrylate, 15	4	300	0.015	82-91	2	88	3.53
7	89	β -Chloroethyl acrylate, 5; acrylonitrile, 6	3	150	0.12	78-91	1.75	92	2.43
8	142.5	Benzyl acrylate, 7.5	4	250	0.03	78-92	2	91	3.80
9	95	Phenyl acrylate, 5	3	150	0.1	75-92	0.83	90	...
10	142.5	β -Methoxyethyl acrylate, 7.5	4	300	0.03	80-92	1.33	93.5	Insol.
11	142.5	β -Cyanoethyl acrylate, 7.5	4	300	0.03	80-92	1.67	91	3.64
12	142.5	2-Me-2-nitro-1-propyl acrylate, 7.5	4	300	0.02	77-92	1.67	91	4.66

^a Sodium alkyl sulfate.^b Triton 720 (8 grams) used; this emulsifier is a sodium salt of aryl alkyl polyether sulfonate (16).

results, but the Luperco A (benzoyl peroxide) and GMF (quinone dioxime) recipes gave good vulcanizates. About 4 hours at 298° F. was necessary for vulcanization with the quinone dioxime formula, and the vulcanizates thus prepared (Tables II and III) had moderately high tensile strengths. Cross linkage occurred much more rapidly with benzoyl peroxide (10 to 20 minutes at 210° F.), but the products were relatively weak. [Cross-linked acrylic resins were produced also by preparing ethyl acetate solutions of the polymeric acrylic ester and benzoyl peroxide (Lucidol), applying the solution to a surface, allowing the solvent to evaporate, and heating the resulting film at about 80° C. for a short time.]

alpha to the carboxyl group, possibly cross linkage occurs through the same type of coupling.

VULCANIZATION OF ETHYL ACRYLATE COPOLYMERS

Ethyl acrylate was copolymerized with various monomers (Table I), and the resulting copolymers were compounded by different recipes and molded to ascertain whether the cyano, halogen, phenyl, ether, and nitro groups in the copolymers would facilitate vulcanization. The results show that several functional groups in the acrylate copolymers are susceptible to cross linkage or vulcanization. It has been believed that olefinic

Table II. Vulcanization of Polyethyl Acrylate and Ethyl Acrylate Copolymers^a

Expt. No.	Copolymerizing Monomers, %	Compounding Recipe	Curing Time at 298° F., Min. ^b	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Tensile Product	Brittle Point, °C.
1	None	Quinone dioxime ^c	240	1390	510	55	710	-16
		Benzoyl peroxide ^d	120	810	440	46	355	-16
		Sulfur ^e /
2	Acrylonitrile, 5	Quinone dioxime ^c	240	1320	260	72	345	-11
		Benzoyl peroxide ^d	180	1000	420	53	420	-7
		Sulfur ^e	240	830	1040	50	860	-7
3	Acrylonitrile, 5	Quinone dioxime ^c	240	1420	340	70	480	-9
		Benzoyl peroxide ^d	120	870	520	52	450	-8
		Sulfur ^e /
4 ^f	γ -Chloropropyl acrylate, 4.8	Quinone dioxime ^c	160 ^h	1610	470	67	756	...
		Sulfur ^e	210 ^h	1240	950	39	1178	...
5	β -Chloroethyl acrylate, 5	Quinone dioxime ^c	120	1610	400	64	645	-15
		Benzoyl peroxide ^d	240	870	500	45	435	-9
		Sulfur ^e	240	1280	880	46	1125	-15
6	β -Chloroethyl acrylate, 10	Quinone dioxime ^c	180	1350	460	56	620	-15
		Benzoyl peroxide ^d	120	1050	280	50	295	-11
		Sulfur ^e	180	1220	720	42	880	-14
7	β -Chloroethyl acrylate, 5; acrylonitrile, 6	Quinone dioxime ^c	240	1180	470	56	555	-8
		Benzoyl peroxide ^d	180	820	560	45	460	-6
		Sulfur ^e /
8	Benzyl acrylate, 5	Quinone dioxime ^c	240	1410	480	65	675	-11
		Benzoyl peroxide ^d	120	640	490	45	315	-10
		Sulfur ^e	240	<100	>2400	40
9	Phenyl acrylate, 5	Quinone dioxime ^c	240	960	180	75	170	-17
		Benzoyl peroxide ^d	20	570	480	42	275	-11
		Sulfur ^e	240	790	780	50	615	-16
10	Methoxyethyl acrylate, 5	Quinone dioxime ^c	240	1090	340	55	370	-17
		Benzoyl peroxide ^d	80	<100	380	40
		Sulfur ^e	240	<100	680	39
11	β -Cyanoethyl acrylate, 5	Quinone dioxime ^c	120	1670	450	65	750	-15
		Benzoyl peroxide ^d	80	510	440	45	225	-13
		Sulfur ^e	120	1090	860	48	940	-16
12	2-Me-2-nitro-1-propyl acrylate, 5	Quinone dioxime ^c	120	470	410	31	190	-14
		Benzoyl peroxide ^d	180	760	440	41	335	-13
		Sulfur ^e /

^a Prepared as described in Table I; brittle points of vulcanizate determined as described in citation (12).^b Cured in 4 × 4 × 0.032 inch molds.^c Compounded: polymer, 100; red lead, 10; quinone dioxime, 2; zinc oxide, 5; stearic acid, 3; Furnex Beads (semireinforcing carbon black), 30.^d Compounded: polymer, 100; iron oxide, 150; Luperco A (benzoyl peroxide), 5.^e Compounded: polymer, 100; Captax (mercaptobenzothiazole), 0.5; zinc oxide, 10; stearic acid, 2; sulfur, 2; Furnex Beads, 30; Tuads (tetramethylthiuram disulfide), 1.^f Specimen unsatisfactory for testing.^h Cured at 303° F.^g Cured in 6 × 6 × 0.075 inch molds.ⁱ Cured at 312° F.

The ester group in polyethyl acrylate apparently is responsible for the vulcanization with benzoyl peroxide and quinone dioxime, since cross linkage did not occur when polyisobutylene (Vistanex) was compounded according to these two recipes and molded. The mechanism of the vulcanization of polyethyl acrylate is not known, but earlier work by Kharasch and Gladstone (7) with a peroxide and isobutyric acid is suggestive. They observed that isobutyric acid is converted into tetramethylsuccinic acid by treatment with acetyl peroxide. Since the polyacrylic ester chain is somewhat similar to isobutyric acid in having one hydrogen

Table III. Preparation and Vulcanization of Copolymers of Ethyl Acrylate with Chloropropyl Acrylate or Chloroethyl Acrylate^a

Expt. No.	Copolymerizing Monomer, Grams	Ethyl Acrylate, Grams	Water, Ml.	Tergitol Penetrant No. 4, Grams	Triton 720, Grams	Ammonium Persulfate, Grams	Time, Hr.	Temp., °C.	Curing Conditions Min. ° F.	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	$\ln \eta_r/c$
1	γ -Chloropropyl acrylate, 32	630	1125	5	..	1.70	5	65-92	180 298	500	1030	42	3.023
2 ^b	Same, 10	90	300	4	..	0.04	3.5	75-92	240 298	990	760	42	4.784
3 ^c	Same, 44	882	3050	40	..	0.05	1	81-88	180 ^d 298	1700	480	68	5.386
4 ^c	Same, 45	897	2860	40	..	0.03	1	80-84	240 298	1200	620	59	
5	Same, 150	3000 ml.	5000	60 (paste)	80	0.180	4.5	82-90	240 298	1510	710	48	
6	Same, 150	3000 ml.	6000	60 (paste)	80	0.040	3	83-90	180 ^d 298	1940	420	76	..
7	Same, 75	1470	3200	28	8	0.020	2	78-90	180 ^d 298	1890	440	75	..
8	Same, 200	4000 ml.	5000	80 (paste)	40	0.035	3	82-90	210 312	1240	950	39	5.273
									150 ^d 303	1610	470	67	5.062
									120 ^d 298	1610	560	63	
									180 312	1210	790	48	
9	β -Chloroethyl acrylate, 125	2375	5000	45	12.5	0.355	6.5	82-88	240 298	1290	900	46	2.820
10	Same, 25	475	1000	9	2.5	0.215	..	82-88	240 298	1440	840	42	3.255
11	Same, 20	380	800	4	2	0.010	1.25	82-91	240 298	1430	860	48	5.079
12	Same, 60	1140	2700	30	15	0.015	2.25	81-92	240 298	740	800	48	1.968
13	Same, 50	950	2250	30	..	0.16	4.5	78-82	240 298	1120	820	45	3.284
14	Same, 25	500	1350	10	..	0.100	2	75-92	180 ^d 298	1300	530	48	

^a Compounded with sulfur and accelerators (footnote ^a of Table II) unless otherwise indicated.^b Methyl acrylate (30 grams) and *n*-butyl acrylate (70 grams) were also used as co-monomers.^c The copolymers prepared in experiments 3 and 4 were combined.^d Compounded with quinone dioxime and red lead (footnote ^c of Table II).

unsaturation is necessary for vulcanization with sulfur, but our findings indicate that cyano, halogen, and phenoxy groups are also adequate in acrylic resins when suitable vulcanization agents are used. We have not ascertained whether these groups are susceptible to vulcanization in the absence of ester groups such as those found in acrylic resins.

The cyano group in the acrylonitrile copolymer did not decrease the time required for quinone dioxime vulcanization (experiments 2 and 3, Table II) or significantly improve the properties of the vulcanizates. It was possible, however, to vulcanize the acrylonitrile copolymer with sulfur. The acrylonitrile segments in the polymer chain raised the brittle point and increased the hardness.

The cyano group in the cyanoethyl acrylate copolymer was advantageous. It decreased the time required for vulcanization with quinone dioxime and permitted sulfur vulcanization (experiment 11, Table II). It did not appear to raise the brittle point.

Acrylic resins containing halogen were prepared by using either γ -chloropropyl or β -chloroethyl acrylate as copolymerizing monomers. The halogen in the polymers was beneficial in that it decreased the time required for the quinone dioxime vulcanization and resulted in good sulfur vulcanizates. Moreover, it did not adversely affect the brittle points of the vulcanizates. Copolymers made from ethyl acrylate and either chloroethyl or chloropropyl acrylate have been prepared several times in this laboratory and given considerable study (Table III).

The phenyl group of benzyl acrylate seemed ineffective for vulcanization purposes, but the phenyl group of phenyl acrylate permitted sulfur vulcanization. The quinone dioxime and benzoyl peroxide vulcanizates prepared from the phenyl acrylate polymers were unsatisfactory, perhaps because of the antioxidant character of the phenyl ester group.

Vulcanizates of poor quality were obtained from the resins containing the ether and nitro groups (Table II). The possibility that molecular weight as well as specific effects of functional groups was responsible for the differences in properties of the vulcanizates of Table II is discussed below.

EFFECT OF MOLECULAR WEIGHT

Ethyl acrylate was emulsion-polymerized under various conditions to obtain polymers of different molecular weight (Table IV). Polymers of relatively high molecular weight (as indicated by viscosity measurements) could be prepared conveniently by refluxing the reaction mixture and using low concentrations of ammonium persulfate (experiment 6, Table IV). The $(\ln \eta_r/c)$ values ranged from 2.6 to 6.3, an indication that the polymer of experiment 6 had an average molecular weight considerably higher than that of the polymer of experiment 1.

The vulcanizates prepared from the seven polymers of Table IV were roughly similar in spite of the considerable differences in average molecular weight. These results suggest that the plateau of the curve showing the relation between the properties and molecular weight (δ) has been reached for polyethyl acrylate and that further increase in molecular weight would not be beneficial from the standpoint of tensile strength, ultimate elongation, and Shore A hardness.

Viscosities of toluene solutions of most of the copolymers shown in Table I were determined to ascertain whether the monomers used with ethyl acrylate had a pronounced effect on molecular weight. Moreover, it was hoped that viscosity data would indicate whether the properties of the vulcanizates (for example, the low tensile strength of the nitroisobutyl acrylate product, item 12 in Table III) could be attributed to differences in molecular weight. Since a copolymer having $(\ln \eta_r/c)$ value as low as 2.43 (experiment 7, Table I) gave a satisfactory vulcanizate and the other copolymers had even higher $(\ln \eta_r/c)$

Table IV. Emulsion Polymerization^a of Ethyl Acrylate and Properties of the Vulcanizates^b

Expt. No.	Ethyl Acrylate, Grams	Tergitol Penetrant No. 4, Grams	Temp., °C.	Time, Hr.	Ammonium Persulfate, Grams	$(\ln \eta_r/c)$	Tensile strength, lb./sq. in.	Vulcanizates—Ultimate elongation, %	Tensile product	Shore A hardness
1	680	30	72-81	0.5	0.30	2.578	1220	520	634	53
2 ^d	540	20	66-7	3	0.45	3.020	1270 ^e	560	710	52
3	550	20	62-75	0.5	0.43	3.552	1290	480	620	60
4	955	30	62-90	0.75	0.60	4.110	1330	480	638	61
5	835	30	62-85	0.5	0.60	4.285	1280	490	626	53
6 ^f	200	3	82-92	1.25	0.003	6.284	1380	480	662	58
7	760	60	62-81	0.75	0.70	4.367	1400	470	668	53

^a Except where indicated, 2 liters of water were used; polymerization yields were 89 to 99%.^b Compounded: polyethyl acrylate, 100; red lead, 10; zinc oxide, 5; stearic acid, 3; GMF, 2; and Furnex Beads, 30; curing time was 4 hours at 298° F.; molded specimens were 4 × 4 × 0.032 inch.^c Viscosities determined with solutions containing approximately 0.05 gram per 100 ml. of toluene.^d 4.15 liters of water used.^e Cured for 3 hours at 298° F.^f 300 ml. of water used.

Table V. Vulcanization of Polyethyl Acrylate^a

Expt. No.	Cure at 298° F., Min.	Parts per 100 Polymer Red lead	GMF	Furnex Beads	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Tensile Product
1	300	5	1	30	1190	360	65	428
2	240	5	2	30	1190	680	49	784
3	300	10	1	30	1110	360	65	408
4	180	10	2	30	1240	610	55	755
5	240	10	2	40	1230	400	63	492
6	240	10	2	50	1360	440	70	598

^a Prepared in experiment 5, Table III. Compounded: polymer, 100; stearic acid, 3.0; ZnO, 5.0; test specimens were 4 × 4 × 0.032 inch.

values, it appears that some specific effect of the functional group was more important than molecular weight.

The methoxyethyl acrylate copolymer was not completely soluble in toluene. Whether this was due to cross linkage or was characteristic of this particular copolymer is not known.

VULCANIZATION WITH QUINONE DIOXIME

The effects of variations in the quinone dioxime (GMF) recipe were studied briefly because this vulcanization method produced satisfactory vulcanizates with polyethyl acrylate and several ethyl acrylate copolymers. Moreover, vulcanization could be achieved in less time with quinone dioxime than with sulfur. Harder and less elastic vulcanizates were obtained by using 1 instead of 2 parts of quinone dioxime (Table V). Use of 5 parts of red lead rather than 10 softened the vulcanizate without causing any significant decrease in tensile strength. The effect of larger proportions of Furnex Beads is shown by experiments 4, 5, and 6, Table V. The vulcanizate prepared with 50 parts of black was harder and stronger but less elastic than the standard vulcanizate (experiment 4) having 30 parts of black.

Pitting sometimes occurred when curing temperatures higher than 298° F. were used. In some instances pitting at 307° F. was not severe, but badly pitted vulcanizates were produced at 312° F. Some of the undercured specimens prepared at 298° F. were pitted, although the vulcanizates cured for a longer time at this temperature were satisfactory. Possibly the tendency of products compounded with the quinone dioxime recipe to pit at temperatures much above 298° F. is related to the exothermic reaction between the dioxime and red lead (1). Products compounded according to the sulfur-Rotax-Tuads recipe showed less tendency to pit, and satisfactory vulcanizates were prepared at temperatures as high as 320° F. (75 pounds steam pressure).

EFFECT OF CARBON BLACK

In a preliminary study of the effect of carbon black, it was observed that greater tensile strengths were obtained when Kosmos, Gastex, and Pelletex were used (50 parts per 100 parts of polymer) instead of Furnex Beads. The elongation and hardness values, however, were less:

Expt. No. ^a	Carbon Black	Modulus, Lb./Sq. In.	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Tensile Product
1	Furnex Beads	970(500%)	1200	620	59	744
2	Kosmos 40	1450(500%)	1530	540	57	826
3	Dixie 20	1110(600%)	1130	610	51	689
4	Gastex	1450	1450	490	55	710
5	Pelletex	1130(400%)	1410	530	54	747

^a Copolymer was prepared from 95% ethyl acrylate and 5% chloropropyl acrylate. Compounded: copolymer, 100; Rotax, 0.5; ZnO, 10; stearic acid, 2; sulfur, 2; Tuads, 1; and semireinforcing black, 50. Cured in 4 × 4 × 0.032 inch molds at 298° F. for 4 hours.

EFFECT OF MONOMER STRUCTURE

Vulcanizates of polymethyl acrylate were harder, stronger, and less rubbery than those prepared from polyethyl acrylate. The samples of vulcanized polymethyl acrylate had brittle points of approximately 0° C. Poly-*n*-butyl acrylate, prepared under the conditions shown in Table I, was softer and tackier than

polyethyl acrylate. When compounded with the quinone dioxime formula (footnote ^c, Table II) and cured for 60 minutes at 298° F., a vulcanizate with the following properties was obtained: tensile strength, 780 pounds per square inch; ultimate elongation, 640%; Shore A hardness, 47; tensile product, 500; and brittle point, about -50° C. (-58° F.).

HEAT AGING

Vulcanizates prepared by the sulfur and quinone dioxime recipes were heated in an oven at 150° C. for periods up to 5 weeks and examined to determine their resistance to aging at elevated temperatures. Heat increased the tensile strength and hardness of both vulcanizates but decreased the elongation and permanent set:

Sample ^a	Aged at 150° C., Days	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Permanent Set—10 min., 75% elongation	At break
1 ^b	0	1580	370	65	25.5	20.4
	1	2170	260	81	..	22
	2	2130	200	84
	4	2240	190	83
	8	1930	90	89
2 ^c	0	1700	480	68	7.1	..
	1	2100	110	82	2.4	..
	4	2430	80	80	10.0	..
	7	2330	50	92	3.1	..
	14	2120	50	97	0	..
	21	2150	80	98
	28	2200	40	100
	35	2320	60	98

^a Specimens were heated in an oven at 150° C.; they were tough instead of brittle at end of test.

^b Polymer prepared in experiment 7, Table IV. Compounded: polymer, 100; red lead, 10; ZnO, 5; stearic acid, 3; quinone dioxime, 2; Furnex Beads, 30. Cured 240 minutes at 298° F. in 6 × 6 × 0.075 inch molds.

^c Polymer prepared in experiments 3 and 4, Table III. Compounded: polymer, 100; Rotax, 0.5; zinc oxide, 5; stearic acid, 2; sulfur, 2; Tuads, 1; Furnex Beads, 30. Cured at 298° F. in 6 × 6 × 0.075 inch molds.

These results show that vulcanized acrylic resins are rather resistant to heat, and suggest that acrylic resins might be useful where rubbery materials are required to withstand relatively high temperatures. It should be possible to improve the heat-aging characteristics of vulcanized acrylic resins by making appropriate changes in the compounding recipe. These changes might include the use of antioxidants, softeners or plasticizers, decreasing the proportion of sulfur and vulcanizing agents, and loading with more suitable reinforcing agents.

BLENDS WITH OTHER SYNTHETIC ELASTOMERS

A copolymer made from ethyl acrylate and 5% γ -chloropropyl acrylate blended readily with Butyl rubber on a small rubber mill. Increasing the proportion of Butyl rubber increased the tensile strength and lowered the brittle point:

Expt. No. ^a	Butyl Rubber, % of Gum ^b	Cure at 298° F., Min.	Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	Tensile Product	Brittle Point, ° C.
1	0	180	500	1030	42	513	-16
2	20	240	1050	830	46	870	-22
3	35	240	1370	900	48	1230	-43
4	60	120	1410	920	40	1300	-49
5	100	180	2340	790	41	1850	-65

^a Butyl rubber A contained 1.5 parts sulfur and 5 parts ZnO.

^b Blends were compounded as follows: gum stock, 100; Captax, 0.5; ZnO, 5; stearic acid, 2; sulfur, 2; Furnex Beads, 30; Tuads, 1. Cured in 4 × 4 × 0.032 inch molds.

Apparently blending with Butyl rubber (and presumably certain other synthetics) constitutes a convenient method of lowering the brittle points of polyethyl acrylate vulcanizates. Other methods of lowering the brittle point consist in using plasticizers or in copolymerizing ethyl acrylate with suitable monomers, such as *n*-butyl acrylate.

Table VI. Vulcanization of Ethyl Acrylate-Chloropropyl Acrylate Copolymer with Various Agents^a

Compound No.	1 ^b	2	3	4	5 ^b	6	7	8	9	10	11	12
Recipe, parts												
Rotax	0.5	0.5	0.5	0.5	0.5	0.38	..	0.5
ZnO	10	10	10	10	5	10	10	10	10	10	..	10
Stearic acid	2	2	2	2	3	2	2	..	2
Sulfur	2	2	2	2	..	2	2
Furnex Beads	30	50	50	75	30	30	30	30	30	30	30	..
Tuads	1	1	1	1	..	1	0.75	..	1
Plasticizer SC	..	5	10	20
Red lead	10
Quinone dioxime	2
Cuprax	0.5	..	0.5
Cumate	1
Polyac	1
Tegul OS
p-Dinitrobenzene	4	..
Litharge	10	..
Witcarb R	80
Curing time, min.	180	240	360	240	60	180	300	300	300	240	360	240
Curing temp., ° F.	312	298	298	298	298	298	298	298	298	298	298	298
Tensile, lb./sq. in.	1210	1170	1190	880	1530	1490	1370	1440	1460	980	1340	1280
Modulus at 600%	830	1080	730	490	1450	660	1070	990	1180	370	..	1240
Ultimate elongation, %	790	690	690	880	650	940	740	790	700	920	560	610
Shore A hardness	48	46	40	40	55	40	43	43	41	38	35	47
Permanent set, %												
At break	13.7	25.5
After 10 min.	21.4	34.9
Tensile product	956	806	822	774	994	1400	1014	1138	1022	902	750	780

^a 100 parts copolymer (prepared in experiment 8, Table III) used. With exception of experiments 1 and 5, compounded mixtures were cured in 4 × 4 × 0.023 inch molds.

^b Compounded mixtures cured in 6 × 6 × 0.075 inch molds.

MISCELLANEOUS VULCANIZATION RECIPES

Samples of copolymer prepared from ethyl acrylate and chloropropyl acrylate (experiment 8, Table III), were vulcanized with various agents, and the vulcanizates were compared with products obtained with the standard quinone dioxime and sulfur-Rotax-Tuads recipes.

Both Cuprax and Cumate (cupric salt of mercaptobenzothiazole and cupric diethyldithiocarbamate, respectively) were effective in promoting sulfur vulcanization (Table VI, experiments 6, 7, and 8). The combination of Cuprax and Tuads gave vulcanizates that were superior to those obtained with combinations of Rotax and Tuads, Rotax and Cumate, and Cuprax and Cumate. Polyac (14) caused vulcanization in the absence of sulfur and gave vulcanizates which compared favorably with those prepared by other recipes. The dinitrobenzene litharge combination also gave satisfactory vulcanizates (experiment 11, Table VI). The vulcanizate obtained with Tegul OS, an organic sulfur compound, Rotax, and Tuads (experiment 10) had high elongation but relatively low tensile strength.

Considerable quantities of plasticizers were used in experiments 2, 3, and 4. In the presence of increased amounts of carbon black the plasticizer decreased tensile strength and hardness while increasing the elongation. Witcarb R (calcium carbonate) functioned as a reinforcing agent when used instead of carbon black.

Although the study of compounding and vulcanization is still in the preliminary stage, the results obtained show that certain saturated acrylic resins can be vulcanized, reinforced, and modified with a variety of agents.

PROPERTIES OF VULCANIZED ACRYLIC RESINS

As Figure 1 shows, the copolymer of ethyl acrylate and 5% chloropropyl acrylate has a tensile strength of approximately 1700 pounds per square inch (cured in 6 × 6 × 0.075 inch molds without cellophane sheets) and an elongation of 500%. Higher tensile values may be obtained by sacrificing elongation and presumably with different blacks or higher loading, as shown above. The stress-strain curve of a quinone dioxime vulcanizate is roughly comparable with those of other synthetic elastomers (2) up to about 400% elongation (Figure 1).

The tear strength by the crescent tear test is about 220 pounds per inch. The permanent set is frequently 20% or less. The brittle point is approximately 0°, -15°, or -50° C., depending upon whether methyl acrylate, ethyl acrylate, or *n*-butyl acrylate is the principal monomer.

The polymers are readily milled without softeners or plasticizers. Different compounding recipes can be used, and several blacks and pigments, such as iron oxide, zinc oxide, and calcium carbonate, can be used as reinforcing agents. The copolymers are soluble in organic solvents, and synthetic rubber cements can be prepared from them.

The vulcanizates have the advantages of resistance to oxygen and aging, which one would expect to find in essentially saturated materials. The acrylic elastomers contain a high proportion of oxygen and are resistant to some oils, particularly those that are paraffinic.

Although in some respects vulcanized acrylic resins do not compare favorably with certain other synthetic elastomers, they have several advantages. The monomers can be made from several raw materials, including whey (5), molasses, corn, sugar, petroleum, and coal. Moreover, more than twice as much acrylic elastomer as elastomers of the butadiene types can be made from carbohydrates.

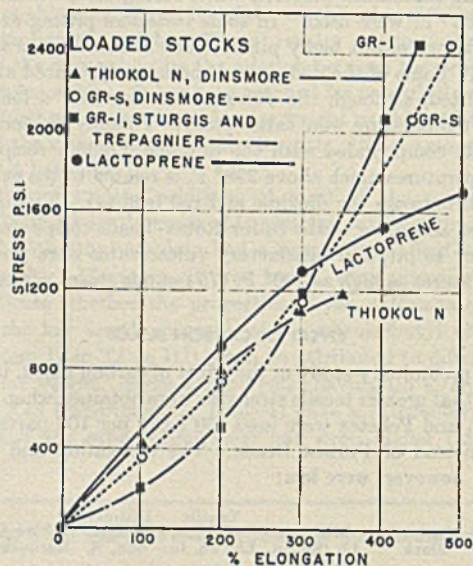


Figure 1. Stress-Strain Curves

Another advantage of acrylic elastomer is that the polymerization can be carried out in simple equipment. Since ethyl acrylate boils at 99° C. at atmospheric pressure, high-pressure reaction vessels are not needed. The time required is short, and polymerization is carried to completion. Polyfunctional monomers are not required, and consequently premature cross linkage and its attendant disadvantages are avoided. Any one of several acrylic esters can be used, or two or more acrylic esters can be copolymerized.

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Vulcanized Acrylic Resins

COPOLYMERS OF ETHYL ACRYLATE AND ALLYL MALEATE

Rubberlike materials were made by copolymerizing emulsified ethyl acrylate with small proportions of allyl maleate and vulcanizing the resulting unsaturated acrylic resins with sulfur and accelerators and with other agents in the absence of sulfur. Acrylonitrile (preferably about 6%) and dodecyl mercaptan had a beneficial effect, possibly because of their tendency to decrease cross linkage. Ammonium persulfate was preferable as polymerization catalyst; a small amount caused polymerization to proceed smoothly. Benzoyl

peroxide was also effective but produced properties, such as insolubility and toughness, that are sometimes attributed to cross linkage. Although not so active as benzoyl peroxide, hydrogen peroxide was moderately satisfactory. Sodium perborate had no advantage. Nonsulfur vulcanization gave promising results. Combinations of quinone dioxime, quinone dioxime dibenzoate, red lead, and lead peroxide produced vulcanizates with considerably higher tensile strength and somewhat greater hardness than did sulfur.

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BECAUSE of their flexibility and certain rubberlike characteristics, acrylic resins have been used in place of rubber for some purposes (4, 6, 7). Since it seemed reasonable that the value of acrylic resins as rubber replacements would be enhanced by vulcanization, an investigation of the preparation and properties of vulcanized or cross-linked acrylic polymers was inaugurated in this Laboratory. An earlier paper (2) described preliminary results, which showed that vulcanizable polymers could be prepared by copolymerizing acrylic esters with small proportions of polyfunctional monomers such as butadiene, isoprene, and allyl maleate. The copolymers prepared were compounded with sulfur, vulcanization accelerators, and carbon black, and vulcanized with the equipment and techniques ordinarily used in processing natural and synthetic rubbers. These vulcanizates were more rubberlike than the unvulcanized acrylic resins and appeared to warrant further study.

The present paper describes the results of investigating certain variables in the production of vulcanized acrylic resins. To simplify the study and decrease the numerous possibilities afforded in copolymerization, compounding, and curing operations, ethyl acrylate and allyl maleate were selected as the acrylic and polyfunctional monomers. Ethyl acrylate was chosen because its polymers are softer and more rubbery than the other acrylic resins examined in the preliminary study. To provide information on suitable monomer concentrations and conditions of polymerization, uniform compounding and curing conditions were used in most experiments.

The monomers were emulsion-polymerized because this operation can be carried out conveniently both in the laboratory and plant, and also because emulsion polymerization ordinarily yields polymers of relatively high molecular weight. Hydrogen peroxide (27.5%) and benzoyl peroxide were used to initiate polymerization in the earlier experiments, but ammonium persulfate was employed after its advantages as catalyst were discovered.

Satisfactory copolymers were prepared with Triton K 60 (10) as emulsifying agent and hydrogen peroxide as catalyst, but an appreciable amount of polymer was usually precipitated during this reaction, necessitating the laborious removal of resin from the stirrer and vessel. Controlling the rate of polymerization offered some difficulties when hydrogen peroxide was used. Triton K 60 could not be employed with ammonium persulfate or sodium perborate catalysts because of precipitation or loss of emulsifying action.

Tergitol Penetrant No. 4 (10) worked satisfactorily with ammonium persulfate, sodium perborate, benzoyl peroxide, or hydrogen peroxide. Little if any polymer precipitated from the emulsion during polymerization. Moreover, the polymer emulsion could be completely broken merely by adding a dilute solution of sodium chloride.

Acrylonitrile and dodecyl mercaptan were used in some of the experiments to decrease or prevent cross linkage (1). Polymerization seemed easier to control in the presence of dodecyl mercaptan when hydrogen peroxide was used as catalyst.

The copolymers were prepared, compounded, cured, and

Table I. Effect of Allyl Maleate and Acrylonitrile

Expt. No.	Monomers, Grams	Dodecyl Mercaptan, G.	Triton K 60, G.	Tergitol No. 4, G.	Catalyst	Ammonium persulfate, g.	Temp., °C.	Time, hr.	Yield, %	Vulcanization Time, min.	Temp., °C.	Tensile Strength, Lb./Sq. In.	Elongation, %	Shore Hardness	Brittle Point, °C.	Tensile Product	% Gain in Weight after Immersion in: Toluene, heptane, Water
1	98	0.1	1.5	0	0	13.7	65.6	5.25	90	180	148	640	1500	43	-15	980	26
2	96	0.1	1.5	0	0	13.7	65.6	5.25	93	120	148	400	790	45	-12	316	23.8
3	94	0.1	1.5	0	0	13.7	65.6	5.25	90	120	148	600	610	45	-12	366	20.7
4	90	0.1	1.5	0	0	12	65.6	5.25	89	120	148	710	380	48	-7	256	20.6
5	90	0.1	1.5	0	0	3.5	82-92	6.75	83	120	148	990	490	47	-8	434	17.3
6 ^a	180	0.6	2	0	0	2.5	82-92	1.08	83	120	148	780	980	48	-11	730	14.2
7 ^b	80	0.1	1.5	0	0	12	65.6	6.5	83	120	148	300	430	50	-10	129	26 ^c
8 ^b	60	0.1	1.5	0	0	22	65.6	6.5	90	240	148	600	620	55	-14	427	24.7
9	97	0.1	1.5	0	0	45	65.6	11.5	95	180	148	560	440	54	-8	247	21.5
10	94	0.1	1.5	0	0	2.35	82-92	1.75	93	180	148	600	580	35	-12	616	13
11	94	0.1	1.5	0	0	30	65.6	8.75	95	120	148	850	770	55	-12	574	17
12	92	0.1	1.5	0	0	17	65.6	5	94	180	148	870	660	59	-7	531	10.3
13	318.5	0.35	1050	7	0	0.03	83-91	3	90	180	148	1130	470	52	0	558	19.8
14	91	0.1	1.5	0	0	25	65.6	6	96	180	148	1510	370	80	+24	410	14.5
15	88	0.1	1.5	0	0	25	65.6	0.5	96	180	148	1640	250	89	...	357	20
16 ^d	88	0.1	1.5	0	0	0.1	82-92	0.5	90	180	148	510	700	41	...	129	8.5
17 ^d	88	0.1	1.5	0	0	0.055	75-92	3.33	86.5	120	148	340	380	48	...	201	16.3
18 ^e	82	0.1	1.5	0	0	0.050	75-92.5	2.97	87.5	180	148	380	570	46	-19	128	...
19 ^f	73	0.1	1.5	0	0	0.055	75-92.5	4.63	83.7	180	148	330	390	48	...	108	...
20 ^g	24	0.1	1.5	0	0	0	82-92	0.72	83	120	148	320	400	45
21 ^h	62	0.1	1.5	0	0	0.5	82-92	0.67	83	120	148	320	400	45
22	98	0.1	1.5	0	0	0	82-92	1.0	...	120	148	320	400	45
23	99.5	0	1.5	0	0	0	82-92	2.33	...	140	148	360	300	48
24	95	0.5 ^a	160	2	0	2	82-92	0.5
25	95	0.25	160	2	0	7	82-92	0.5
26	475	1.0	600	8	0	5.5	82-92	0.5
27 ^{a,i}	500	55 (10%)	700	8.5	0	5.5	82-92	0.5

^a Reported in another paper (2). ^b Copolymer was inelastic. ^c Specimen was weakened. ^d Copolymer was soft and tackylike. ^e About one third of the mixture foamed out of the flask. ^f Copolymer was hard and slightly rubbery. ^g Copolymer was hard and inelastic. ^h Mercaptan 3B, 0.5 grain. ⁱ Forty parts of black was used.

tested as described previously (2). The following ingredients were used (parts per 100 parts of polymer): Captax (mercaptobenzothiazole), 0.5; zinc oxide, 5; stearic acid, 2; sulfur, 2; Furnex Beads (carbon black), 30; and Tuads (tetramethylthiuram disulfide), 1. Tensile product was calculated from the formula:

$$\text{tensile product} = \frac{(\text{tensile strength})(\text{elongation})}{1000}$$

Copolymers prepared in the present work were incompletely soluble at room temperature in several common organic solvents, possibly because of cross linkage. Hence, data on molecular weight based on viscosity measurements would be difficult to obtain and of questionable significance. A relation has been observed (8), however, between the swelling characteristics of the insoluble fraction and the viscosity of solutions of the soluble fraction for styrene-butadiene copolymers.

EFFECT OF ALLYL MALEATE AND ACRYLONITRILE

The copolymers prepared from a monomer mixture containing as little as 1% allyl maleate (Table I, experiment 1) were found to be vulcanizable with sulfur and accelerators. When used with an equal quantity of acrylonitrile, the following changes in properties of the vulcanizate occurred as the proportion of allyl maleate was increased to 5% (experiments 1 to 5): The amount of hydrocarbon mixture (50% toluene-50% heptane) sorbed by the

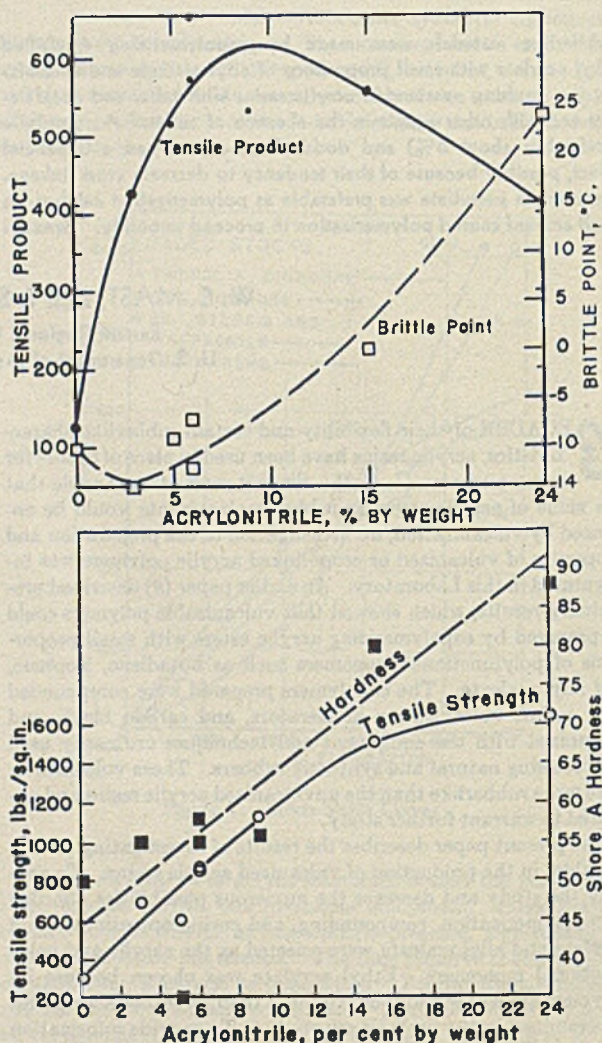


Figure 1. Effect of Acrylonitrile on Tensile Product, Brittle Point, Tensile Strength, and Hardness of Vulcanizates

Table II. Effect of Catalyst, Catalyst Concentration, and Time of Polymerization^a

Expt. No.	Triton K 60, G.	Tergitol No. 4, G.	Catalyst		Polymerization		% Yield of Co-polymer	Vulcanization		Tensile Strength, Lb./Sq. In.	Elongation, %	Shore A Hardness	Brittle Point, °C.	Tensile Product	% Gain in Wt. after Immersion in Toluene-Heptane
			H ₂ O ₂ , ml.	Benzoyl peroxide, g.	Ammonium persulfate, g.	Temp., °C.	Time, hr.	Time, min.	Temp., °C.						
3	1.5	0	12	0	0	65.6	3.5	90	148	600	610	45	-12	360	..
12	1.5	0	30	0.5	0	65.6	8.75	91	240	560	440	54	-8	247	..
11	0	2	2.35	0	0	83-91	1.75	93	180	490	620	55	-14	427	..
28	1.5	0	15	0	0	83	3	94	300	580	430	60	-12	241	17.4
29	0	2	0	0	0	70	2.75	87	240	510	600	55	-10	306	14
30	1.5	0	0	0.85	0	70	1.75	86
31	0	2	0	0	0.25	70-92	0.33	96	240	510	330	56	-10	168	14 ^c
32	0	2	0	0	0.1	70-92	0.75	95	240	570	430	53	-12	245	14.5
33	0	2	0	0	0.05	80-92	0.5	97	240	520	380	55	-11	197	14.2 ^c
34	0	2	0	0	0.05	70	4	96	120	440	600	50	-10	264	20.8 ^c
35	0	2	0	0	0.1	80	7.25	7
36	0	2	0	0	0.014	83-92	1.1	81	240	590	630	47	-12	372	23.6
37	0	2	0	0	0.1	60	15	53	240	650	610	58	-16	396	26.7
38	0	2	0	0	0.007	83-92	1.25	85	180	590	730	48	-13	431	19.1
39	0	2	0	0	0.003	83-89	2.5	76	180	730	930	50	-16	678	26.7
40	0	2	0	0	0	83	7.25	0

^a Polymerization mixtures included 94 g. ethyl acrylate, 3 g. acrylonitrile, 3 g. allyl maleate, 300 ml. water, and 0.1 g. dodecyl mercaptan (no mercaptan was used in expt. 12). The polymers were soft and elastic with the exception of that obtained in expt. 30.

^b Catalyst was 0.85 g. NaBO₃·4H₂O. ^c Vulcanizate was weakened.

vulcanized polymer decreased, the tensile strength increased, the ultimate elongation decreased, the brittle point (9) was raised, and the vulcanizate became harder. The copolymers obtained from monomer mixtures containing 10% or more of allyl maleate were relatively tough and inelastic and were unsuitable for milling. The effects mentioned above could be attributed to increased cross linkage or increased amounts of acrylonitrile or both.

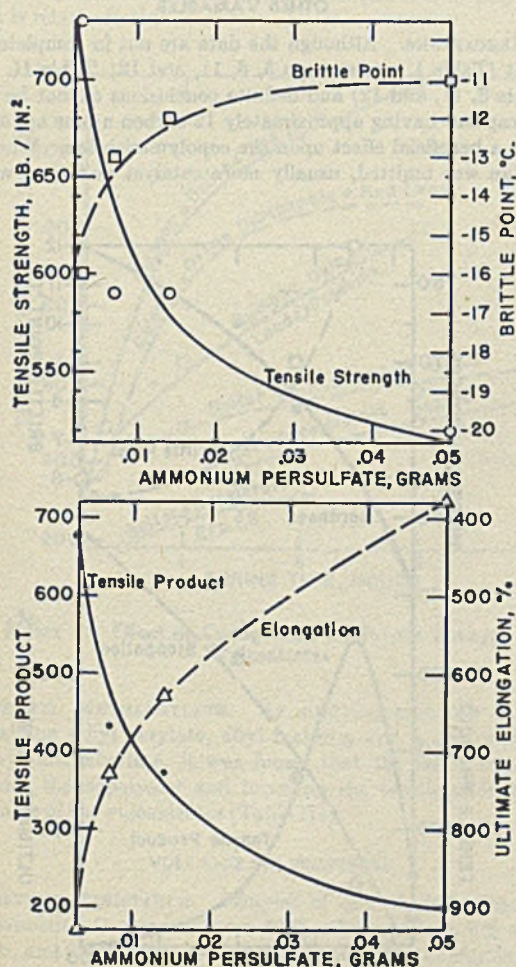


Figure 2. Effect of Ammonium Persulfate on Tensile Strength, Brittle Point, Tensile Product, and Ultimate Elongation of Vulcanizates

In the absence of acrylonitrile, both the tensile strength and ultimate elongation decreased as the proportion of allyl maleate was increased (experiments 22 to 27). In one series (experiments 9 to 21) the proportion of allyl maleate was kept constant and various amounts of acrylonitrile were used. The effect of increasing proportions of acrylonitrile may be summarized as follows: Resistance to hydrocarbons increased; the brittle point was raised (after an apparent initial drop); hardness and tensile strength increased; and ultimate elongation increased up to about 5% acrylonitrile and then decreased (Figure 1). The over-all effect of acrylonitrile seems beneficial, particularly when used as approximately 3 to 9% of the monomer mixture.

