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The photograph above shows two Dorr thickeners treating dust-laden waste waters from gas scrubbers connected with a blast furnace at the Cleveland plant of Republic Steel Co.

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INDUSTRIAL AND ENGINEERING CHEMISTRY
REPORTS
ON THE CHEMICAL WORLD TODAY

Technology

Concrete from Coral. Rock, sand, cement, and water are the essential materials from which concrete is made. The removal of any one of these ingredients would seriously handicap the construction engineers. The denial of two—in this instance, American rock and fresh water—would virtually forbid the mixing of concrete. This is what was threatened in Bermuda when the Government erected one of its most important outlying military bases.

Although American varieties of rock are not found in Bermuda, the islands abound in coral, the skeleton structure created by the tiny marine animal known as the polyp. Travelers have admired the beauty of coral in southern Atlantic waters and on the islands and atolls of the Pacific because the polyp is a marine architect of no mean ability. The concrete man, of course, was more concerned with the engineering qualities of coral, and it appeared highly probable that the constructors would have to use coral for the base. Coral is perforated with innumerable tiny holes; therefore it is highly absorbent and light in weight. Aggregates made with coral would have moisture-retaining properties which might introduce corrosion in the steel reinforcing.

Water was another problem because it is available in Bermuda only for household use. For this purpose rain is caught on whitewashed roofs and run into underground reservoirs. There would be none available for construction unless new catchment areas were built, which would require a great deal of time and labor. After a suggestion that water be imported had been vetoed, it was decided to use sea water. The National Bureau of Standards and the cement industry had conducted research on the use of sea water for mixing concrete, and on the basis of this work the engineers could proceed with at least some assurance. It was found that sodium and other chlorides in sea water would not induce corrosion. Sulfides might, but these are present only in minute quantities.

The contractors established a laboratory on the islands and experimented with many variations of the concrete formula. The objective was a high-impact-strength concrete for buildings, ammunition magazines, storage tanks, warehouses, and electrical conduits. A parallel line of investigation was conducted in the United States. Various mixes were made up with coral aggregates and sea water brought in from Bermuda and cured in the usual manner. These mixes were then compression-tested against concrete made from American granite and fresh water. This work and the trials conducted in Bermuda proved that good concrete can be made from coral aggregates and sea water.

Cement and water provide the mortar or binder which fills in the voids resulting from a mixture of stone and sand. Engineers in Bermuda obtained a considerable reduction in the water-cement ratio by including an admixture in their formulas, although as a rule such additions are frowned upon. The admixture is a pozzolanic compound (calcium lignosulfonate[1]); in this instance it reduced water requirements about 17%. It also facilitated control of the mixes, the setting of which was hastened unduly by Bermuda's wind and hot sun. Concrete, testing over 4000 pounds per square inch, was obtained.

The Bermuda military base project has given the construction industry an appreciation of scientific approach. By overcoming these serious raw material deficiencies, we were able to complete this essential link in our defenses shortly after we found ourselves engulfed in the cataclysm of the second world war.

Citrus Peel Oil. One of the problems in the industrial separation of citrus juices is to obtain maximum expression of juice without including any of the bitter oil from the skin. Mechanical juicers are adjusted to certain sizes of fruit, and variations in size or thickness of skin will either leave some of the juice or squeeze oil out of the skin. Peel oil deteriorates and may help to reduce the keeping quality of juice. A little oil is thought to improve the flavor. Too much oil, however, tastes unpleasant to most people and actually upsets digestion. Tests conducted at the University of Florida have shown that 85% of the people who were asked to choose between the flavor of juice from peeled oranges and juice to which 0.05% peel oil had been added (maximum for grade C—the limit for grade A is 0.03%) said they preferred the oil-free juice. (*Continued on page 8*)

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[1] Ernsberger, F. M., and France, W. G., Ind. Eng. Chem., 37, 598 (1945)

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

Ten per cent liked better the juice containing oil, and 5% could not tell the difference. But regardless of likes or dislikes, the added oil made everybody burp.