POLYMERIZATION CATALYSTS

Several conclusions were drawn regarding the relative merits of hydrogen peroxide, benzoyl peroxide, sodium perborate, and ammonium persulfate as catalysts (Table II). Hydrogen peroxide, which has the advantage of not leaving nonvolatile materials in the polymer, was moderately satisfactory. It was not so active or effective, however, as benzoyl peroxide or ammonium persulfate. Benzoyl peroxide was an active catalyst and was used in some instances (Table I, experiments 8, 10, and 12; Table II, experiment 30) when hydrogen peroxide seemed ineffective. Benzoyl peroxide, however, appeared to promote ef-

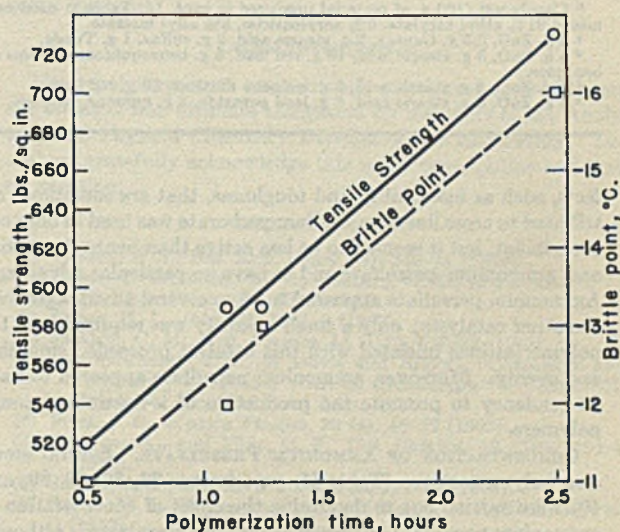


Figure 3. Effect of Polymerization Time on Tensile Strength and Brittle Point of Vulcanizates

Table III. Effect of Methyl Methacrylate^a

Expt. No.	Monomers, G.			Polymerization			Characteristics of Polymer	Vulcanization		Tensile Strength, Lb./Sq. In.	Elongation, %	Shore A Hardness	Tensile Product
	Ethyl acrylate	Methyl methacrylate	Ammonium Persulfate, G.	Temp., °C.	Time, hr.	Yield, %		Time, min.	Temp., °C.				
41	92	5	0.020	75-93	2	95	Elastic, rubbery, tough	120	148	370	440	51	163
42	87	10	0.025	80-95	2.33	94	Fairly elastic, tough	120	148	680	570	51	387
43	77	20	0.055	74-92	2	95	Tough, hard	60	148	1200	390	65	458

^a Polymerizations were carried out in presence of 3 g. allyl maleate, 300 ml. water, 2 g. Tergitol Penetrant No. 4, and 0.10 ml. dodecyl mercaptan.

Table IV. Effect of Solvents on Sulfur-Vulcanized Acrylic Resin (Sample 14) after Immersion for 4 Days

Solvent	Increase in Wt., %	Properties ^a	Dimensions, In. ^b		
			Length	Width	Thickness
Acetone	26.5	W	3 1/4	3/4	0.052
Toluene	87.0	W	3 1/4	3/4	0.052
1,4-Dioxane	145.0	W	3 1/4	1	0.053
Ethyl acetate	19.2	SI W	2 1/4	1/4	0.035
Butyl acetate	125.0	W	3 1/4	7/8	0.042
Cyclohexanol	18.5	E, S	2	1/4	0.032
Methanol	22.0	W	2	1/4	0.032
Ethanol	17.0	W	2	1/4	0.032
n-Butyl alcohol	16.5	W	2	1/4	0.032
Isopropyl alcohol	16.0	SI W	2	1/4	0.032
Methyl lactate	314.0	W	3 1/4	3/4	0.050
Methyl acetate	10.0	S	2	1/4	0.032
Carbitol	58.0	W	2	1/4	0.032
Isomyl alcohol	14.0	S	2	1/4	0.032
Water	19.0	E, S	2	1/4	0.034
Sulfuric acid, 30%	0.3	E, S	2	1/4	0.034
Sulfuric acid, 3%	8.0	E, S	2	1/4	0.032
Sodium chloride, 10%	1.6	E, S	2	1/4	0.034
Sodium carbonate, 2%	9.5	E, S	2	1/4	0.034
Hydrogen peroxide, 3%	100.0	W	2 1/4	3/4	0.043
Sodium hydroxide, 1%	8.2	E, S	2	1/4	0.033
Sodium hydroxide, 10%	0.7	E, S	2	1/4	0.034
Nitric acid, 10%	100.0	W	2 1/4	3/4	0.041
Hydrochloric acid, 10%	0.3	E, S	2	1/4	0.032

^a W = weak, S = strong, E = elastic, SI = slightly.

^b Original dimensions were 2 × 0.5 × 0.0032 inch.

Table V. Effect of Compounding Formula and Carbon Black on Properties of Vulcanizate^a

Expt. No.	Vulcanization Method	Carbon Black, G.		Min. of Cure at 148° C.	Tensile Strength, Lb./Sq. in.	Elongation at Break, %	Shore A Hardness	Brittle Point, °C.
		Furnace Beads	Micro-nex Beads					
14-1	Formula 1 ^b	15	0	180	420	810	40	-12
14	Formula 1 ^b	30	0	180	850	770	55	-12
14-2	Formula 1 ^b	45	0	180	740	630	64	-9
14-3	Formula 1 ^b	60	0	240	660	480	75	-6
14-4	Formula 1 ^b	40	20	180	1090	370	71	-9
14-5	Formula 1 ^b	100	0	120	780	320	85	-6
14-6	Formula 1 ^b	0	30	180	860	660	60	-
14-7	Formula 2 ^c	60	0	120	1050	360	81	-4
14-8	Formula 3 ^d	60	0	180	1280	300	84	-6
14-9	Formula 4 ^e	60	0	180	1010	420	73	-7

^a Copolymer (100 g. of material produced in expt. 14, Table I) used contained 91% ethyl acrylate, 6% acrylonitrile, 3% allyl maleate.

^b 5 g. ZnO, 0.5 g. Captax, 2 g. stearic acid, 2 g. sulfur, 1 g. Tuads.

^c 5 g. ZnO, 3 g. stearic acid, 10 g. red lead, 6 g. benzoquinone dioxime dibenzoate.

^d 5 g. ZnO, 3 g. stearic acid, 2 g. quinone dioxime, 10 g. red lead.

^e 5 g. ZnO, 3 g. stearic acid, 6 g. lead peroxide, 2 g. quinone dioxime.

fects, such as insolubility and toughness, that are sometimes attributed to cross linkage. Sodium perborate was used in only one experiment, but it seemed to be less active than benzoyl peroxide and ammonium persulfate and to have no particular advantage. Ammonium persulfate appeared to have several advantages over the other catalysts; only a small quantity was required, and the polymerizations initiated with this catalyst proceeded smoothly and evenly. Moreover, ammonium persulfate appeared to have no tendency to promote the production of inelastic and tough polymers.

CONCENTRATION OF AMMONIUM PERSULFATE. Several emulsion polymerizations (Table II, experiments 33, 36, 38, 39, and 40) were carried out to determine the effect of concentration of ammonium persulfate on properties of the vulcanizate. Although no appreciable amount of polymerization occurred at 83° C. in 7.25 hours in the absence of a catalyst, as little as 0.003 gram

of catalyst (0.003% of the monomer mixture) was employed satisfactorily in experiment 39. Not only was it possible to carry out the polymerization with small proportions of ammonium persulfate, but the quality of the vulcanizates seemed to be inversely proportional to the amount of catalyst. The brittle point, tensile strength, ultimate elongation, tensile product, and polymerization time varied markedly with small changes in concentration of ammonium persulfate when the concentration was less than about 0.015% of the monomer mixture (Figure 2). Tensile strength, brittle point, and ultimate elongation were approximately straight-line functions of the time required for virtually complete polymerization for this series of experiments (Figure 3).

Comparison of experiments 31 and 32 indicates that improved vulcanizates are obtained also by using less ammonium persulfate in the polymerization at 70° to 92° C.

OTHER VARIABLES

MERCAPTANS. Although the data are not in complete agreement (Table I, experiments 5, 6, 11, and 12; Table II, experiments 3, 11, and 12) and definite conclusions cannot be drawn, mercaptans having approximately 12 carbon atoms appeared to have a beneficial effect upon the copolymerization. When mercaptan was omitted, usually more catalyst and time were re-

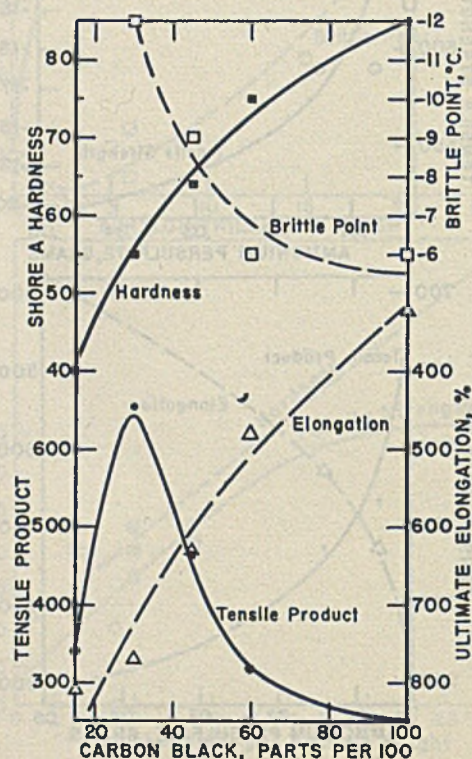


Figure 4. Effect of Carbon Black on Physical Properties of Vulcanizates

Table VI. Effect of Curing Time on Properties of Vulcanizates

Expt. No.	Properties	Curing Time at 148° C., Min.							Vulcanization	Carbon Black, Parts
		10	15	60	90	120	180	240		
15	Tensile strength, lb./sq. in.	640	720	870	820	Standard S	30
	Ultimate elongation, %	700	640	680	570		
	Shore A hardness	59	57	59	55		
39	Tensile strength	460	..	630	730	..	Standard S	30
	Ultimate elongation	1060	..	960	930	..		
	Shore A hardness	48	..	48	50	..		
14	Tensile strength	550	..	720	850	..	Standard S	30
	Ultimate elongation	860	..	850	770	..		
	Shore A hardness	49	..	51	55	..		
14-5	Tensile strength	780	750	790	Standard S	100
	Ultimate elongation	320	250	270		
	Shore A hardness	85	88	89		
14-8	Tensile strength	350	320	1050	..	1240	1380	..	Quinone dioxime & red lead	60
	Ultimate elongation	510	540	370	..	320	300	..		
	Shore A hardness	72	73	75	..	78	84	..		

quired for the polymerization and curing, the Shore hardness and brittle point were higher, and the tensile product was lower.

TEMPERATURE. Polymerization proceeded readily at 67° C. or higher in the presence of catalysts, but at 60° it was considerably more difficult to effect the polymerization and more time was required. Although only a few experiments were suitable for indicating the effect of temperature on properties of the vulcanizate, it appears that lower temperatures have a beneficial effect (Table II, experiments 3, 28, 32, 33, 34, and 37). This is in general agreement with other observations which indicate that improved vulcanizates are obtained when the rate of polymerization is relatively low.

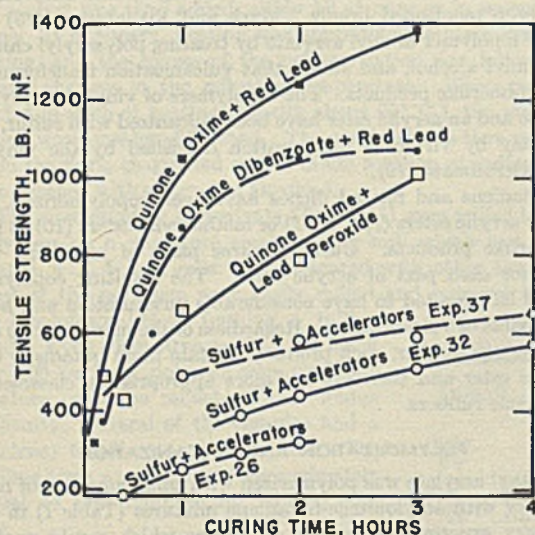


Figure 5. Effect of Curing Time on Tensile Strength of Vulcanizates

METHYL METHACRYLATE. By studying monomer mixtures containing ethyl acrylate, allyl maleate, and 5, 10, or 20% of methyl methacrylate, it was found that the latter compound hardens the copolymer and increases the tensile strength and hardness of the vulcanizates (Table III).

VULCANIZATE PROPERTIES

SOLVENT RESISTANCE. Samples of one of the vulcanizates (experiment 14) prepared from 91% ethyl acrylate, 6% acrylonitrile, and 3% allyl maleate and vulcanized by the standard sulfur formula (Tables I and II) were immersed for 4 days in water, solvents, and various aqueous solutions, and then examined to determine the effect of this treatment. Several of the organic solvents had a weakening effect on the vulcanizate, but only five

of the solvents caused great changes in the weight and dimensions of the samples (Table IV). Water and most of the aqueous solutions had little effect. Hydrogen peroxide solution and 10% nitric acid weakened the specimens, which doubled in weight after immersion in these solutions.

COMPOUNDING AND CURING.

A brief study was made of the effect of carbon black on the properties of the vulcanizates. One of the copolymers (Table I, experiment 14) was vulcanized by nonsulfur methods (Table V,

experiments 14-7, 14-8, 14-9). As the carbon black was increased from 15 to 100 parts per 100 parts of copolymer (Table V and Figure 4), ultimate elongation decreased, hardness increased, and the brittle point was raised. The tensile product increased as the content of carbon black was raised to 30 parts, and then decreased (Figure 4). A harder carbon black (Micronex Beads) with Furnex Beads increased tensile strength and decreased elongation without hardening the sample or raising its brittle point.

Preliminary study of nonsulfur vulcanization methods (5) gave promising results (Table V). Combinations of quinone dioxime, quinone dioxime dibenzoate, red lead, and lead peroxide, developed by Fisher (3) as agents for vulcanizing rubber, produced vulcanizates having higher tensile strengths and greater hardness than the sulfur vulcanizates. Vulcanization with the nonsulfur formulas also decreased the ultimate elongation slightly but had little effect on the brittle point.

Since only one vulcanizing or curing time is listed for each experiment in Tables I and II, additional curing data are given in Table VI and Figure 5 to indicate the effect of curing time at 148° C. on the tensile strength of the vulcanizates. These data show that after the first one or two hours, further changes in the time of curing have no pronounced effect on the tensile strength when the sulfur formula is used. It can be concluded, therefore, that in the study of polymerization conditions (Table I and II) additional curing experiments to determine the optimum time of curing at 148° C. would not have given vastly different results.

The data in Table VI and Figure 5 show also that at 148° C. nonsulfur formulas produced vulcanization more rapidly than did sulfur formulas.

ACKNOWLEDGMENT

The copolymers were compounded, cured, and tested for tensile strength and ultimate elongation by members of the Analytical and Physical Chemistry Division of this Laboratory. The authors gratefully acknowledge this major contribution and their cooperation.

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PRESENTED before the spring meeting of the Division of Rubber Chemistry, AMERICAN CHEMICAL SOCIETY, in New York, N. Y.

.. Lactoprene.. New Synthetic Rubber

Acrylic ester copolymers containing vulcanizable unsaturation were prepared by polymerizing methyl acrylate or ethyl acrylate with small quantities of polyfunctional monomers, such as butadiene, isoprene, and allyl maleate. Compounding the soft copolymers with sulfur and accelerators, followed by curing, produced rubbery

vulcanizates. Several abundant carbohydrates can be converted, through lactic acid as an intermediate, into approximately an equal weight of vulcanized acrylic resins. Because of the key role played by lactic acid in this transformation, the name "Lactoprene" is proposed for synthetic rubber of this type as described here.

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UNLIKE many polymerized methacrylic acid derivatives, polymers prepared from the α -alkyl acrylates (16) are soft and elastic at room temperature. The rubberlike properties of the polymerized acrylic esters have been pointed out by several workers, and the acrylic resins are actually being used as rubber substitutes for certain purposes (20, 29).

Although elastic plastics such as the acrylic and vinyl resins have many uses, it appeared that proper cross linkage or vulcanization might transform these essentially linear polymers into products more nearly resembling rubber. The method of cross linking first selected consisted in copolymerizing the lower alkyl acrylates with small proportions of a polyfunctional monomer and vulcanizing the resulting copolymer (assumed to have olefinic unsaturation) according to the technique and with the agents used in the rubber and synthetic rubber industries.

Vulcanization effected with sulfur, accelerators, and other agents used in rubber compounding, transformed the acrylic resins into rubberlike products that appear to have attractive possibilities. Although this study of vulcanized acrylic resins is not complete, the results are reported because of the unusual current interest in synthetic rubbers (9). Several normally abundant carbohydrates can be transformed, through lactic acid (27) as intermediate, into approximately an equal weight of these new rubberlike materials. Because of the key role played by lactic acid in this transition of carbohydrates into rubber substitutes, the name "Lactoprene" is proposed for vulcanized acrylic resins of the type described in this paper.

The first patent obtained by Rohm (22, 23), who pioneered the industrial exploitation of acrylic resins, was concerned with making artificial rubber. Rohm prepared his rubber substitute by mixing a polymerized acrylic ester with sulfur and "vulcanizing" the mixture at about 40° C., for 2 hours. The mechanism and nature of this vulcanization of essentially saturated acrylic polymers were not described.

Rohm and Bauer (24) described the preparation of acrylic resin mixtures, containing mineral fillers and other materials, which they claimed were suitable for the manufacture of skid-proof tires. According to the reports of other investigators (11, 13), rubberlike materials have been made by the emulsion polymerization of acrylic esters, and the rubberlike properties of acrylic resins have been enhanced by the admixture of tannic acid, ferric acetate, copper powder, and antimony potassium tartrate (25).

Nowak (17, 18, 19) claimed that vulcanization does not occur when polyacrylic esters and sulfur mixtures are heated

VULCANIZATION OF ACRYLIC RESINS

unless a surface catalyst, such as carbon black, is present. His process of making rubberlike materials consisted in incorporating sulfur, β -naphthol, carbon black, and talc into polymerized ethyl acrylate

by milling at 90° to 110° C.

Vulcanization of acrylic polymers having olefinic unsaturation has been mentioned briefly. Mark and Fikentscher (15) prepared a polymer of allyl acrylate by treating polyacrylyl chloride with allyl alcohol, and stated that vulcanization transformed it into rubberlike products. The copolymers of vinyl β -methylcrotonate and an acrylic ester have been vulcanized with sulfur, presumably by virtue of unsaturation furnished by the vinyl β -methylcrotonate (12).

Butadiene and related dienes have been copolymerized with either acrylic esters (1, 6, 8, 31) or methacrylic esters (10) to form rubberlike products. Usually three parts of butadiene were used for each part of acrylic ester. The resulting copolymers would be expected to have considerable unsaturation and hence be capable of vulcanization. Regardless of the merits of this type of synthetic rubber, such products contain more butadiene than acrylic ester and therefore are more appropriately classified as butadiene rubbers.

POLYMERIZATION AND VULCANIZATION

Methyl acrylate was polymerized with small amounts of butadiene or with acrylonitrile-butadiene mixtures (Table I) in preliminary experiments to find conditions which would produce soft, rubberlike polymers. Most of these polymerizations were carried out in a bottle in an electrically heated oven. Agitation was provided by rotation of the bottle, and the temperature of the oven was controlled automatically. In experiment 9 the monomers were dissolved in ethyl acetate prior to polymerization in a three-neck flask. The polymer of experiment 10 was prepared by mass polymerization in a closed test tube. A glass vessel or liner located in an autoclave was used for some of the experiments described in Table I.

In Experiment 28 (Table II), the monomer mixture containing benzoyl peroxide (2.45%) was polymerized with stirring or kneading in a stainless-steel mixer (one-quart capacity) in the absence of solvent or dispersing medium. The mixer was fitted with an efficient reflux condenser because of the exothermic nature of the polymerization. During this mass or bulk polymerization, at reflux temperature, the monomer mixture was added in portions.

The emulsion polymerizations of Table II were carried out in round-bottom, three-neck, Pyrex flasks fitted with thermometer

Table I. Polymerization of Mixtures of Methyl Acrylate, Acrylonitrile, and Butadiene

Expt. No.	Monomers, Grams			Water, Ml.	Aerosol OT, Grams	Sodium Oleate, Grams	Rennet Casein, Grams	Other Components, Grams	Catalyst, Benzoyl Peroxide, Grams	Time, Hr.	Temp., °C.	Properties
1 ^a	14.25	0	0.75	60	0.5	0.5	0.5	Lecithin, 0.5	0.15	18	40	Hard and tough
2 ^a	14.25	1.0	0.75	60	0.5	0.5	0.5	Lecithin, 0.5	0.15	18	40	Elastic and strong
3 ^a	15.1	0	1.6	115.0	1.0	0.5	1.5	Gum tragacanth, 0.1; n-amyl alcohol, 0.25 ml.	0.17	Hard and tough
4 ^a	18.7	1.2	3.7	230	2.0	2.0	2.0	Lecithin, 2	0.19	18	50	Hard and dark
5 ^a	19.5	2.2	2.3	230	2.0	2.0	2.0	Lecithin, 2	0.2	18	60	Hard and tough
6 ^a	60.2	8.0	4.8	240	2.0	2.0	2.0	Lecithin, 2	0.6	18	45	Rubbery
7 ^a	60.2	16.0	4.8	240	2.0	2.0	2.0	Lecithin, 2	0.6	18	45	Hard, tough, amber-colored
8 ^a	45.0	2.5	2.5	210	2.0	2.0	1.0	Starch derivative, 2.0 ^b	0.22	22	40	Rubbery
9 ^c	31.5	1.75	1.75	Ethyl acetate, 140 ml.	0.15
10 ^d	9.0	0.5	0.5	0.04	24	55	Rubbery; good retraction
11 ^a	55	1.5	3.0	210	2.0	2.0	1.0	Starch derivative, 2.0 ^b	0.3	Very rubbery
12 ^a	45	1.5	5.0	180	1.5	1.5	0.6	...	60	Rubbery
13 ^a	100	10	25	470	4.0	4.0	4.0	...	1.05	24	55	Extremely rubbery; bounced
14 ^d	60	0	22.2	310	2.0	2.0	2.0	...	0.6	22	60	Tough; not rubbery
15 ^d	43	2.0	14.4	230	1.5	1.5	0.62	20	68	Hard and tough
16 ^d	40	0	6.0	130	1.0	1.0	1.0	...	0.8	9	80	Soft and rubbery
17 ^d	40	2	6	130	1.0	1.0	1.0	...	0.8	2	85	Soft and rubbery
18 ^a	62	3	59.5	425	2.5	2.5	2.5	...	1.9	5	75-107	Soft and granular

^a Polymerized in rotating bottle located in oven.^b Product prepared from starch and chloroethyl ether by S. G. Morris of this Laboratory.^c Solution polymerized, with stirring, in a three-neck flask.^d Polymerized in a sealed tube.^e Polymerized in a glass-lined rotating bomb.

well, reflux condenser, and water-sealed stirrer (ground-glass joints). The stirrers were paddle, anchor, or half-moon type and were rotated at 75 to 150 r.p.m. The monomer mixture was added to the water and emulsifier (Triton K60S, solution of cetyl dimethyl benzyl ammonium chloride, 30) in the flask, stirred, and heated to refluxing temperature. The desired amount of catalyst was then added, either all at once or in several portions. If necessary, heating was applied to maintain gentle refluxing, and the course of the polymerization was followed by noting changes in the refluxing temperature. When refluxing ceased in spite of heating (usually about 92° C.), the polymerization was considered finished. The emulsion was then removed from the flask, coagulated with a dilute solution of sodium chloride, washed with water, and air-dried.

The compounding ingredients (Table III) were milled into the polymers on a miniature compounding mill which had steam-heated, 4 × 8 inch rolls. As compared with other synthetics, most of the polymers were easily milled and required little or no breakdown before forming a rolling bank. Even when 60 parts of carbon black per 100 parts of polymer were used, the mixture could be milled without undue difficulty. Several of the samples had a tendency to adhere to the back roll. The milling time was short and approximately equal to that required for natural rubber.

The compounded mixtures were cured in stainless-steel "sandwich" molds to obtain sheets having the dimensions 4 × 4 × 0.025 inch. In the initial stages of the study, the cured specimens adhered to the sandwich and removal from the mold was difficult. The method of curing the specimens between two sheets of cellophane was then adopted and used in the later experiments.

In most instances the polymers were compounded according to a Butyl rubber formula. The following ingredients were used (parts per 100 parts of polymer): Captax (mercaptobenzothiazole), 0.5; zinc oxide, 5; stearic acid, 2; sulfur, 2; Furnex Beads (carbon black), 30; Tuads (tetramethylthiuram disulfide) 1. The

compounded mixtures were cured under various conditions, but only the conditions leading to best results are reported in Table III. The best compounding formula and optimum curing conditions were not determined.

The tensile strength, ultimate elongation, and hardness (Shore A durometer) were determined by standard methods, except that the specimen was not of standard thickness. The behavior of some of the samples in a hydrocarbon solvent (50% toluene-50% heptane) was determined by immersing a weighed specimen in the solvent for periods of 1 to 4 days, allowing it to dry for 30 minutes, and then weighing. The results are given in Table III. The brittle points of some of the samples were determined with apparatus of the type described by Selker, Winspear, and Kemp (14, 26). The bath liquid was petroleum ether. Specific gravity was determined by suspending the sample in standard zinc chloride solutions, according to a previously described method (2). The specific gravity of the samples examined was approximately 1.31. Natural rubber, Neoprene GN, Buna S, Thiokol F, Koro-

Table II. Polymerization of Acrylic Esters in the Presence of Polyfunctional Monomers

Expt. No.	Monomers, Grams	Water, Ml.	Triton K60S, Grams	Time, Min.	Catalyst, Ml. ^a
19	Ethyl acrylate, 90; allyl lactate maleate, 10	150	2.0	60	H ₂ O ₂ , 1
20	Ethyl acrylate, 180; allyl lactate maleate, 20	250	3.0	55	H ₂ O ₂ , 1
21	n-Butyl acrylate, 60; allyl lactate maleate, 20; methyl acrylate, 120	250	3.0	80	H ₂ O ₂ , 1
22	Ethyl acrylate, 500; allyl maleate, 55	700	8.5	30	H ₂ O ₂ , 5.5
23	Methyl acrylate, 85; 2-ethyl hexyl acrylate, 10; allyl maleate, 5	150	2.0	60	H ₂ O ₂ , 2
24	Ethyl acrylate, 98; isoprene, 2	150	2.0	210	H ₂ O ₂ , 14; benzoyl peroxide, 2 g.
25	Ethyl acrylate, 250	300	4.0	20	H ₂ O ₂ , 0.5
26	Ethyl acrylate, 99.5; allyl maleate, 5	150	2.0	45	H ₂ O ₂ , 0.5
27	Ethyl acrylate, 98; allyl maleate, 2	150	2.0	55	H ₂ O ₂ , 0.5
28 ^b	Ethyl acrylate, 380; isoprene, 20	130	Benzoyl peroxide, 10 g.
29	Methyl acrylate, 140; n-butyl acrylate, 42; allyl lactate maleate, 20	275	3.0	...	H ₂ O ₂ , 4
30	Methyl acrylate, 46.5; n-butyl acrylate, 46.5; allyl lactate maleate, 12	150	2.0	...	H ₂ O ₂ , 2; benzoyl peroxide, 0.5 g. Benzoyl peroxide, 0.7 g.
31	Methyl acrylate, 70; acrylonitrile, 3; butadiene, 13.5	250	"	26 hr.	H ₂ O ₂ , 3.5
32	Ethyl acrylate, 90; acrylonitrile, 5; allyl maleate, 5	150	2	6	H ₂ O ₂ , 2 ^d
33	Ethyl acrylate, 95; allyl maleate, 5	150	2	40	H ₂ O ₂ , 2.5 ^e
34	Ethyl acrylate, 180; acrylonitrile, 10; allyl maleate, 10	250	2	65	H ₂ O ₂ , 2.5 ^e

^a The concentration of hydrogen peroxide was 30%.^b Mass polymerization.^c Emulsifying agents were 2 grams Aerosol OT, 2 grams sodium oleate, and 2 grams casein.^d Mercaptan 3B (0.5 ml.) also was present during the emulsion polymerization.^e Dodecyl mercaptan (0.5 ml.) also was present during the emulsion polymerization.

Table III. Vulcanization and Test Data^a

Expt. No.	Deviations from Standard Formula, Parts	Curing Conditions		Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	% Gain in Wt. after Immersion in		Brittle Point, °C.
		Min.	° F.				50 toluene, 50 heptane	Water	
19	2 Tuads	180	274	290 ^b	800	35
20A	20 Furnex Beads	120	274	270 ^b	210	48
20B	Furnex Beads omitted	150	274	190 ^b	300	35
20C	30 Micronex in addition to Furnex	90	274	890 ^b	140	77	12.5 ^c	4.1	-18
21A	40 Furnex Beads	120	274	830	160	77	15.5	4.9	-11
21B	None	150	274	820 ^b	260	63
22	40 Furnex Beads	140	294	360 ^b	300	48
23	None	30	298	1070 ^b	270	78
24	None	80	298	350 ^b	1020	50	22.0 ^c
25A	None	80	298	290 ^b	>2700	47	^d
25B	Only 95 polymer and 5 S	360	122
25C	10 allyl lactate maleate	80	298	0	>2800	32
26	None	80	298	310 ^b	380	48	8.5
27	None	80	298	510 ^b	700	41	20.0	1.6
28	None	110	298	440 ^b	160	50
29	2 Tuads	15	287	960	500	-6
30	3 S; 15 Furnex Beads	10	307	270	160	55
31	2 Tuads	120	274	1840 ^b	120	77	15.0
32	None	120	298	990 ^b	490	47	17.3 ^c	3.5	-8
33	None	120	298	380 ^b	530	46	16.3 ^c	3.5	-19
34	None	120	298	760 ^b	960	48	14.2	5.8	-11

^a Standard compounding formula (parts by weight): Polymer, 100; Captax, 0.5; stearic acid, 2; zinc oxide, 5; sulfur, 2; Furnex Beads, 30; Tuads, 1.

^b Apparently optimum curing conditions for maximum tensile strength were not reached.

^c Samples were weakened. ^d Polymer dissolved. * Vulcanization did not occur.

seal, and Hycar OR have densities of 0.92, 1.24, 0.96, 1.38, 1.33, and 1.00, respectively (7).

The *n*-butyl acrylate (21), 2-ethyl hexyl acrylate, allyl maleate, and "allyl lactate maleate" used in some of the experiments were prepared in connection with other investigations. The *n*-butyl and 2-ethyl hexyl acrylates were prepared by alcoholysis (21) of methyl acrylate. Allyl maleate was prepared by direct esterification. The allyl lactate maleate, which was made by the interaction of allyl lactate and maleic anhydride, is believed to consist mainly of di-(1-carboalloxy ethyl) maleate. Commercial grades of butadiene and isoprene (95%) were used after purification.

Several of the copolymers were insoluble in organic solvents and, hence, were probably cross linked. Presumably cross linkage was not extensive enough to preclude the presence of olefinic linkages. Probably the copolymers had olefinic unsaturation and were transformed into thermosetting products through genuine sulfur vulcanization. It should be pointed out, however, that the only evidence supporting this view is the fact that treatment with sulfur and suitable accelerators effected changes in the physical properties that roughly resembled those occurring with rubber or Butyl rubber under similar conditions.

DISCUSSION OF RESULTS

The preliminary polymerization experiments showed that soft, elastic polymers could be made from methyl acrylate and butadiene under certain conditions (Table I). With the exception of experiment 16, a tough or hard polymer was obtained when methyl acrylate and butadiene were polymerized in the absence of acrylonitrile. Probably cross linkage was responsible for the fact that these polymers were not rubberlike.

Ethyl acrylate was used in several of the experiments listed in Table II because the polymers of this ester are unusually similar to rubber in appearance and feel. Mixtures of methyl acrylate with other alkyl acrylates (*n*-butyl or 2-ethyl hexyl) were polymerized because the copolymers thus prepared were softer than the methyl acrylate polymers obtained under the same conditions. The relatively hard and tough methyl acrylate polymers could be softened by plasticization, but soft copolymers were selected for study in preference to plasticized methyl acrylate polymers.

In view of claims made by earlier workers (17, 18, 19, 22, 23, 24), attempts were made to vulcanize the polymer of ethyl acrylate (Table II, experiment 25). No effect that could be attrib-

uted to vulcanization was observed when mixtures of ethyl acrylate polymer containing sulfur alone or sulfur, carbon black, and other agents (Table III, experiment 25A and 25B) were heated under curing conditions. These results were expected, since the polymers of alkyl acrylates have little or no unsaturation.

In preparing the copolymers listed in Table II, only small amounts of the polyfunctional monomers (2 to 13.5% of the total monomer mixture) were used because the primary purpose of the copolymerization was to furnish olefinic linkages in the polymer chains. Acrylonitrile was used because it had appeared to inhibit cross linkage during the polymerization of butadiene-methyl acrylate mixtures in the preliminary experiments (Table I). Dodecyl mercaptan was used also in some experiments to prevent or retard cross linkage. The polymerization appeared to proceed smoothly and with less violence when dodecyl mercaptan was present. Possibly xanthogen disulfides, carbon tetrachloride, and other agents (7) could

be used for the same purpose.

Unlike the simple alkyl acrylate polymers (Table II, experiment 25), the unsaturated copolymers were readily vulcanized when compounded suitably with sulfur, carbon black, and certain active accelerators sometimes used with Butyl rubber (Table III). Relatively inactive accelerators were less suitable. The vulcanized samples were rubberlike in appearance and feel, and were distinctly superior to the unvulcanized products. Before vulcanization, the samples could be drawn out almost indefinitely and had negligible tensile strength. The vulcanized samples had tensile strength as high as 1840 pounds per square inch, and the elongation ranged in most instances from 200 to 800%. Shore A durometer hardness ranged from 32 to 78 (Table III). As little as 2% of the polyfunctional monomer (Table II, experiments 24 and 27) provided enough unsaturation for vulcanization.

Results obtained with an ethyl acrylate polymer plasticized with allyl lactate maleate (Table III, experiment 25C) indicate that the vulcanizable products were true copolymers. The ethyl acrylate-allyl lactate maleate copolymer (experiments 19 and 20) was vulcanizable, whereas the ethyl acrylate polymer plasticized with allyl lactate maleate could not be vulcanized under comparable curing conditions (Table III, 25C).

Although the ethyl acrylate polymer was soluble in a mixture of toluene and heptane (equal portions), the vulcanized products were insoluble in this mixture. The vulcanized products, however, swelled and absorbed some of the hydrocarbon mixture during immersion tests (Table III). Some of the products tested (21A, 21B, and 24) were noticeably weakened by immersion in the toluene-heptane mixture. The vulcanized products increased in weight as much as 5.8% when immersed in water, but no other effect was apparent.

Brittle temperatures of the samples tested (Table III) ranged from -6° to -19° C. According to Trommsdorff (28), the polymers of methyl, ethyl, and *n*-butyl acrylate have softening points of +8°, -20°, and -40° C.

POSSIBLE USES AND SOURCES

Although vulcanized acrylic resins in their present stage of development are not suitable substitutes for rubber for all purposes, it is expected that Lactoprene will prove useful as an elastomer in several fields (9). Moreover, it seems reasonable to expect that further research will improve the rubberlike properties of vulcanized acrylic resins and extend the scope of their usefulness. Even

in the present stage of development, Lactoprene is superior in tensile strength and ultimate elongation to some of the products (4, 5) now being used to replace rubber. On the basis of the results shown in Table III and the structure of vulcanized acrylic resins, Lactoprene would be expected to resist oils and aging better than natural rubber. Fisher (9) listed several fields in which oil-resistant synthetic rubbers, but not natural rubber, can be used.

POSSIBLE USES AND SOURCES

Although acrylic esters can be made from either coal or petroleum, carbohydrates merit consideration as a starting material because of their abundance in normal times, low cost, and reproducibility. Carbohydrates can be converted to acrylic esters by the following steps (27): fermentative production of lactic acid, esterification of lactic acid with methanol, acetylation of methyl lactate, and pyrolysis of the acetylated methyl lactate (3). Yields are high; one pound of carbohydrate can be transformed into approximately one pound of Lactoprene.

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Vinyl Butyrals in the Rubber Industry

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IN RECENT years there has been a strong tendency toward the use of certain plastic materials in the rubber industry, a trend which has been strongly accelerated by the war. The types of synthetic plastics which have shown themselves adaptable to rubber processing techniques are commonly known as elastomers and are to a large extent based on vinyl resins. One group which is closely related to rubber in methods of processing is vinyl acetals, particularly the vinyl butyrals.

Vinyl acetals were originally developed in Canada in the late 1920's. The method of manufacture is essentially to polymerize vinyl acetate, hydrolyze the polymer to polyvinyl alcohol, and react the polyvinyl alcohol with an aldehyde to form an acetal. The properties of the resulting resin depend on several factors, including the viscosity of the original polyvinyl acetate which indicates the chain length of the molecule, the degree of completion of both the hydrolysis and acetalization, and the particular aldehyde used in the acetal reaction. The viscosity of the polymer is generally made as high as commercially possible because

greater toughness at elevated temperatures results; but for applications where the resin is to be used in solution, lower-viscosity polymers are also made to allow thinner solutions with higher solid contents. In any vinyl acetal the hydrolysis reaction is never complete so that some acetate groups always remain in the polymer chain. It is also customary to acetalize only a portion of the polyvinyl alcohol so that generally several hydroxyl groups are also on the chain. Since the remainder of the molecule is acetal, it is evident that any vinyl acetal can be widely varied, depending on the quantity of the three groups present on the one molecular chain—hydroxyl, acetate, or acetal. Finally, the longer the molecule used to form the acetal, the more easily is the resin plasticized. For example, if formaldehyde is used, the resin requires almost equal quantities of a liquid plasticizer to form an elastomer. If octyl aldehyde is employed, the resin itself is fairly flexible with no plasticizer added at all.

When butyraldehyde is the aldehyde in the acetal reaction with polyvinyl alcohol, a resin is formed of varying properties

depending on the degree of completion of the reaction. The usual vinyl butyrals have a weight analysis of less than 2% vinyl acetate and 8 to 22% vinyl alcohol, the remainder of the molecule being vinyl butyral. In its original form it is a white granular flake which coalesces at about 240° F. to a clear, hard, tough solid of a light amber color.

The addition of plasticizer progressively softens this material until, with fairly large amounts, a flexible and extensible stock is obtained.

The first major use for vinyl butyral was in a plastic containing about 40 parts of a plasticizer such as dibutyl sebacate and nothing else. This compound was calendered or extruded into continuous sheets 0.015 inch thick which were used as the inner layer of the glass-plastic-glass sandwich, safety glass. With the cessation of automobile production, large quantities of the resin were suddenly made available. A natural field to approach was that of cloth coating or the preparation of pure gum film which had been gradually invaded by vinyl chloride type materials.

Vinyl butyral, like all vinyl resins, is thermoplastic. The first experiments in the cloth coating field were made with compounds containing resin, fairly large proportions of a suitable plasticizer, pigments, fillers, and a lubricant. These compounds coated well, and a fair amount of coated fabric was used by the Quartermaster Corps. However, plasticized butyral has a lower softening point than is desirable, and much difficulty was encountered when these coatings became sticky or even soaked into the fabric at temperatures as low as 160° F. The next step, then, was to reduce this thermoplasticity.

A number of attempts were made to cross link two molecule chains of vinyl butyral, presumably by condensation through the hydroxyl group, but none was commercially successful until the spring of 1942 when a process was developed by J. L. Haas of Hodgman Rubber Company, Inc., which made possible a heat-curing material. Although this cross linking was apparently a condensation reaction, it was physically if not chemically analogous to the vulcanization of rubber. Since that time, largely owing to the commercial practicability of the Haas process, many thousands of miles of fabric have been coated in rubber proofing plants by means of thermosetting vinyl butyral plastics, and a

Polyvinyl butyral is one of the new elastomers that has found widespread use in the rubber industry during the war. Originally developed for safety glass, it has been adapted to rubber processing for such applications as waterproof fabrics, free film, tubing, and many other articles. It has been rendered vulcanizable to reduce its thermoplasticity and is otherwise easily handled on all standard rubber-processing equipment. Its transparency, elasticity, strength, durability, and attractiveness make it a new raw material available to the rubber industry for its expansion into the field of plastics.

number of other applications have been developed as well.

COMPOUNDING

The compounding agents for vinyl butyral can be divided into five classes—plasticizers, curing agents, fillers, colors, and miscellaneous ingredients such as stabilizers and lubricants. The amount and type of plasticizer

is the main variable in determining flexibility. Esters either of the chemical type, such as phthalates, or the vegetable oil type, such as ricinoleates, are commonly used, and the quantity varies from 30 to 120 parts per 100 parts of resin. Plasticizers are either of the solvent type, which have unlimited ability to absorb resin until a gel or clear solution is formed, or the mechanical type, which tend to exude if more than a limited quantity is incorporated with the resin. Greater nerve and toughness are usually obtained with the latter, softness and flexibility with the former; a mixture of the two types is usually prescribed for a specific application. If the plasticized resin is slabbed out (a process which requires thorough and severe mastication in internal mixers and strainers and cannot be performed well on a rubber mill), then this slab can be considered analogous to raw, crude, or synthetic rubber.

Further compounding follows rubber practice closely and can be readily performed on a rubber mill. Curing agents are selected for the particular purpose required, and are available for cure rates varying from rapid at temperatures as low as 150° F. to slow at 300° F. The nature of most of these ingredients is under a Patent Office secrecy order at the present time.

Fillers are added either for cheapening or reinforcing. The best filler for simple loading is fine ground whiting, and quantities as high as 100 parts per 100 parts of resin have little effect on physical properties of the stock. For example, adding 100 parts of atomite to a typical stock raised Young's modulus at -35° C. from 31,000 pounds to only 40,000 pounds per square inch, and raised the brittle temperature from -60° to -40° C. It has no effect on tensile strength or elongation at break. Other fillers, such as clay or Silene, dry out the stock with greater toughness and stiffness as a result. Any common filler can be used with no harmful chemical effect on the resin. Carbon blacks reinforce but not to the extent common in rubber. Fifty parts of lamp-

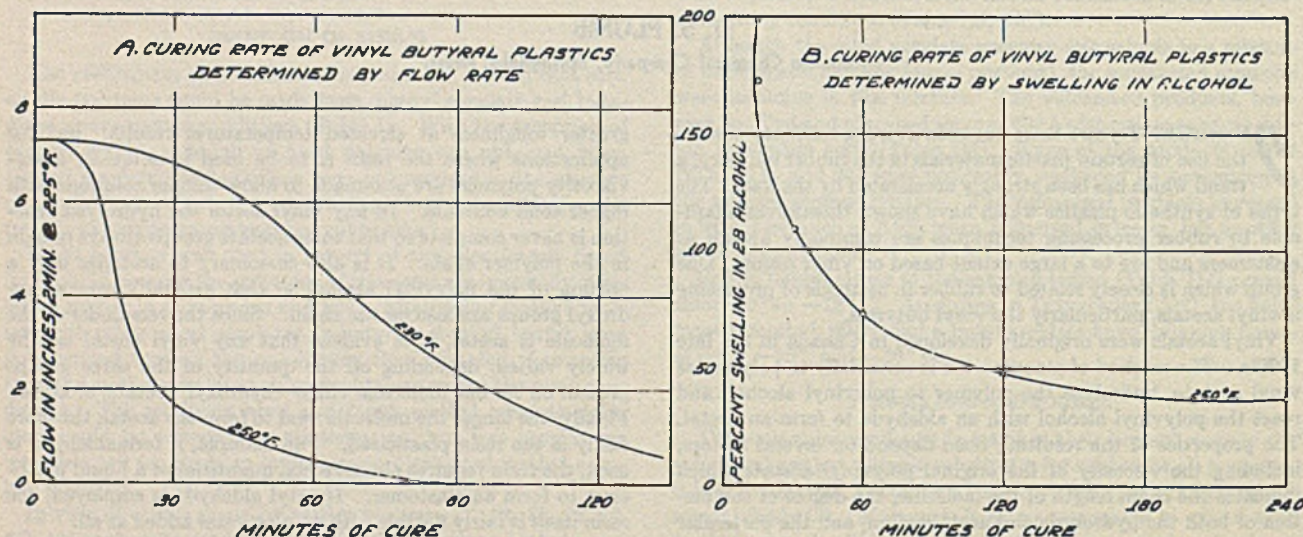


Figure 1

black in the stock described above raised the tensile strength from 1200 to 1900 pounds per square inch, the brittle temperature to -45°C. , and Young's modulus at -36°C. to 39,000 pounds per square inch. Very fine channel blacks have the same effect as lampblack, but less is required.

Colors must be selected only on the basis of their permanence except when two colors are to be cured in juxtaposition; in the latter case oil-soluble dyes might bleed one into the other, a fact which must be determined experimentally. Common lubricants are used as in rubber compounding.

PROCESSING

Unlike those resins requiring extremely high temperatures, the butyral is amazingly easy to process on the usual rubber equipment. The average stock runs perfectly on a calender at about 210°F. , and no stock requires a higher temperature than 250°F. With the usual curing ingredients the stock can be handled for a matter of hours at 220° to 230°F. without scorching but will cure rapidly in air at 270°F. Frictioning can be performed readily if the center roll is first wiped thoroughly with a rag dipped in plain milk.

Coatings or pure gum taken from a calender are surface-treated with dust or lacquer exactly as rubber, soapstone and mica being commonly used. Curing of finished fabrics or fabricated articles is best accomplished in hot air, the usual cure being one hour at 260 – 270°F.

Extrusion of vinyl butyrals offers no problems to the rubber tuber, the average stock running at 180 – 220°F. Extruded articles can be wrapped and cured on mandrels in open steam. Molding requires special compounding and is facilitated by the use of carbon black, although black is not essential. The butyrals tend to soften rapidly with heat before they set up; therefore excessive flash is frequently encountered where mold clearances are high. With a cycle of 5–7 minutes at 320 – 340°F. , good moldings are obtainable provided the pressure is adjusted to avoid flash. Pieces as complicated as a gas mask facepiece have been molded on production lines. Heat-curing butyrals are contrasted to thermoplastic vinyl resins in their ability to be pulled hot from the mold. Molded sponge of both the open-cell and unicell type can also be made by standard rubber-expanding processes.

The chief differences in behavior faced by the rubber processor are in fabrication. Like all vinyls and many synthetic rubbers, tack is not obtainable without moistening with solvent. However, as soon as operators become familiar with the necessity for a solvent-wet surface to obtain tack, most fabrication problems on

uncured stock can be met with no difficulty. By incorporation of tackifiers, such as rosin derivatives and some alkyds, some cements have been prepared which have excellent tack while wet with solvent and give a longer working life than is experienced with pure solvent. Cured plastics are insoluble in all solvents so far tested, so that fabrication is extremely difficult although air-curing cements with fair strength will adhere to a carefully prepared surface.

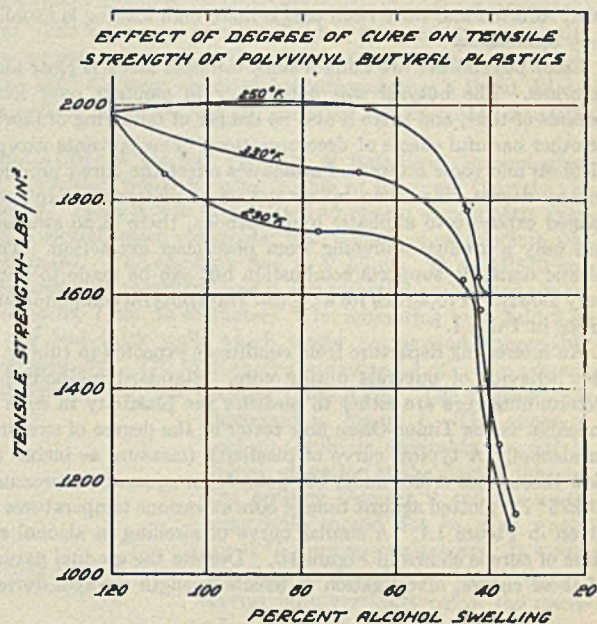


Figure 2

Uncured vinyl butyrals are generally soluble in all alcohols although one commonly used resin is soluble only in ethyl alcohol or ethyl acetate. No other active solvents except alcohols are of commercial importance, but alcohol solutions are commonly diluted with naphtha, aromatics, or practically any other solvent to give smoother drying rates and lower cost. Butyral solutions are used for coating of fabrics, casting of film, or preparation of dipped articles.

Dispersions of thermoplastic butyrals have been made with some success, and it is expected that a butyral latex will be available for all types of compound shortly; this work is still experimental.

PROPERTIES

The properties of vinyl butyral render it particularly useful in coated fabrics where it has demonstrated major military importance, in free film, and in applications where its particular properties such as transparency can be employed. It has excellent abrasion resistance, extreme flexibility, softness and warmth of texture, and good resistance to age, oxidation, and sunlight. Its water absorption runs about 3%. The permeation of water vapor is fairly high compared to such materials as Saran. It has poor flex fatigue life, particularly where flexing is rapid, as it is a "dead" material and builds up heat when flexed rapidly. Although most stocks have poor compression sets, a set as low as 25% at 160°F. (A.S.T.M. constant-deflection method) is readily obtainable. The tensile strength varies from 1000 to 3500 pounds per square inch, depending on compound with corresponding ultimate elongation of 400 to 200%. Tensile strength usually falls off rapidly at temperatures higher than 140°F. , but reinforcing blacks assist in maintaining considerable strength up

Table I. Physical Properties of Typical Thermosetting Vinyl Butyral Compound

Tensile strength, lb./sq. in.	1470
Elongation (A.S.T.M. Method D-412), %	300
Tear strength (A.S.T.M. D-624), lb./in.	120
Permanent set (A.S.T.M. D-395, constant deflection), %	
25°C.	27
71°C.	25
Brittle temp. (A.S.T.M. D-746), $^{\circ}\text{C.}$	-40
Modulus of elasticity in flexure (A.S.T.M. D-747), lb./sq. in.	
$+25^{\circ}\text{C.}$	About 200
-35°C.	68,000
-57°C.	220,000
Water absorption in 24 hr. at 25°C. (A.S.T.M. D-570), %	2.2
% plasticizer loss after:	
Water absorption test	0.2
Heating 72 hr. at 82°C.	1.6
Abrasion resistance in Du Pont abrader, cc./hp. hr.	107

CHEMICAL RESISTANCE AFTER 7-DAY IMMERSION AT 25°C. (COR. FOR EXTRACTABLES)

Solution	% Absorption	Effect
3% sodium chloride	2.1	None
10% sodium hydroxide	7.4	Color darkened
30% sulfuric acid	3.4	Color darkened
100-octane gasoline	9.2	Slight stiffening after drying
Toluene	67	Bad softening

to 200° F. Prolonged exposure to 180° F. has no effect so long as nonvolatile plasticizers are used.

Like most vinyls, the butyral has a tendency to stiffen at low temperatures, Young's modulus changing from 200 pounds per square inch at +77° F. to 16,000 pounds at -5° F., 40,000 pounds at -40° F., and 235,000 pounds at -70° F. However, brittle temperatures are usually very low, generally below -40° F., and some stocks are below -90° F. The specific gravity of the base resin is 1.06; finished compounds can run as high as 1.4. Since the covering power and most of the properties are not seriously affected and since resin cost is high, high loading is usually very economical.

Color possibilities are infinite since the base stock is clear and colorless. The butyral will not yellow in sunlight over long periods of time, and there is also no danger of tendering of fabric or other harmful effects of decomposition. Few solvents except alcohols and some esters and aromatics affect the cured product to any degree other than by extraction of plasticizer. In prolonged exposure to aliphatic hydrocarbons, there is no swelling but only a gradual stiffening from plasticizer extraction. The plastic normally supports combustion but can be made to burn very slowly. Properties for a typical vinyl butyral compound are given in Table I.

An interesting departure from conditions expected in rubber is the behavior of butyrals during cure. Standard methods for determining cure are either to measure the plasticity in such a machine as the Tinius-Olsen flow tester or the degree of swelling in alcohol. A typical curve of plasticity (measure as inches of flow through an orifice under 100 pounds per square inch pressure at 225° F.) plotted against time of cure at various temperatures is given in Figure 1A. A similar curve of swelling in alcohol vs. time of cure is shown in Figure 1B. Despite the gradual nature of these curves, investigation of tensile strength changes during

cure shows a more abrupt change and, contrary to rubber, a change downward. Figure 2 presents such a curve with tensile strength plotted against alcohol swelling for three different curing temperatures. It is evident that overcuring is harmful chemically and that optimum cure is obtained where the curve starts to drop. No explanation is given for this behavior as yet, but since the overcure point is far beyond most practical cures, this phenomenon does not appear to be serious.

APPLICATION

Military applications have consumed all the vinyl butyrals since the stoppage of safety glass manufacture. Chief uses have been army raincoats, double-textured waterproof clothing, water, food, and clothing bags, and flotation gear. On a smaller scale, production items include 18-ton pontoons, heavy-duty hose, film for waterproof (but not vaporproof) packaging, soft and hard sponge, miscellaneous tubing and molded parts. A specialty use has taken advantage of its resistance to mustard and other vesicant gases for the coating of large quantities of fabric for the Chemical Warfare Service.

For civilian applications the properties of beauty, attractive softness, and chemical resistance will be of advantage. The possibilities in waterproof fabrics and film ranging from crib sheeting to industrial aprons, clothing to tablecloths, are infinite. It may even be an ingredient of the experimental but much dis-cussed plastic shoe sole.

Vinyl butyral is not to be considered a competitive material for crude or synthetic rubber. It offers some properties unavailable in rubber, combined with ability to be processed by rubber mills. It is thus a new raw material available to the rubber industry for expansion into the field of plastics.

PRESENTED before the spring meeting of the Division of Rubber Chemistry, AMERICAN CHEMICAL SOCIETY, in New York, N. Y., 1944.

Viscosity of Liquid Styrene and Butadiene

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FOR styrene an open Ostwald viscometer was employed of the standard type suitable for liquids of medium viscosity. The upper bulb held roughly 2 ml., the capillary was 8.0 cm. long, and the average head during a run was some 12 cm. The volume of liquid added was about 5 ml., enough to fill the lower bulb always to the same level with the liquid warmed to the temperature of the run. The viscometer was immersed in a transparent water jacket with a stirrer and calibrated thermometer.

Calibrating runs with distilled water were made at nine temperatures between 24° and 77° C. Water is a suitable cali-

brating liquid because its kinematic viscosity is close to that of styrene. The temperature in the water runs was varied in order to cover a range of viscosities, since the principal source of error under the conditions was end effects (δ). The viscometer constant in the form v/θ was plotted against θ^{-2} . This is a convenient plot, since a straight line should be obtained if the head lost in end effects is proportional to the velocity head. This may be shown by writing Poiseuille's law explicit for head and adding the term $\alpha(u^2/g)$. On rearranging,

$$\left(\frac{v}{\theta}\right) + \frac{\alpha Q}{8\pi L} \left(\frac{1}{\theta}\right)^2 = \frac{\pi H D^4 g}{128 Q L}$$

The viscosity of liquid styrene and liquid butadiene monomers was determined in Ostwald type viscometers over a useful range of temperatures. The primary purpose of the experiments was to obtain values of viscosity which are sufficiently accurate for the design of heat transfer equipment involving these compounds.

On plotting the water runs in this way it was apparent that a straight line was a satisfactory curve. The line obtained by the method of averages gave an average deviation in v/θ , for all the points, less than 0.5% from the line. From the slope, α was calculated to be 0.78; from the

Table I. Viscosity of Liquid Styrene and Liquid Butadiene

Styrene at Atm. Pressure				Butadiene at Satn. Pressure			
Temp., °C.	Viscosity		Density (4), G./Ml.	Temp., °C.	Viscosity		Density (4), G./Ml.
	Centi- poises	Centi- stokes			Centi- poises	Centi- stokes	
0	1.060	1.186	0.9240	-20	0.245	0.366	0.6687
10	0.882	0.965	0.9148	-15	0.229	0.346	0.6631
20	0.751	0.829	0.9058	-10	0.215	0.327	0.6574
25	0.696	0.773	0.9010	-5	0.201	0.309	0.6518
30	0.650	0.725	0.8965	0	0.189	0.293	0.6457
35	0.607	0.681	0.8919	5	0.178	0.279	0.6396
40	0.567	0.640	0.8873	10	0.168	0.265	0.6336
45	0.534	0.605	0.8827	15	0.158	0.252	0.6274
50	0.504	0.574	0.8781	20	0.149	0.240	0.6212
55	0.478	0.547	0.8735	25	0.141	0.229	0.6150
60	0.455	0.524	0.8689	30	0.133	0.219	0.6085
65	0.435	0.503	0.8643	35	0.125	0.208	0.6022
70	0.414	0.482	0.8597	40	0.119	0.199	0.5957
75	0.394	0.461	0.8551	45	0.112	0.191	0.5891
80	0.375	0.440	0.8506	50	0.106	0.183	0.5822
90	0.340	0.404	0.8414	55	0.101	0.175	0.5754
100	0.310	0.372	0.8322	60	0.095	0.168	0.5684
110	0.290	0.352	0.8230				
120	0.270	0.332	0.8138				
130	0.250	0.311	0.8047				
140	0.233	0.293	0.7955				
145	0.225	0.284	0.7909				

intercept, D was 0.0494 cm. These values are only approximate since Q , L , and the average value of H were not measured accurately. By filling with mercury and weighing the mercury, D equaled 0.0491 cm. The v/θ intercept at $\theta = \infty$ was 0.0001080 stoke per second, and v/θ decreased about 6% over the range of the tests. This method of calibration assumes α is approximately the same for both liquids, which seems reasonable in view of its practical constancy for water over the temperature range used.

The styrene was shipped in a 5-gallon can from the Institute, W. Va., plant of Carbide & Carbon Chemicals Corporation on September 21, 1943. Their analysis showed:

Sp. gr., 20/20° C.	0.9069
Styrene, % by wt.	99.03
Aldehydes (as benzaldehyde), % by wt.	0.011
Peroxides (as hydrogen peroxide), % by wt.	<0.001
Polymer, % by wt.	<0.50
Solubility of polymer	Complete
Viscosity, centipoises at 20° C.	0.76
Inhibitor, p.p.m. <i>p</i> -tert-butylcatechol	10

The polymer analysis is by methanol dilution (L.M. 2.2.6, Method II of Rubber Reserve Company). Method I (L.M. 2.2.6, vacuum distillation) shows an average of less than 0.01% polymer (2). Thus, not enough high-molecular-weight polymer is present to affect the viscosity appreciably. The runs on styrene were made 20 days later. There had apparently been negligible polymerization in the interim, since the viscosity at 20° C. had not changed appreciably. Duplicate runs 5 to 10 minutes apart were made at eight temperatures between 25° and 75° C. The duplicates checked almost exactly, an indication of no polymerization during the interval. Furthermore, the viscosities found closely checked several values obtained on a previous shipment. A new styrene sample was employed for each temperature.

From the calibration curve and the observed θ , v then μ were calculated from given values of ρ (4). A differential Porter plot against benzene was prepared by plotting the temperature of the styrene viscosity runs against the difference between that temperature and the temperature at which benzene would have the same viscosity (3). The average deviation of the temperature difference points from the smooth curve was less than 0.3° C. By this method of interpolation μ and v for styrene were obtained for each 5° C. interval from 25° to 75° C., and v checked well with a direct plot of the original kinematic viscosity-temperature data. The values are listed in Table I and probably are not in error by more than 1%. The values of μ and v down to 0° and up to 145° C. were obtained by extrapolating a linear Porter plot against water (3) and are probably correct within 2 to 3%.

BECAUSE of the low viscosity of butadiene, the end-effect correction would be considerable in the usual Ostwald viscometer. Since it was also desired to exceed atmospheric pressure, a special sealed viscometer with a long helical capillary was constructed. The capillary had $L = 63$ cm., $D = 0.0570$ cm. (measured with mercury), and it was smoothly coiled into almost three turns, 7 cm. in diameter. The measuring bulb held 2.80 cc. and had thick walls which would not expand appreciably under pressure. The total charge was some 4.1 cc. The average head during a run was between 7 and 8 cm. The viscometer is illustrated in Figure 1. The upper or hold-up bulb is desirable to obtain smooth operation at the start of the run. The opening between it and the measuring bulb should not be very small; about $1/16$ inch is satisfactory. It would probably be desirable to locate the receiving bulb vertically below the measuring bulb (6). In this case, however, it was not deemed necessary since the liquid levels were measured during each run in any case. White (6) showed that error due to curvature of the capillary (using a smoothed curve through his tabulated values) is negligible for a value of the Reynolds number times the square root of the capillary to coil diameter ratio of less than about 10.

Calibrating runs were carried out with distilled water at room temperature and with *c.p.* diethyl ether, which has a viscosity approaching that of butadiene, from 20° to 75° C. Because of the inconvenience of changing the amount of liquid in the viscometer at each temperature in order that the average head remain constant, the same charge of ether was employed in all runs, and the head in the upper and lower bulbs was read eight or ten times during each run, by parallel scales to avoid parallax. The differential head was graphically integrated against time to give its average value, and the viscometer constant calculated in the form $(v/\theta H_{av})$. Actually, the average level of the upper bulb was always practically the same, and the level of the lower bulb did not change very fast or unevenly. Thus it was necessary only to determine three or four levels of the lower bulb to compute H_{av} for a given run, once

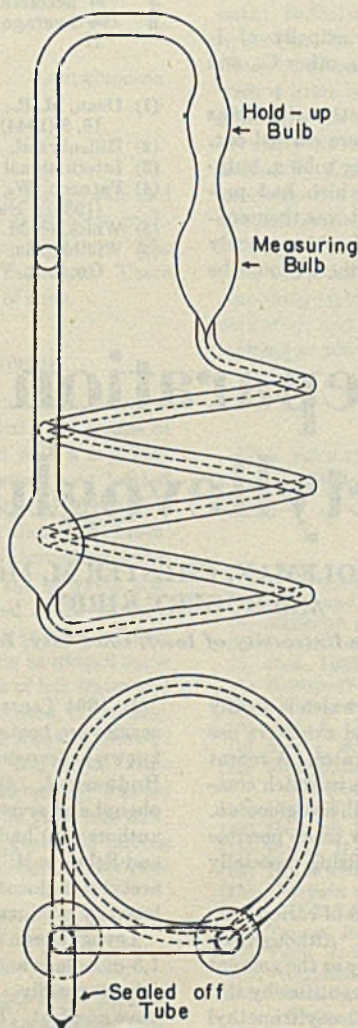


Figure 1. Scaled Viscometer

the average for the upper bulb had been determined with respect to a fixed mark on the viscometer.

The six water runs at 24.1° C. gave an average ($v/\theta H_{av.}$) of 0.000001502 cm./sec.², with an average deviation of 0.3% and no curvature error. Ether was run twenty-seven times between 17° and 70° C. The average ($v/\theta H_{av.}$) of the runs was 0.000001494 with an average deviation of 0.9%, suggesting slight end and curvature effects. However, the separate ether runs showed consistently increasing values of ($v/\theta H_{av.}$) at decreasing viscosities, up to 0.000001512 at 70.7° C., 215.5 seconds efflux time, and 0.231 centistoke. This variation is in the opposite direction from that expected. Furthermore, the available viscosity data may be appreciably in error (3). Thus, the more precise water-run viscometer constant was adopted. With this value the capillary diameter was calculated to be 0.0576 cm. As a further check, using the same value of α as for the styrene viscometer, at the shortest efflux time with butadiene (197 seconds), the correction, $\alpha(\mu^2/g)$, amounts to less than 0.3% of the total head; thus end effects are probably negligible.

The butadiene was shipped February 5, 1944, in a 5-gallon cylinder also from the Institute, W. Va., plant and stored out of doors. The analysis was reported as follows:

1,3-Butadiene, % by wt.	98.1
Acetylenes	Nil
Aldehydes, p.p.m. CH_3CHO	20
Peroxides	Nil
Water, entrained	Nil
Inhibitor, p.p.m. <i>p</i> -tert-butylcatechol	100
Nonvolatile matter, % by wt.	0.03

The remainder of the impurities consisted principally of 1-butene and *cis*- and *trans*-2-butene. Traces of C_3 , other C_4 , and C_5 hydrocarbons also may have been present (2).

The runs on butadiene were made some two months after it was received, in the same way that the ether runs were carried out. After evacuation of the viscometer and connecting tubing, butadiene vapor was admitted from the cylinder which had previously been partially emptied by vaporization; it was then condensed in the viscometer, which was sealed off. In this way only negligible amounts of lighter compounds or polymers should be

present in the viscometer. Four groups of five runs each were made at, roughly, 0°, 12°, 25°, and 36° C. The average deviations of the calculated kinematic viscosities in each group averaged under 0.9%. The runs took less than a day, and no noticeable polymerization occurred. Because of the low viscosity of butadiene, the curvature correction was applied. It was considerable at the higher temperatures, varying from 4% at a Reynolds number of 215 at 36° down to 0.4% at 0°. The viscometer should have had twice as many turns to make the curvature correction negligible with butadiene.

It was found that the points lay practically on a straight line when $\log \mu$ was plotted against $\log T$. This curve was used for interpolation to give the values in Table I and was also extrapolated 20° C. in each direction. It is estimated that the values of viscosity listed up to 35° are correct within 2%, roughly, and those at the higher temperatures have an increasing possible error up to 5%.

NOMENCLATURE

μ	= absolute viscosity, poises
ν	= kinematic viscosity, stokes
ρ	= density, grams/cc.
α	= number of viscous flow velocity heads, (u^2/g), dissipated in end effects
θ	= efflux time, sec.
D	= capillary diameter, cm.
L	= capillary length, cm.
$H_{av.}$	= total head, time average, cm.
Q	= volume of liquid timed, cc.
g	= acceleration of gravity, cm./sec. ²
u	= average liquid velocity in capillary, cm./sec.

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Preparation of Triacetyllevoglucosan

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TEOVGLUCOSAN (1,6-anhydro-D-glucose), which is readily prepared from its triacetate (22), has found extensive use as a synthetic agent in the field of carbohydrates. A recent patent (9) describes a pharmaceutical application in which compounds of the sulfanilamide type are combined with levoglucosan. The ready availability of levoglucosan should now make possible investigation of other industrial applications utilizing especially its unusual stability to heat and alkali.

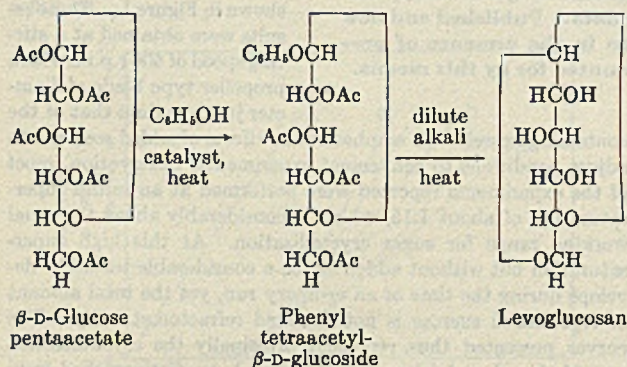
The preparation of levoglucosan by the pyrolysis of various carbohydrates (2, 6, 14, 17) has been described. Although the yields are good on a small scale, they fall off rapidly as the amount is increased (4) so that the preparation of large quantities by this method has not been feasible. The use of glucosyltrimethyl ammonium halide (7) and an alkali involves the expensive tetraacetylglucosyl halide as an intermediate and is thus not practical.

In 1894 Tanret (16) observed that, when several natural glucosides are heated with an alkali, an anhydroglucose results now known as levoglucosan. Recently Montgomery, Richtmyer, and Hudson (11, 12) showed that this reaction is characteristic of phenyl and several substituted phenyl β -D-glucosides. The same authors (10) had previously modified the procedure of Helferich and Schmitz-Hillebrecht (3) for the preparation of phenyl tetraacetyl- β -D-glucoside by the exchange of phenyl for acetyl as catalyzed by *p*-toluenesulfonic acid.

Levoglucosan is a trihydroxy inner acetal. It possesses both a 1,3-dioxolane and a pyranose ring. Water and warm alcohol dissolve it readily. Acids hydrolyze it slowly to glucose, but alkalis have no effect. The unsubstituted compound or its derivatives are split readily to glucose derivatives by reagents such as a mixture of sulfuric acid and acetic anhydride (1), phosphorus pentabro-

mide, liquid hydrobromic acid (8), and titanium tetrachloride (20). It polymerizes to dimers, tetramers, hexamers, etc., under the influence of heat and zinc chloride, platinum black (13), or zinc dust (5). It forms crystalline trimethyl ether (4) and tribenzyl ether (21) as well as a crystalline triacetate (18) and a crystalline tribenzoate (18). The trimethyl ether has been reported to give phenol under the influence of sodium in liquid ammonia at room temperature (15). Levoglucosan has been identified as a constituent of tobacco smoke (19).

The present synthesis involves the preparation of phenyl tetraacetyl- β -D-glucoside from phenol and β -D-glucose pentaacetate. This glucoside is simultaneously deacetylated and converted to levoglucosan by heating with alkali. The isolation of crystalline levoglucosan was not found practical since impurities prevented complete crystallization. Isolation was therefore accomplished through the triacetate which crystallizes readily:



This method of preparing phenyl tetraacetyl- β -D-glucoside and triacetyllevoglucosan can be used for relatively large-scale preparation of these compounds with little further modification. The runs were varied from 0.3 to 3 moles of starting materials. There was no change in yield with variation in the size of runs.

PHENYL TETRAACETYL- β -D-GLUCOSIDE

To a solution of 15 grams of *p*-toluenesulfonic acid monohydrate in 1000 grams of warm phenol were added 1170 grams of β -D-glucose pentaacetate. The flask was fitted with a capillary tube and arranged for distillation. The mixture was heated strongly on a steam bath under a reduced pressure of 20 mm. for 30 minutes after the liquid began to distill, then under 10–12 mm. for 15 minutes. At this point distillation was interrupted and a solution of 5 grams of sodium hydroxide in 300 ml. of warm phenol was added. The distillation was continued at 10–12 mm. until distillation nearly ceased. The pressure was then reduced to about 1 mm. and distillation continued as long as phenol came over. The thick residue was stirred with 2 liters of hot water and the mixture allowed to cool. The water was decanted, the residue dissolved in 1 liter of hot 95% alcohol, and the solution allowed to stand at room temperature for 15–20 hours. During this time crystallization occurred. The crystals were filtered off, washed with 300 ml. of 70% alcohol, and air-dried. The yield was 825–965 grams (65–76%) of phenyl tetraacetyl- β -D-glucoside having a melting point of 120–122° C. The product was sufficiently pure for the preparation of levoglucosan.

TRIACETYLLEVOGLUCOSAN

To a solution of 858 grams of sodium hydroxide in 6.7 liters of water were added 1100 grams of phenyl tetraacetyl- β -D-glucoside. The mixture was heated in an oil bath at gentle reflux for 20 hours. At the end of this period the solution was cooled to

The practical preparation of triacetyllevoglucosan from β -D-glucose pentaacetate is described. The scale of laboratory operation was limited only by the size of equipment available. An interesting property of levoglucosan, which may add to its commercial value, is its unusually high stability to heat and alkali.

room temperature and neutralized by the addition of 908 grams of concentrated sulfuric acid previously diluted with an equal weight of ice. The solution was concentrated to dryness under reduced pressure, the residue was thoroughly extracted with 5 liters of boiling alcohol, and the undissolved salts were washed with additional solvent. Considerable bumping was experienced during the concentration when the salts started to separate if the flask was heated only on a steam bath. This difficulty was overcome by the use of an internal steam coil. Coils made of both block tin and of copper were used satisfactorily. The alcohol solution was concentrated to dryness under reduced pressure and the residue acetylated by the cautious addition of 3 liters of acetic anhydride. Warming was sometimes necessary to start the reaction.

The acetylation mixture was heated for one hour on the steam bath. Sufficient water (250 ml.) was then continuously added to hydrolyze the excess acetic anhydride, and the acetic acid was removed under reduced pressure. The solid residue was extracted with 4 liters of chloroform in order to dissolve the triacetyllevoglucosan, and the resulting solution was washed twice with 1 liter of water to remove suspended salts. The chloroform was removed by distillation on a steam bath, reduced pressure being used near the end. The sirupy residue was mixed with 300 ml. of 95% alcohol and allowed to crystallize. The crystals were filtered off and the filtrate concentrated to a sirup. It was then diluted with 100 ml. of ether and placed in the ice box to crystallize. The combined crystalline products were triturated with 400 ml. of ice cold ether and filtered. The yield of product was 550–600 grams, melting at 108–109° C. (73–80%).

ACKNOWLEDGMENT

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Kinetics of Sucrose Crystallization

PURE SUCROSE SOLUTIONS

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MUCH work has been reported on the rates of crystallization of sucrose from pure and impure solutions. Sugar refining processes operate under the latter condition, and the time factor in such a case is vastly different from that under ideal conditions of high purity. Nevertheless it is imperative to have a satisfactory description of the kinetics in pure solutions before a successful understanding of the actual working process can be expected.

The complete course of crystallization consists of the consecutive processes of nuclei generation and the subsequent growth of these nuclei. In ordinary commercial practice the operation of the first factor is subdued by "graining". However at high supersaturation, high temperature, and rapid agitation, seed generation is manifest as "false grain" which will operate to augment the observed rate of crystallization (31).

RELATIVE CRYSTALLIZATION VELOCITY

Two general methods of investigating the kinetics of the crystallization of pure sucrose are available: (a) the direct evaluation of the growth velocity by direct measurement of individual crystals suspended in excess of sirup, and (b) the change in concentration of sirup in which a large number of seed crystals are growing. The second method is the more convenient of the two, yet it is not generally utilized for the determination of the absolute velocity of crystallization since it has not been possible to estimate with certainty the large surface of the growing crystals. Since comparative results were the primary interest of this work, the second method was used, as described in detail by Whittier and Gould (37). The refractive index of strong sirups is approximately linear in terms of the supersaturation coefficient,

$$S = \frac{\% \text{ sucrose in sirup}}{\% \text{ sucrose in satd. sirup}} = a(n - n_{\infty}) + 1$$

where n , n_{∞} = refractive indices of sirup and satd. sirup, respectively

and thus may be substituted directly in place of S in the integrated form of the monomolecular growth equation; i.e.,

velocity = $-(dc/dt) = k(c - c_{\infty})$ with $S = c/c_{\infty}$ gives:

$$k = \frac{1}{t} \log \frac{S_0 - 1}{S - 1} =$$

$$\frac{1}{t} \log \frac{n_0 - n_{\infty}}{n - n_{\infty}}$$

The enhanced velocity of crystallization of sucrose from pure aqueous solutions at high supersaturations may be accounted for on the basis of the increased activity of sucrose in solution. The fundamental rate equation is:

$$\text{velocity} = k(a - a_{\text{satd.}})$$

The activities are estimated by rather long but reasonable extrapolations of vapor pressure data. Published and new data on velocity of growth, even in the presence of pronounced false grain, can be accounted for by this means.

This simple order is the one indicated by the results of the majority of workers, and on this basis typical results at 30° C. for the adjustment of seeded sugar solutions are shown in Figure 1. These results were obtained at a stirring speed of 400 r.p.m. with a propeller type blade of diameter just less than that of the

containing vessel. To emphasize the effects of added seed and to adjust conditions to convenient experimental observation, most of the experiments reported were performed at an initial supersaturation of about 1.15, which is considerably above the usual working range for sugar crystallization. At this high supersaturation but without added seeds, a considerable turbidity develops during the time of an ordinary run, yet the total amount of crystallized sucrose is not detected refractometrically. The curves presented thus represent principally the crystallization on added seed and false grain developed, as distinguished from spontaneously generated nuclei. A seed to sirup ratio of 1 to 20, of 40-60 mesh seeds, was used. Larger amounts of this standard size seed, or equal amounts of smaller size seed, shortens and eventually eliminates the induction period with a simultaneous increase in the slope of the major curve. This behavior immediately relates the observed induction period with an area-producing mechanism. Consistent results above coefficients of 1.20 were not obtained and therefore are not included in the analysis. Close adherence to a standardized procedure was necessary to obtain duplicate results, especially in the presence of ammonium and the trivalent metal salts. Inversion and caramelization effects were minimized by heating the solution only sufficiently to form the sirup and then cooling immediately. The acidity of all the sirups examined except at extremely high salt concentrations did not differ from that of a corresponding pure sucrose solution.

The general features of these curves are an initial slow rate of adjustment which is emphasized as an induction period (or even

a slight peak), the higher the original supersaturation, followed by a uni-molecular section extending from about one quarter to more than three quarters of the maximum amount of crystallizable sucrose, and then a section indicating lagging velocity. The linearity is extended by using supersaturation in terms of sucrose to water ratios in place of the usual coefficients, but for the present discussion the improvement

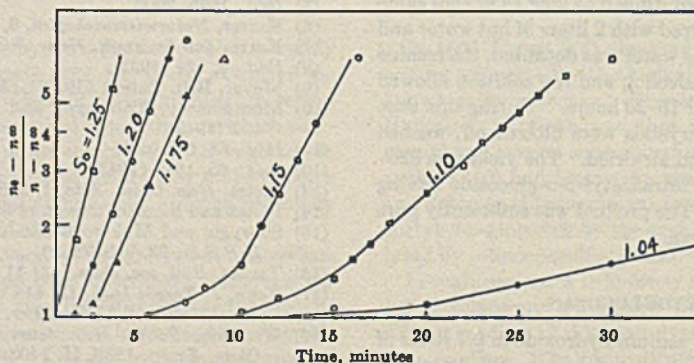


Figure 1. Monomolecularity of Sucrose Crystallization at Different Supersaturations (30° C., 400 R.P.M., 1/10 of 40-60 Mesh Seeds)

is not necessary. Over not too large a concentration range the two modes of expressing concentration are proportional to one another.

The factors responsible for the deviating parts of the curve are considered to be:

EARLY SECTION

1. Establishment of a large and effectively constant seed area, principally by disintegration
2. Nonisothermal conditions due to evolved heat of crystallization
3. Enhanced solubility of small grains

LATE SECTION

4. Slowly decreasing area available for crystallization due to accretion and aging or perfecting of crystals
5. Diminishing crystallizing activity of sucrose

Undoubtedly other explanations are possible and may operate. Of those suggested, factor 1 is considered most determinative in the early part of the curve and factor 4 in the later part, with factor 5 becoming more significant with the more concentrated solutions.

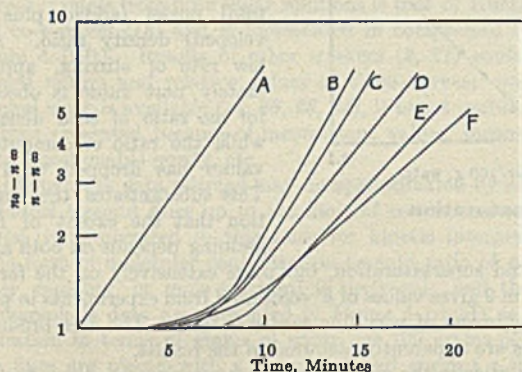


Figure 2. Effect of Stirring Speed on Crystallization Speed Sucrose ($S_0 = 1.16$, 30°C. , $1/20$ of 40–60 Mesh Seeds)

- | | |
|---|---------------|
| A. $1/16$ of xxxx seed, directly on refractometer prism | C. 250 r.p.m. |
| B. 400 and 500 r.p.m. | D. 150 r.p.m. |
| | E. Piston |
| | F. 85 r.p.m. |

FACTOR 1. The little that is known regarding nucleation of sugar sirups may be summarized by Webre's criteria (36) that spontaneous crystallization occurs above a coefficient (weight per cent) of 1.07–1.08, whereas only added seeds will grow below 1.03–1.06. In between is a region of false grain, in which added seeds beget more seeds. In this work these criteria were confirmed, in the main, for gently stirred sirups using well developed and consolidated seeds over relatively short periods of time. (Surface dust is eliminated from dry seed by suspending in a saturated sirup and superheating $10\text{--}20^\circ$ for a short time, 21). If stirring is more violent or if the observation time is sufficiently long, spontaneous nucleation inevitably occurs, even in sirups at very low coefficient. False graining seems to become more pronounced the higher the supersaturation, the greater the number of seeds (glass beads substitute effectively), and the more violent the stirring (11, 38).

Microscopically the growth of individual crystals in over-saturated sirups is irregular and not uniform. Nodules form which may be swept off if agitation is sufficient and thus give rise to new centers of crystallization. This action is accompanied by sluffing off of corners and edges. The subsequent perfection of sucrose crystals is a slow process which takes place at concentrations close to saturation. The action is emphasized with unconsolidated but well-graded seed crystals. Undoubtedly the incipient fractures of the previous processing enhance the stresses and strains of the solution \rightleftharpoons crystallization forces involved in the nonuniform growth of added nuclei. This mechanism conforms with the current concept of crystallization and precipitation, which regards the initially formed and fresh surface

as being quite different in nature and extent from the well aged and developed crystal (12).

This interpretation that false grain is principally the disintegration and erosion fragments of the added seed is supported by observations on the effects of rate of stirring on the velocity curves. In general, maximum and minimum rates of crystallization are attained with increasing or decreasing rates of stirring in the same equipment. With a given initial supersaturation the induction period is retained although it becomes less certain at lower rates of stirring. These results are represented schematically in Figure 2, where 85 r.p.m. was the slowest practical speed for the stirrer used. Below this speed the crystals were not evenly suspended in the sirup, and very erratic results were obtained because of this nonuniformity. However with an excess ($1/15$) of finer seed (xxxx), good results may be obtained by allowing crystallization to occur directly in the smear on the refractometer prism. This is a reasonable technique according to the subsequent discussion, and in view of greater convenience much of the later data was obtained in this way. Suspension of the coarser seed by a reciprocating sieve gave approximately the same limiting value. Between these limiting values the relation of velocity constant to stirring speed is roughly linear.

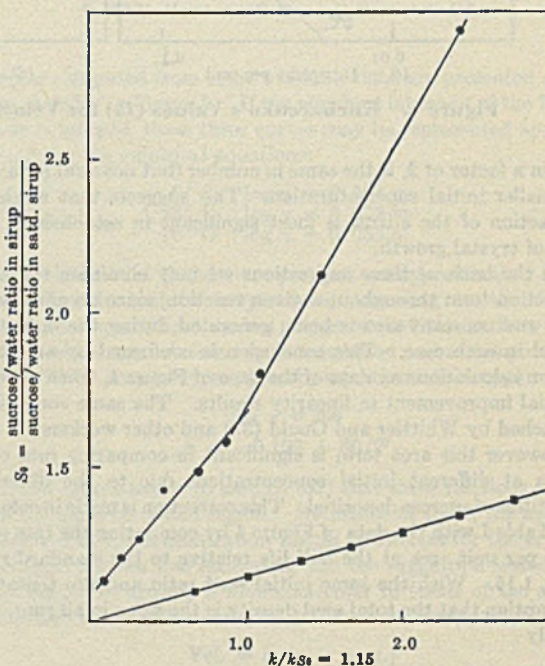


Figure 3. Velocity Constant vs. Initial Supersaturation at 30°C.

- This work (column 5, Table I).
 ■ Amagasa (1), area uncorrected, large excess of seed.

Since the velocity of crystallization may not be limited by a diffusional mechanism even at slow rates of stirring, as will be shown later, the upper critical stirring speed suggests a marked and severe shattering action of the stirring mechanism itself; the lower limit (if real) and the persistence of the induction period suggest that this erosion process is assisted (perhaps preceded) by a disintegration of the crystal lattice upon immersion in the supersaturated sirups. The persistence of the lagging period of crystallization at low initial concentration and high rates of stirring (Figure 1) are in agreement with this suggestion. The effects of low stirring rates at low initial concentrations are too uncertain to separate these two factors. It is also observed that sugar crystals can be disintegrated by agitating in saturated sirup even at low rates. Likewise the seed count at $100\times$ of a reaction, $S_0 = 1.16$, just after the induction period is approximately the same as it is near the end of this same reaction and,

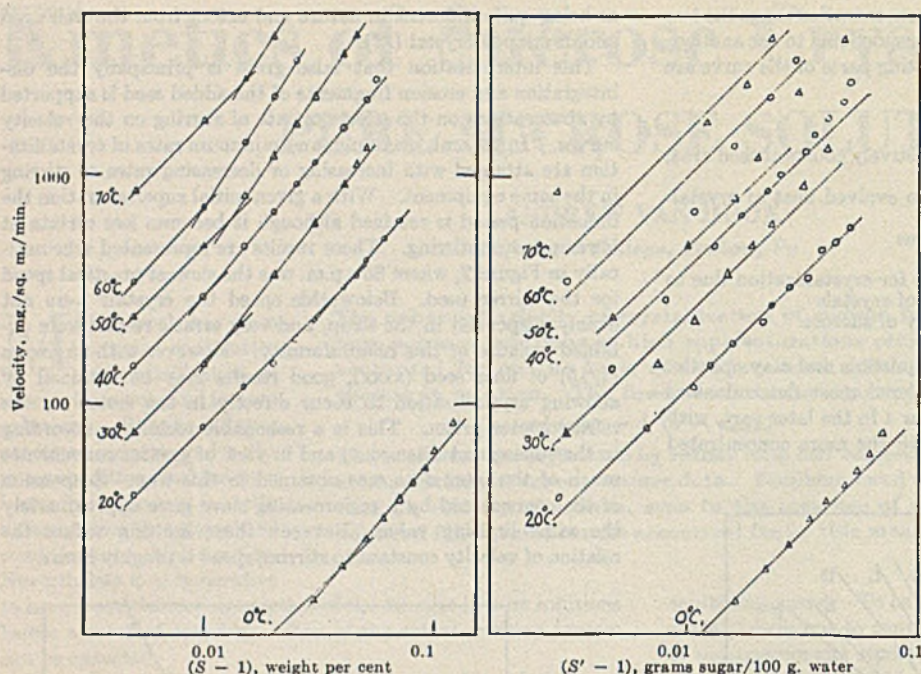


Figure 4. Kucharenko's Values (13) for Velocity vs. Supersaturation

within a factor of 2, is the same in number (but not size) for a run of smaller initial supersaturation. This suggests that mechanical action of the stirrer is most significant in establishing the area of crystal growth.