De-oilers have been used which give the juice a quick boil under vacuum with the object of removing the more volatile oil before the flavor essence starts coming off. But although the oil should theoretically be removed completely by a 1% distillation, a false equilibrium is encountered, and as much as 5% of the juice must be boiled off during this process. Some of the essence is recovered by returning the aqueous fraction to the juice, but the better solution is to avoid oil in the juice in the first place, especially since the de-oiling equipment costs nearly as much as the entire juicing plant. Efforts to avoid getting too much peel oil in the juice are largely centered on giving the fruit a 1–2 minute treatment in hot water. This softens the peel and allows the juice to be pressed out without breaking too many of the oil cells.

Citrus peel oil is in fair demand as a flavoring agent (its largest use is in beverages), but less oil is produced than could be; its recovery is more or less optional in canning operations for oranges and grapefruit. Lime oil at $12.50 per pound is a different story. Formerly all lime oil was distilled, but cold-pressed lime oil was produced in quantity for the first time only last year. Cold-pressed oil is obtained by squeezing the peel either on a screen or screw press and centrifuging the resulting emulsion. Distilled oil is recovered from de-oiling or from the concentration of press water to give a by-product molasses, but its composition is different from that of the pressed oil, and it brings a lower price.

A way around the comparatively low price for orange oil ($1.40 to $1.75 per pound) has been sought by one Florida canner who makes a concentrated oil. A 10 to 1 concentration removes most of the limonene, the terpene which constitutes about 90% of orange oil and is largely responsible for its instability. The concentrate keeps better than the original oil, and the limonene finds application as a perfume or odor killer in cheap soaps.

New Chemical Markets. It is possible for a large industry to penalize itself through its own efficiency and fail to find outlets for greatly expanded production. This is being witnessed to an extent in the petroleum industry. In addition to providing billions of barrels of fuels and lubricants for prosecution of the war, petroleum plants performed the astounding feat of supplying 3,001,496,000 pounds of organic chemical materials during 1944, about double the amount produced in the previous year. These war materials would be surplus during peacetime, if a large share were not finding a market which did not exist prior to 1939.

The products which figured largely in this total on a volume basis were toluene, xylene, ethylene, rubber-grade butadiene, 1-butene and 2-butene mixture, propane, and propylene. The industry is shutting down the production of toluene which was required in heavy volume for explosives. This will affect catalytic dehydrogenation and hydroforming plants which were making toluene chiefly, but similar units will remain in operation to supply marketable products.

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During the war blank spaces followed "toluene" in statistical compilations of chemical production, but we now learn from the United States Tariff Commission that it attained a production volume of 134,000,000 gallons last year, compared with 43,000,000 in 1942, and these figures do not include toluene made in plants under ordnance control. It is probable that all toluene production at the peak of the war effort was eight to ten times the amount supplied in prewar years through coke-oven sources. Considering its value as a solvent, especially in rubber manufacture, we may require annually more than the 25,000,000 gallons which were formerly consumed each year.

Through their demonstrated ability to provide raw materials for elastomers, the petroleum plants are assured of steady outlets for this purpose, provided national and international political influences are not permitted to handicap unduly our new rubber industry. Our synthetic needs for 1946 have been placed at 1,200,000 tons, an increase of 200,000 tons over the current year, and approximately 600,000 tons over what is considered our normal peacetime needs.

It may be necessary to suspend certain processes which have been converting butanes to butylenes for aviation fuel; but, to supply the base stock for synthetic rubber, *n*-butane and *n*-butylenes will still have to be made in some volume. These are processed into 1,3-butadiene, which attained the huge total last year of 488,945,000 pounds, an output expansion in only one year of 375%. The startling circumstance in connection with this is that butadiene was also being derived from alcohol, and that butylenes were being diverted into the production of high-test aviation fuel.

Here we have a large-scale illustration of the industrial resourcefulness which contributed to winning the war. Few people realize that as many as thirty thousand different rubber products were supplied to the Army and Navy, and that these had to be produced in large measure from man-made intermediate materials. Through catalytic processes were obtained the olefins, isoparaffins, aromatics, and other items upon which we are certain to establish new chemical and petroleum industries with undreamed of possibilities for the future.