On the basis of these suggestions we may eliminate the area correction term throughout a given reaction, since an effectively large and constant area is being generated during the induction period in each case. This conclusion is confirmed by area correction calculations on data of the type of Figure 1, when no substantial improvement in linearity results. The same conclusion is reached by Whittier and Gould (37) and other workers.

However this area term is significant in comparing rate constants at different initial concentrations due to the different quantities of sucrose deposited. This correction is made in column 6 of Table I with the data of Figure 1 by computing the rate constant per unit area at the half life relative to the standard run, $S_0 = 1.15$. With the same initial seed ratio and the tentative assumption that the total seed density is the same in all runs, obviously

$$\frac{k}{k_{S_0=1.15}} = \left(\frac{k_{\text{obsvd.}}}{k_{S_0=1.15}} \right) \left(\frac{A_{S_0=1.15}}{A_{1/2}} \right)$$

where $k_{S_0=1.15}$ is the specific reaction rate constant per unit reference area, and k is the same at a different concentration.

Apparently the area term is insufficient to explain the variation of velocity with supersaturation (column 6); the ratio of velocity constants at $S_0 = 1.06$ and 1.2 is about 1/6. By actual count the ratio of the seed density in the two cases at the half life is about 1/1.5; with the plunger type of stirring it becomes much less but is still insufficient to explain the wide variation. Apparently some factor other than nucleation, such as suggested in factor 5 above, is operating.

In this situation the velocity equation, as developed later, becomes

$$\frac{-dS'}{dt} = k'(\gamma S' - \gamma_{\text{satd.}})$$

in place of

$$\frac{-dS'}{dt} = k(S' - 1)$$

where the primes indicate supersaturation coefficients in terms of the more significant sugar/water ratios rather than the previous unprimed weight percentages, and γ is the activity coefficient of sucrose in aqueous solution. Then

$$k = \frac{k'(\gamma S' - \gamma_{\text{satd.}})}{S' - 1}$$

Using values of γ presented later in this report, the values of k' given in column 7 (Table I) were computed. The spread of values between $S_0 = 1.06$ and 1.2 is in the ratio of 1/2, which is just about the observed total nuclei (added plus developed) density ratio. At a low rate of stirring, approximately unit value is observed for the ratio of seed densities, while the ratio of computed k values has dropped to 1/1.2. This substantiates the suggestion that the extent of false-graining depends on both agitation and supersaturation, but more extensively on the former. Column 9 gives values of k' computed from experiments in which a large excess of very fine seed was used. The area-producing factors are apparently obscured in the results.

Analytically the above equation approximates at not too high supersaturations to a linear dependence of the velocity constant on the supersaturation. This is borne out in Figure 3 with Amagasa's data (1) and at low concentrations with the present data. Since Amagasa does not specify the amount of seed employed in his experiments, it is not possible to compare these results in an absolute way.

FACTOR 2. It is observed that a temperature rise of about 0.3° C. occurs in the reaction mixture during a run, even at stirring speeds in excess of the upper critical rate. This maximum is reached at about one third life when $S_0 = 1.16$ and is insufficient to account for the initial slow period, although it contributes in part because of decreased supersaturation coefficient. The subsequent fall in temperature also contributes, although to a small extent, to the latter falling part of the curves.

FACTOR 3. The small grains formed during the early period will have a transitory solubility exceeding the usual value and

TABLE I. VELOCITY CONSTANTS

1	2	3	4	5	6	7	8	9
S_0	S'_0	$A_{1/2}$	$k_{\text{obsvd.}}$	$k_{\text{obsvd.}} \cdot \frac{A_{S_0=1.15}}{A_{1/2}}$	Relative Velocity Constant/Unit Area	k'	k' by Graphic Integration	k' , Excess xxx
1.04	1.14	0.68	0.168	0.10	0.15	0.32	0.38	0.91
1.06	1.215	0.75	0.33	0.19	0.25	0.54	0.53	...
1.08	1.25	0.81	0.488	0.29	0.36	0.68	0.70	1.09
1.10	1.41	0.88	0.700	0.41	0.46	0.70
1.11	1.47	0.91	1.15	0.68	0.75	0.97	0.93	1.02
1.125	1.55	0.96	1.43	0.84	0.88	0.97
1.15	1.72	1.00	1.70	1.00	1.00	1	1	1.0
1.175	1.91	1.13	2.10	1.24	1.10	1.0
1.20	2.14	1.20	2.50	1.50	1.25	1.08	...	1.10
1.25	2.59	1.38	4.01	2.36	1.70	1.21	1.32	...

$$* k_{\text{obsvd.}} = \frac{1}{t} \log \frac{n_0 - n_{\infty}}{n - n_{\infty}}$$

hence will inhibit the observed rate of crystallization until they grow to effective planar size.

FACTOR 4. Freshly formed surfaces age rapidly (12), and as a result of this agglomeration a diminishing area is available for further growth which thus reduces the observed velocity constant. Ostwald "ripening" (12) may be significant. A surface active agent (0.2% Aerosol OT) seems to sustain the initial rate of growth for a longer reaction time, perhaps as a result of its dispersing action.

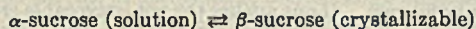
FACTOR 5. Diminishing activity of sucrose in less concentrated solutions may account for part of the fall in this section of the curves, especially at higher initial supersaturations.

ABSOLUTE VELOCITY OF SUCROSE CRYSTALLIZATION

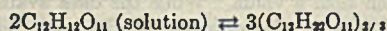
Most of the published data on the rate of crystallization of sucrose is for seeded solutions, simulating production conditions, and presumably the effect of spontaneous nucleation is negligible. The most extensive and consistent data on the growth of single sucrose crystals from pure sugar solutions is that of Kucharenko and co-workers (13) and is represented in compressed form in Figure 4 (left). Results of other workers (2, 21) confirm the general nature and relative values of these curves; while additional work is available (14, 28, 29, 34), it is not useful for the analysis presented because of inconsistent values, inconvenient units, questionable purity, etc.

Although the data selected may be approximated by a family of double straight lines up to the limit of concentration represented, it is unsuited in this form for kinetic interpretation. Some form of molecular concentration (weight ratio of sugar to water, molality, or mole fraction) is preferred; and therefore Kucharenko's data are presented in Figure 4 (right) as supersaturation in terms of grams of sugar per 100 grams of water. The lines are placed with a slope of 1 and suggest a limiting monomolecular mechanism in terms of this ratio of supersaturation, with some factor operating to accelerate this growth at higher supersaturations and temperatures. Two possibilities are obvious: (A) increased nucleation and induced grain at higher supersaturation and temperature, and (B) increased activity in the crystallizing potential of sucrose.

Suggestion A may be rejected immediately since Kucharenko's technique consisted in the measurement of single, growing crystals. Concerning suggestion B, it is not unreasonable to expect that the effective concentration of crystallizable sucrose in solution may be different from its true weight concentration as a result of hydration effects (18) and/or the variety of isomeric alterations possible of the sucrose molecule (5, 7). Orth (22) reviews the literature on this subject and explains the apparent acceleration of the growth velocity of sugar as the result of a favorable shift of the equilibrium:



From boiling point data Orth calculates the effective molecular weight of the crystallizable form of sucrose to be 228; the above equilibrium may then be represented as



In view of the recognized limitations of boiling point determinations (3, 17), the preceding representation is somewhat uncertain.

The activity is a superior function representing alterations in the form and concentration of crystallizable sucrose, and is independent of any specific molecular form of the modification under consideration. A variety of methods have been employed to evaluate the activity of sucrose in dilute aqueous solution. At ordinary temperatures and low concentrations the results of different workers are in agreement, but at concentrations approaching or exceeding saturation and temperatures above 30° C. few data are available. Values of the activity coefficient of

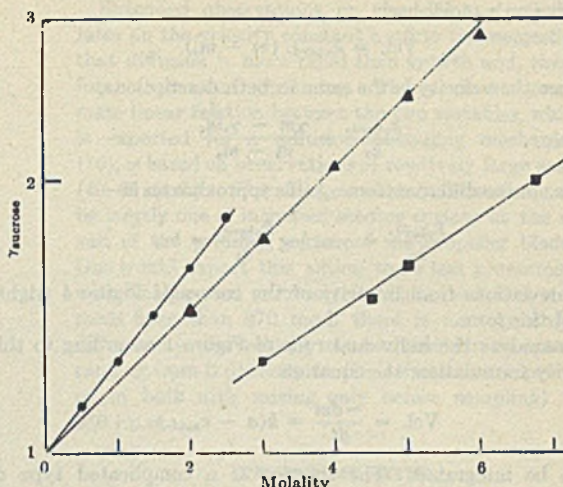


Figure 5. Activity Coefficients of Sucrose in Aqueous Solution

- 0° C., Smith and Smith (27).
- ▲ 25° C., Scatchard (25), Robinson et al. (24).
- 70° C., Perman (23), Landolt-Börnstein (15).

sucrose computed from some available data are presented as log γ vs. molality in Figure 5. If the apparent intercept of the 70° C. curve is ignored, these three curves may be represented approximately by the empirical equations:

$$\begin{aligned} 0^\circ \text{ C. : } \log \gamma &= 0.101 m \\ 25^\circ \text{ C. : } \log \gamma &= 0.079 m \\ 70^\circ \text{ C. : } \log \gamma &= 0.055 m \end{aligned}$$

The coefficients of the above equations are approximately linear in reciprocal absolute temperature, according to the Gibbs-Helmholtz equation; this fact suggests that the activity coefficients of sucrose solutions up to saturation and at temperatures of 0–70° C. may be represented by equations of the type:

$$\begin{aligned} \log \gamma &= bm \\ b &= -0.122 + 60/T \end{aligned}$$

It is not unreasonable to assume (32) that these relations extend into the supersaturated region. By means of them, the activity of sucrose in the concentration ranges of interest for the crystallization of sucrose was estimated, and the suggestion tested that the velocity of growth is monomolecular in terms of the supersaturation expressed as activities or effective concentrations:

$$\text{Vel.} = k_0 (a - a_{\text{satd.}})$$

This same kind of expression is suggested by an activated complex interpretation (9) of the mechanism of growth; i.e., in the equilibrium sucrose \rightleftharpoons complex:

$$\begin{aligned} K^* &= \frac{a_{\text{sucrose}}}{a_{\text{complex}}} = \frac{\gamma_{\text{sucrose}} m_{\text{sucrose}}}{\gamma_{\text{complex}} m_{\text{complex}}} \\ \text{Vel.} &\approx m_{\text{complex}} \approx \frac{a_{\text{sucrose}}}{K^* \gamma_{\text{complex}}} \end{aligned}$$

If γ_{complex} is effectively constant, this expression, when formulated more properly in terms of supersaturations, is identical with the preceding form.

The computed values are presented as points in Figure 6, and the line is drawn with a slope of one corresponding to a monomolecular growth. The agreement is gratifying, considering the different sources of data used and the extended assumptions required to apply them to the range of interest.

The same conclusion obtains from direct consideration of the curves of Figure 4; i.e., in terms of activities,

$$\text{Vel.} = k_0 (a - a_s)$$

whereas on a molal basis,

$$\text{Vel.} = k_{\text{obsvd.}} (m - m_s)$$

Since the velocity is the same in both descriptions,

$$\frac{k_{\text{obsvd.}}}{k_0} = \frac{\gamma m - \gamma_s m_s}{m - m_s}$$

If γ is not too different from γ_s , this approximates as

$$\frac{k_{\text{obsvd.}}}{k_0} = \gamma \text{ or } \log \frac{k_{\text{obsvd.}}}{k_0} = b m$$

The deviations from linearity of the curves of Figure 4 (right) are of this form.

To analyze the individual runs of Figure 1 according to this activity formulation, the equation

$$\text{Vel.} = \frac{-dm}{dt} = k(a - a_{\text{satd.}})$$

must be integrated. The solution is a complicated type of gamma function, and for the present purpose it is advantageous to integrate graphically. The equation is restated in the form,

$$\frac{-dS'}{dk} = k(\gamma S' - \gamma_{\text{satd.}})$$

where $S' = m/m_{\text{satd.}}$

$$a = \gamma m = m e^{b m}$$

$$\text{Then: } k = + \int_{S_0}^{S_1} \left(\frac{1}{S - \gamma_{\text{satd.}}} \right) dS$$

An area term should be inserted in the expression under the integral sign; but in view of the previous remarks regarding nucleation and for not too extended reaction life, this factor may be applied, as before, as $A_{1/2}/A_{1/2}^{S_0=1.15}$. The results of such calculations are presented as relative values in column 8, Table I, and are of the same order of value and significance as those in column 7. These computations are especially significant since they extend the application of the analysis beyond the range of Kucharenko's concentration limit of $S_0 = 1.10$ into the higher concentration range. It would be interesting to extend

the comparison of theory and observation still further, but more quantitative information about the graining mechanism must first be available.

An additional test of this activity interpretation which is free from the manifold area-correction terms is possible with data of runs performed with a large excess of finely divided seeds (1/5 of xxx powder). In this case the induction period is absent and the observed velocity applies at the commencement of the crystallization when the area term is common at different initial concentrations. The results on an activity basis are given in column 9, Table I.

As mentioned previously, the evaluation of the absolute crystallization velocity from experiments involving many small crystals is somewhat uncertain on account of the difficulty of determining this surface. Nevertheless this was attempted microscopically, by settling, and by dye adsorption. By the first method an average area of 0.12×10^{-4} sq. cm. per seed was estimated for the crystals at the half life of the reaction whose initial supersaturation was 1.08. By settling (36), an average value of 0.10×10^{-4} sq. cm. per seed was realized; dye adsorption was unsuccessful. The velocity of growth corresponding to the former value is 2700 mg. per square meter per minute which compares well with Kucharenko's value of 2000 at these conditions. Better agreement was realized by computation from a run without stirring at $S_0 = 1.035$ with a large excess of very fine, graded seeds. The value of 1000 mg. per square inch per minute in comparison with Kucharenko's value of 755, was obtained. The search will be continued for a suitable dye method, despite the fact that it is generally unsuitable for the evaluation of absolute specific surface, since relative values would be fruitful in the interpretation of the nucleation process.

TEMPERATURE COEFFICIENT OF CRYSTALLIZATION

The Arrhenius equation, $k = e^{-E/RT}$, suggests a semilogarithmic representation, such as Figure 7, for the temperature-velocity constant relation. On this plot values of the velocity constant relative to the value at 30° C. are plotted according to the relation,

$$\frac{k}{k_{30^\circ \text{ C.}}} = e^{\frac{E}{R} \left(\frac{1}{T_{30^\circ \text{ C.}}} - \frac{1}{T} \right)}$$

and the slope is determinative of activation energy E . The curve is drawn only through points \circ and \square rather than through the points in terms of activities, since the former are more significant for the subsequent discussion. The curve indicates a 10° C. temperature coefficient which increases rapidly at lower temperatures from an apparently limiting value of $k_{70^\circ \text{ C.}}/k_{60^\circ \text{ C.}} = 1.54$. Similar high coefficients are realized from most of the rate values reported by McGinnis, Moore, and Alston (19) for a low-purity fillmass. If one applies the not irrevocable criterion that temperature coefficients below 1.5 indicate the controlling operation of a physical process such as diffusion (30), then the crystallization process represented in Figure 7 is not regulated by such a factor, since only above 60° C. does the slope of the curve approach such a value. While the data available on the temperature index of the diffusion coefficient of sucrose into water (15) conform with the criterion stipulated, there are indications in these and additional data (20, 39) that this index may increase to a value much greater than 1.5 at the supersaturation concentrations of interest in the case of crystallization. The rapid increase of the corresponding temperature coefficient of viscosity (16, 39) in supersaturated solutions strengthens this suggestion. If, however, one computes the temperature index of viscosity of sucrose solutions at constant degree of supersaturation at the varying temperatures (it would seem that such a variable would be more significant than a constant weight concentration in the interpretation of the mechanism of crystallization), then the result is a value below 1.3 for the

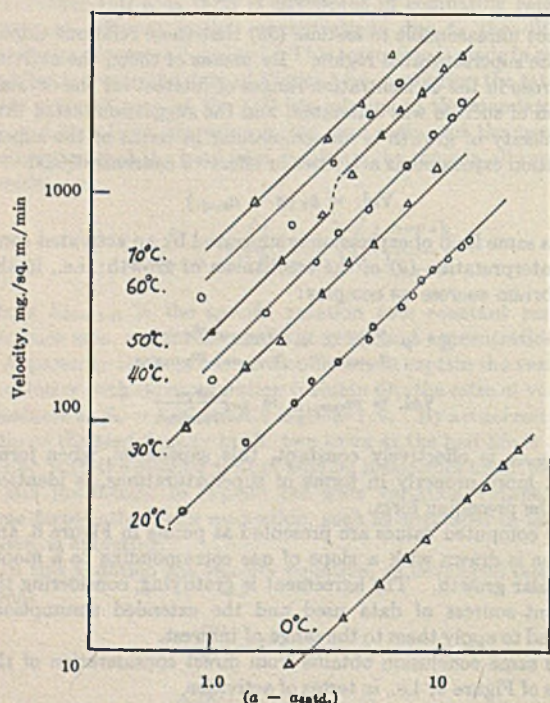
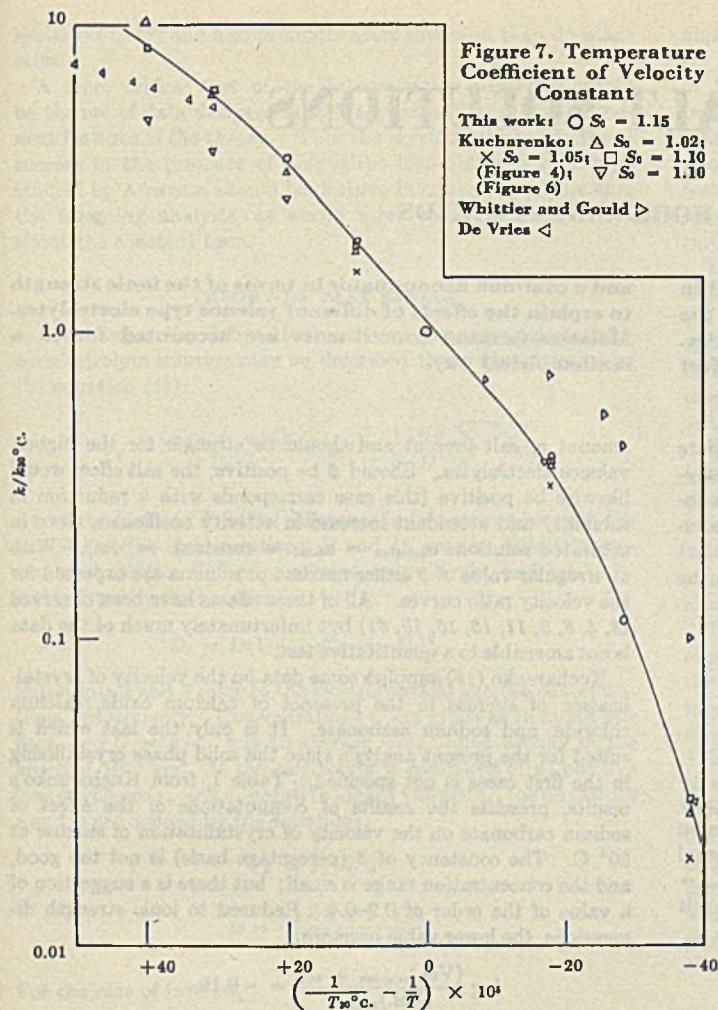


Figure 6. Velocity vs. Activity Potential



complete temperature range. This again suggests that the controlling step is not a simple physical process. This conclusion corroborates the circumstance that the viscosity factor has never been satisfactorily included, and is apparently only a secondary factor, in the velocity equations of crystallizing sucrose (4, 11, 21, 22).

In terms of activation energy, values of 6500 to 22,000 calories per mole are estimated from Figure 7 at high and low temperatures, respectively. A similar analysis of the crude data available on the rate of nucleation of sucrose sirups indicates that diffusion may very well (33) control this initial act in the spontaneous growth of a complete sucrose crystal. The incomplete data of van Ginneken and Smit (8) roughly confirms a unimolecular mechanism for the formation of sucrose crystals in super-saturated sirups. Application of this conclusion to the data of Fouquet (6), with the specification that a definite minimum number of nuclei are necessary for identification in an arbitrary time, leads to relative values of the specific reaction rate constant; when plotted these values give a fairly straight line with a slope corresponding to an activation energy of about 3000 calories per mole.

The results with gum acacia and invert sugar (page 1048) increase and decrease the viscosity (η), respectively, yet have no effect or a decelerating effect, respectively, on the velocity of crystallization. A complete examination of the diffusivity of sucrose at high concentrations would decide whether the controlling step in the crystallization might be an ordinary physical process or an "activated" one.

Extended observations on the effect of stirring rates on the velocity constant confirm the suggestion that diffusion is more rapid than growth and, therefore, is not rate determining. The previous approximate linear relation between the two variables, which is expected for a diffusion-controlling mechanism (10), is based on observations of relatively large seeds (40-60 mesh). The effect, as already intimated, may be largely one of increased seeding surface as the result of the grinding action of the propeller blades. One would expect this action to be less pronounced with smaller seed material; it is observed that with seeds finer than 270 mesh there is no appreciable difference in the velocity constants at stirring speeds ranging from 0 (directly on the refractometer prism, or in bulk with mixing only before sampling) to 640 r.p.m.

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SUCROSE-SALT SOLUTIONS

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The activity theory of sucrose crystallization developed in the preceding paper is applied to the crystallization in the presence of electrolytes and nonelectrolyte impurities. Interionic theory indicates a maximum in the salt effect

SALTS generally reduce the velocity of crystallization of pure sucrose solutions (2, 6, 9). In terms of the preceding analysis this reduction in velocity may be interpreted as a consequence of the effect of electrolyte on the activity of the nonelectrolyte (salt effect). Direct experimental information is not available to test this suggestion; therefore we shall assume the applicability of the reasonable equation (10, 23):

$$\log \gamma_{\text{sucrose}} = \beta \mu$$

where β = constant of proportionality

$$\mu = \text{ionic strength} = \frac{1}{2} \sum m_i z_i^2$$

This type of equation was first derived by Debye and McAulay (7), and Scatchard (20) to describe the effect of electrolytes on nonelectrolyte activity, and was validated by the experimental work of Belton (3). Coupled with the result that $\log \gamma_{\text{sucrose}} = bm$ for the sucrose concentration effect alone, for sucrose-salt solutions

$$\log \gamma = bm + \beta \mu$$

The velocity equation, $\text{Vel.} = k_0(a - a_{\text{satd.}})$, then becomes for pure sucrose and sucrose-salt solutions, respectively:

$$(\text{Vel.})_{\text{sucrose}} + k_0 a_{\text{satd.}} = k_0 a = k_0 \gamma m = k_0 m e^{bm}$$

$$(\text{Vel.})_{\text{sucrose} + \text{salt}} + k_0 a_{\text{satd.}} = k_0 m e^{bm + \beta \mu}$$

Since the saturated solutions in both cases are in equilibrium with the same solid phase, it is possible to eliminate the term $k_0 a_{\text{satd.}}$ from these equations by taking the difference. However the result,

$$(\text{Vel.})_{\text{sucrose}} - (\text{Vel.})_{\text{sucrose} + \text{salt}} = k_0 m e^{bm} (1 - e^{\beta \mu})$$

is not particularly advantageous, and the ratio

$$\log \frac{(\text{Vel.})_{\text{sucrose} + \text{salt}} + k_0 a_{\text{satd.}}}{(\text{Vel.})_{\text{sucrose}} + k_0 a_{\text{satd.}}} = \beta \mu$$

is preferred, for it accounts directly and qualitatively for the observed effects of salts upon the crystallization velocity of sucrose. If $k_0 a_{\text{satd.}}$ is ignored relative to the velocity factors, this equation reduces to

$$\log \frac{(\text{Vel.})_{\text{sucrose} + \text{salt}}}{(\text{Vel.})_{\text{sucrose}}} = \log \frac{k_{\text{salt}}}{k_{\text{sucrose}}} = \beta \mu$$

β is usually negative, and therefore a decelerating effect of salts is expected. This reduction should be proportional to the

amount of salt present and should be stronger for the higher-valence electrolytes. Should β be positive, the salt effect would likewise be positive (this case corresponds with a reduction in solubility and attendant increase in activity coefficient, since in saturated solutions $a_{\text{solution}} = a_{\text{solid}} = \text{constant} = \gamma m$). With an irregular value of β either maxima or minima are expected for the velocity ratio curves. All of these effects have been observed (2, 4, 8, 9, 11, 13, 15, 19, 21) but unfortunately much of the data is not amenable to a quantitative test.

Kucharenko (16) supplies some data on the velocity of crystallization of sucrose in the presence of calcium oxide, calcium chloride, and sodium carbonate. It is only the last which is suited for the present analysis since the solid phase crystallizing in the first cases is not specified. Table I, from Kucharenko's results, presents the results of computations of the effect of sodium carbonate on the velocity of crystallization of sucrose at 50° C. The constancy of β (percentage basis) is not too good, and the concentration range is small; but there is a suggestion of a value of the order of 0.2-0.4. Reduced to ionic strength dimensions, the lower value becomes:

$$\log \frac{(\text{Vel.})_{\text{sucrose} + \text{salt}}}{(\text{Vel.})_{\text{sucrose}}} = -0.19 \mu$$

Compared to the generalized result of Figure 1, $\log (k_{\text{salt}}/k_{\text{sucrose}}) = -0.057 \mu$, it is surprising that the constants evaluate within a ratio of 3, in view of the wide differences in the velocity data used.

In Figure 1 the data of Amagasa are represented in the coordinates suggested by the above equation; except for sodium sulfate, which Amagasa mentions as being unusual, the result is gratifying. The general trend seems to be a linear curve, represented by $\log (k_{\text{salt}}/k_{\text{sucrose}}) = -0.057 \mu$, which falls off at higher salt concentrations. Similar results were obtained with sodium sulfate at high concentrations in this investigation. It was observed that this salt does not follow the usual additive rule for

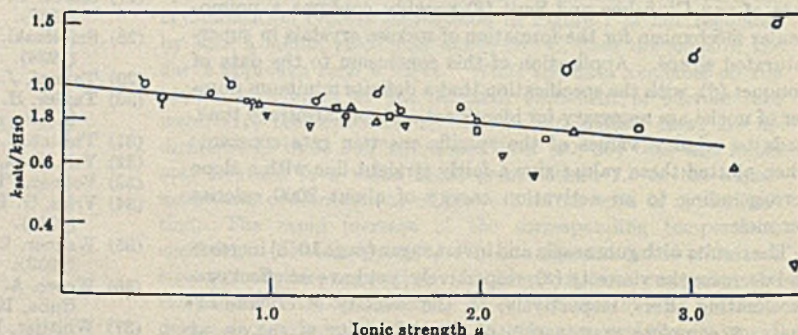


Figure 1. Effect of Electrolytes on Velocity Constant at 30° C., According to Amagasa (2)

○ NaCl; □ KCl; △ Na₂CO₃; ▽ K₂CO₃; ♦ Na₂SO₄; + Na₂C₂O₄; ○ K₂C₂O₄.

refractive index and also promotes more inversion than do other salts.

A more critical test of the interpretation suggested would be the use of data designed specifically according to the prominent features of the theory. Thus the crystallization velocity of sucrose in the presence of polyvalent ions above the 1-2 type studied by Amagasa should be decisive in approving or rejecting the foregoing analysis, as would more revealing information about the constant term.

THEORY OF SALT EFFECT

According to the Debye-Huckel theory an aqueous electrolyte-nonelectrolyte solution may be described thermodynamically by the equation (17):

$$F_s = \frac{(\alpha_2 n_2 + \alpha_3 n_3)}{2 D_0 V b} \nu w n_2 \epsilon^2 - \frac{1}{3} \frac{\epsilon^2 \kappa x}{D} \sum n_i z_i^2$$

where the function F_s is the difference in free energy between the actual and the ideal solution; D and D_0 are the dielectric constants of solution and pure solvent, respectively, and are to be interrelated by the equation,

$$D_0 = D(1 + \alpha_2 C_2 + \alpha_3 C_3)$$

Subscripts 2 and 3 refer to the electrolyte and sucrose concentrations, respectively. Concentrations C are given as in moles per liter, and $C = n/\nu$. b is an average ionic radius usually of the order of 10^{-8} cm. If the electrolyte is composed of ν_+ positive ions of valence z_+ and ν_- negative ions of valence z_- , the quantities ν and w are defined by the equations:

$$\nu = \nu_+ + \nu_-$$

$$w = \frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu}$$

For the case of interest,

$$\nu w n_2 = \sum n_i z_i^2 = 2\mu$$

μ is the ionic strength, ϵ is the unit electronic charge, $1/\kappa$ is the effective diameter of the ion atmosphere, and x is a function of κ and a , the effective finite diameter of the ion.

Since $\partial F_s / \partial n_2 = kT \ln \gamma_2$, the above equation gives the following result:

$$\ln \gamma_2 = \frac{2\epsilon^2 \alpha_2}{D_0 kT} \left(\frac{1}{2b} - \frac{1}{3} \kappa x \right) \mu$$

Experimentally α_2 is a positive quantity; hence the net sign and size of the total coefficient depends on the relative magnitudes of b , κ , and x —all positive quantities. In the limiting case the second term under the brackets reduces to zero, and the equation becomes:

$$\log \gamma_2 = \frac{\epsilon^2 \alpha_2}{b D_0 kT} \mu$$

Upon inserting usual values for the various items in the coefficient, and using the value of $\alpha_2 = 0.21$ at $S_0 = 1.2$ from approximate dielectric constant measurements, the value of the coefficient in Brigg's logarithmic terms becomes 0.60. This

limiting value is inserted in Figure 2, and there seems to be rough conformity. However, at a not unreasonable value of 10^{-7} for the ion radius, a , the net value of the bracketed term becomes negative and increasingly so at higher concentrations. Hence the complete $\log \gamma_2 - \mu$ curve should exhibit a maximum and steadily decreasing slope thereafter. This first feature is exhibited by sodium acetate in Figure 1, and the second feature is displayed by all the salts reported except sodium sulfate.

This same equation accounts qualitatively for the effect of salts on the solubility of sucrose. Since the same solid phase of the same activity occurs in all cases in equilibrium with the various saturated solutions, and since γ first increases and then decreases, the solubility should exhibit a reciprocal behavior of passing through a minimum. This is true for the majority of salts for which data are available (2, 16).

The results of Amagasa (2) were extended, especially with higher-valence type salts and at low concentrations, and are given graphically in Figure 2. Most of the results were obtained at an initial sucrose supersaturation of 1.15; although additional values at other concentrations confirm the indication of the above equation that the salt effect should be independent of the non-electrolyte concentration.

The refractive index was ascertained to be additive in the case of added salt as reported by Amagasa (2), with sodium sulfate the only exception as already noted. Trivalent cations seemed to promote discoloration which, however, could be minimized by rapid cooling after solution.

The nature of the coefficients in the dielectric constant equation, $D_0 = D(1 + \alpha_2 C_2 + \alpha_3 C_3)$, was determined by a resonance method. As reported by Akerlof (1), it was found that the addition of sucrose to water decreased the dielectric constant, and the effect continued regularly into the supersaturated region up to a coefficient of 1.2. A value for α_3 , of approximately 0.21 was realized at this concentration. At any definite sugar concentration the addition of electrolyte (NaCl, KCl, Na_2CO_3 , $\text{NaC}_2\text{H}_3\text{O}_2$, and Na_2SO_4 were observed) increased the dielectric

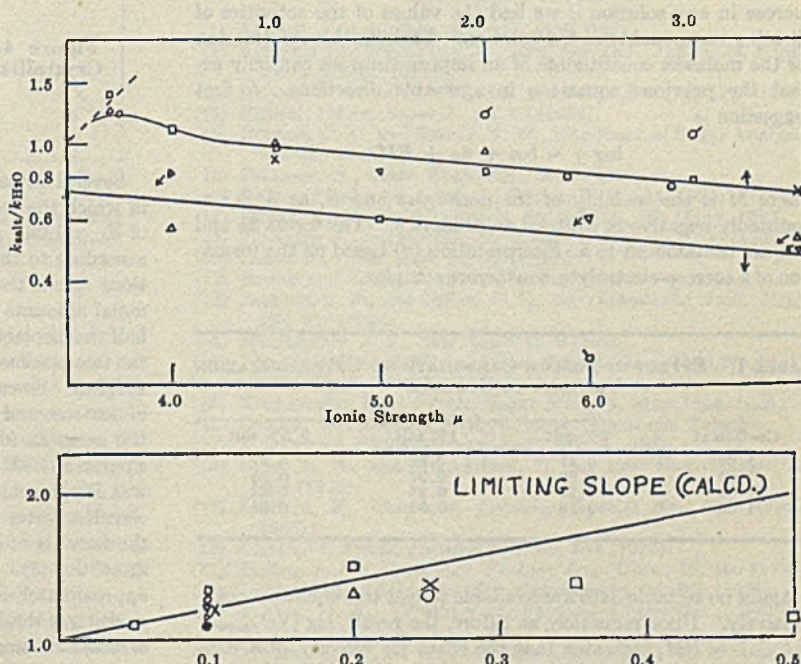


Figure 2. Effect of Electrolytes on Velocity Constant at 30° C., According to Van Hook and Shields (Semilog Scale)
 ○ NaCl; □ KNO₃; △ MgSO₄; ▽ Na₂PO₄; ◊ Na₂SO₄; ▴ (NH₄)₂SO₄; × sodium citrate;
 ● K₂Fe(CN)₆ and K₃Fe(CN)₆.

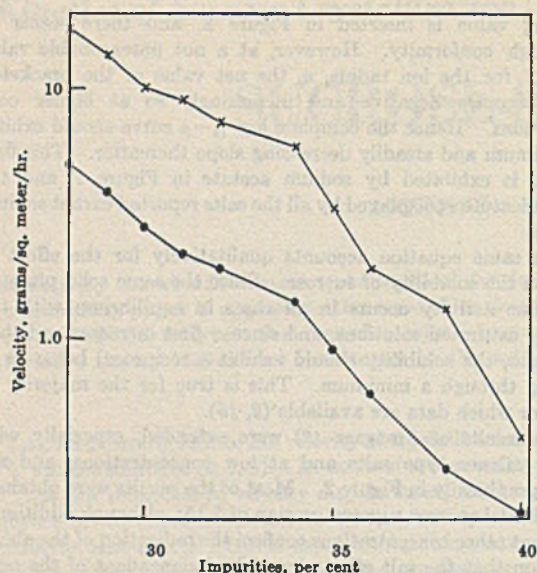


Figure 3. Effect of Molasses Impurities on Crystallization of Sucrose (Semilog Scale)

× $S_0 = 1.071$; ○ $S_0 = 1.04$

constant but not quite linearly. Precise measurements were not made and the limit of measurement with the apparatus used was only to a value of $\Delta D = 20$ and a salt concentration of $\mu = 0.05$ (KCl).

MOLASSES CRYSTALLIZATION

The complete description of intensive properties of any solution is given by the Gibbs-Duhem equation,

$$\sum_i n_i d\mu_i = 0$$

which reveals that we would be able to compute the activity of sucrose in any solution if we had the values of the activities of all other components of the solution. Lacking this information for the molasses constituents of an impure sirup we can only extend the previous equations in agreeable directions. A first suggestion is

$$\log \gamma = b_m + \beta\mu + BM$$

where M is the molality of the nonsugars and B , as β , is undoubtedly negative in contrast to positive b . The terms $\beta\mu$ and BM are tantamount to an interpretation (6) based on the formation of a sucrose-electrolyte-nonsucrose complex.

TABLE I. EFFECT OF SODIUM CARBONATE ON CRYSTALLIZATION VELOCITY OF SUCROSE

Coefficient	β , Percentage Basis		
	2% salt	1% salt	0.5% salt
1.02	0.27	0.38	0.47
1.03	0.20	0.27	0.36
1.04	0.19	0.25	0.32
1.05	0.18	0.24	0.31

Again no suitable data are available to test this equation quantitatively. Upon reduction, as before, the result, $\log (\text{Vel.}_{\text{impure}} / \text{Vel.}_{\text{pure}}) = BM$, indicates that the effect on velocity of a non-electrolyte impurity should be exponential in terms of its concentration, and that the relative effect will be greater at lower supersaturations. Table II, assembled from Kucharenko's data (15), confirms this suggestion in a qualitative way.

Figures 3 and 4 approve the suggestion that a semilogarithmic plot is superior to Cartesian coordinates for representing data in a linear manner. The values for these plots are taken from Figure 4 of Nees and Hungerford's paper (18), and the purities are represented directly without conversion to a molal basis. At any fixed purity the approximate equation suggests that the ratio of intercepts should be in the ratio of the velocities of pure sucrose solutions. The ratios are 3.5 at the left-hand side of the curve and 2 at the less pure side; the ratio for pure solutions is 2.3 (15).

Additional observations (14, 22) confirm in a qualitative way the general features of this activity interpretation of crystallization from molasses.

TABLE II. EFFECT OF CARAMEL ON VELOCITY OF CRYSTALLIZATION OF SUCROSE

	Relative Velocity at supersatn. Coefficient of:			
	1.01	1.02	1.03	1.04
1% caramel	0.91	0.90	0.88	0.90
3% caramel	0.64	0.67	0.79	0.73
8% caramel	0.37	0.50	0.75	0.60

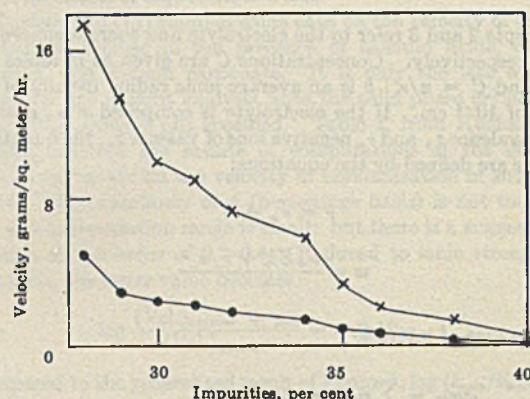


Figure 4. Effect of Molasses Impurities on Crystallization of Sucrose (Cartesian Coordinates)

× $S_0 = 1.071$; ○ $S_0 = 1.04$

Several series of experiments (Figures 5 and 6) were performed in which the initial sirup was, in most cases, at a concentration of $S_0 = 1.08$. As observed in the case of added electrolyte and according to theory, experiments at different sucrose concentrations reveal the same relative lowering of the velocity by equimolal amounts of impurities. The dextrose curve is just about half the displacement of the invert sugar curve; on a weight basis the two become identical on account of the 1/2 ratio of molecular weights. Since the invert sugar used was an equimolal mixture of dextrose and levulose, the results for levulose would have to be the same as for dextrose. The caramel was made by heating sucrose at 200° C. under vacuum until 60% of the initial weight was lost, leaching with hot methyl alcohol, and evaporating the clarified water solution. A molecular weight corresponding to the formula of saccharan, $C_{12}H_{22}O_{11}$, was employed for expressing molalities (5). Ammonia, phenol, aniline, and ethyl alcohol fall approximately on a common curve, out to about 2M with apparently a diminishing effect at still higher concentrations. All of these substances have a depressing effect on the solubility of sucrose in water at the concentrations used (12, 16) and therefore should have a contrary accelerating effect on the basis of any straightforward supersaturation theory of reaction velocity. Amagasa (2) finds similarly that solubility cannot be completely

correlated with velocity effects, although the pattern found in the preceding paper with electrolytes follows that demanded by salting-out theory. In general, salts (noncomplex formers) have an initial depressing effect on the solubility of sucrose in water, changing to increasing solubility at higher concentrations (2, 16). This leads to the maximum observed in the velocity ratio curves.

In most of the mixtures investigated, the refractive indices were additive in terms of the concentrations of constituents of the solution. For working purposes a linear calibration curve was drawn between the refractive index and the supersaturation coefficients in terms of the sucrose and water constituents. In several cases the linear additive rule was confirmed by a complete series of synthetic mixtures. Only in the case of sodium sulfate, aniline, and gum acacia was the rule found to be unreliable. The de Whalley rule for invert sugar mixtures did not apply at the high concentrations used (24).

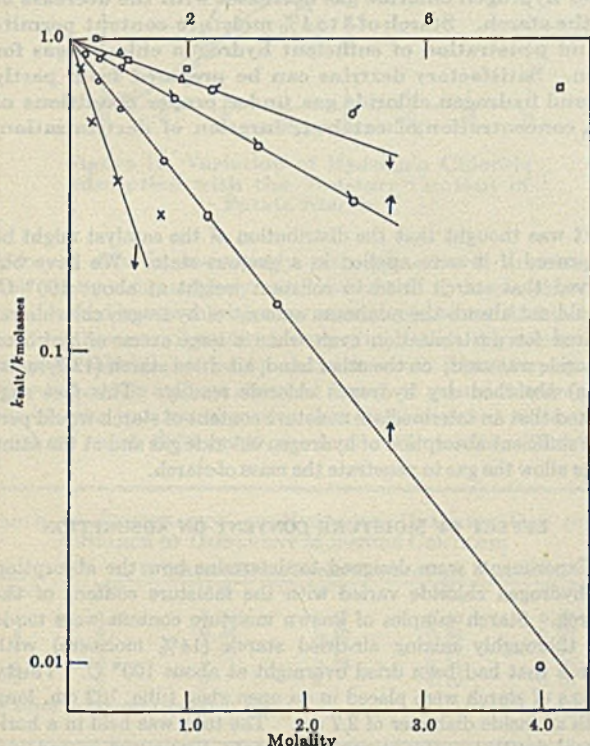


Figure 5. Effect of Nonelectrolytes on Velocity Constant

○ invert sugar; ◇ dextrose; □ ammonia; △ phenol; ▽ aniline; + ethyl alcohol; × caramel

The effects of colloids are of interest and, perhaps, of practical significance. Since such materials have little effect on the activity of solutes, it follows, according to the present activity interpretation and the inference that viscosity is not a rate-determining factor, that colloids should have little effect on the rate of crystallization of sucrose. A sirup was made up in which the amount of gum acacia was approximately one sixth the amount of sucrose which, with the water present, was equivalent to a coefficient of 1.08. The viscosity of this sirup, by the rising bubble method, was approximately twenty-five times that of pure sirup of the same sucrose-water ratio. The velocity of crystallization observed was practically the same (99%) as that of pure sirup. Similarly it was observed that amounts of starch up to 5% of the weight of sucrose had no effect on the velocity of crystallization of these seeded solutions.

The crystals grown at a reduced rate in the presence of phenol, aniline, ammonia, acacia, and several electrolytes were tested

for these substances, and only in the case of ammonia was an amount found sufficient to indicate appreciable adsorption; 4.7% of the original ammonia (4 M) was found on the crystals. The behavior of the majority in this way would seem to eliminate the possibility that the diminished velocity is the result of an impeding adsorbed layer; possibly this does occur with ammonia.

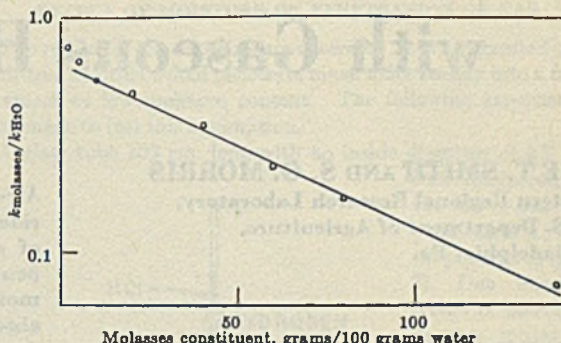


Figure 6. Effect of Molasses Constituent on Velocity Constant

A composite run was performed in which the contaminants were 2 M sodium chloride and 2 M invert sugar. A reduction of $\log (\text{Vel.}_{\text{impure}}/\text{Vel.}_{\text{pure}})$ to 0.30 was computed from the individual results; that observed was 0.27, confirming the equation:

$$\log \frac{(\text{Vel.})_{\text{impure}}}{(\text{Vel.})_{\text{pure}}} = \beta\mu + BM$$

The results in Figure 6 are for blended mixtures of pure sucrose, water, and a cooking molasses which was arbitrarily assumed to contain 50% of molasses constituent, 30% sucrose, and 20% water. This arbitrary assumption probably accounts for the deviations in the early part of the curve.

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Dextrinization of POTATO STARCH with Gaseous Hydrogen Chloride

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COMPARATIVELY few studies of the dextrinization of starch have been reported in the scientific literature. Most of the papers are general discussions of the dextrin industry and reviews of methods of manufacture (4, 5, 8, 11, 12). Bauer (1) in four experiments investigated the effect of acidity and time on the roasting of dextrins. Detailed information on dextrinization is confined chiefly to the patent literature. Numerous patents related to the dextrinization of starch have been granted, most of which claim improvements in dextrinization procedure. The first patent on dextrin in this country was granted to Bloede in 1867 (2).

The method used today for dextrinization of starch is substantially the same as that employed for the last forty years or more. It consists in heating or roasting powdered or granular starch which has been treated with a catalyst, usually an aqueous mineral acid. Early in the industry, starch was heated in shallow trays placed in tiers in large ovens. The modern dextrinizer is a cylinder, placed either horizontally or vertically, in which the starch can be agitated or thoroughly mixed during the heating process. Fans are provided for drawing off the excess water vapor and other gases liberated during the roasting of the starch.

The following references are given, not because they are important to the development of the dextrin industry but because the catalyst applied to the starch was in a gaseous or vapor state, as in the method used here. Fielding (6) dextrinized starch in a revolving cylinder mounted on trunnions, one of which was hollow. A mixture of atomized acid and steam was conducted through the trunnion to the starch while the cylinder was rotated. Thompson and Morrice (9) modified starch by heating it with sulfur dioxide under pressure. Thompson and Berge (10) used the combination of sulfur dioxide and steam under pressure to dextrinize starch. Browning and Barlow (3) acidified starch for dextrinization by conducting the vapors from boiling concentrated hydrochloric acid into the starch as it was mixed in a rotary converter. Frary and Dennis (7) prepared dextrins experimentally by treating 20-gram samples of starch (12.7% moisture) with dry hydrogen chloride. The starch was then heated in stoppered glass tubes.

One of the difficulties in dextrinizing starch is to distribute the small amount of catalyst evenly throughout the comparatively large mass. For example, in some dextrinizations only 1 to 2 pounds of hydrochloric acid are used per ton of starch. The usual method is to spray an aqueous solution of hydrochloric acid into the starch as it is being stirred (5). Obviously, regardless of the efficiency of the atomizer or stirring arrangement, this method of distribution cannot give every starch granule an equal portion of acid.

Air-dry starch (about 12% moisture) readily absorbs hydrogen chloride gas but does not permit penetration of the gas through the mass of starch. Both the absorptive capacity and the resistance to penetration of hydrogen chloride gas decreases with the decrease of moisture in the starch. Starch of 3 to 4% moisture content permits absorption and penetration of sufficient hydrogen chloride gas for dextrinization. Satisfactory dextrins can be prepared from partly dried starch and hydrogen chloride gas under proper conditions of temperature, concentration of catalyst, duration of dextrinization.

It was thought that the distribution of the catalyst might be improved if it were applied in a gaseous state. We have observed that starch dried to constant weight at about 100° C. would not absorb the minimum amount of hydrogen chloride required for dextrinization even when a large excess of hydrogen chloride was used; on the other hand, air-dried starch (12% moisture) absorbed dry hydrogen chloride readily. This fact suggested that an intermediate moisture content of starch would permit sufficient absorption of hydrogen chloride gas and at the same time allow the gas to penetrate the mass of starch.

EFFECT OF MOISTURE CONTENT ON ABSORPTION

Experiments were designed to determine how the absorption of hydrogen chloride varied with the moisture content of the starch. Starch samples of known moisture content were made by thoroughly mixing air-dried starch (14% moisture) with starch that had been dried overnight at about 100° C. Thirty grams of starch were placed in an open glass tube, 102 cm. long with an inside diameter of 2.7 cm. The tube was held in a horizontal position. The starch was evenly distributed in one end of the tube for a distance of 40 cm., and this end was closed with a one-hole rubber stopper. A known quantity of hydrogen chloride mixed with air was then conducted into the tube at the stoppered end.

Hydrogen chloride was generated by dropping concentrated hydrochloric acid into concentrated sulfuric acid at approximately 1 ml. per minute. At the same time a current of air, 700 ml. per minute as measured by a flowmeter, was passed through the sulfuric acid of the generator to carry the hydrogen chloride along and to dilute it with air in the ratio of about 3 volumes of air to 1 of hydrogen chloride. After the required volume of hydrogen chloride had been generated, the air was allowed to flow for another minute and a half. The generator was then disconnected from the tube, and the starch was thoroughly mixed. To determine the quantity of hydrogen chloride absorbed, a 4-gram sample of the starch in water suspension was titrated with 0.1*N* sodium hydroxide solution (phenolphthalein indicator).

Figure 1 shows the variation in the absorption of hydrogen chloride with the moisture content of the starch. Curves A and B, which represent the absorption when 0.36 and 1.46 grams of

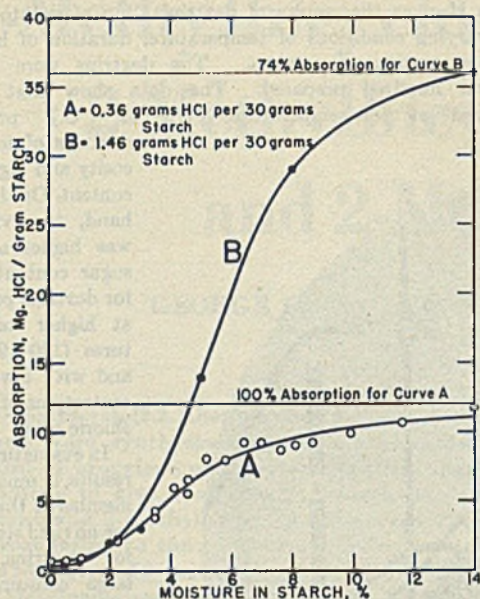


Figure 1. Variation of Hydrogen Chloride Adsorption with the Moisture Content of Potato Starch

hydrogen chloride, respectively, were passed over the starch, show that a comparatively small amount of hydrogen chloride was absorbed by starch with a low moisture content. At 3 to 4% moisture, however, it readily absorbed more than the amount of hydrogen chloride needed for dextrinization. Moreover, up to 4% moisture the amount absorbed from 1.46 grams of hydrogen chloride was not much greater than that absorbed when one fourth as much (0.36 gram) was used. The leveling-off of the

TABLE I. PENETRATION OF HYDROGEN CHLORIDE GAS INTO STARCH OF DIFFERENT MOISTURE CONTENTS

Section No.	% HCl Absorbed by Starch with Moisture Content of:				
	12%	3%	2%	1%	0%
1	1.5	0.94	0.57	0.43	0.25
2	0	0.66	0.50	0.30	0.22
3	0	0.16	0.35	0.24	0.22
4	0	0	0.23	0.14	0.22
5	0	0	0	0.10	0.20

^a Dried to constant weight at 100° C.

TABLE II. PROPERTIES OF POTATO STARCH DEXTRINS PRODUCED UNDER VARIOUS CONDITIONS

Sample No.	Starch, Grams	% Moisture in Starch	HCl Addition		Conversion		Viscosity, Centistokes ^a	Sugar ^b , as % Dextrose
			Temp. of starch, ° C.	Gram/g. of starch	Temp., ° C.	Min. to attain temp.	Time at temp. Hr. Min.	
1	349	2	Room	0.0037	95-100	11	1 24	62.4
2	500	4	Room	0.0035	95-100	16	1 33	31.4
3	500	4	Room	0.0035	110-113	9	0 53	29.8
4	170	4	Room	0.0042	85-88	10	2 27	38.7
5	170	4	Room	0.0042	140-142	24	2 6	21.6
6	157	4	Room	0.0042	140-142	25	0 4	10.7
7	170	3	Room	0.0020	135-138	21	0 27	29.6
8	173	3	Room	0.0015	135-138	21	1 12	40.9
9	170	3	Room	0.0026	75	17	23	8.3
10	170	4	95	0.0030	95	12	19	34.0
11	170	4	130	0.0024	130-132	12	1 10	48.5
12	170	4	Room	0.0025	110-111	8	2 57	8.8
13	2600	4	Room	0.0008	179-180	39	2	73.0
14	4100	4	Room	0.0008	180-181	39	2 50	67.2
15	200	2	Room	0.0008	190	22	0 33	43.5
16	5000	4	Room	0.0010	190-193	35	1 42	44.9
17	200	4	180	0.0012	180-182	23	0 42	69.4
18	200	3	180	0.0013	180	17	1 8	77.9
19	4875	3	180	0.0009	180-185	31	1 32	48.2
20	4000	3	180	0.0010	180-185	34	1 36	76.5
21	200	3	Room	0.0012	180-184	23	0 59	93.0
22	200	3	Room	..	180	22	1 ^c	56.8

^a Viscosities of 50 per cent water solutions of the dextrans (density approximately 1.22) were determined with a modified Ostwald viscosimeter tube No. 300.

^b Munson and Walker method (8A).

^c Four minutes before removal from the converter the pH was changed from 2.73 to 4.50 with ammonia gas.

curves is partly due to the limited amount of hydrogen chloride present. For example, the highest point on curve A represents about 90% of the hydrogen chloride applied, a high figure considering that the starch was not stirred during passage of the hydrogen chloride and that the gas was in contact with the starch for only a short time as it passed through the tube.

EFFECT OF MOISTURE ON PENETRATION OF GAS

The results of the experiments described above suggested that hydrogen chloride would penetrate much more readily into a mass of starch of low moisture content. The following experiments were made to test this assumption.

A glass tube 102 cm. long with an inside diameter of 2.7 cm.

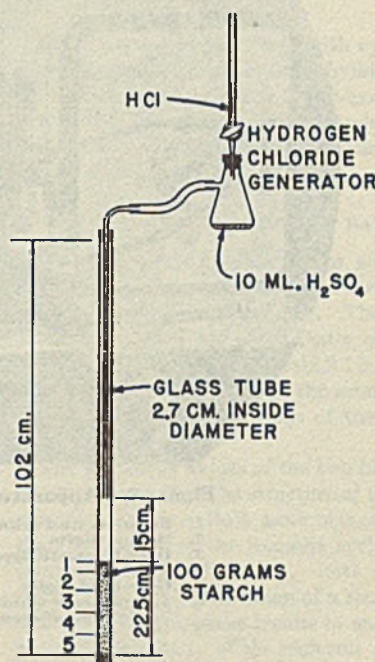


Figure 2. Apparatus for Determining Penetration of Hydrogen Chloride Gas into a Mass of Powdered Potato Starch

was stoppered at the lower end and mounted in a vertical position (Figure 2). One hundred grams of starch of known moisture content were placed in the tube and made a column approximately 22.5 cm. high. Hydrogen chloride gas was generated in a flask by adding 1 ml. of concentrated hydrochloric acid drop by drop over a 5-minute period to 10 ml. of concentrated sulfuric acid. The hydrogen chloride gas was conducted to the starch by a glass tube which extended to within 15 cm. of the top surface of the starch. To permit displacement of the air during the generation of hy-

drogen chloride, the tube containing the starch was loosely stoppered at the upper end. After 30 minutes an additional milliliter of concentrated hydrochloric acid was added to the sulfuric acid. Then the tube containing the starch and hydrogen chloride was tightly stoppered. After 24 hours the starch was removed from the tube in such a way that the column could be separated into five sections. The top section was 2.5 cm. long; each of the other four was approximately 5 cm. Starting at the top, the sections were numbered consecutively from 1 to 5. The quantity of hydrogen chloride in each section was determined. This experiment was carried

out with five starch samples of different moisture contents (Table I).

The results show that hydrogen chloride, even in concentrations several times that required for dextrinization, does not penetrate deeply or diffuse into a mass of starch containing 12% moisture; sections 2, 3, 4, and 5 contained no hydrogen chloride. The affinity between this starch and the hydrogen chloride was so great that the surface layer of the starch (2.5 cm.) absorbed all the hydrogen chloride and thus prevented it from penetrating into the mass. In contrast, the hydrogen chloride penetrated the entire length of the dry starch column (22.5 cm.). In the starches with 3, 2, and 1% moisture, respectively, the distribution was intermediate between the two extremes.

HYDROGEN CHLORIDE IN STARCH DEXTRINIZATION

The three main factors which influence the dextrinization of starch are: quantity of catalyst present, duration of heating period, and temperature of heating. A change in one factor requires a compensating change in at least one of the others to attain the same degree of dextrinization.

Potato starch was acidified and dextrinized in the apparatus shown in Figure 3. This consisted essentially of a 2-quart, stainless steel, revolving cylinder, 1, supported on hollow shafts and mounted horizontally in an electrically heated oven, the temperature of which was controlled by a variable transformer, 13. This cylinder had an operating capacity of about 200 grams and was rotated at a rate of 35 r.p.m. For larger-scale operations an oven was assembled to accommodate cylinders made from 5- and 8-gallon milk cans, which had operating capacities of 10 and 15 pounds (4.5 and 7 kg.), respectively.

Hydrogen chloride gas was generated by dropping concentrated hydrochloric acid into concentrated sulfuric acid at a rate of 3 to 4 ml. per minute. A current of air was bubbled through the sulfuric acid to dilute the hydrogen chloride in the ratio of about 3 parts of air to 1 of hydrogen chloride. The air and hydrogen chloride gas were conducted through flowmeter 7 and the hollow shaft of the cylinder to the starch as it was being mixed in the dextrinizer. The acidity of the starch was determined by titrating 5-10 gram samples as described previously. In most cases the hydrogen chloride was added before heating; in a few cases it was added after the dextrinization temperature had been reached.

The starch was dextrinized by heating until a sample of the dextrin dissolved almost entirely in cold water. The cylinder was then removed from the oven, and the dextrin was emptied into open trays to hasten cooling.

Table II gives the results of dextrinization of potato starch under varying conditions of temperature, duration of heating, and concentration of catalyst. The dextrins were typical of several hundred prepared. The data show that starch dextrinized at low-temperatures (75-142° C.) produced

dextrins of low viscosity and high sugar content. On the other hand, the viscosity was higher and the sugar content lower for dextrins prepared at higher temperatures (180-193° C.) and with lower concentrations of hydrochloric acid.

In evaluating these results, it must be remembered that there are no rigid standards for dextrins. Each large consumer has specifications for the particular dextrin used. It has been generally accepted, however, that high viscosity and low sugar content, together with satisfactory solubility in cold water, are the desirable properties of dextrins, particularly for gums that are to be remoistened.

The results obtained when the catalyst was added at room temperature did not differ significantly from those obtained when the catalyst was added at the dextrinization temperature. To some of the samples ammonia gas was added at the end of roasting to prevent overdextrinization of starch and to increase the pH of dextrin; this increase is desirable because it improves taste and odor. It was found, however, that complete neutralization darkened the resulting product. The pH should not be increased above 5.

Some of the best samples prepared in the course of this investigation fully satisfied the specification of U. S. Bureau of Engraving and Printing for dextrins used as adhesive for postage stamps.

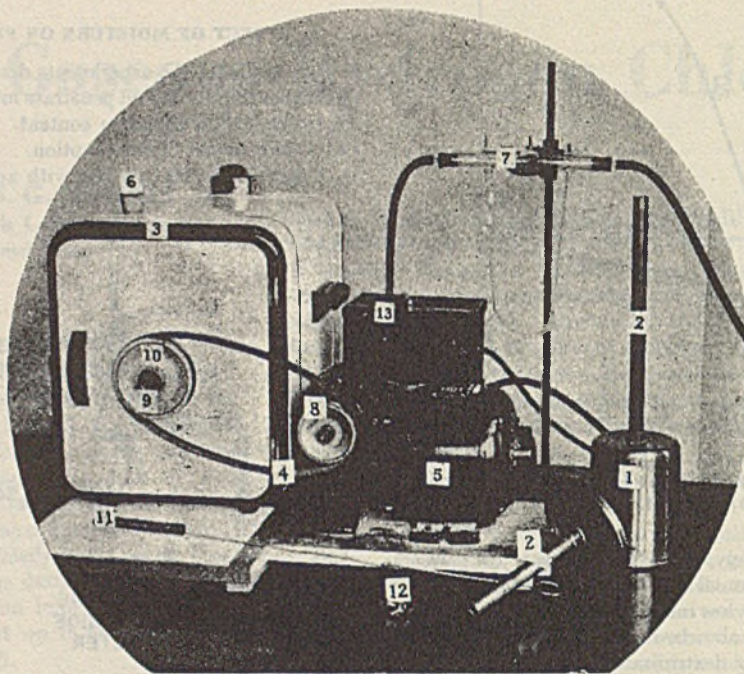


Figure 3. Apparatus for Dextrinizing Starch

- | | |
|---|--------------------------|
| 1. Stainless steel cylinder | 7. Flowmeter |
| 2. Hollow shafts | 8, 10. Pulleys |
| 3. Oven (domestic type) | 9. End of hollow shaft |
| 4. V-belt | 11. Sampler |
| 5. Gear-head motor | 12. Wing nuts |
| 6. Thermometer admitted to interior of oven | 13. Variable transformer |

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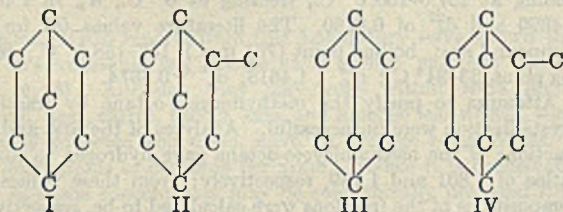
2-Methylbicyclo [2.2.1] 5-heptene, 2-Methylbicyclo [2.2.1] heptane, and 2-Methylbicyclo [2.2.2] octane

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2-Methylbicyclo[2.2.1]heptane and 2-methylbicyclo [2.2.2]-octane were synthesized through Diels-Alder condensations of propylene with cyclopentadiene and 1,3-cyclohexadiene to give, respectively, 2-methylbicyclo[2.2.1]5-heptene and 2-methylbicyclo [2.2.2]5-octene, followed by hydrogenation to the respective bicycloalkanes. The octane numbers of 2-methylbicyclo [2.2.1] 5-heptene and the two bicycloalkanes were found to be 97, 70, and 51, respectively. These octane numbers are compared with those of bicyclo[2.2.1]2-heptene, bicyclo [2.2.1] heptane, and several isomeric cycloparaffins.

HYDROCARBONS of compact structure generally have higher antiknock values than the isomeric compounds of straight-chain or less highly compact structure (7). Models of the molecules of such compounds as bicyclo [2.2.1] heptane and bicyclo[2.2.2]octane, having carbon skeletons I and III,



show that these compounds are very compact and, hence, might be expected to have high antiknock values. However, because of their high melting points (87° C. for the heptane and 169° for the octane) the antiknock evaluation of these two hydrocarbons is not of practical interest. The 2-methyl derivatives, however, which have carbon skeletons II and IV, have relatively low melting points and were deemed to be of interest for testing as high-antiknock fuels.

These two bicyclic hydrocarbons, 2-methylbicyclo[2.2.1]heptane and 2-methylbicyclo[2.2.2]octane, have been prepared previously only by Zelinski and co-workers (8, 10) through Diels-Alder reactions. Interaction of acrolein with cyclopentadiene and 1,3-cyclohexadiene, respectively, produced bicyclo[2.2.1]5-heptene-2-al and bicyclo[2.2.2]5-octene-2-al. These compounds were converted to the respective hydrazones which were decomposed by heating with potassium hydroxide to give 2-methylbicyclo[2.2.1]5-heptene and 2-methylbicyclo[2.2.2]5-octene. Hydrogenation of the olefins over platinum or palladium gave the corresponding bicycloalkanes.

The recent work of Joshel and Butz (5), who prepared bicyclo[2.2.1]2-heptene by the interaction of ethylene and cyclopentadiene, suggested that the two methylbicyclo compounds might be prepared more directly through similar Diels-Alder condensations of propylene with cyclopentadiene and 1,3-cyclohexadiene, followed by hydrogenation of the resulting bicycloalkenes. This was found to be the case.

Condensation of propylene with cyclopentadiene or its dimer dicyclopentadiene, gave 2-methylbicyclo[2.2.1]5-heptene, and interaction of propylene with 1,3-cyclohexadiene gave 2-methylbicyclo[2.2.2]5-octene. Both bicycloalkenes were readily converted to the corresponding bicycloalkanes by hydrogenation with a nickel catalyst.

ANTIKNOCK RATINGS

The two methylbicycloalkanes and 2-methylbicyclo[2.2.1]5-heptene were knock-rated in a nonsupercharged, variable-compression, single-cylinder engine. The results are given in Table I. Also included are the recently obtained ratings of bicyclo[2.2.1]2-heptene and bicyclo[2.2.1]heptane (9) and the values given in the literature (1) for the isomeric hydrocarbons obtained by splitting one of the rings of the bicycloalkanes to produce cycloparaffins.

The antiknock values of the two bicycloalkanes were found to be much lower than the structure of the two molecules had given reason to expect. Both have octane numbers somewhat lower than the better of the isomeric cycloparaffins listed but somewhat higher than the worse. Both show high susceptibility to tetraethyllead. Substitution of a methyl group into the nucleus of bicyclo[2.2.1]heptane results in an increase in octane number while the symmetry of the molecule decreases. Both 2-methylbicyclo[2.2.1]5-heptene and bicyclo[2.2.1]2-heptene have high antiknock values but low susceptibility toward tetraethyllead.

2-METHYLBICYCLO [2.2.1] 5-HEPTENE

In a typical experiment 624 grams (4.7 moles) of 70% dicyclopentadiene (kindly supplied by United Gas Improvement Com-

TABLE I. ANTIKNOCK RATINGS OF CYCLO- AND BICYCLOPARAFFINS

Compound	Octane No. ^a	
	Clear	Plus 3 cc. EtPb/gal.
2-Methylbicyclo[2.2.2]octane	51 ^b	66 ^b
Propylcyclohexane	18	..
Isopropylcyclohexane	63	..
1-Methyl-4-ethylcyclohexane	54	..
1-Methyl-3-ethylcyclohexane	58	..
1-Methyl-2-ethylcyclohexane	74	..
2-Methylbicyclo[2.2.1]heptane	70 ^b	86 ^b
Propylcyclopentane	31	..
Isopropylcyclopentane	81	..
1-Methyl-3-ethylcyclopentane	49	..
1,2-Dimethylcyclohexane	81	..
Bicyclo[2.2.1]heptane	56 + 5 ^c	..
Ethylcyclopentane	62	..
1,3-Dimethylcyclopentane	72	..
Methylcyclohexane	75	..
2-Methylbicyclo[2.2.1]5-heptene	97 ^b	99 ^b
Bicyclo[2.2.1]2-heptene	95 + 5 ^c	..

^a Except as otherwise noted, ratings were obtained from Dose (1).

^b Measured by a modified Research Method, at 350° F. intake temperature.

^c Measured by A.S.T.M. Procedure D357-41T on a 20% blend in 80% iso-octane-40% n-heptane (9).

pany) and 646 grams (15.4 moles) of propylene were charged into an autoclave (2). (Cyclopentadiene and dicyclopentadiene were used in this condensation reaction with equally good results. The mechanism of the dicyclopentadiene-propylene reaction probably involves the preliminary dissociation of the dimer to the monomer, which then reacts with the propylene.) Rocking of the autoclave was started, and its temperature was raised to 228° C. and maintained for 2.5 hours. The maximum pressure attained was 2530 pounds per square inch at 175° C.; this dropped to 1500 pounds at 228° C. at the end of the run. After cooling the autoclave and venting the excess propylene, distillation of the product yielded 543 grams of crude methylbicycloheptene, distilling at 95–128° C. (mainly at 114–116°). The yield of crude product was 73%, based on the diene content of the dicyclopentadiene charged. Seven runs made in this manner gave 3423 grams of this product.

Fractional distillation of 1458 grams of the crude bicycloheptene through an efficient column yielded 1156 grams of material having a boiling range of 115.9–116.3° C. (760 mm.); d_4^{20} , 0.8653–6; and n_D^{20} , 1.4598. The literature values for 2-methylbicyclo[2.2.1]heptene (10) are: boiling point (750 mm.), 115.5–117.0° C.; d_4^{18} , 0.8668; n_D^{18} , 1.4606.

2-METHYLBICYCLO[2.2.1]HEPTANE

The remainder of the crude methylbicycloheptene (1965 grams) was hydrogenated in an autoclave at 100° C. over nickel catalyst. The product, after separation from the catalyst by distillation, was shaken with concentrated sulfuric acid, washed with sodium bicarbonate solution, and refluxed over metallic sodium. Fractional distillation of the chemically purified material through an efficient column yielded 1710 grams of product boiling at 126.9–127.3° C. (760 mm.); d_4^{20} , 0.8544; and n_D^{20} , 1.4540. The literature values (10) for 2-methylbicyclo[2.2.1]heptane are: boiling point (745 mm.), 124.5–126.0° C.; $d_4^{16.5}$, 0.8561; $n_D^{16.5}$, 1.4553.

2-METHYLBICYCLO[2.2.2]OCTANE

PREPARATION OF 1,3-CYCLOHEXADIENE. 1,2-Dibromocyclohexane was prepared by bromination of cyclohexene (Eastman Kodak Company) following the method of Greengard (3). The yields of crude product from individual batches varied from 76% to 99%.

1,2-Dibromocyclohexane was dehydrobrominated to 1,3-cyclohexadiene by passage over calcium oxide at 375–400° C. under a pressure of approximately 10 mm., following the general method of Schmidt, Hochschwender, and Eichler (8). The yield of crude product, distilling at 80–81° C. at 760 mm., was 46%. A sample of this product was separated by fractional distillation into twelve fractions. These fractions varied in refractive index from n_D^{20} 1.3770 to 1.4731, and in density from d_4^{20} 0.8594 to 0.8393, an indication that the cyclohexadiene contained appreciable amounts of other compounds. The latter were probably benzene, cyclohexene, and cyclohexane, all of which boil in the temperature range 80–83° C.

CONDENSATION OF 1,3-CYCLOHEXADIENE WITH PROPYLENE. The condensation of propylene with 1,3-cyclohexadiene to yield 2-methylbicyclo[2.2.2]octene was considerably more sluggish than the dicyclopentadiene-propylene condensation, required a higher temperature, and was accompanied by considerable polymerization of the propylene, apparently because of the high temperature (4). In order to speed up condensation and minimize polymerization, the method ultimately employed consisted of pumping the cyclohexadiene slowly into an excess of propylene at 300° C. This gave considerably better yields than the method of simply charging the reactants into the autoclave and heating the mixture to the desired temperature; but even so, the product contained considerable amounts of propylene polymerization products, largely nonenes, as shown by fractional distillation of the crude product after hydrogenation.

In a typical run the autoclave was evacuated and charged

with 421 grams (10 moles) of propylene. Rocking and heating were started, and when the temperature had reached 300° C., 168 grams (2.1 moles) of crude cyclohexadiene were pumped into the autoclave at a uniform rate during a period of 2 hours. This was accomplished by means of a piston-type hydraulic pump fitted with a double-ball check valve on the exit side. When the addition was completed, heating and rocking were continued for 3 hours. During the addition and subsequent heating period, the pressure fell from 2280 pounds per square inch at the start to 1525 pounds at the end. Distillation of the product removed after venting the excess propylene gave 95 grams of low-boiling material (boiling point, 110° C., 106 grams of crude methylbicyclo-octene (boiling at 110–145° C., mainly at 144–145°) and 137 grams of residue. The yield of crude methylbicyclo-octene was 41% based on the cyclohexadiene and 19% based on the cyclohexene. A total of 2042 grams of crude product was prepared in this manner.

Redistillation of the low-boiling material gave largely material boiling at 80–81° C., which on systematic recrystallization gave both benzene and 1,3-cyclohexadiene. When the low-boiling material was rerun with propylene, very low yields of the desired adduct were obtained.

HYDROGENATION AND PURIFICATION OF PRODUCT. The crude methylbicyclo-octene was hydrogenated over nickel catalyst at 100° C. in the autoclave, and the product was treated chemically as described above for methylbicycloheptane. Fractional distillation of 1828 grams of the chemically purified product through an efficient column gave 109 grams of material boiling at 70.3–88.0° C. (760 mm.) with n_D^{20} of 1.4462–1.4204 (largely cyclohexane); 528 grams of material boiling at 88.0–157.0° C. with n_D^{20} of 1.3994–1.4615 (largely branched-chain nonanes resulting from hydrogenation of the nonenes formed by polymerization of propylene); 938 grams of 2-methylbicyclo[2.2.2]octane boiling at 157.0–160.1° C., freezing at 6° C., n_D^{20} of 1.4659–1.4690 and d_4^{20} of 0.8780. The literature values (6) for the compound are: boiling point (761 mm.), 157–158.5° C.; freezing point, 33–34° C.; $n_D^{40.5}$, 1.4613; $d_4^{40.5}$, 0.8674.

Attempts to purify the methylbicyclo-octane by fractional crystallization were unsuccessful. Analyses of the first and last fractions of the methylbicyclo-octane gave hydrogen to carbon ratios of 1.801 and 1.789, respectively; from these values the compositions of the fractions were calculated to be, respectively, $C_8H_{16.1}$ and $C_8H_{15.1}$. Assuming the impurity to be C_8 paraffins, the amounts of impurity in the two fractions were calculated to be 5.5 and 2.5 mole %, respectively. These figures are in good agreement with those based on the refractive index and density data, using the literature values (6) for methylbicyclo-octane and the values n_D^{20} 1.4030 and d_4^{20} 0.7120 for the C_8 impurities. Hence the combined methylbicyclo-octane was judged to have a purity of at least 95 mole %.

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CAROTENE CONCENTRATES from VEGETABLE LEAF WASTES

Certain vegetable leaf meals are rich sources of carotene, ranging in potency from 300 to 700 micrograms per gram. Petroleum ether solvents combine good solvent properties for carotene in leaf meals with relatively poor solvent properties for other plant pigments. A number of procedures for the preparation of carotene concentrates from vegetable leaf meals have been devised. Most of them are based on the rapid saponification of chlorophyll in petroleum ether solution, followed by adsorption treatment with hydrated lime. Upon removal of the solvent, deep red carotene concentrates equivalent to 20,000–200,000 I.U. vitamin A per gram are obtained. The yield of purified carotene is from 85 to 95% of the carotene in the original extract.

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PREVIOUS reports from this Laboratory have shown that dry vegetable leaf wastes have a high carotene content (2, 3). Although they may vary within wide limits, spinach, beet, carrot, turnip, kale, and broccoli leaf wastes, when properly collected and dried, have an average range of 300 to 700 micrograms of carotene per gram. Hence it is conceivable that carotene concentrates may be economically prepared from these materials. This paper describes and compares various procedures devised for preparing carotene concentrates from vegetable leaf wastes. The chief operations involved are extraction of carotene and purification of the extract.

The leaf wastes, obtained from local packing houses and farms, were trucked to the Laboratory, where they were either dried at once or stored for a few days at 4° C. After the wastes were dried in a through-circulation air dryer, the leaves were separated from the stems by screening according to the method of Kelley, Wall, and Willaman (3). The initial moisture content ranged from 80 to 90%; in most cases the final moisture content was 5%.

To determine carotene and xanthophyll, these pigments must be dissolved in petroleum ether. If they are dissolved in other solvents, the solvent must be removed under vacuum and the residue taken up in petroleum ether. An aliquot containing 50 to 500 micrograms each of carotene and xanthophyll was adsorbed on a mixture of 3 parts Hyflo Supercel and 1 part activated magnesia No. 2641. The carotene was separated from xanthophyll and chlorophyll by washing the adsorption column with a solution of 5% acetone in Skellysolve B, according to the method of Wall and Kelley (11). The xanthophyll was then removed from the column by washing with a solution of 20 to 30% acetone in Skellysolve B.

Chlorophyll was determined by direct reading in a photoelectric colorimeter, according to the method of Petering, Wolman, and Hibbard (7).

CAROTENE EXTRACTION

Extractions were made in a Soxhlet and percolation apparatus. Most of the large-scale extractions were carried out in a Soxhlet apparatus of 4.5-kg. (10-pound) capacity (Figure 1), which was similar in some respects to that described by Rose, Freeman, and Mc-

Kinney (8). The material to be extracted was ground 30 to 40 mesh in a Wiley mill and put in bags holding 450 grams each. A 4.5-kg. charge was put into flask X. After the bags were soaked with solvent, 12 to 14 liters of solvent was poured into flask U. Steam was run through condenser V, and the extraction started. For rapid extraction, the solvent was boiled at such a rate that siphoning took place two or three times per hour. Since considerable back pressure develops, the height of the siphon tube must be experimentally adjusted.

The apparatus was converted for distillation by removing the siphon tube and substituting a 22-liter tubulature flask, with the tubulature closed during distillation. For reflux operations, the siphon tube and condenser W were removed, an auxiliary reflux condenser was attached to condenser V, and cold water was run through the condensers.

Carotene has been extracted from plant material with a large number of organic solvents. The solvents tested here included

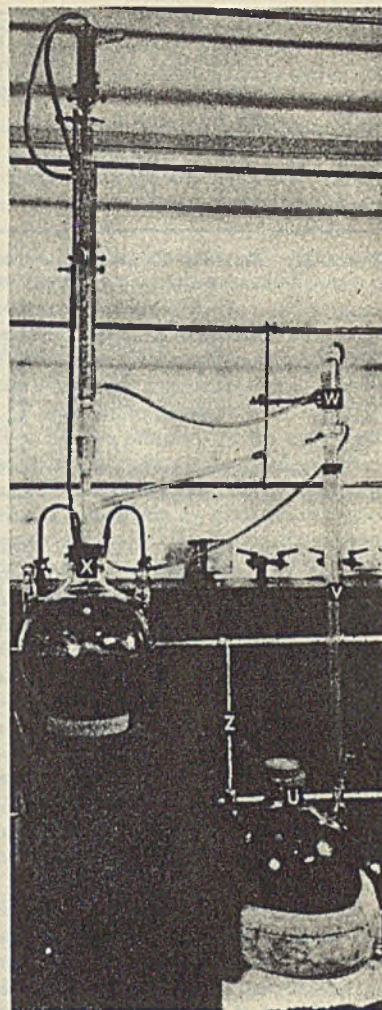


Figure 1. Large Soxhlet Extractor

- U. 22-Liter Pyrex 3-neck flask, heated with Glas-col 22-liter hemispherical mantle or an internal steam coil
- V. Condenser, used with either steam or cold water
- W. Friedrich condenser (Pyrex 3440)
- X. 3-Neck, Pyrex, 22-liter flask with tubulature at bottom
- Y. Several auxiliary condensers
- Z. Siphon tube attached to flask U and tubulature of flask X

TABLE I. RATE OF EXTRACTION OF CAROTENE FROM BROCCOLI LEAF MEAL WITH VARIOUS SOLVENTS

Time, Hr.	% of Total Carotene Extracted				
	SK F	SK B	SK C	Acetone	Trichloroethylene
1	77.5	89.0	90.5	83.0	93.0
2	86.0	95.0	93.0	91.5	94.0
3	90.0	100.0	95.0	100.0	99.5
4	100.0	100.0	97.5	100.0	98.0
5	100.0	100.0	100.0	100.0	100.0

TABLE II. PIGMENT COMPOSITION^a OF BROCCOLI LEAF MEAL EXTRACTS PREPARED WITH VARIOUS SOLVENTS

Solvent	Carotene, %	Xanthophyll, %	Chlorophyll, %	Ratio, Carotene to:	
				Xanthophyll	Chlorophyll
SK F	18.1	24.4	57.5	0.74	0.31
SK B	15.2	25.6	59.2	0.59	0.26
SK C	10.8	28.0	60.6	0.38	0.18
Acetone	4.8	6.4	88.8	0.75	0.05
Trichloroethylene	5.0	15.2	79.8	0.33	0.06

^a Only carotene, xanthophyll, and chlorophyll are considered in this table.

Skellysolve F (b.p. 35° to 59° C., primarily pentane), Skellysolve B (b.p. 65° to 70° C., primarily hexane), Skellysolve C (b.p. 88° to 98° C., primarily heptane), acetone, chloroform, trichloroethylene, and carbon tetrachloride. All extracted large proportions of other plant pigments and lipoids along with the carotene. The amount and type of these contaminants varied widely, depending on the solvent used.

The rate of extraction of carotene from broccoli leaf meal by different solvents was determined in a Soxhlet apparatus of 1-pound capacity. The results are shown in Table I. All the solvents extracted 100% of the carotene in 4 to 5 hours. Skellysolves B and C and trichloroethylene extracted approximately 90% in 1 hour; Skellysolve F and acetone extracted it somewhat less rapidly.

The quantity of xanthophyll and chlorophyll extracted by the various solvents was determined in the 5-hour extracts. The results are shown in Table II. The pigment composition of the extracts varied widely, depending on the solvent used. Since all the extracts had approximately the same total carotene content, the differences in percentages of these pigments in Table II are due primarily to variations in xanthophyll and chlorophyll extracted by the different solvents; chlorophyll showed the greatest variation. Skellysolve F extracted about three times as much chlorophyll as carotene; the others extracted increasing amounts until approximately twenty times as much chlorophyll as carotene was obtained with acetone and trichloroethylene.

It has been reported that petroleum ether will not extract either chlorophyll or xanthophyll from plant material (9, 12). With the various leaf meals tested, appreciable quantities of chlorophyll and xanthophyll were extracted with a wide range of petroleum ethers. Although pure xanthophyll and chlorophyll are only slightly soluble in low-boiling petroleum ether, the solubilities of these compounds seem to be markedly affected by other fat-soluble substances in plant material.

PURIFICATION OF EXTRACTS BY DIRECT ADSORPTION

Since there is relatively little demand for crystalline carotene, efforts were centered on preparing a concentrate of carotene in the natural plant lipoids. Skellysolve B, which has many advantages from the standpoint of both purity of the extract and cost, was used for most of the large-scale extractions. A 4.5-kg. batch of leaf meal was extracted in the large Soxhlet apparatus, and the extract concentrated to 3 or 4 liters. Little or no loss of carotene occurred even when the concentration took place at atmospheric pressure. The concentrated extract was used for the purification experiments.

This procedure was based on the use of activated magnesia No. 2641 (Westvaco Chlorine Products Company), extensively em-

ployed by Strain (10) as an adsorbent for separation of carotenoid mixtures and also used by Wall and Kelley (11) in the determination of carotene in leaf tissue.

Attempts to purify concentrated plant extracts in large chromatographic columns composed of Hiflo Supercel-activated magnesia mixtures were not successful, since the chlorophyll spread through practically the whole length of the column before carotene separated.

When the extract was stirred directly with magnesia, the slurry could be filtered in relatively shallow layers on large Büchner funnels without a filter aid. The carotene was then washed off the adsorbent with pure Skellysolve B or 5% acetone in Skellysolve B. The clear red extract obtained was free of chlorophyll and had little or no xanthophyll. From 0.20 to 0.45 kg. of magnesia was required for every kg. of leaf meal extracted, depending on the source of the extract. The adsorbent was thoroughly stirred with the extract and filtered on a large Büchner funnel, and the cake was well broken and washed three or four times with a total of 6 to 8 liters of Skellysolve B. The yield of carotene averaged about 85% of the quantity initially present. The solvent was removed *in vacuo*, leaving a deep-red oil which solidified on cooling. From 0.45 to 0.56 gram of carotene in 30 to 45 grams of plant lipoids was obtained per kg. of broccoli leaf meal.

PURIFICATION BY SAPONIFICATION OF CHLOROPHYLL

The amount of adsorbent could be greatly reduced if the chlorophyll could be removed from the extract before adsorption. Although chlorophyll may be separated from carotene by direct saponification of the plant material, according to the method of Holmes and Leicester (1) or by procedures based on the classical Willstätter-Stoll procedure (12), such methods are time consuming and do not lend themselves to commercial practice. Therefore, saponification of chlorophyll was attempted in the petroleum ether extract.

As a result of these experiments a rapid and simple method of removing chlorophyll from plant extracts was developed. In certain respects the method is similar to the analytical procedure of Kuhn and Brockmann (4). It was found that 95% ethanol containing 5% potassium hydroxide or saturated with sodium hydroxide was completely miscible with petroleum ether, and when a petroleum ether plant extract was mixed with the alcoholic potassium hydroxide and boiled, most of the chlorophyll was rapidly saponified.

To determine optimum conditions, a study was made of the effect of alkali concentration, length of heating period, and ratio of alcohol to petroleum ether. Concentrations of alkali used were 1, 5, and 10% potassium hydroxide in 95% ethanol; the time of boiling was 0.5, 1, and 2 hours; and the ratio of alcohol to Skellysolve B ranged from 1:4 to 1:1. All combinations of these factors, with the exception of 1% potassium hydroxide, yielded practically the same results. In most cases 97 to 99% of the total chlorophyll was saponified, which left a residual chlorophyll amounting to 10 to 5%, respectively, of the total pigment mixture in the petroleum ether extract. The combination of 5% potassium hydroxide or saturated solution of sodium hydroxide in 95% ethanol, 0.5-hour reflux time, and a 1:4 ratio of alcohol to Skellysolve B was selected as most economical and effective.

The following method was thus evolved: The concentrated Skellysolve B extract (3 to 4 liters) from a 4.5-kg. batch of leaf meal is mixed with 1 liter of 95% ethanol containing 5% potassium hydroxide. The mixture is vigorously refluxed for 0.5 hour and then cooled. Sufficient water (187.5 ml.) is added to make the final alcohol concentration 80%. The extract is shaken and then allowed to stand about 15 minutes. Two layers are formed. The lower consists of the aqueous alcohol with dissolved saponification products and also some xanthophyll; the upper consists of the Skellysolve B extract, from which most of

TABLE III. EFFECT OF SAPONIFICATION ON CHLOROPHYLL IN PETROLEUM ETHER EXTRACT OF BROCCOLI LEAF MEAL

Conditions after:	Mg. per Kg. of Leaf Meal	% of Original Chlorophyll	% of Total Pigment
Original extraction	2640	100.0	74.5
First saponification	111	4.2	15.3
Continuous 80% ethanol extraction	43	1.6	10.5
Second saponification	34	1.3	7.2
Third saponification	34	1.3	7.2

TABLE IV. RECOVERY AND PURIFICATION OF CAROTENE FROM PETROLEUM ETHER EXTRACT OF MIXED VEGETABLE LEAF MEAL

Conditions after:	Carotene		Xanthophyll		Chlorophyll	
	Mg./kg. leaf meal	% of total pigment	Mg./kg. leaf meal	% of total pigment	Mg./kg. leaf meal	% of total pigment
Original extn.	240	17.0	162	11.5	1010	71.5
Saponification	226	63.5	90	25.0	39	11.5
Adsorption on magnesia, 400 g.	220	100.0	0	0.0	0	0.0

TABLE V. EFFICIENCY OF ADSORBENTS IN PURIFYING A SAPONIFIED PLANT EXTRACT IN SKELLYSOLVE B

Adsorbent, Grams	% Carotene in Total Pigment	G. Adsorbent/G. Activated Magnesia
Activated magnesia, 200	73.6	1.0
Hydrated lime ^a , 1200	67.0	6.0
Lime, 1200	66.7	6.0
Magnesium carbonate, 800	77.0	4.0
Calcium carbonate, 2400	63.0	12.0
Bauxite, 1200	69.0	6.0

^a Through courtesy of the Warner Company, we recently received specially prepared, dolomitic hydrated limes which were active adsorbents. These lime preparations have an adsorption ratio of 2.0, or half the adsorptive capacity of activated magnesia No. 2641.

the chlorophyll and some xanthophyll have been removed. The aqueous alcohol layer contains little carotene, and therefore it is discarded for recovery of the alcohol. A 6-liter separatory funnel, well illuminated, is used to separate the two layers.

At this stage the Skellysolve B extract is usually dark brown, probably owing to small amounts of unsaponified chlorophyll remaining in solution. It is wet and contains traces of alkali, but the subsequent treatment renders any drying or removal of alkali unnecessary.

Table III shows the percentage of chlorophyll remaining after saponification of an extract from 4.5 kg. of broccoli leaf meal. The saponified extract was subjected to a continuous 80% ethanol extraction, after which the extract was twice resaponified. The first saponification removed about 96% of the chlorophyll; subsequent treatment with alcohol removed an additional 2 to 3%, which was probably emulsified in the petroleum ether solvent. Two further saponifications failed to remove the remaining 1%. This remnant probably was a decomposition product. All the extracts obtained by the various treatments were dark brown, owing to the fact that the remaining 1% of chlorophyll or its decomposition products constituted from 5 to 10% of the total pigment.

PURIFICATION BY SAPONIFICATION AND ADSORPTION

Although the extract, after saponification and separation of saponification products, can be used to make a crude concentrate, for many purposes a purer extract is desirable. The saponified petroleum ether solution is stirred with 200 to 400 grams of activated magnesia No. 2641 and filtered on a large Büchner funnel, after which the adsorbent is washed three times with a total of 3 to 6 liters of Skellysolve B. A deep red carotene preparation, free of water and alkali, results. Recovery and purification of carotene in a typical experiment are shown in Table IV. This procedure results in a carotene solution free of chlorophyll and xanthophyll. Carotene yields of 85 to 95% have been consistently obtained.

Although the saponification procedure greatly reduced the quantity of magnesia required for purification, the cost of the

magnesia was still too high for commercial use. A number of less expensive materials were therefore tested, including technical calcium oxide, technical calcium hydroxide, calcium carbonate, *sec*-calcium phosphate, magnesium oxide, magnesium carbonate, *sec*-magnesium phosphate, activated alumina, aluminum oxide, and certain grades of bauxite (a natural aluminum oxide). Acidic compounds, extremely alkaline compounds, and various carbon blacks destroy carotene or adsorb it so firmly that it cannot be removed.

The relative efficiency of the adsorbents was determined by stirring aliquots of a saponified extract with increasing increments of adsorbent. The percentage of carotene in the total pigment mixture was determined after each increment of adsorbent. Using the results obtained with activated magnesia as a standard, the weights of the various adsorbents required to give approximately the same degree of purification obtained with activated magnesia were noted. The relative efficiency of the adsorbents could then be determined from the ratio of grams of adsorbent to grams of activated magnesia. Some typical results are shown in Table V. The adsorbents tested can be divided into three groups in order of decreasing efficiency: (1) activated magnesia No. 2641, activated alumina; (2) CaO, Ca(OH)₂, MgCO₃, MgO, bauxite; (3) CaCO₃, CaHPO₄, MgHPO₄.

As a result of these tests, technical hydrated lime was selected for large-scale experiments. It is readily available and although it is only about one sixth as active as activated magnesia, it costs only about one fiftieth as much. The following example illustrates the use of hydrated lime: A 4-liter concentrate of a saponified extract of 4.5 kg. of leaf meal was thoroughly stirred with 1.0 to 2.0 kg. of commercial hydrated lime and filtered. The filter cake was thoroughly washed three or four times with 6 to 8 liters of Skellysolve B. A deep red solution was obtained in which 70 to 80% of the total pigment was carotene and 30 to 20% xanthophyll. The yield of carotene was from 85 to 95% of that originally present in the crude extract.

A number of commercial hydrated limes were tested. All removed the remaining chlorophyll and variable proportions of xanthophyll from the saponified extracts. It is not practical to remove all the xanthophyll since an inordinately large bulk of lime is required. Moreover, the product can be made xanthophyll-free economically by further treatment with 80 to 85% ethanol. For many purposes the xanthophyll in the extracts is not objectionable.

Saponification followed by lime adsorption removed about half the plant lipids in a Skellysolve B extract of broccoli leaf meal. About 0.45–0.56 gram of carotene in 20 grams of plant lipids was obtained per kg. of meal.

CHOICE OF SOLVENTS

Similar experiments were conducted with Skellysolves F and C. Saponification of chlorophyll proceeded equally well, but in general greater adsorption was obtained in Skellysolve F than in the other petroleum ether solvents. Skellysolve F extracted less xanthophyll and chlorophyll from plant materials than Skellysolves B or C, and a pure carotene extract was obtained with less adsorbent. On the other hand, Skellysolve F has a low boiling point, and consequently solvent losses might be high.

Since the use of petroleum ether solvents is attended with fire and explosion hazards, experiments were conducted with chlorinated solvents, particularly trichloroethylene and carbon tetrachloride. These solvents extracted about three to four times as much chlorophyll in two to three times as much xanthophyll from plant material as did the petroleum ether solvents. The saponification reaction with these solvents gave variable results. (With these chlorinated solvents the upper layer is aqueous alcohol.) In both cases about 90 to 95% of the chlorophyll was saponified. There was little loss of carotene when trichloroethylene was used but great loss with carbon tetrachloride, which

TABLE VI. RECOVERY AND PURIFICATION OF CAROTENE OBTAINED FROM A TRICHLOROETHYLENE EXTRACT OF BROCCOLI LEAF MEAL

Conditions after:	Carotene		Xanthophyll		Chlorophyll	
	Mg./kg. leaf meal	% of total pigment	Mg./kg. leaf meal	% of total pigment	Mg./kg. leaf meal	% of total pigment
Original extn.	570	4.8	1160	9.6	10,350	85.6
Saponification	530	25.0	955	45.4	625	29.6
Adsorption on hydrated lime, 6000 g.	489	35.0	910	65.0	0	0

TABLE VII. PIGMENT COMPOSITION OF EXTRACTS PREPARED FROM BROCCOLI LEAF MEAL BY VARIOUS METHODS

Method	Color	Carotene, %	Xanthophyll, %	Chlorophyll, %	Vitamin A ^b , I.U./G. Solids
1. Petroleum ether extn. and saponification	Green-brown	50-60	20-30	10-20	30,000-40,000
2. Same as 1, plus lime treatment	Red	70-80	20-30	0	30,000-40,000
3. Same as 1, plus 80% ethanol extn.	Brown	80-90	5-10	5-10	30,000-40,000
4. Same as 2, plus 80% ethanol extn.	Red	100	0	0	30,000-40,000
5. Same as 2, plus removal of fats from SK B soln. by chilling	Red	95-100	0-5	0	160,000-180,000
6. Same as 5, plus adsorption on 1:1 activated magnesia (Hi-Su Supercel)	Red	100	0	0	200,000-220,000
7. Crystallization of extract 6	Red	100	0	0	1,660,000

^a On basis of total pigment.

^b Values obtained by multiplying micrograms of carotene found by chemical analysis by conventional conversion factor 1.66.

was undoubtedly due to decomposition of the solvent in alcoholic potassium hydroxide. There is risk of such decomposition with all chlorinated solvents commonly used.

The quantity and purification of carotene obtained from a trichloroethylene extract of 4.5 kg. of broccoli leaf meal are shown in Table VI. After adsorption the solution was deep red; 35% of the total pigment consisted of carotene and 65% of xanthophyll. The yield of carotene was 86% of that in the original extract. Little xanthophyll was removed in the saponification procedure because it was necessary to dilute the ethanol 50% with water to separate the trichloroethylene and alcohol layers. Practically no xanthophyll was removed by adsorption on hydrated lime. If desired, the xanthophyll left in the lime-treated extract could be removed with aqueous alcohol.

Chlorinated solvents are relatively expensive, and large amounts of adsorbent are required for purification. On the other hand, the cost of equipment for these solvents would be lower, owing to the greatly reduced fire hazard.

In other experiments the leaf meal was extracted with trichloroethylene, which was removed in vacuum, and the residue taken up in a much smaller amount of Skellysolve B. No loss of carotene occurred. In this procedure there is the advantage of conducting the large volume phase of the process with a non-flammable solvent. The carotene can then be purified much more efficiently in petroleum ether.

LIQUID-LIQUID PURIFICATION

Use of aqueous ethanol in purifying the leaf meal extracts was studied. A continuous extractor of a type used for extracting light liquids with heavier ones was devised for this purpose. Aqueous ethanol of approximately 60% concentration was boiled, and the vapors (80 to 85% ethanol) were condensed, passed through a tall column of petroleum ether extract, and returned to the boiling flask. When a saponified Skellysolve B solution was thus extracted, a solution was obtained in which 85 to 90% of the total pigment was carotene and the remainder was xanthophyll and unsaponified chlorophyll. There was little loss of carotene in this operation. The extract was dark brown, as contrasted with the clear, deep red extracts obtained by the adsorption technique. Such a carotene concentrate may have uses for which the color is not objectionable.

Purification by layering was also investigated. Petroleum

ether extracts were shaken in separatory funnels with 80 to 85% ethanol. Various ratios of alcohol to petroleum ether were tested. The higher the ratio of alcohol to petroleum ether, the more rapid the removal of alcohol-soluble impurities. As in the liquid-liquid extractor, a dark brown carotene extract was obtained in which 85 to 90% of the total pigment was carotene.

Similarly, extracts containing xanthophyll but no chlorophyll after adsorption were purified by the alcohol treatment. Such a procedure is practical only when a pure carotene extract is desired.

ACETONE EXTRACTION

The procedures described for extraction and purification of carotene were compared with the methods of Petering *et al.* (5, 6) originally described for use with alfalfa leaf meal. Carotene yields of 68-89% were secured, the lower results with the use of technical barium hydroxide and the higher with c.p. grade. The acetone-barium hydroxide procedure not only resulted in lower yields of carotene when technical reagents were used, but also required more steps and somewhat more expensive chemicals than the petroleum ether extraction and saponification procedure.

POSSIBLE CAROTENE PRODUCTS

Carotene concentrates of varying degrees of purity may be prepared for specific markets by the procedures outlined. Table VII summarizes the methods used and the pigment composition of the extracts prepared by the various methods.

The product obtained in method 1 by saponification only was a crude extract, partly purified in respect to xanthophyll and chlorophyll. The extract freed of solvent might be suitable for a crude animal feed supplement. When this extract was treated with lime (method 2), a deep red concentrate free of chlorophyll was formed. This concentrate contained 18,000 to 24,000 micrograms of carotene (30,000 to 40,000 International Units of vitamin A) per gram of concentrate. It was easily soluble in vegetable oils, and might be suitable for a food or feed supplement. Treating the saponified extract with 80 to 85% ethanol or 90% methanol produced a concentrate which contained relatively less pigment impurities than the concentrate from method 2. Owing to the presence of a small amount of chlorophyll or its degradation products, this concentrate was brown instead of the red color of a typical carotene concentrate. It would probably be acceptable where an off-color was not objectionable. The concentrate from method 4, resulting from the further treatment of that from method 2 with 80 to 85% ethanol or 90% methanol, yielded a carotene preparation free of xanthophyll and chlorophyll. The concentrates from methods 1 to 4 had about the same provitamin A content, 18,000 to 24,000 micrograms (30,000 to 40,000 I.U. of vitamin A) per gram. When the concentrate from method 2 was dissolved in petroleum ether and chilled, a copious precipitate of various lipoidal substances was obtained. Most of the carotene remained in solution and was filtered off. In this way high-potency concentrates containing 97,000 to 108,000 micrograms of carotene (160,000 to 180,000 I. U. of vitamin A) per gram of solids were obtained. Further treatment of this concentrate with a mixture of activated magnesia and Hi-Su Supercel removed some impurities, and the resulting oil contained 120,000 to 134,000 micrograms of carotene (200,000 to 222,000 I.U. of vitamin A) per gram. Crystalline carotene (melting at 171° to 173° C., corrected) was obtained from the concentrates from methods 5 and 6 by low-temperature crystallization.

Methods presented in this paper for the preparation of carotene concentrates will be tested in the pilot plant to de-

termine their suitability for large-scale operation and to obtain data on the cost of the various steps.

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Composition of Vapors from Boiling Binary Solutions

WATER-ACETIC ACID SYSTEM AT ATMOSPHERIC AND SUBATMOSPHERIC PRESSURES

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DURING a study of the correlation between vapor-liquid equilibria and partial heats of solution, the vapor-liquid equilibria for the system water-acetic acid were determined at pressures of 760, 500, 250, and 125 mm. of mercury. The method adopted for experimentally determining the vapor-liquid equilibria has been described (7, 9, 10). The temperature and pressure are directly observed, whereas the composition of

the liquid and vapor states in equilibrium are determined by suitable analysis of samples of the liquid withdrawn from the still and distillate trap, respectively. The correlation of these data have already been discussed (11).

The details of the equilibrium still were given in another paper (9); the heating arrangement is shown in Figure 3 of that paper. The coil was wrapped around the larger of the reflux heating tubes between layers of asbestos cloth and was rated at 500 watts (considerably more than needed). Power input was controlled by a Variac transformer.

The arrangement of the apparatus is shown in Figure 1, as prepared for use at subatmospheric pressures. For work at atmospheric pressure, the constant-pressure device was replaced by a small mercury manometer having a slope of about 1 to 10 with the horizontal, and open to the atmosphere. The pressure on the system was then maintained at 760 mm. by adding air to or venting air from the reservoir through cock E. The column of the still was lagged with many layers of cloth. Cock A served to expel noncondensable gases; cocks B and C allowed liquid and condensate samples to be withdrawn; and the three-way cock D, venting to the atmosphere, served to isolate the still from the reservoir while samples were being withdrawn. The 12-liter flask, used as a reservoir, maintained steady conditions by absorbing fluctuations of pressure. Both absorption tubes contained soda lime and calcium chloride to

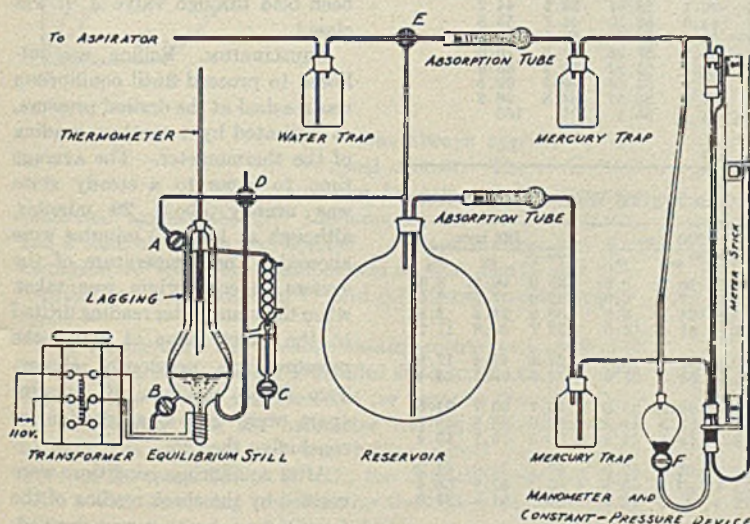


Figure 1. Arrangement of Apparatus for Subatmospheric Pressure
For use at atmospheric pressure the apparatus to the right of stopcock E and of the reservoir was replaced with a simple inclined-tube manometer.

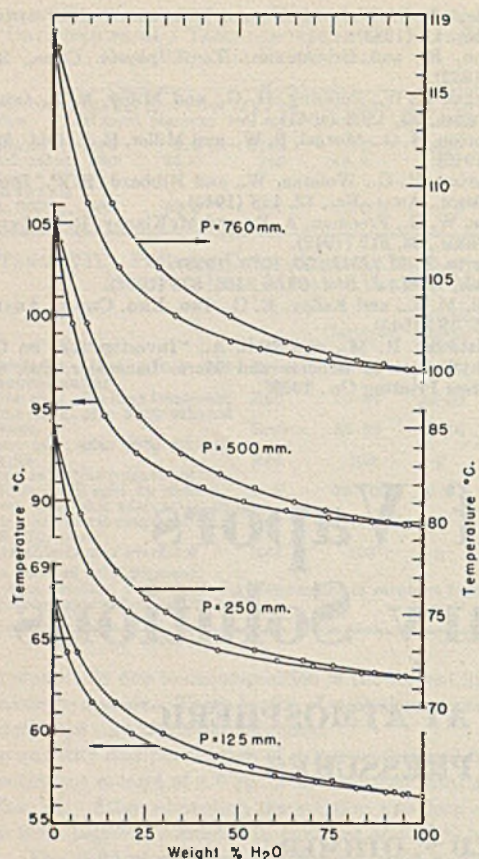


Figure 2. Phase Equilibria of Acetic Acid-Water System

Upper line at each pressure is for vapor and lower line is for liquid, both plotted against temperature.

TABLE I. VAPOR-LIQUID EQUILIBRIA OBSERVATIONS (IN WEIGHT PER CENT WATER)^a

P = 760 Mm.			P = 500 Mm.			P = 250 Mm.			P = 125 Mm.		
T° C.	% x	% y	T° C.	% x	% y	T° C.	% x	% y	T° C.	% x	% y
118.4	0	0	105.2	0	0	85.5	0	0	67.8	0	0
117.5	0.45	1.15	99.55	5.0	9.1	80.42	4.6	8.3	64.25	3.9	7.1
109.1	8.9	15.6	94.28	14.0	23.3	77.33	10.5	17.5	61.53	10.7	17.0
105.6	17.3	28.1	92.64	22.8	34.8	75.86	16.5	25.5	59.83	21.4	29.8
103.0	32.85	47.6	91.43	31.6	45.4	75.12	20.8	30.7	58.61	35.6	44.2
101.6	47.4	62.4	90.74	40.7	55.0	73.76	34.2	44.6	58.10	45.7	53.8
101.2	55.75	68.5	89.94	51.8	65.4	73.09	45.0	55.0	57.68	60.1	68.2
100.9	63.6	74.5	89.63	63.4	74.0	72.51	61.0	68.2	57.28	71.3	75.6
100.59	74.3	81.7	89.20	74.9	82.2	72.23	70.8	76.1	56.92	82.2	85.4
100.37	84.0	88.6	88.98	86.6	90.8	71.87	83.9	87.5	56.68	90.2	92.5
100.12	95.4	96.8	88.83	95.5	97.0	71.63	95.7	93.8	56.57	94.8	96.3
100.00	100	100	88.7	100	100	71.6	100	100	56.4	100	100

^a x = liquid; y = vapor.

TABLE II. SMOOTHED DATA OF VAPOR-LIQUID EQUILIBRIA FOR SYSTEM WATER-ACETIC ACID^a

Liquid		Vapor											
		760 mm.			500 mm.			250 mm.			125 mm.		
x ₁	w ₁	T° C.	y ₁	w ₁	T° C.	y ₁	w ₁	T° C.	y ₁	w ₁	T° C.	y ₁	w ₁
5	1.5	115.7	10.1	3.2	103.0	10.1	3.2	83.3	10.2	3.3	65.9	10.2	3.3
10	3.2	114.3	18.1	6.2	101.8	18.0	6.1	82.3	17.7	6.0	65.0	17.6	6.0
15	5.0	111.9	25.5	9.3	99.6	25.0	9.1	80.1	24.5	8.9	63.6	24.3	8.8
20	7.0	110.3	32.7	12.6	98.0	32.3	12.4	78.8	31.4	12.0	62.7	30.8	11.7
30	11.3	107.8	44.7	19.4	95.5	44.2	19.1	77.1	43.4	18.6	61.4	42.1	17.8
40	16.6	105.8	55.5	27.1	93.8	54.9	26.6	75.9	53.5	25.6	60.5	52.1	24.4
50	22.9	104.4	64.9	35.6	92.5	64.2	34.9	74.9	62.3	33.0	59.7	60.7	31.5
60	30.9	103.2	73.7	45.4	91.5	72.8	44.3	74.0	70.3	41.4	59.0	68.8	39.7
70	41.0	102.2	81.3	56.4	90.7	80.7	55.3	73.3	78.1	51.3	58.3	76.7	49.4
80	54.3	101.3	87.5	67.6	89.9	87.3	67.2	72.7	85.0	62.9	57.7	84.0	61.2
85	62.8	101.1	90.4	73.9	89.6	90.2	73.6	72.4	88.5	68.8	57.5	87.8	68.4
90	73.0	100.8	93.4	80.9	89.2	93.3	80.7	72.2	92.3	78.2	57.2	91.8	77.0
95	85.0	100.3	96.6	89.3	89.0	96.7	89.6	71.8	96.3	88.6	56.8	96.0	87.9
97.5	91.9	100.1	98.2	94.3	88.8	98.3	94.5	71.6	98.2	94.3	56.6	98.2	94.0
99	96.7	100.0	99.2	97.6	88.7	99.3	97.8	71.6	99.3	97.7	56.5	99.2	97.6

^a x = mole % in liquid; y = mole % in vapor; w = weight % in liquid; w' = weight % in vapor; subscript 1 = water.

The vapor-liquid equilibria and boiling points were determined for the binary system water-acetic acid at the constant pressures of 760, 500, 250, and 125 mm. of mercury by the method previously described (9). The experimental data are presented in graphs and tables, including one for smoothed data obtained from the graphs. A comparison with other data in the literature is given for boiling points and vapor compositions at atmospheric and subatmospheric pressures.

protect the mercury from acid or water vapor. Two mercury traps prevented any mercury from being lost if sudden surges took place; the water trap prevented any water from the aspirator from being sucked into the system if sudden changes in water pressure took place. Three-way cock *E* was used for rapidly evacuating the system to approximately the correct pressure before suction was permitted by way of the pressure regulator, which maintained the pressure at any desired value. Cock *F* of the constant-pressure regulator (4) enables the correct amount of mercury to be added to the manometer to obtain the arbitrarily chosen pressure.

CHARGING STILL. The still was charged with about 200 cc. of pure acetic acid, and the boiling point was determined at each pressure. By adding the correct amount of distilled water and draining the corresponding amount of solution after each run, about ten evenly spaced values of weight per cent water for the liquid composition were obtained for each pressure.

CORRECT PRESSURE. The system was closed off from the atmosphere by turning cock *D* so as to connect the still with the reservoir. With cock *A* opened, the system was evacuated through cock *E* with the pressure regulator by-passed. When the desired pressure was nearly reached, cock *E* was turned so that all aspirated gas would have to pass through the regulator which had been previously set at the desired pressure. With the system at the correct pressure, the liquid was brought to a steady boil by regulating the heat input by means of the transformer. When all non-condensable gases appeared to have been bled through valve *A*, it was closed.

EQUILIBRIUM. Boiling was allowed to proceed until equilibrium was reached at the desired pressure, as indicated by a constant reading of the thermometer. The average time to come to a steady state was usually about 20 minutes, although at least 40 minutes were allowed. The temperature of the system in equilibrium was taken when the manometer reading drifted to the exact value at which the pressure was previously chosen. Two check readings, 10 minutes apart, were used as a criterion for concluding the run.

After equilibrium conditions were verified by the check reading of the temperature, heating was stopped; the still (but not the reservoir) was opened to the atmosphere through cock *D*.

WITHDRAWAL OF SAMPLES. Samples of the liquid in the still and in the reservoir were withdrawn into previously weighed flasks, each containing 25 cc. of approximately 0.2 *N* barium hydroxide and 2 drops of phenolphthalein, just to remove the pink coloration. The flasks were immediately stoppered and weighed. For the first set of runs, two samples were withdrawn from both the still and condensate trap as a check on the method, which was found to be more accurate and convenient than any other attempted.

The titrating buret was so arranged that solution could be added directly without any contact with the air. The solution was standardized against certified potassium acid tartrate obtained from the National Bureau of Standards. From the titers, the compositions of the vapor and liquid in equilibrium at the given pressure and measured temperatures were obtained.

CALIBRATIONS AND SMOOTHING OF DATA

The 0.1° C. thermometer for subatmospheric runs was calibrated by the National Bureau of Standards for total immersion; a stem correction

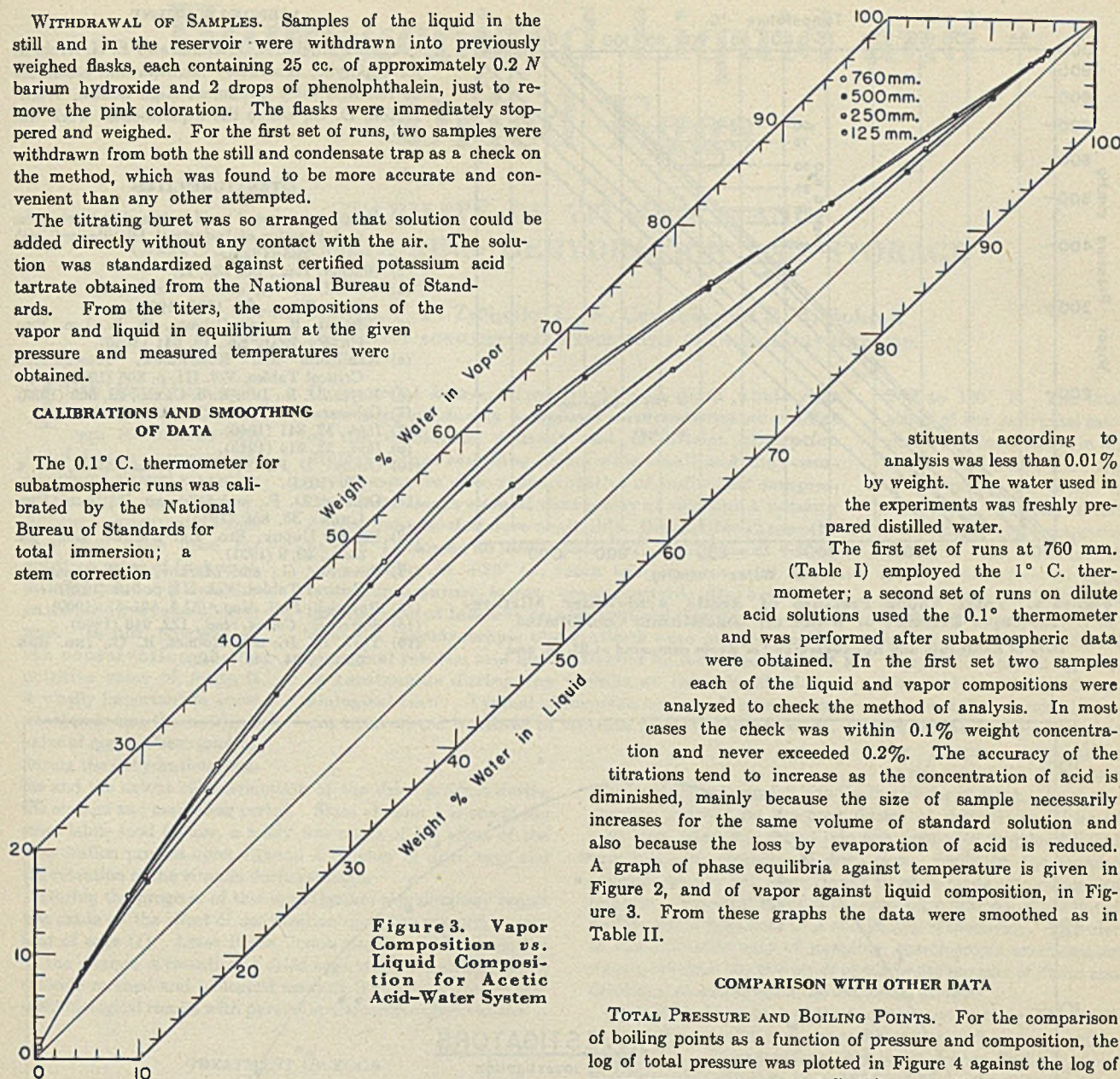


Figure 3. Vapor Composition vs. Liquid Composition for Acetic Acid-Water System

was always applied in the usual manner. The 1° C. thermometer for atmospheric runs was calibrated against the 0.1° thermometer for total immersion, and a stem correction was applied. A magnification glass was employed to read the thermometers so that tenths and hundredths were estimated on 1° and 0.1° thermometers, respectively.

The temperature and pressure measurements were calibrated by taking the boiling points of distilled water at several pressures. The pressure reading was corrected for vapor in the manometer by comparison with the barometer reading. The agreement between the observed and true boiling points was excellent; between the range 55° to 85° C., the deviation was less than 0.2°. With increasing temperatures the boiling point read too high and was in error by 0.7° at 100° C.

Titration showed the reagent-grade acetic acid to contain 99.8% acid by weight; the bulk of the remaining constituents were assumed to be water as the total amount of other con-

stituents according to analysis was less than 0.01% by weight. The water used in the experiments was freshly prepared distilled water.

The first set of runs at 760 mm. (Table I) employed the 1° C. thermometer; a second set of runs on dilute acid solutions used the 0.1° thermometer and was performed after subatmospheric data were obtained. In the first set two samples each of the liquid and vapor compositions were analyzed to check the method of analysis. In most cases the check was within 0.1% weight concentration and never exceeded 0.2%. The accuracy of the titrations tend to increase as the concentration of acid is diminished, mainly because the size of sample necessarily increases for the same volume of standard solution and also because the loss by evaporation of acid is reduced. A graph of phase equilibria against temperature is given in Figure 2, and of vapor against liquid composition, in Figure 3. From these graphs the data were smoothed as in Table II.

COMPARISON WITH OTHER DATA

TOTAL PRESSURE AND BOILING POINTS. For the comparison of boiling points as a function of pressure and composition, the log of total pressure was plotted in Figure 4 against the log of vapor pressure at constant liquid composition, as previously described (8). Included are data from two other sources. The data of Keyes (6) show deviations since the experimenter was essentially concerned with vapor composition rather than temperature measurement; the data of Kahlbaum and Konowalow (5) are in better agreement. The latter investigators used the static method of determining total pressure at a given temperature which gives larger errors at decreased pressures.

VAPOR-LIQUID EQUILIBRIA AT ATMOSPHERIC PRESSURE. A large plot was made of $(y-x)$ against x (Figure 5) to compare the experimental values of this investigation with those from available literature (1, 2, 3, 7, 12-16). The difference plot emphasizes small variations. Wherever possible, the original observations of the investigator were chosen rather than smoothed data.

Another article (11) has discussed the correlation of these data by means of heats of solution and by means of several new methods of plotting developed for handling these p - t - x - y data.

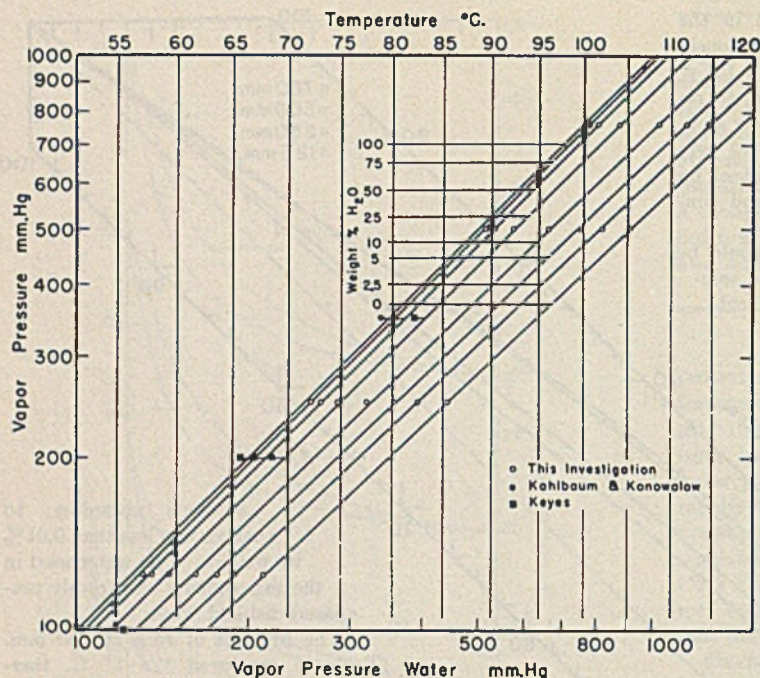


Figure 4. Total Vapor Pressure of Acetic Acid-Water Mixtures vs. Vapor Pressure of Water on Logarithmic Coordinates

Data of Kahlbaum and Konowalow and of Keyes compared at 25, 50, and 75 % weight water.

ACKNOWLEDGMENT

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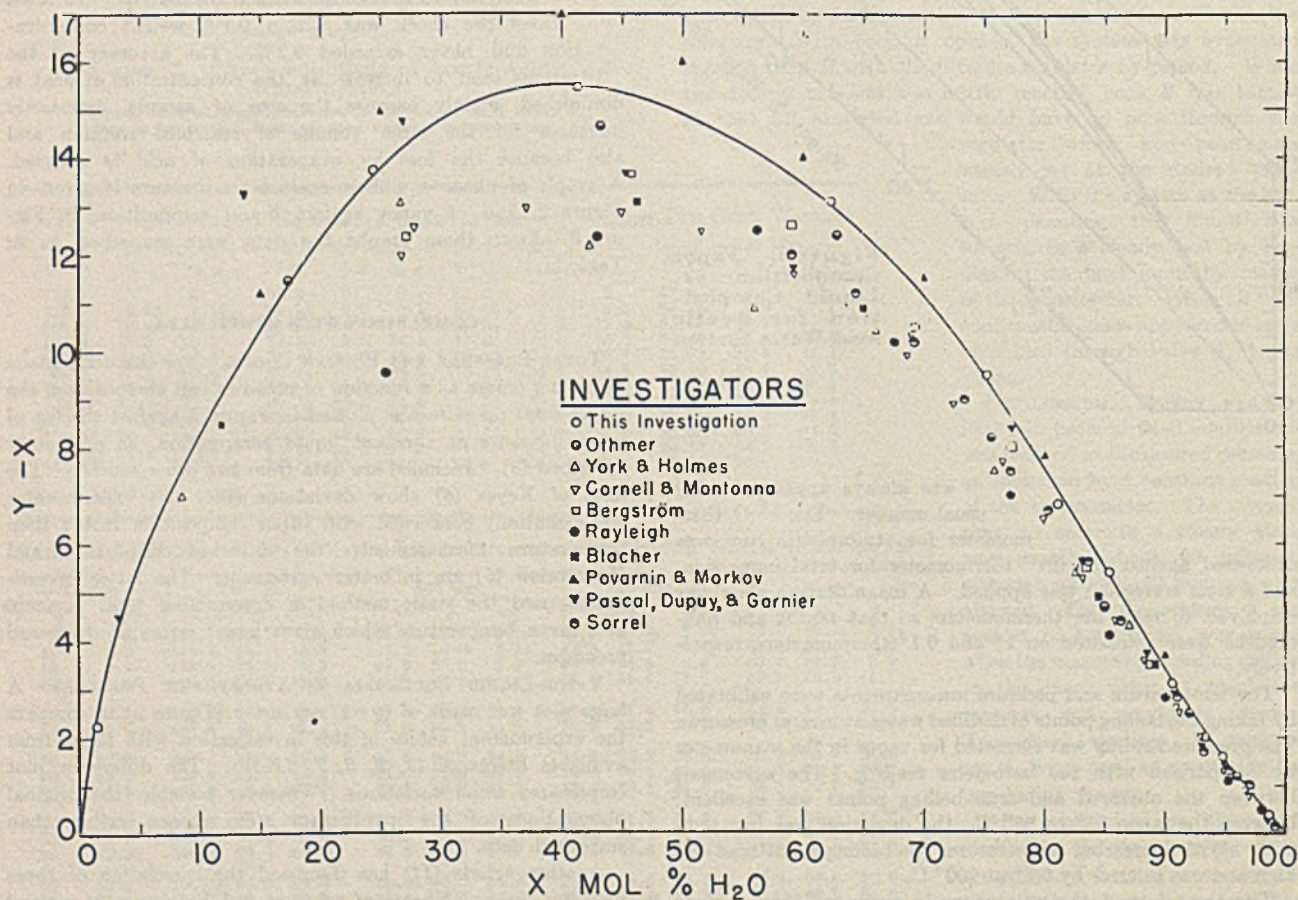


Figure 5. Difference in Vapor and Liquid Compositions (in Mole Per Cent) of Acetic Acid-Water System vs. Mole Per Cent Water in Liquid

Homogenized Liquid and Dried Eggs

STABILITY OF VITAMIN A AND CAROTENOIDS DURING DEHYDRATION AND STORAGE

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THE demand for enormous quantities of dried eggs for military and Lend-Lease purposes has stimulated a rapid expansion in the dried egg industry. Although extensive studies have been made upon the nutritive value of fresh eggs, little information is available on the nutritive value of dried eggs. In the program on the conservation of the nutritive value of foods, it is vitally important to know whether or not the nutritive value of eggs has been lowered during the dehydration process and the extent of deterioration of the dried product during the storage and marketing period. Since vitamin A is one of the most labile food factors, a study was made of the effect of the dehydration process upon vitamin A potency of dried eggs and the retention of the vitamin during storage.

During the progress of this investigation a preliminary report was made on the effect of dehydration upon the vitamin A content of eggs (1). Later Klose, Jones, and Fevold (2) reported on the vitamin A retention in dried eggs, using the antimony trichloride method and biological assays. The present paper presents biological results with parallel spectroscopic observations.

TREATMENT OF EGGS

SOURCE AND PROCESSING. The homogenized liquid and dried eggs used in these experiments were prepared in a commercial plant on May 4, 1942, from current receipts of fresh shell eggs (not over 12 days old) from central Indiana, Kentucky, Tennessee, and Illinois. The eggs (none of which were at temperatures above 70° F.) were broken in the conventional manner with the elimination of any objectionable eggs. The liquid eggs were transferred to a churn for mixing and then passed through a Hansen Liquid Egg Strainer into a cooled storage tank where the mix was held at 36° F. with agitation for a period not exceeding 8 hours. The mixed liquid eggs were homogenized and sprayed through eight double-opening nozzles of 0.042 inch diameter under a pressure of approximately 2600 pounds per square inch into the chamber of the Mojonner dryer, accompanied by preheated air ranging in temperature from 370° to 380° F. The dryer was operated under slightly reduced pressure by means of suction fans which removed the dried egg powder to the collector; then it was sifted through screens and packed in barrels. The temperature of the exhaust air leaving the dryer was 153° F. The dried egg powder, as it came from the screen, varied from

Commercial homogenized liquid and dried whole eggs were sampled during a day's run. Spectroscopic studies of the carotenoid content and ultraviolet absorption indicated that sampling errors were small and that composite samples were representative of individual samples. Biological assays showed that losses of vitamin A potency during dehydration were negligible. Storage for 12 months at -18° C. caused no loss of potency. The losses at +5° C. were small. At +20° C., room temperature, and warehouse temperature, losses were appreciable after 3 months, but the rate of loss was greatly reduced during the next 9 months. Spectroscopic observations were parallel to the biological results, and also indicated no loss of vitamin A or carotenoids during the periods of time required for biological tests. Typical absorption curves of egg extracts are interpreted in terms of vitamin A potent carotenoids.

90° to 120° F. The total solids of the individual samples of powder as tested in the plant varied from 96 to 98%.

SAMPLING. In order to minimize sampling errors which might arise from variations in the vitamin A potency of individual eggs, paired samples of fresh liquid homogenized eggs and of dehydrated eggs were collected every half hour during a 6-hour period. The liquid samples were drawn from the bypass of the homogenizer. The dry samples were taken approximately 3 minutes

later as the dried eggs fell into the barrels for packing. From the samples collected on the hour (series A) definite quantities of each were taken and mixed into one composite sample of liquid eggs and one composite of dried eggs. Similarly, the samples collected on the half hour (series B) were made into composite samples. The total solids of the composite samples of the liquid and the dried eggs were 27.4 and 96.3%, respectively. In order to test the uniformity of sampling, spectroscopic examinations were made upon the two series of composite samples of liquid and dried eggs as well as upon the individual samples.

STORAGE. From each of the two composite samples (A and B) of dried eggs, twelve portions of 400 grams each were packed in Mason jars. Three jars from each series were packed in cartons to exclude light and stored at -18° C., +5°, +20°, and room temperature. At the end of each storage period (i.e., 3, 6, and 12 months) one sample jar of each series was removed from each carton and stored at -18° C. for testing. In addition, composite samples of both series were packed in two small barrels with double paper liners and left at the plant for storage in the warehouse. These were sampled at the end of 6 and 12 months. All samples were preserved at -18° C. during the test period.

ANALYSES

SPECTROSCOPIC EXAMINATION. For the spectroscopic observations, samples were saponified and extracted with ether by the method described earlier for butterfat (7). Ten-gram and three-gram samples were employed for homogenized and dried eggs, respectively. The weighed egg samples were reconstituted by moistening with 8 ml. of water for 1 hour at room temperature before saponification. The photoelectric spectrophotometer and spectroscopic methods were the same as those employed earlier in studies on butterfats (7) and vitamin A (6). Wave length 3240 Å. was considered best for vitamin A deter-

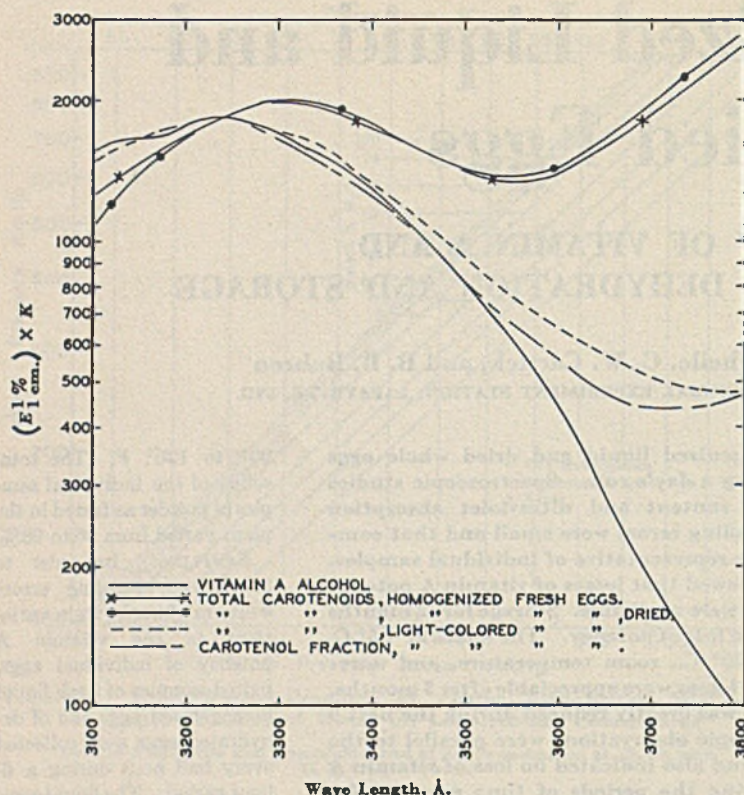


Figure 1. Absorption Spectra of Egg Extracts in Ether Solution

mination because the absorption maximum of vitamin A alcohol in ether solution occurs at this wave length. Wave length 4370 Å. was employed for estimation of total carotenoids for comparative purposes. Although the absorption of β -carotene at this wave length is essentially unchanged by heat isomerization, no such definite information is available for the carotenols.

BIOLOGICAL ASSAY. The samples were assayed for vitamin A by the usual rat growth method, using U.S.P. reference oil diluted with Wesson oil as a standard. To overcome the problem of uniform sampling during the assay of the liquid eggs, the composite samples of liquid eggs were broken down into weighed portions of 25 grams each; these were stored at -18°C . until needed for the feeding tests, when they were diluted to 500 ml. with 1% saline solution. For convenience in weighing the test doses, the dried egg samples were diluted with four times their weight of the vitamin A deficient diet. The vitamin A potencies of all samples were calculated upon a moisture-free basis.

SPECTROSCOPIC EXAMINATION

UNIFORMITY OF SAMPLES. Absorption values are compared in Table IA for six individual samples of both the A and B series and for the composite samples. Much greater uniformity was observed at 4370 Å. than at 3240 Å., an indication of greater variations in ultraviolet absorption which involves vitamin A carotenoids, and miscellaneous substances, than in visible absorption due only to carotenoids. The deviations for dried samples were slightly higher than those for liquid samples. Changes induced by drying appear to be of little practical significance. Composite samples agreed well with the corresponding averages of the individual samples of liquid eggs. Agreement was equally good at 4370 Å. for dried eggs. At 3240 Å. for dried eggs, discrepancies of about 7% occurred, in accordance with the greater deviations found in the ultraviolet region. The data on the dry basis also agree better at 4370 Å. than at 3240 Å. Slightly increased absorption in the ultraviolet follows drying.

It is clear from Table IA that the spectroscopic deviations among the six samples are negligible. In so far as these absorption measurements indicate uniformity of chemical composition, the composite samples are adequately representative of the individual samples.

STABILITY OF EGGS AT -18°C . DURING BIOASSAY. Spectroscopic observations were made on composite samples at intervals during the first bioassay period, with results presented in Table IB. Differences for the same sample at different times are approximately equal to those observed among different samples reported in Table IA. No trend in results was observed with increasing periods of storage.

STABILITY OF VITAMIN A DURING DEHYDRATION. The results of the spectroscopic examinations (Table IA) and the biological assays show that little or no deterioration of the vitamin occurred during the dehydration process. The paired samples of liquid and dried eggs of series A were found to have potencies of 45 and 43 I.U. per gram, respectively; those of series B had 44 and 45 I.U. per gram, respectively, when compared on a moisture-free basis.

Since the spectroscopic observations failed to reveal any deterioration of either the liquid or dried egg samples during the assay period (Table IB), it is probable that no losses occurred in the liquid eggs during the assay period which might compensate for losses in the dried eggs during the dehydration process and assay period.

Therefore, the biological values have added significance. These observations on the retention of vitamin during dehydration are substantiated by work of Klose, Jones, and Fevold (2).

RETENTION OF VITAMIN A DURING STORAGE

The effects of time and storage conditions upon the vitamin A potencies and spectroscopic values of the dried eggs are shown in Tables II and III, respectively. These two series of results are approximately parallel. It is apparent that the samples stored at -18° and $+5^{\circ}\text{C}$., the usual storage and refrigerator temperatures, respectively, retained most of their original vitamin activity; in the samples stored at the higher temperatures, considerable deterioration had taken place although the losses of

TABLE I. SPECTROSCOPIC STUDY OF HOMOGENIZED LIQUID AND DRIED WHOLE EGGS

Series	$(E_1^{\%} \text{ cm.}) \times 1000$							
	Homogenized liquid				Dried			
	3240 Å.		4370 Å.		3240 Å.		4370 Å.	
	A. Sampled during a Day's Run							
	A	B	A	B	A	B	A	B
Sample 1	13.0	14.1	70.4	74.2	53.0	45.7	268	276
Sample 2	12.6	13.0	71.4	75.1	44.5	45.3	268	264
Sample 3	12.0	12.8	72.3	72.5	43.4	46.7	269	269
Sample 4	12.4	12.8	70.3	73.4	46.4	41.7	263	254
Sample 5	11.1	12.4	72.5	72.6	41.9	44.3	264	259
Sample 6	10.8	12.0	70.3	73.7	45.5	39.6	257	261
Av.	12.0	12.8	71.2	73.6	45.8	43.9	265	264
Av. deviation, %	5.8	3.5	1.2	1.0	6.8	5.2	1.3	2.2
Max. deviation, %	10.0	10.1	1.8	2.0	11.8	9.8	3.0	4.5
Composite samples	12.3	12.7	72.8	73.9	49.0	47.3	263	261
Dry basis	45.0	46.4	266	270	50.7	49.0	272	270
B. Effect of Short-Time Storage at -18°C .								
0 days	12.3	12.7	72.8	73.9	49.0	47.3	263	261
23 days	13.6	12.1	73.7	75.5	47.6	45.7	266	271
51 days	12.5	11.4	73.3	74.7	45.1	43.2	263	264
105 days	11.2	12.7	69.9	76.1	47.4	45.1	260	256

vitamin A potencies were not so great as might have been expected. The greatest losses were observed in samples held at room temperature, where the losses were about 40% in 12 months. The samples stored in the warehouse retained about 70% of their vitamin activity, which may be considered satisfactory. Klose, Jones, and Fevold (2) reported somewhat greater losses in their samples at comparable temperatures. This suggests that these variations may be due to effects of difference in dehydration process or to effects produced by difference in the rations of hens producing the eggs.

Table II shows that the rates of loss of vitamin A were greatest during the first 3 months, after which the vitamin appeared rather stable. Similar deductions can be made from results of the bioassays by Klose, Jones, and Fevold (2). No explanation can be offered at this time for the apparent inhibition of losses after 3 months of storage.

ABSORPTION CHARACTERISTICS OF EGG FRACTIONS

To permit a more critical study of changes during dehydration, more extensive absorption measurements were made. Typical characteristic curves of egg extracts are presented in Figures 1 and 2. The same as $E_{1\text{ cm.}}^{1\%}$ values are plotted on a logarithmic scale. Curves of identical substances are then superposable, regardless of concentration, through multiplication of the $E_{1\text{ cm.}}^{1\%}$ values by a constant, K . An attempt was made to study vitamin A independently of other carotenoids. To this end light-colored eggs were produced by hens on a special low-carotenoid diet. The yolks were very pale but not free of color. The carotenol fractions were transferred to ether from 90% methanol solutions which had been washed with hexane.

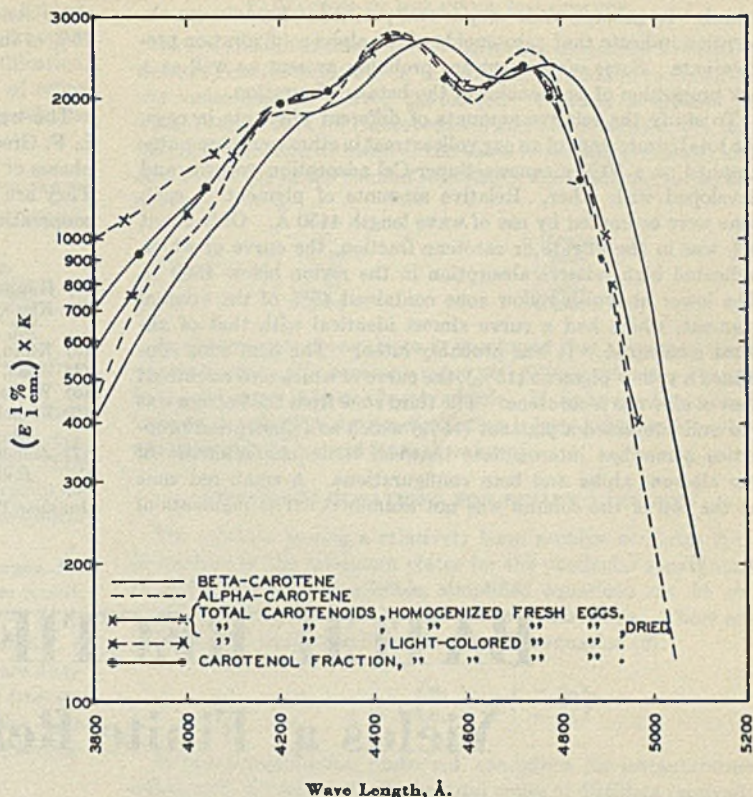


Figure 2. Absorption Spectra of Egg Carotenoids in Ether Solution

Figure 1 gives the ultraviolet curves in comparison with that of vitamin A alcohol. All curves were made to coincide at 3240 Å., the absorption maximum of vitamin A alcohol (6). Differences between the curves for fresh homogenized eggs before and after drying were small, an indication of little change during dehydration. These curves are very different from that of vitamin A, both in position of maximum and in shape. These differences are due principally to the high content of other carotenoids. The curve for the light-colored egg more nearly approaches that of vitamin A, but the presence of other carotenoids is indicated by comparatively high absorption near 3800 Å. The carotenol fraction was free of carotenes but contained vitamin A; hence, slightly better agreement with absorption characteristics of vitamin A was observed.

In Figure 2 the standard curves of all-*trans* α -carotene (4) and β -carotene (5) are presented for comparison. Curves agree at 4497 Å., a wave length at which the α - and β -carotene curves intersect. In general, the predominant carotenoid of eggs is luteol (3), which has the configuration of α -carotene. Curves for fresh homogenized eggs before and after drying were identical, indicating little if any change in the carotenoids, even by isomerization, during dehydration. The close agreement between the curves for total carotenoids and the carotenol fractions of the light-colored egg indicates the comparatively low content of carotenes in the yolk, particularly β -carotene.

None of these curves can be analyzed as binary mixtures of well-known pigments whose curves have been accurately deter-

TABLE II. EFFECT OF STORAGE TEMPERATURE AND TIME ON VITAMIN A POTENCY OF DRIED EGGS

Series	Storage Period, Months	-18° C.		+5° C.		+20° C.		Room		Warehouse	
		Vita-min A, I.U. ^a	Reten-tion, %	Vita-min A, I.U.	Reten-tion, %	Vita-min A, I.U.	Reten-tion, %	Vita-min A, I.U.	Reten-tion, %	Vita-min A, I.U.	Reten-tion, %
A	0	43	100	43	100	43	100	43	100	43	100
	3	43	100	41	95	29	67	32	74	28	65
	6	41	95	38	88	29	67	25	58	28	65
	12	43	100	30	70	27	63	32	74
B	0	45	100	45	100	45	100	45	100	45	100
	3	40	89	39	87	32	71	28	62
	6	40	89	38	80	28	62	24	53	30	67
	12	40	89	38	80	28	62	24	53	30	67

^a I.U. per gram of moisture-free egg.

TABLE III. SPECTROSCOPIC STUDY OF EFFECT OF LONG-TIME STORAGE ON DRIED WHOLE EGGS AT DIFFERENT TEMPERATURES^a

Storage Time, Months	-18° C.		+5° C.		+20° C.		Room		Warehouse	
	Absorp-tion ^b	Reten-tion, %	Absorp-tion ^b	Reten-tion, %	Absorp-tion ^b	Reten-tion, %	Absorp-tion ^b	Reten-tion, %	Absorp-tion ^b	Reten-tion, %
Wave Length 3240 Å.										
0	48.1	100	48.1	100	48.1	100	48.1	100	48.1	100
3	47.8	99	44.2	92	40.3	84	37.5	78
6	49.2	102	46.2	96	40.7	85	40.6	85	42.1	87
12	42.8	89	33.5	70	33.5	70	32.2	67
15	43.1	90	33.0	69	33.3	69	36.1	75
Wave Length 4370 Å.										
0	282	100	282	100	282	100	262	100	262	100
3	257	98	248	95	216	82	202	77
6	267	102	238	91	190	72	188	71	190	72
12	243	93	160	61	158	60	166	63
15	238	91	160	61	161	61	173	66

^a These figures are averages of the A and B series.

^b $(E_{1\text{ cm.}}^{1\%}) \times 1000$.

mined. In general, their shapes and positions of maximum absorption indicate that carotenoids of the alpha configuration predominate. Some *cis*-isomers are probably present as well as a low proportion of carotenoids of the beta configuration.

To study the relative amounts of different pigments in eggs, the total carotenoids of an egg yolk extract in ether were chromatographed on a 50% magnesia-Super-Cel adsorption column and developed with ether. Relative amounts of pigment in each zone were estimated by use of wave length 4450 Å. Only about 5% was in the filtrate or carotene fraction, the curve of which indicated high relative absorption in the region below 4300 Å. The lower brownish-yellow zone contained 45% of the original pigment, which had a curve almost identical with that of all-*trans* α -carotene. It was probably luteol. The next zone contained a yellow pigment (15%), the curve of which also resembled that of all-*trans* α -carotene. The third zone from the bottom was red and contained a pigment (15%) which had absorption properties somewhat intermediate between those characteristic of the all-*trans* alpha and beta configurations. A small red zone at the top of the column was not examined. The pigments of

these zones were not purified further. In the egg studied, over 75% of the recovered pigments were of the alpha configuration.

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BATCH RECTIFICATION

Yields at Finite Reflux Ratios

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A general method is described for calculating yields from batch rectification of binary mixtures under constant distillate conditions for any given final reflux ratio. The method allows for the effect of column holdup. Simplified equations are derived for both binary and complex mixtures which are applicable to certain cases in which holdup is negligible.

AN EARLIER paper (2) described a method of calculating the final yield of distillate from batch rectification, allowing for the effect of column holdup, when the reflux ratio is continuously increased to infinity in such a manner as to keep the distillate composition constant. This was termed "batch rectification under constant distillate" (c.d.) conditions. In the present paper a general method is presented for cases where the final reflux ratio has a finite value. This enables a curve to be plotted showing the relation between final reflux ratio and yield fraction, the *Ry* curve, which is important to the plant designer.

Such a curve was, in effect, proposed by Bogart (1), who carried out a number of McCabe and Thiele constructions at different reflux ratios, keeping the distillate composition constant, and plotted reflux ratio against composition of residue. He did not, however, allow for the effect of column holdup.

BINARY MIXTURES WITH COLUMN HOLDUP

The previous paper (2) showed that the moles of lighter component *A* held up in the column is equal to $Q\Sigma$, where Q = total moles of the mixture held up per theoretical plate, and

$$\Sigma = a_1 + a_2 + a_3 \dots + a_N$$

It was further shown that in the special case where the reflux ratio is infinite, Σ can be calculated from a_p , N , and α .

Consider a batch rectification under c.d. conditions in which the final reflux ratio is only moderately high, so that the yield of

distillate is substantially lower than when the final ratio is infinite. The column is assumed to be empty at the beginning of the operation. If it is not, its contents must be added to the charge, and the quantity and composition of the latter modified accordingly.

A McCabe and Thiele construction for the desired final reflux ratio gives the final bottoms composition a_w ; gives the sum of the final plate-to-plate liquid compositions, $a_1 + a_2 + a_3 \dots + a_N = \Sigma$; and enables $Q\Sigma$, the total column holdup of *A*, to be calculated. Taking material balances at the end of the batch rectification:

$$P + W = F - QN$$

$$Pa_p + Wa_w = Fa_f - Q\Sigma$$

whence

$$P = F \frac{a_f - a_w}{a_p - a_w} - Q \frac{\Sigma - Na_w}{a_p - a_w}$$

Substituting $y = Pa_p/Fa_f$ and $Q/F = q$ gives the required yield:

$$y = \frac{a_p[(a_f - a_w) - q(\Sigma - Na_w)]}{a_f(a_p - a_w)} \quad (1)$$

By carrying out a number of computations of a_w for different reflux ratios and repeating the above calculations, the complete *Ry* curve can be drawn, showing the variation of reflux ratio with yield fraction required to maintain a given distillate composition.

This is essentially Bogart's curve (1) corrected for column holdup, except that residue composition is replaced by yield fraction, which is more easily observed during the course of rectification. Graphical integration of this curve gives the quantity of reflux which must be vaporized for a given yield of distillate, whence the economic limit of reflux ratio can be decided upon.

TABLE I. DATA FOR Ry CURVE IN RECTIFICATION OF CHLOROBENZENE AND BROMOBENZENE

R	a_w	Σ	y	y_o
4	0.443	8.177	(-0.365)	(-0.196)
7	0.260	7.253	0.319	0.476
12	0.157	6.552	0.563	0.723
20	0.117	6.190	0.659	0.803

As an example, take the separation of chlorobenzene and bromobenzene, using the volatility data published by Young (4). Assume $N = 10$, $a_f = 0.40$, $a_p = 0.98$, $Q/F = q = 0.01$. The latter is a high value, taken to exaggerate the column holdup effect for purposes of illustration. For rectification at atmospheric pressure the average value of α is 1.8896.

By carrying out several McCabe and Thiele constructions for different reflux ratios, the corresponding values of a_w are found. For each value of a_w the plate-to-plate compositions $a_1 + a_2 + a_3 + \dots + a_N$ are read off and added together to give Σ . y is then calculated from Equation 1. The calculations are summarized in Table I. For comparison with y , the yield fraction taking account of column holdup, a calculation has also been made of y_o , the yield fraction for a corresponding value of a_w neglecting holdup:

$$y_o = \frac{a_p(a_f - a_w)}{a_f(a_p - a_w)}$$

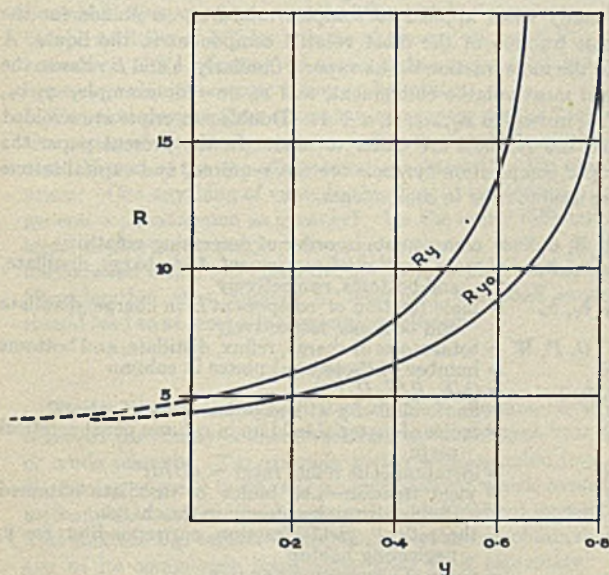


Figure 1. [Final] Reflux Ratio vs. Yield Fraction, without and with Column Holdup, for Chlorobenzene-bromobenzene

These results are plotted in Figure 1. The negative value of y for $R = 4$ shows that this reflux ratio is below the required initial value. It can, however, be used for plotting the lower end of the Ry curve and saves calculation of the initial reflux ratio. The Ry_o curve corresponds to Bogart's curve, neglecting column holdup.

VARIATION IN RELATIVE VOLATILITY

In continuous distillation it is legitimate to assume a constant average relative volatility in the column. In batch rectification the value changes during distillation. Plotting α against a_w from Young's data for chlorobenzene and bromobenzene (4), and taking the arithmetic mean of the value in the still (variable) and that at the top of the column (constant), the following values are obtained:

a_w	α (average)
0.40	1.8949
0.30	1.8943
0.20	1.8894
0.15	1.8867

In the example given above, it was found that the use of these values in place of a constant value of 1.8896 produced a change in the Ry curve that was barely visible. If, however, the change in relative volatility during distillation is large, the correct average value should be used for each value of a_w .

SIMPLIFIED EQUATIONS FOR BINARY MIXTURES

For columns having a relatively large number of plates (i.e., in relation to the minimum plates for the particular separation) in which holdup is negligible, simplified equations can be obtained requiring no McCabe and Thiele construction. These are derived from Underwood's minimum reflux equation (3):

$$R = \frac{1}{\alpha - 1} \left(\frac{a_p}{a_w} - \alpha \frac{1 - a_p}{1 - a_w} \right)$$

In batch rectification under c.d. conditions the instantaneous reflux ratio R varies with P , the total moles of distillate received; i.e., $R = dO/dP$. a_w is also a function of P . From material balances

$$a_w = \frac{F a_f - P a_p}{F - P}$$

Putting $P/F = p$ and substituting for a_w ,

$$R = \frac{1 - p}{\alpha - 1} \left[\frac{a_p}{a_f - p a_p} - \frac{\alpha (1 - a_p)}{(1 - a_f) - p (1 - a_p)} \right] \quad (2)$$

or substituting the yield fraction $y = p (a_p/a_f)$,

$$R = \frac{a_p - y \alpha}{\alpha - 1} \left[\frac{1}{a_f (1 - y)} - \frac{\alpha (1 - a_p)}{a_p (1 - a_f) - y \alpha (1 - a_p)} \right] \quad (3)$$

These equations define the manner in which reflux ratio should vary with p and y , respectively, to maintain a constant distillate composition of a_p in an infinite column. They can be applied with fair accuracy to finite columns in which the value of α^{N+1} is greater than about 5000 and holdup is negligible.

The total vaporization required to secure p_r moles of distillate per mole of charge, or a yield fraction of y_r , can be calculated by integrating Equation 4. Putting $R = dO/dP = do/dp$,

$$\begin{aligned} o &= \int_0^{p_r} \frac{1 - p}{\alpha - 1} \left[\frac{a_p}{a_f - p a_p} - \frac{\alpha (1 - a_p)}{(1 - a_f) - p (1 - a_p)} \right] dp \\ &= \frac{a_p - a_f}{\alpha - 1} \left[\ln \frac{a_f}{a_f - p_r a_p} + \frac{\alpha \ln \frac{1 - a_f}{(1 - a_f) - p_r (1 - a_p)}}{1 - a_p} \right] - p_r \\ o &= o + p_r \\ &= \frac{a_p - a_f}{\alpha - 1} \left[\ln \frac{a_f}{a_f - p_r a_p} + \frac{\alpha \ln \frac{1 - a_f}{(1 - a_f) - p_r (1 - a_p)}}{1 - a_p} \right] \quad (4) \end{aligned}$$

Substituting the yield fraction $y_r = p_r (a_p/a_f)$,

$$v = \frac{a_p - a_f}{\alpha - 1} \left[\frac{\ln \frac{1}{1 - y_r}}{a_p} + \frac{\alpha \ln \frac{a_p(1 - a_f)}{a_p(1 - y_f) - y_r a_f(1 - a_p)}}{1 - a_p} \right] \quad (5)$$

These equations give the total moles to be vaporized per mole of charge in order to produce p_r moles of distillate per mole of charge, or a yield fraction of y_r , under c.d. conditions. They are applicable to finite columns under the same conditions as Equations 2 and 3—namely, when α^{N+1} is more than 5000 and holdup is negligible.

SIMPLIFIED EQUATIONS FOR COMPLEX MIXTURES

Similar equations can be derived for complex mixtures. Consider a mixture consisting of components A, B, C , etc., from which a distillate is to be prepared containing a relatively high proportion of A , the lightest component present. A and B are the key components, and the distillate may, without serious error, be assumed to consist of these components only. Provided the components obey Raoult's law, the minimum reflux equation applies to the key components as if they constituted a binary mixture—that is,

$$R = \frac{1}{\alpha - 1} \left(\frac{a_p}{a_w} - \alpha \frac{b_p}{b_w} \right)$$

From material balances,

$$a_w = \frac{F a_f - P a_p}{F - P}; \quad b_w = \frac{F b_f - P b_p}{F - P}$$

Putting $b_p = 1 - a_p$ and $P/F = p$, substituting for a_w and b_w , and integrating as for binary mixtures,

$$v = \frac{a_p - a_f}{\alpha - 1} \left[\frac{\ln \frac{a_f}{a_f - p_r a_p}}{a_p} + \frac{\alpha \ln \frac{b_f}{b_f - p_r (1 - a_p)}}{1 - a_p} \right] \quad (6)$$

or putting $y_r = p_r (a_p/a_f)$,

$$v = \frac{a_p - a_f}{\alpha - 1} \left[\frac{\ln \frac{1}{1 - y_r}}{a_p} + \frac{\alpha \ln \frac{a_p b_f}{a_p b_f - y_r a_f (1 - a_p)}}{1 - a_p} \right] \quad (7)$$

The above equations are applicable to complex mixtures only when the more volatile of the key components is the lightest material present. They cannot, for example, be applied to petroleum distillation where the distillate has a relatively wide boiling range.

As an example of the use of these simplified methods, consider the rectification of a commercial mixture containing the following mole percentages of components: benzene, 47.4; toluene, 43.5; xylenes, 9.1. It is desired to extract 99% of the total benzene in the charge by batch rectification, and the distillate is required to contain 98.0 mole % of benzene. The column to be used has fifteen theoretical plates. Holdup is negligible. A constant boil-up rate will be maintained in the still, and the overhead temperature will be held constant, automatically or otherwise, by continuously increasing the reflux ratio as distillation proceeds.

In order to calculate the heat input per gallon of product, and hence the duration and cost of the operation, it is desired to know the total moles which must be vaporized in the still per mole of distillate to secure the desired degree of exhaustion of the bottoms.

The temperature at the top of the column will be 80° C. throughout, and the relative volatility of benzene and toluene at this temperature is 2.545. The temperature in the still is estimated as 96° C. at the beginning of distillation, 118° C. at the end. The relative volatilities of benzene and toluene at these

temperatures are 2.428 and 2.295, respectively. Hence the average relative volatility in the still over the whole operation is 2362, and the mean between this and the relative volatility at the top of the column is 2.453. This is the value taken for α .

To check whether the simplified equations are applicable, evaluate α^{N+1} : $2.453^{16} = 171,900$. Evidently the column can be considered as infinite and the equations apply. The other quantities required are: $a_f = 0.474$; $b_f = 0.435$; $a_p = 0.980$; $y_r = 0.99$. Substituting in Equation 7 and solving: $v = 2.585$. That is, 2.585 moles must be vaporized in the still per mole of distillate to secure the desired degree of fractionation of the product and exhaustion of the charge.

CONCLUSION

The methods presented in this and the previous paper (2) rest upon the observation that under constant distillate conditions the equations for batch rectification are very much simplified. Since these are also the conditions for minimum heat input per pound of distillate (for a given final reflux ratio), they represent the most economical procedure as well. For binary mixtures and for complex mixtures, the distillate from which is required to contain a high proportion of the lightest component, a sensitive overhead temperature controller combined with a constant boil-up rate should automatically give the proper Ry curve.

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NOMENCLATURE

The nomenclature used is based upon that of Underwood (3), which has certain advantages over the usual $x-y$ system, especially when applied to complex mixtures. a stands for the mole fraction of the most volatile component in the liquid, A for the mole fraction in the vapor. Similarly, b and B refer to the next most volatile component, and so on—for example, a_f , b_p , C_{n+1} instead of x_{of} , x_{bp} , y_c , $n + 1$. Double subscripts are avoided and the symbols are easier to read. In the present paper the vapor composition symbols are not required, and capital letters are used to refer to components.

A, B, C	= components in order of decreasing volatility
a, a_p, a_w	= mole fraction of component A in charge, distillate, and bottoms, respectively
b, b_p, b_w	= mole fraction of component B in charge, distillate, and bottoms, respectively
F, O, P, W	= total moles of charge, reflux, distillate, and bottoms
N	= number of theoretical plates in column
o, p, q	= $O/F, P/F, Q/F$
p_r	= final value of p at end of batch rectification
Q	= moles of material held up in column per theoretical plate
R	= instantaneous reflux ratio = dO/dP
y	= yield fraction—i.e., moles of distillate obtained divided by moles present in the charge.
y_o	= theoretical yield fraction corresponding to y , neglecting holdup
y_r	= value of y corresponding to p_r
α	= average relative volatility of components A and B —i.e., arithmetic mean of values in still and top of column throughout distillation
Σ	= sum of plate-to-plate liquid compositions, $a_1 + a_2 + a_3 + \dots + a_N$

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Synergy in Industrial Chemistry

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Synergy, or nonadditive nonideal behavior in mixtures and polycomponent systems, is common in all branches of chemistry. Solvents, catalysts, emulsions, surface-active agents, and plastics offer many examples of its practical utilization. Synergic mechanisms can be classified generally as involving stepwise action, direct interaction, or complementary functioning of the components. Self-association, packing effects, dissymmetry, and interaction of components appear to be among the factors underlying all truly synergic phenomena as distinguished from combined, stepwise processes which are only apparently synergic.

SYNERGY—the force that can make $2 + 2 = 5$ —is an effective agent in chemistry. While this term is better known to the medical and pharmaceutical professions, the chemist has encountered the principle under such designations as catalyst promoters, activators, latent solvents, builders, and the like.

The use of sesame oil in pyrethrum and rotenone insecticides is an illustration (8). A millimolar solution of pyrethrins in refined kerosene (roughly one third the concentration of satisfactory household fly sprays) causes only 8% mortality among test flies; by the addition of 5% by volume of sesame oil, mortality is increased to 88%. Sesame oil alone, either pure or diluted with kerosene, exhibits no toxic action on houseflies.

The dictionary defines synergism or synergy as the “cooperative action of discrete agencies such that the total effect is greater than the sum of the two effects taken separately”. The question arises: Can anything of value to the chemist be learned from so general a phenomenon as synergy? Do the many different systems displaying synergy possess any common factors in their mechanisms which can guide the industrial chemist in his work? Consideration of a number of seemingly unrelated examples should lead to at least a few general conclusions.

SOLVENTS

When synthetic solvents first made their appearance, it was observed that many of them were inferior to old-type “natural” or crude solvents. For example, methylacetone made from the distillation of wood is actually a mixed solvent which consists of methanol and acetone, with some esters and higher ketones (21). This mixture has certain desirable properties not obtainable by any of its component ingredients when used separately. For this reason “synthetic methylacetone” made to simulate it, is not a chemical individual. Similarly amyl acetate manufactured from fusel oil has superior solvent properties over synthetic amyl acetate which lacks the impurities of the other.

The term “mix solvency” has been coined for synergy in solvents for resins (26) and for soaps (27). The process is pictured as one of statistical solvation by means of van der Waals forces or hydrogen bonding of different portions of the solute molecule by the different components of the solvent mixture. The efficiency of the solvents is increased in the presence of higher concentrations of solute since there are more attachments per

unit time. On this basis Palit has been able to account for the behavior of resins in certain mixtures of nonsolvents where solubility is improved by increasing the amount of solute as expressed by his rule of resinous or lyophilic solubility. The turbidity and precipitation which are known to occur upon the dilution of many resin solutions (18) are explained on the same basis.

SURFACE-ACTIVE AGENTS

The most common case of synergy among surface-active agents is the building of soaps and synthetic detergents by salts which themselves display little or no surface activity. Many of the relatively low-cost sodium alkyl aryl sulfonates, as marketed, contain large amounts of sodium sulfate formed during neutralization. This so-called inert material greatly increases the surface-active properties of the sulfonate. Alone it does not have such a good balance of solubilizing against hydrocarbon groups under the usual conditions of use.

The addition of salts in suitable amounts to solutions of ionic surface-active agents promotes micelle formation and reduction of surface tension (1). The first appears to play an important role, not clearly understood at present, in deflocculating, dispersing, and solubilizing action (20); the second, or rather a corresponding reduction of interfacial tension, is important in wetting and emulsification. An explanation (28) of the reduction in surface tension is that the added salt reduces the extent to which the charged heads of the sorbed surface-active ions repel one another. This results in a closer packing which makes possible an increase in the amount of surface-active material in the sorbed layer.

Advantage has been taken of this effect in the marketing of wetting agents which have practically no surface activity in water alone but are very effective in concentrated salt solutions. Dibutyl sodium sulfosuccinate (1) is extremely soluble in water. A 0.1% solution has a surface tension of 67.5 dynes per cm. A 0.1% solution in 20% sodium sulfate, however, has a surface tension of only 37.6 dynes per cm. This wetting agent is soluble even in a 75% solution of zinc chloride. Similarly, a polymer of about 90 molecules of ethylene oxide is very soluble in water and has little effect on surface tension, but in a high concentration of any strong electrolyte it shows substantial surface tension reduction.

An important technical application of synergy in surface-active agents is the so-called solutizer process (5) for sweetening gasoline. The mercaptans are removed from gasolines by extraction with a solution of a solutizer, such as potassium isobutyrate in concentrated aqueous potassium hydroxide. Under these conditions micelles of the otherwise nonsurface-active potassium isobutyrate are formed, and the mercaptans are apparently dissolved within these micelles. The mechanism of solution in micelles has been studied (22).

Synergic lowering of the surface tension of surface-active agents can also occur as a result of their direct interaction. Thus capronic acid and *o*-aminobenzoic acid together lower the surface tension of their mutual solutions more than could be expected from a summation of their separate effects (24). An addition product which possesses greater surface activity than either of the constituents is presumably formed in this case.

EMULSIONS AND EMULSIFIERS

Emulsions containing mixtures of emulsifying agents for which enhanced stabilizing properties are claimed have been the subject of a number of patents (3). A mixture of two or more emulsifying agents selected from four different classes (33) have a mutual stabilizing action such that the mixed emulsifiers are more effective than the separate emulsifiers. Synergy was also observed in the increased viscosity of solutions containing these mixed emulsifiers. A specific instance of increased stability is an emulsion prepared by the use of a mixture of lecithin and methylcellulose, which is much more stable than emulsions obtainable with either lecithin or methylcellulose alone (25).

Instead of increasing viscosity in an emulsion, a synergic effect may be just the opposite. For instance, in concentrated emulsions and suspensions, viscosity is sometimes reduced by the use of mixed particle sizes in the disperse phase. Thus the production of a "pourable" bituminous emulsion of high bitumen content by the creation of both large and small dispersed particles in the same system has been reported (34, 35). Two 60% asphalt dispersions, alike except for particle size, were prepared. One had an average particle size of 2 to 3 microns, the other of less than 1 micron. Mixtures of these two emulsions possessed viscosities considerably lower than those of the separate emulsions. The decrease in viscosity is ascribed to the packing effect of the large and small particles. This applies only to concentrated dispersions where some state of packing exists.

Particle-size distribution is no doubt a more important factor than particle size itself in regulating the viscosity of concentrated disperse systems (36). The principle of maximum close packing, recognized and applied in making concrete (32), is thus carried over into the field of emulsions.

Two possible mechanisms for synergy in emulsifiers are suggested. The first is an improvement in molecular balance as a result of interaction of the component emulsifiers, which might cause an increase in the toughness and stability of the interfacial sorption film. The second is the possibility of closer packing of mixed emulsifier molecules in the interfacial film, leading to increased stability of the film and a lower interfacial tension. The influence of molecular interaction and packing of emulsifiers on emulsion stability has been studied (10, 14, 31). Increased packing in the sorbed layer can occur as a result of differences in the chain lengths, of improved balance of polar and nonpolar groups in the molecules, or of a decrease within limits of the solubility of the emulsifiers in the mixture.

CATALYSIS

A promoter has been defined as a substance which increases the catalytic activity to an extent exceeding many times the additive effect of the mixture. Catalytic promotion is thus characterized by a much greater yield at the same temperature or by the same yield at a substantially lower temperature. In

synergy as applied to catalysis, a distinction can be made between a promoter which is not a catalyst and one which is a catalyst in its own right. Examples of promoter action in catalysis are well known and have been ably discussed elsewhere by workers in that field (4).

Synergic catalysts need not be mixtures in the ordinary sense; they may be intramolecular mixtures. Thus a catalyst prepared from the mixed heteropoly acid, silicomolybdotungstic ($H_4SiMo_8W_2O_{40}$), gives considerably higher conversions in the vapor-phase oxidation of naphthalene to phthalic anhydride (8) than the catalysts prepared from either of the parent acids, silicomolybdic ($H_4SiMo_{12}O_{40}$) or silicotungstic ($H_4SiW_{12}O_{40}$).

MISCELLANEOUS EXAMPLES

Many varied applications of synergy are in use today. One example is in weed control (15). Sodium chlorate sprays to control weeds among sugar cane are harmful to both weeds and cane crop at effective concentrations. By the addition of spreaders and activators such as pentachlorophenate, spray concentrations can be reduced to a point at which weeds are destroyed without affecting the sugar cane.

In the field of plastics, it has been shown that styrene-methyl methacrylate copolymers are stronger than either polymer alone (7). Definite compressive strength maxima occur at 30 and 50% styrene. This may be regarded as an intramolecular effect, with the synergy probably a result of the nonuniformity or dissymmetry introduced into the polymer chains by copolymerization.

Addition of a few per cent of halogenated aromatic hydrocarbons raises the breakdown potential of saturated hydrocarbons by 30-40% whereas greater additions lower it (29). This is probably a case of true interaction between the components.

The synergic action produced by the joint use of caustic soda and sodium peroxide in the modern fur-carroting process (36) results from combining two steps, hydrolysis and oxidation, into one.

Examples of natural materials which are synergic mixtures are carnauba wax and shellac. Although synthetic wax esters such as cetyl stearate, myricyl palmitate, and the like are known, they are not used commercially as waxes. Indeed, pure wax esters have had notoriously poor success in commercial applications despite many attempts in this direction. Carnauba wax, toward whose duplication most synthetic waxes are aimed, is a mixture of wax esters and uncombined wax alcohols. The synergy operating here has been approached with some success in the manufacture of synthetic waxes by oxidation of hydrocarbons to a mixture of wax acids and alcohols, which are then partially condensed to esters, leaving a certain amount of uncombined acids and alcohols (11).

Similarly, shellac (12) is a mixture composed largely of the complex esters of several different polyhydroxy acids together with a proportion of uncombined acids. The individual components are devoid of film-forming characteristics.

SYNERGY IN THEORETICAL CHEMISTRY

Although theoretical methods for dealing with pure substances and ideal systems are well developed, the opposite is true in the case of nonideal systems and synergic mixtures where empirical methods are the rule. But the development of such methods for dealing with the admittedly more complex, nonideal mixtures has lagged far behind the accumulation of data and the demands of technology. This may be largely the result of a lack of uniform methods in the evaluation and presentation of data, the use of arbitrary assumptions as to what constitutes ideal behavior in complex systems, and a failure to appreciate the presence and significance of synergy in many cases.

The latter point is illustrated by the work of Michaelis and Timénez-Díaz (23) on ionic synergy. They point out that the

various rules of Hardy, of Schultze, and of Freundlich, describing the coagulating power of electrolytes for colloids, were hindered from quantitative development by their failure to recognize that in aqueous solution one has to deal with hydrogen and hydroxyl ions, as well as the ions of the electrolytes. The coagulation of Congo Rubin sols was studied with sodium and potassium salts at various pH values, and it was shown that the coagulation power was a function of both pH and pI (where I indicates alkali metal ion concentration), both ions acting synergically. On the basis of this study, they formulated a quantitative "law of ionic synergism" which enables the true coagulating powers of the individual ions to be determined. The observation (28) that the effect of salts of polyvalent ions in reducing the interfacial tension of surface-active agents is analogous to the Schultze-Hardy rule for the coagulation of colloids, is very suggestive in this connection. It is possible that this phenomenon may yield to quantitative treatment according to the "law of ionic synergism" or along similar lines.

AUTOSYNERGY

For the sake of completeness the possibility of autosynergy should be considered. Pure substances which, upon dilution in an inert medium, are nonideal in their behavior may be regarded as autosynergic. Mixtures of the lower fatty alcohols and acids with hydrocarbons are typical, the polar molecular aggregates dissociating upon dilution with the nonpolar hydrocarbons. The increased rate of tanning of leather obtained upon dissolving formaldehyde in nonpolar solvents has been ascribed (30) to dissociation of the formaldehyde polymers in such solvents.

The solution of nitrocellulose in mixtures of alcohol and ether may also be regarded as a case of autosynergy according to the mechanism suggested by Barr and Bircumshaw (2). Alcohol alone, which is highly associated, is a poor solvent, but mixture with ether (a nonsolvent) is believed to lessen the degree of aggregation of the alcohol and thereby improve its solvent powers for nitrocellulose.

ROLE OF DISSYMMETRY

A large role in synergic phenomena is apparently played by the factor of dissymmetry. Molecular dissymmetry in catalysts and plastics has been cited, and the effects of mixed particle sizes, representing a type of dissymmetry, in emulsions and fillers have been noted. The influence of mixed molecular sizes and shapes on the stability of sorption layers of emulsifying agents has also been suggested.

Mixtures of sodium palmitate and sodium laurate in water illustrate the influence of dissymmetry in mutual solubilization (19). Mixed micelles of smaller size, less orientation, and greater solubility than those of the pure soaps are attributed to the occurrence of the shorter laurate molecules among the longer homologs. This results in micelles of nonuniform internal structure.

The transformation of a symmetrical into a nonsymmetrical system produces changes in polarity, orientation, packing effect, etc., depending on the type of system involved, and is reflected in changes in various properties such as viscosity, elasticity, melting point, fiber strength, and the like. The organic chemist dealing with polyfunctional molecules and the formulator having at his disposal many grades of the same material differing as to chain length or particle size may consider with advantage the synergic possibilities of employing mixed reactants or mixed grades.

PATENTS

The word "synergy" appears in the title of at least one patent (9), on sesame oil as a synergist or activator for pyrethrum insecticides. The use of mixtures to obtain enhanced or synergic effects, if so demonstrated and claimed, may be classed as new, novel, and unexpected and be patentable, even though the use of

the separate components may be the subject of previous patents. In a patent (15) covering the use of aliphatic amino derivatives or their salts as plasticizers for hydrophilic organic colloids, the statement that a mixture of amines is more effective than a single amine may be important. Because it is unpredictable, the possibility of synergy should always be considered in drawing up patents involving classes of materials, polyfunctional reactants, multistep processes, etc.

QUANTITATIVE DETERMINATION

To determine quantitatively the presence or absence and the degree of synergy in various systems is by no means so simple as might appear from the definition. The choice of a suitable measure or norm, which if exceeded indicates the occurrence of synergy, is not difficult from the practical point of view where evidence of improved performance, lower cost, and time saving is sufficient. The difficulty arises when a measure is sought such that deviations from it will be quantitatively significant—for example, in stoichiometrically establishing molecular association or in making valid comparisons as to the extent of synergic action among different systems.

Many of the mixed systems for which synergy has been claimed are actually dispersions or solutions of the active agents in a medium which is assumed to be completely inert. Insecticides, antiseptics, tanning agents, and surface-active agents are typical examples. In such cases the significant properties vary with the concentration, and it may be difficult to determine just what the "sum of the two effects taken independently" really is because of such complicating factors as dilution effects or autosynergy and differences in synergic mechanisms.

In the case of a mixture of two substances with or without an inert diluent, the sum of the independent effects, or the norm against which the actual behavior of the system is compared, may be represented by the expression,

$$\frac{P_1c_1 + P_2c_2}{c_1 + c_2}$$

where c_1 and c_2 represent the concentration of each component; P_1 and P_2 represent the value of the property of each pure component, taken at a concentration of $c_1 + c_2$ when the property in question is extensive.

This is often considered a true measure of ideal or nonsynergic behavior, particularly in binary liquid mixtures. However it has not always been appreciated that the validity of this measure depends entirely upon the use of significant and additive quantities. Not all property scales or measures of concentration can be validly used in this measure. A binary liquid system is usually treated graphically by plotting a property such as viscosity in centipoises against composition, as in mole per cent. The ordinates at 0 and 100 mole per cent represent the viscosities of the pure components. A straight line drawn between the two extreme compositions is often assumed to represent the ideal behavior of the system, and the actual curve is compared with this straight line which may be represented by the expression $(P_1c_1 + P_2c_2)/(c_1 + c_2)$. Such a practice is in this case entirely intuitive and arbitrary, since other viscosity scales such as the logarithmic or reciprocal and other concentration units such as volume or weight per cent might be used with equal validity, yet give entirely different results.

Irany (16, 17), in an important series of studies of the viscosity function, has investigated this matter in detail and has shown how a considerable degree of confusion regarding compound formation and association in binary systems has appeared in the literature as a result of arbitrary graphical interpretations of viscosity data. An additive viscosity scale is developed empirically, and volume per cent is shown to be the correct composition unit for graphical treatment. On this basis a large number of recorded erroneous observations are corrected, and the whole mat-

ter of the existence, stoichiometry, and stability of molecular aggregates is greatly simplified; closer agreement with independent thermodynamic data is shown in many cases by way of confirmation.

CLASSIFICATION

From a study of known phenomena, synergy may apparently occur in at least three fundamentally different ways:

1. As a result of a combined stepwise action such that one component acts upon the result of the other component. Groups of components may be involved in each step of the process.
2. As a result of direct mutual interaction of the components such that a new entity or product is formed with a structure and properties of its own.
3. As a result of the complementary functioning or indirect interaction of the components, each acting in its own way toward the same effect.

More than one of these mechanisms may be involved in any particular case of synergy, and many actual cases will defy a simple classification into one of the above groups. This formal classification of the basic mechanisms is conveniently made, however, for analytic and critical purposes.

Important distinctions can be made between these classes of synergic mechanisms. The first represents processes which can be dealt with by the ordinary means employed with pure substances. The total process can be separated into parts and each dealt with separately. Such processes are usually the most easily analyzed among those displaying synergy. Combined stepwise processes are of practical importance in effecting savings in time, costs, space, and equipment.

The second type of mechanism, involving mutual interaction, differs fundamentally from the first and is of far greater importance. Nonideal binary and multicomponent systems offer typical examples. The results of mutual interaction cannot be adequately described in terms of the components alone, and special methods are required to deal with such mixtures. This type of interaction may be involved in the creation of novelty in nature, and thereby play a role in both organic and inorganic evolution.

The third synergic mechanism involves an indirect type of interaction resulting from the simultaneous action of the components of a mixture upon the substance being acted upon. Thus, although synergy is attributed to a binary solvent mixture in which different portions of the solute molecule are solvated by the two solvent components, it is really the ternary system of two solvents and a solute which manifests synergy. The solute acts as a unifying element or intermediary for the interaction of the entire system.

On the basis of these classifications it is possible to distinguish between true and apparent synergy. Possibly the concept of synergy should be limited to include only such phenomena as involve some type of mutual interaction; purely stepwise processes which are only apparently synergic would be thereby excluded. The purpose of such a restriction is to bring into sharper focus those essential features of synergy which can be of most value to the creative chemist.

CONCLUSIONS

This generalization of the nature of synergy and the factors underlying it—namely, self-association, packing effects, dissymmetry and interaction of components, represents no new discovery of principle. It does offer a valuable orienta-

tion or approach to the problems of industrial chemistry. Heretofore the application of synergy has often been the result of years of accumulated experience or of a special theory about some particular process or even the result of chance discovery. An awareness of the nature of synergy can be an important addition to the blend of experience, theory, and imagination, often called the "know how" of the chemist.

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OCTOBER'S HEADLINES

Events during the Month, of Interest to
Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ OCTOBER 1. Industry executives urge cancellation of commission plan in Anglo-U. S. oil agreement, putting it purely on basic principles of oil policy.~~Reynolds Metals Co. maps program of postwar manufacturing ranging from aluminum-treated food containers to aluminum freight cars.~~Consolidated Edison of N. Y. and system companies announce survey of manufacturing facilities in metropolitan area to aid industry in obtaining postwar work.~~Mexican company arranges for alkali plant to utilize lake brines near Mexico City, American Cyanamid to serve as technical adviser¹.~~Buffalo Electrochemical announces process for making solutions of acetyl peroxide safe to handle.~~Rubber Chemicals Division of Du Pont states it will have completely equipped technical service laboratory in Akron.~~Industry leaders draw plans for private institutions to bring young men to this country from all over the world for training in industrial and mercantile establishments.

¶ OCTOBER 2. General Tire & Rubber announces construction of new \$500,000 research laboratory.~~Elmer K. Bolton, chemical director of Du Pont, to receive Perkin Medal award of American Section, Society of Chemical Industry².

¶ OCTOBER 3. President Roosevelt signs Surplus War Property bill and War Mobilization and Reconversion bill, and announces interim appointment of James F. Byrnes as director of new Office of War Mobilization and Reconversion.~~WPB announces sulfuric acid industry will reach peak capacity of 9,426,600 tons by June 30, 1945.~~WPB lifts all government controls on use of magnesium for civilian goods.~~B. F. Goodrich Co. develops new synthetic shoe-soles and top-lift material made of Koroseal.

¶ OCTOBER 4. Chemicals Bureau of WPB lifts allocations controls for civilian use over various materials used in manufacture of plastics.~~Office of Price Administration announces increase of about 80% in prices for certain cinchona alkaloids sold by Defense Supplies Corp. to other government agencies.~~Petroleum Administrator Ickes recommends that minimum of 27,000 oil and gas wells be drilled in 1945, of which 5000 should be exploratory.~~Pennsylvania Salt Mfg. Co. dedicates Whitmarsh Research Laboratories near Philadelphia³.

¶ OCTOBER 5. WPB Chairman Krug says there will be no shortage of metals after V-E day cutbacks have taken effect.~~WPB assures that, one year after defeat of Germany, industry will have steel, copper, and aluminum in greater

supply than during record producing peace year 1937.~~Standard Oil Development holds Forum on Future of Industrial Research in New York, in celebration of Silver Anniversary⁴.

¶ OCTOBER 6. U. S. Tariff Commission predicts that serious competition between imported natural rubber and domestic synthetic is unlikely for a year or two after reconquest of rubber-producing areas of Far East.~~WPB says supplies of rotenone, pyrethrum, arsenic, and copper fungicides may have to be allocated after V-E day.~~F. A. Howard resigns as president of Standard Oil Development; R. P. Russell, executive vice president, succeeds him⁵.

¶ OCTOBER 8. Foreign Economic Administration announces about 78,000 tons of crude rubber are to be shipped to U. S. from the British Commonwealth.

¶ OCTOBER 9. Reynolds Metals plans new uses for aluminum foil, including wrapping of bread, cake, crackers, and citrus fruit.~~Petroleum Administrator Ickes announces October output of 100-octane gasoline will exceed Allied Nations' combat training requirements for first time.

¶ OCTOBER 10. Annual report of E. R. Squibb & Sons states production of penicillin is being carried on in 15,000-gallon instead of 1-gallon tanks as used a year ago.~~Directors of Independent Petroleum Association, meeting in Dallas, ask for defeat of proposed Anglo-American petroleum agreement.~~WPB says nearly all government production controls over copper industry will be lifted following V-E day.

¶ OCTOBER 11. Toilet Goods Association announces research program to determine effects of cosmetics, first co-operative venture of this kind in the industry.

¶ OCTOBER 12. National Foreign Trade Convention adopts recommendations giving view of business and industry on future foreign trade policy.~~Chairman Krug tells press conference WPB is mapping steps for each industry and government, leading to reconversion when Germany collapses.~~U. S. S. R. mission sent to Iran is negotiating for oil concession.~~Walter Rice, vice president of Reynolds Metals Co. and president of Reynolds Mining Corp., tells press conference his company has long-term plans for bauxite mining in Jamaica⁶.

¶ OCTOBER 13. WPB abolishes Controlled Materials Plan Division and Production Controls Bureau, and announces departure of five dollar-a-year men.~~American industry

¹ Chem. Eng. News, 22, 1811 (Oct. 25, 1944).

² Ibid., 22, 1690 (Oct. 10, 1944).

³ Ibid., 22, 1682 (Oct. 1944).

⁴ Ibid., 22, 1752 (Oct. 25, 1944).

⁵ Ibid., 22, 1800 (Oct. 25, 1944).

soon will have access to 45,000 patents seized by Alien Property Custodian, Heyward C. Hosch, southeastern consultant of Smaller War Plants Corp., tells Georgia business leaders. ~Albert Hayes, chief, WPB leather branch, at annual meeting of Tanners Council of America, says cutbacks affecting leather industry will not exceed 20% on V-E day. ~Association of Pulp Consumers requests continued control of wood pulp allocations after defeat of Germany. ~William Blum, chief of Electrochemistry Section, National Bureau of Standards, receives Acheson Gold Medal of Electrochemical Society.

¶ OCTOBER 14. American Cyanamid manufactures "Lana-set" for process to control wool shrinkage. ~Diamond Alkali of Pittsburgh purchases Emeryville Chemical Co. of San Francisco. ~Deputy Petroleum Administrator Davies says new superfuel will give planes of United Nations even greater superiority over Japanese air fleets.

¶ OCTOBER 16. Foreign Policy Association urges control of public and private cartels by international supervision after war. ~WPB orders manufacturers of paper and paperboard to hold 35% of total output of groundwood, printing, book, writing, and coarse wrapping papers for future distribution. ~War Manpower Commissioner McNutt says all offices of U. S. Employment Service must tighten controls and have workers prove availability as prerequisite to employment when they move into new area. ~OPA rules that producers of synthetic resins containing more than 50% of gum rosin may apply for increases in ceilings if they cannot maintain production at present ceilings.

¶ OCTOBER 17. Gilbert H. Montague of N. Y. Bar Association, in address before Boston Conference on Distribution, urges immediate consideration of changing and conflicting views on international trade agreements and cartels by an international group. ~State Department undertakes to expand foreign service personnel and facilities to furnish foreign trade information to federal agencies. ~Control of metals after war to ensure that enemy countries will never again possess sinews of war, urged by Walter S. Tower, president of American Iron and Steel Institute in address to American Society for Metals at National Metal Congress. ~Union Carbide & Carbon forms new plastics group to correlate company activities in plastics. ~WPB maps program to increase output of sulfuric acid to meet ordnance needs⁶.

¶ OCTOBER 18. State Department is prepared to revise Anglo-U. S. oil pact if necessary to allay industry's fears.

¶ OCTOBER 19. New nylon coating for wire, applicable at rates over 1000 feet per minute, announced by J. W. Strackleton, Plastics Department of Du Pont. ~Charles J. Brand, executive secretary and treasurer of National Fertilizer Association, receives decoration from Ambassador of Chile on behalf of his government for valuable services.

¶ OCTOBER 20. WPB eases restrictions on copper in 17 civilian and commercial items. ~Attorney General Biddle says Department of Justice filed amended counterclaim as intervening defendant in case of Wisconsin Alumni Research Foundation vs. Douglas Laboratories for alleged infringement by Douglas of so-called Steenbock patents on production of vitamin D. ~Appellate Division of N. Y. Supreme Court reverses a decision requiring Climax Molybdenum and certain directors of American Metal Co. to account to American Metal

for profits, and absolves Climax Molybdenum from charges of improper use of facilities of American Metal. ~Three-dimensional pictures of views through electron microscope demonstrated publicly for first time at 29th annual meeting of Optical Society of America.

¶ OCTOBER 22. Leo T. Crowley, head of FEA, announces he will relax export controls as soon as compatible with wartime exigencies and reconversion possibilities. ~Iran rejects American, British, and Soviet propositions for oil concessions and postpones further discussions until after war. ~WPB eases restrictions on some types of laboratory equipment; places acrylonitrile, penicillin, and chlorinated paraffin under control of M-300 (general chemicals order) and lifts allocation controls from thiamine hydrochloride. ~U. S. Rubber is spending more than \$29,000,000 to expand tire production facilities.

¶ OCTOBER 23. WPB Chairman Krug says control over leather and cotton textile industries must be maintained after Germany's fall. ~Federal Trade Commission files bill setting forth 15 charges against Potash Export Association. ~Monsanto Chemical announces perfection of new synthetic resin which will practically eliminate size as restrictive factor in postwar plastics, it is claimed.

¶ OCTOBER 24. East Coast distillers of industrial alcohol to shift to grain after January 1, following request from War Food Administration to WPB.

¶ OCTOBER 25. J. H. Pew, president of Sun Oil tells Petroleum Industry War Council that Anglo-U. S. petroleum agreements give Government a blank check which could embroil domestic industry in vicious cartel system. ~Clark H. Minor, president, International General Electric Co., defends cartels as logical development of international trade before House Committee on Postwar Economic Policy and Planning.

¶ OCTOBER 26. Owners of Universal Oil Products set up Petroleum Research Fund with Guaranty Trust Co. of N. Y. as trustee. Management of UOP to be vested in a board of directors, to be appointed by Guaranty Trust. Net income from the trust to flow to ACS for research in petroleum and natural gas fields. ~Mathieson Alkali announces sodium methylate available commercially. ~Secretary Ickes asks petroleum industry to submit constructive suggestions for amending proposed Anglo-U. S. world oil agreement. ~Nobel Foundation announces 1943 Nobel Prize in Medicine goes to Edward A. Doisy, professor of biochemistry, St. Louis University School of Medicine, and to Henrik Dam of Copenhagen (now of Strong Memorial Hospital, Rochester) for discovering chemical nature of vitamin K.

¶ OCTOBER 27. Diamond Match Co. answers antitrust suit claims by saying that it fought Swedish International match cartel. ~Milo Perkins proposes that Congress allow American business to join international cartels under strict regulation by State Department.

¶ OCTOBER 30. National Patent Planning Commission's second of three reports on possible changes in American patent system is ready for submission to President.

¶ OCTOBER 31. Longest pipe line of kind in world begins delivering daily output of 200,000,000 cubic feet of natural gas from Texas to Pittsburgh-Youngstown-Cleveland area. ~Colorful plastic shoes from Union Carbide's Vinylite will be ready for Easter wear, according to announcement at National Shoe Fair in Chicago.

⁶ I. & E. C. REPORTS, advertising page 16, this issue.

the growing utilization of alkylation processes will probably serve to keep sulfuric consumption at high levels in that industry next year. It may not be just hopeful postwar guessing to expect that the higher acid-consuming rate in petroleum refining processes for this reason will be projected beyond the end of the war.

It should also be noted that other sulfuric-using industries have expanded or are planning to expand capacity. The steel industry in this country, for example, has increased its ingot-making capacity to 94,055,000 tons, from 81,829,000 in 1939, along with facilities for rolling, finishing, and acid pickling its product into sheets with high brilliant surfaces and durability for automobiles, refrigerators, and many other necessities.

The chemical industry is one of its own best customers when it comes to sulfuric acid, as the above table shows. In this war it has increased all chemical production 233% if comparison is made with 1939; and some related processing fields, notably rayon, paints, pigments, metallurgical manufacture, have also expanded wartime productive facilities. It is only reasonable to expect that the greater part will remain after the war to supply billions of dollars in consumer goods in what may prove to be the greatest of industrial eras and provide new outlets for sulfuric acid and many other chemicals.

New sulfuric acid plants will be constructed but will not be in the production picture until March of next year, if then. In the interim the tight situation will continue, and it may be necessary to deny virgin acid to superphosphate makers entirely until the new plants are ready.

Sponge Iron. Among the many controversies that waxed warm in the earlier days of WPB was the advisability of adopting the sponge iron process in certain sections of the United States during the war period. In the Far West particularly, pressure was brought to bear to try the process on low-content western and Texas ores, despite opposition from the steel industry which insisted the process was not feasible. Now Republic Steel is ready to go into production at its million-dollar Warren, Ohio, low-temperature reduction plant. Republic will operate with high-grade magnetite, but some of the answers long debated should be found in results at the new plant.

White Glove Fuel. Briquetted fuel is by no means a wholly new idea, but despite certain apparent advantages, the idea never has been fully exploited. The entrance of Blaw-Knox into the field of briquets (a combination of anthracite and bituminous "fines") will be watched closely. An asphalt is used as a binder, and the "white glove" fuel will be pressed into 3 × 3 × 3 inch cubes. A kraft paper will serve as wrapper for the cubes. The new plant will be located near Philadelphia, will be financed by Defense Plant Corporation, and will cost approximately four hundred thousand dollars. The War Production Board and the Solid Fuels Administration have endorsed the project as a means of assisting in the relief of fuel shortages.

EQUIPMENT AND DESIGN

Discussed by Charles Owen Brown

NOVEMBER, 1944, is an excellent time to begin presentation of discussions of equipment and plant design since the progress normally made in eight or ten years has been concentrated into the last four by the necessity of defense and war programs. Shortly much of this new knowledge may be available for wider and more humane uses. This opportunity is unique in the fast-moving history of the chemical industry. Equally true it is that the end of the war will make available much idle equipment for industrial use. Some of this equipment can be used in the way for which it was designed. A far larger portion, however, must be modified, knocked down, and reconstructed for special purposes. No one knows how much equipment will be thrown on the market by government agencies, but it is certain to be enormous, measured by any previous standard. The list will include entire plants, some of which will have a fair value exceeding a hundred million dollars, while millions of dollars represent equipment and apparatus valued from a few cents to several hundred thousand dollars for individual pieces. There is a considerable economic problem attached to this huge surplus storehouse. To assist in a better knowledge of this equipment, with satisfaction to both seller and buyer, will be but one of the many objects of this column. There seems to be a good possibility that the wonderful work of the scientific research groups

will evolve new processes which can be constructed from the stocks of surplus equipment and thus convert both to useful productive plants.

Recently the Blaw-Knox Company designed and built a plant, installed in a new building 70 feet high, which makes possible the mixing of carbon black (a product of natural gas) with liquid rubber. The milling time needed to make a certain grade of rubber is thereby cut by one third. A simple flow diagram of the process is shown in Figure 1. The carbon black is delivered by railroad cars on the left, taken by the air-activated conveyor into the storage room, and sent as needed to the hopper. The arrows show the course of the carbon black as it is pumped into the main synthetic rubber plant for mixture with latex before the rubber coagulates into plastic form. Previously the mixing was done after the rubber had coagulated. Blaw-Knox engineers received the basic information on how the scientists had been able in the laboratory to mix carbon black with liquid latex successfully and began work on blueprint layouts and building. The blueprinting was completed by July 1, and on August 16 the first rubber was turned out, properly processed. The flow diagram indicates that this project could have been assembled promptly from surplus equipment, since much of it is typical of that used in unit operations of chemical engineering—the air conveying system, pumps, scales, and tankage. The highly important result of shortening the compounding time for a special rubber came from fundamental research and good engineering. These two tools of the chemical industry can accomplish the same wonders in adapting surplus material to postwar needs.

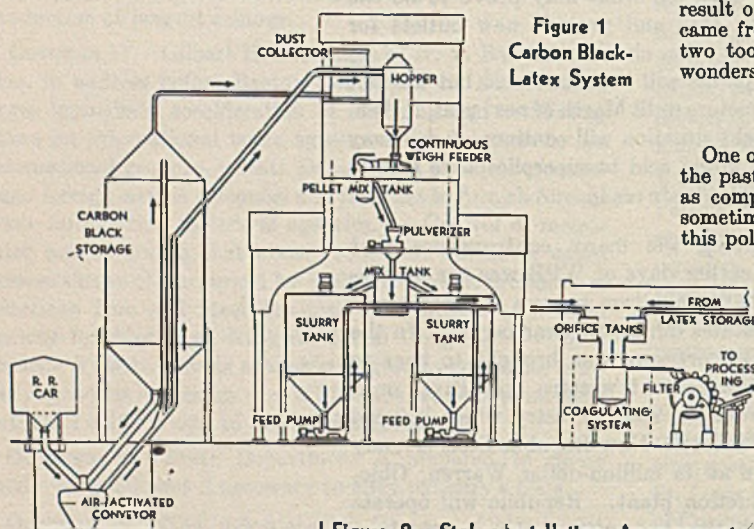


Figure 1
Carbon Black-
Latex System

Packaged Units

One of the most useful innovations in the technical field during the past three years has been the fuller development of "units" as complete, ready-to-operate plants. The generic principle is sometimes referred to as packaged units. The extent to which this policy has been developed is remarkable. In the chemical equipment field the packaged unit idea often consists in placing or properly installing motors, instruments, regulating controls, and secondary foundations on a principal piece of equipment at the point of manufacture before shipment. When the apparatus is boxed, it is actually a complete plant. On arrival at destination it is unpacked, placed in the desired location, and is ready to perform as soon as water, electrical power, or steam can be connected. The packaged unit idea is permanent; it will be more widely used. To this principle, more than to anything else, can be attributed the success of domestic oil burners, the Iron Fireman, and conditioned atmosphere furnaces. Developed first as a domestic house heater purely to serve those districts where oil was not available with a laborless heating device and to hold coal sales in competition with automatic oil burners, the Iron Fireman has "grown up". It is now a completely packaged unit serving the light industrial field. One frequent application is in connection with HRT boilers of 1500 and 2000 square feet of heating surface. Boilers of this capacity and type have long been the old reliable work horses of small manufacturing plants throughout the country but have not been known, especially, for efficiency under hand-firing conditions. The modernized firing methods with such devices as the Iron Fireman coal-flow underfeed stoker (shown diagrammatically in Figure 2) change many

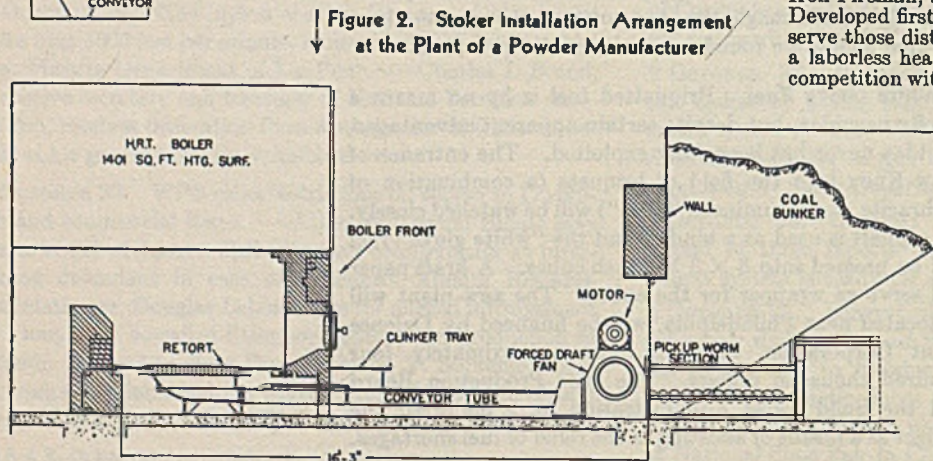


Figure 2. Stoker Installation Arrangement
at the Plant of a Powder Manufacturer

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Equipment and Design

old boiler room conditions vastly for the better. While carrying a slightly higher load, the steam pressure is maintained more nearly constant with fewer man-hours in the boiler room. Financially important is a saving of 22.5% in coal consumption. It is a safe guess that one of the most interesting developments to come out of the thousands of new designs utilized in war activities will be the fuller use of the wonderful properties of new alloys and materials. While the tensile strength of certain alloy steels has been steadily increased to over 200,000 pounds per square inch, ordinary machining and tool operations also have become more precise; heavier safe loads are thus permissible on each separate part. One example out of many to illustrate the results that this combination of improvements will yield is the Hycon oil pump, patented and manufactured by the New York Air Brake Company. The size and weight of this small precision alloy pump may be judged from the two half-inch pipe openings in the top of the casing, but its normal capacity is 6 gallons per minute of oil against a head of 3000 pounds per square inch (6950-foot head) at 4500 r.p.m.

It is hoped that one of the results from these articles will be to increase the use of old devices in new applications. There are great rewards within reach of those who will extend a successful, proved device into a new duty and thereby make some piece of equipment more useful. Consider the water-sealed gas holder. These storage tanks of two or three lifts can be raised and lowered to change their volume from zero to full capacity. A series of two or three inverted steel bells dip into water and permit the bells to move up or down while sealed to the atmosphere. This old device applied to the top of tanks for the storage of light volatile liquids has recently been improved by Graver Tank & Manufacturing Company. The new "expansion roof" built into the top of any tank operates the same as the single lifts or bells of the gas holder. The tank roof is built as a self-supporting, shallow, inverted bell, the skirt of which moves in a concentric layer of water constructed at the top of the tank. During the temperature change in the vapor over the liquid stored in the tank due to a noon sun, the roof simply raises until the increased volume of the vapor at the higher temperature has been provided. At night, as a result of lower temperature, the vapor volume contraction is replaced, not by creating a vacuum or drawing in air, but simply by the fall of the roof until normal vapor pressure exists. Valuable vapors of the materials stored in the tank are not lost with rising temperatures or diluted with air by falling temperature. The proportion of the tank proper, usually added for the gas-holder adaptation roof, for gasoline storage tanks is:

Barrels Stored	Roof Expansion Capacity, Cu. Ft.
5000	3,613
80,000	54,225

The saving in gasoline due to this type of expansion roof, valued at 7 cents per gallon, will exceed six thousand dollars per year.

Charles Owen Brown is a consulting chemical engineer identified with the nitrogen fixation industry for over a quarter of a century. Active in this field as Lieutenant Colonel of Ordnance during the last war, he has since been connected with the chemical industry, here and in Europe. His present office was established in 1937, specializing in high-pressure technique, synthetic ammonia, nitric acid, alkali, alcohols, and aldehydes. His experiences are closely related to many types of equipment and plant layout. One of the large synthetic ammonia plants of the present defense program was designed and put into operation under his supervision. Brown has lectured in chemical engineering economics at Brooklyn Polytechnic Institute; he is a member of the State of New York Industrial Commission and of War Production Board, and is a consultant to the Army Engineer Corps.



Current Developments in INSTRUMENTATION

THE art or science of using instruments for measurement or control can be called "instrumentation". Instruments were developed to enable us to obtain more quantitative information about the materials and processes with which we work than is possible by our unaided senses. After instruments for measuring became available, recorders and controllers developed from them.

Our need for instrumentation stems from a desire to obtain better yields of purer products from poorer raw materials with less capital investment and less labor. Batch processes usually require a minimum of instrumentation. There is generally time for manual measurement of important process variables, such as pH, or for chemical analysis to determine completeness of reaction. When, in our effort to improve quality and lower costs, we go to continuous processes, it becomes imperative that we have methods which will indicate without lag the condition of the process at each of its important stages. During the time required to run control tests suitable for batch processes, a continuous one may get so far out of balance as to require hours to correct and may make large quantities of off-grade product during that time. In other cases serious danger to personnel and damage to equipment can result.

The instrumentation for a process should develop along with the process, starting with the laboratory work and advancing to the pilot plant and full-scale plant along with the process itself. In the laboratory the chemist must determine which are the significant process variables and how closely they must be controlled. With the aid of a physicist and perhaps an instrument engineer, he must decide whether thermal conductivity, infrared methods, ultraviolet methods, a mass spectrograph, or straight chemical

The electronics industry is becoming increasingly aware of the instrument field as a new market for its products.

gas analysis methods will give most satisfactory results with the particular gas mixture involved in his process. Speed and accuracy of method must be balanced against cost of equipment required and skill needed to operate it. The method selected should usually be given a laboratory trial, because there the chemist can arrange his experiment to cover the widest range of conditions to be expected without bothering plant production and without the expensive equipment changes so often required for even a simple experiment in the plant. Later, measurements should be made in the plant, or at least on plant materials, so that there will be no trouble from unexpected impurities or plant conditions. Small amounts of impurities that are not supposed to be there often cause methods, which seem suitable at first sight, to fail entirely in actual plant use.

Cases of this kind are the failure of the antimony electrode for pH measurement in the presence of traces of copper, and the failure of dielectric constant methods for determining the dryness of a liquid hydrocarbon when small but variable amounts of other high-dielectric-constant impurities are present. When manual measurements in laboratory and plant have demonstrated the usefulness of a control method, the next step is installation of recording or recording and controlling instruments in the plant.

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Discussed by Ralph H. Munch

Ralph H. Munch is a physical chemist who specializes in control methods and instruments for plant processes. After receiving his Ph.D. degree in physical chemistry at Northwestern University, he became Rockefeller Research Assistant at the University of Chicago. There he experimented on the application of visible and ultraviolet absorption methods to biochemical problems. In 1937 Munch became research chemist in the Organic Division of Monsanto Chemical Company, working on electro-organic processes and on catalysts, among other things. He is now group leader in charge of the Physicochemical Group of Monsanto's St. Louis research laboratory. His reputation is growing as a "trouble shooter" for knotty problems in the instrumentation field. As such the Editors welcome his monthly contributions to this column.

Instrumentation

If the preceding steps have been well carried out and a wise choice of recorder or recording controller has been made, the plant installation will function successfully.

Trend to Electronic Instruments

Those of us who are interested in instrumentation are becoming increasingly aware of electronic methods for achieving our aims. Likewise, the electronic industry, expanded to several times its prewar size, is becoming increasingly aware of the instrument field as a new market for its products. Evidence of this trend can be seen in the increasing number of articles on electronic instruments for both laboratory and plant uses in such publications as *Electronics*, *Radio News*, and *Electronic Industries*. Other evidence of this trend can be seen in the programs of such meetings as the Gibson Island, Md., conference on instrumentation, of the American Association for the Advancement of Science, and of the National Electronics Conference recently held in Chicago.

One of the difficult operations encountered in plant work is the separation of an oily layer from an acid layer by allowing the constituents to settle out in a tank and then drawing off the lower layer. The two layers are often so dark colored that no change can be seen in a sight glass when one layer gives way to the other. J. W. Broadhurst describes "An Electronic Indicator for Liquid Separation" in the *Journal of Scientific Instruments*, Volume 21, page 108 (1944). His indicator consists of a Hartley oscillator with the tank coil wound around a section of glass pipe in the decant line. The circuit is adjusted to oscillate when the oil is passing through the coil and to stop oscillating as a result of eddy current loss when the conducting acid enters the tube. A relay operates a signal lamp when the circuit ceases to oscillate. While the device described by Broadhurst should be easy to construct and operate, it seems that it would be possible to use one of the commercial liquid-level indicators operating on the same principle. At any rate, this method seems to be a nice solution to a difficult problem.

"Industrial Electronic Control", by W. D. Cockrell (McGraw-Hill Book Company) is a very timely book in view of the great interest of instrument users and manufacturers in electronic devices. Many books similar to "The Fundamentals of Vacuum Tubes" by A. V. Eastman have been written on the theory of vacuum tubes. The practical use of electron tubes has been the subject of many others, such as "Electron Tubes in Industry" by Kieth Henney. Cockrell's book falls in a class between these two. Its first section is a simple résumé of the properties of the various types of electron tubes. The various circuit components used with electron tubes are described in the second section. Section three shows how these elements are combined in the basic electronic circuits. A fourth section then applies the information covered in the preceding ones to the analysis of a selected group of typical industrial electronic circuits.

"Industrial Electronic Control" is written primarily for electronic service and maintenance engineers. The subject matter outlined above is covered simply and clearly. Its objective is to give an understanding of electronics sufficient for the reader to recognize the basic circuits found in industrial control devices and to understand the manner in which the electron tubes and circuit components associated with them function in these basic circuits. The book can be heartily recommended to the group for whom it was written and to chemists interested in understanding industrial electronic control devices or in devising and constructing electronic devices for their own use.

Current Developments in

PLANT MANAGEMENT

MANY difficulties will have to be overcome in order to find the right job for our returning soldiers. A study of the situations we will have to face and a knowledge of the Government's rehabilitation plans will enable us to establish the basis of a successful re-employment program before the need for action arises. Government agencies have, or are making, plans for the rehabilitation of veterans. Of immediate importance to the manufacturer are steps taken by the selective service system, charged with carrying out a program for re-employment assistance to veterans. Selective Service Director L. B. Hershey recently issued instructions to local draft boards which should be of considerable interest to every manufacturer. The highlights are:

1. Seniority rights accumulate during the period of active military or naval service. Time is credited in the same manner it would have accumulated had the person remained continuously at work in his civilian occupation.
2. Where a position has been upgraded, a returning veteran, in order to claim reinstatement in such position, must be qualified to perform the duties and functions of that new position. If unable to qualify for the upgraded job, he is nevertheless entitled to a position equal in seniority, status, and pay to the one which he left.
3. A returning veteran is entitled to reinstatement in his former position or one of like seniority, status, and pay even though such reinstatement necessitates the discharge of a nonveteran with greater seniority.
4. A veteran is entitled to his former position or one of like seniority, status, and pay, and may refuse another even though the pay is greater and offers other advantages.
5. If, upon a veteran's return from military service, he finds that his employer has entered into employment agreements with others setting up conditions of employment different from those which existed at the time the veteran left, the veteran cannot be deprived of his re-employment rights by reason of these agreements.

How shall we re-employ our former workers? This problem becomes more acute as the end of the war approaches.

These instructions clearly show the Government's intention to deal with this problem in detail in order not to leave the proper execution of the rehabilitation program to chance.

In addition to the selective service system, other federal and state agencies are making plans and issuing instructions. All will want to cooperate fully in making the readjustment of veterans a success. Nevertheless, many of us will wonder how we, technically, will be able to accomplish this without impairing the efficient execution of postwar programs. In what problems will we become involved and how can we arrive at a solution?

At the time our soldiers will seek employment, industry will be in the midst of reconversion. Many plants will be temporarily closed or at a low volume of production. We may, therefore, find that the number of veterans who will have to be absorbed will represent the majority of people who can be kept busy. Common sense will tell us that we cannot discharge a great number of our present employees without seriously hampering operations.

To avoid confusion and dissatisfaction, we should now determine the number of employees needed for reconversion and the number of veterans who can safely be absorbed. For the remaining veterans we will have to find a temporary place to work. This may be accomplished by the establishment of training schools which will prepare the discharged soldier for the job he will have to perform after reconversion has taken place; this will give him an opportunity either to brush up on his former job, learn a new job, or prepare himself for a higher skilled operation.

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Discussed by Walter von Pechmann

Walter von Pechmann is an industrial engineer with fifteen years of production experience to his credit. For many years he supervised one of the most intricate of chemical manufacturing processes, the making of photographic emulsions. As cost analyst he had the opportunity to familiarize himself with all phases of plant operation and management problems. Von Pechmann is also familiar with accounting procedures; as advisor on matters pertaining to production, he worked for some time on the installation of cost systems. He is the author of several articles on management problems and is now working on rehabilitation problems. At present he is connected with the Binghamton, N. Y., plant of General Aniline and Film Corporation.

Plant Management

It may be well to keep in mind that the training period will give the ex-soldier an opportunity to adjust himself gradually to the normal way of life. It may therefore be advisable, when selecting employees to be trained, to give preference to persons who find it hard to adjust themselves.

Setting aside sentimental feelings, we must come to the conclusion and deal with the fact that the veterans may not qualify for their former jobs. Anyone who has had the opportunity to talk with employees now in service cannot fail to realize the change that has taken place in our soldiers' outlook on life. The youth who saw in his job nothing but the source of money, to be spent as soon as received, has now become a man who prefers the chance for advancement to temporarily higher pay; the man who was satisfied with performing a routine operation tells us that he never will be able to return to his former job.

In order to put the right man into the right job and to build the foundation for a healthy future employee-employer relationship, it will be necessary to interview every returning soldier. The personnel department of each concern will play an important part in our rehabilitation program, and the staff of this department must be able to appreciate and understand soldier's problems. The staff which successfully handled war problems may not necessarily be successful in handling rehabilitation problems.

Frequently thought of, but seldom discussed, is the question of how organized labor will react to our re-employment plan. One often finds the attitude of "not crossing the bridge until we come to it", because asking organized labor to express its opinion now will only add to the many problems we are trying to solve. This point of view is shortsighted. Labor's attitude towards an organized rehabilitation program must be known now if we are to plan properly. It may be advantageous to familiarize labor representatives with the difficulties we anticipate in our plants and to seek active participation in planning for the re-employment of veterans.

Unfortunately many soldiers will return disabled. These men will want neither to be celebrated as heroes nor treated as charity cases. They will want to adjust themselves as quickly as possible to the normal way of life and will expect us to assist them in this undertaking. Contrary to general belief, earning power is not the most important factor from the disabled veterans' point of view. His objectives, listed in order of importance, will be (1) to attain the working capacity of a normal person engaged in a specific type of work; (2) to have a chance for advancement; and (3) to attain immediately an earning capacity based on his former standard of living.

Only in rare cases can full working capacity be achieved if the disabled soldier is trained to perform operations according to prevailing working standards. The writer has repeatedly advocated less emphasis on training the handicapped to adjust themselves to normal working conditions and greater effort in adjusting the working conditions to fit the need of the incapacitated. Private enterprise can be, if cognizant of this important distinction, of real help to the disabled veterans.

The problems discussed are only a few of the many we will have to solve in order to give our boys a fair break and to bring reconversion from war work to civilian production to a successful conclusion. Because of the variety of problems and the difference of importance which has to be attached to each problem, there will be no fixed pattern which can be followed; every manufacturer will have to work out his own plans and we had better start now, if we do not want to be caught unprepared in welcoming home the boys who have risked everything so we may live in peace.

Last-Minute Flashes FROM THE EDITOR'S DESK

CONSIDERABLE export demand for copper sulfate is anticipated—destination Italy and France, for use on potato and grape crops. No increase in productive capacity in this country is believed necessary.

★ Large quantities of fats are expected to move overseas to liberated parts of Europe, according to the Food Research Institute of Stanford University.

★ When the war is won in Europe, look for the lifting of most War Production Board controls except on chemicals, forest products (including paper, of course), and textiles. This seems to be WPB's plan at the moment.

★ October chemical allocations by WPB indicate little immediate easing in the over-all supply situation.

★ From a raw material point of view, ejection of the Japanese from the Philippines will mean large quantities of sugar, copra (coconut oil), and hemp; but considerable time will be needed to put the country back on the export list in a major way. Capture of the Philippines will mean denying Japan access to much of the spoils—rubber, tin, etc.—because we will bomb her shipping day and night.

★ The Office of Coordinator of Inter-American Affairs has just concluded an interesting survey of the Latin American market for industrial equipment—total, some 10 billion dollars. Scientific apparatus is listed at 111 million in the report; if the term is used as we generally understand it, this should mean a lot of research to the south of us.

★ The output of glycerol is such that diethylene glycol, propylene glycol, and noncrystalline sorbitol isomeric mixtures have been removed from allocation.

★ Vitamin A is reported scarce because of the shortage of high-potency livers. The output of synthetic vitamins continues to grow by leaps and bounds.

★ Considerable differences of opinion exist in Washington as to just how extensive industrial cutbacks will be after the defeat of Germany. One thing is practically certain: 1944 will be the peak production year. This means that we are rather close to the necessity for making a number of important decisions; despite the present slow progress on the western front, there seems to be optimism that Hitler will be defeated before the middle of December. Transportation is the biggest problem at the moment and will be corrected shortly.

★ Petroleum Administrator Ickes reveals that October output of aviation gasoline has exceeded requirements, permitting production of a new superfuel for B-29 and B-32 bombers.

★ Our present consumption of quartz crystals has jumped fifty times over prewar levels, with Brazil playing an important role.

★ According to J. A. Woods, president of Chilean Nitrate Sales Corporation, that company has negotiated with U. S. Government agencies to supply 850,000 tons of Chilean nitrate for the 1944-45 season; availability of ships is the only bottleneck in supplying still larger quantities.

★ "Postwar National Income" by Joseph Mayer (published by Bookings Institution) sounds a warning: "The widespread erroneous impression that the war has placed the American people upon a new plateau of national income is due to failure to take account of the abnormal current increase in wages, prices, and employment; also to confusion of thought and unsound statistical projections."