Thermoplastic Laminates. Phenol-formaldehyde resins have been foremost in the field of laminated plastics. When they are used in combination with ordinary fragile materials such as paper, textiles, and thin strips of wood, products of almost unbelievable strength are obtained. Heretofore a large volume of the thermoplastics (principally cellulose acetate and ethylcellulose) have entered molding, film, and other products where their toughness and color possibilities could be utilized.

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More recently manufacturers of cellulosic resins have been engaged in an interesting line of research which may lead to the introduction of cellulose acetate and ethylcellulose in the lamination industry. One advantage is their ability to take a deep draw in forming operations. For example, roomy pieces of luggage may be formed in a press from cellulosic materials, and the suitcase will be light, strong, easy to keep clean, and sound deadening.

Before the close of the war a fuel tank was fabricated from cellulose laminations in teardrop design, and it was assembled without rivets, bolts, or gaskets. Blows from a sledge hammer failed to inflict any damage on this tank. The resin product has been found to possess a high energy absorption factor.

It is too early to forecast the exact turn which this newest plastics development will take, but sufficient research has been conducted to indicate that combinations of cellulose acetate or ethylcellulose with wood, paper, mica, Fiberglas, cotton, and nylon will find specific applications in a number of manufacturing lines. One distinct advantage which sets cellulose acetate apart from many other plastics is its property of taking a wide range of colors. This means that artistically executed prints on cotton and rayon can be permanently fabricated into the laminate. For pigmentation, dyes such as Luxol Fast Brown R or Pink may be combined with titanium, or carbon black with aluminum powder, etc. Phenolics and urea resins are somewhat restricted in this respect.

When cellulose resins are employed in conjunction with glass fiber or cotton duck, laminates of unusual strength and light weight result. A Pasadena manufacturer constructed, from the latter material and cellulose acetate, a five-passenger boat which weighed only 60 pounds. High elastic modulus and impact strength were obtained with glass fabric as a laminating material; asbestos paper gave an elastic modulus of close to 2,000,000. Generally, the cellulose laminates appear to have excellent electrical characteristics.

Thermoplastic laminates, on the other hand, possess characteristics which may disqualify them for many other industrial uses, for which the phenolic and urea materials are better suited. It is a promising new line of development in an industry which is constantly and restlessly moving forward.

Preview of a Revolution. Chemistry's contributions to textiles have been glamorized and publicized with lavish abandon in the past, but there is much more to come. We have already paraded mannikins attired from head to foot with exciting test tube creations, against which the vaunted Queen of the Nile was a very plainly dressed person. Postwar now finds manufacturers and stylists getting out a new series of fabrics from synthetic fibers which strongly suggest that we are witnessing a large-scale revolution in textiles.

Satins never seen before, manufactured from acetate, have just made their debut. According to the dictionary, satin is "A silk fabric of thick texture

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with glossy face and dull back", but the chemist and his style-conscious following will have to rewrite that definition somewhat. Acetate is entering one synthetic satin that is "fluorescent gold and rose striped". In a more serviceable role it finds inclusion in a foundation garment, and in still another acetate application the satin is "two-faced gold and platinum".

Some half dozen other synthetic fabrics have been introduced at the same time. Fine-denier viscose rayon of multifilament type has been made into underwear fabric with silklike qualities. Techniques for combining fibers have been developed along new lines. A taffeta of very fine-denier acetate also includes some nylon in the warp. Viscose rayon of the same fine construction is combined with acetate, and the result is an unusual satin. The finest denier acetate rayon yarn is twisted with 50-denier Cordura rayon, and a new material becomes available for evening gowns and lingerie. These combinations are considered triumphs in fabric construction.

The fibers have come home from the wars to take up permanent and more profitable civilian outlets. Nylon's long-chain molecules of amine and carboxyl groupings, capable of many variations, evidently will find many fields of service outside of hosiery. Nylon is a tough crystalline material, yet soft threads may be made from it for wool-like materials such as socks and sweaters.

Vinyon, a copolymer of vinyl chloride and vinyl acetate, can be supplied in filaments which are finer than silk. A yarn of the stuff consisting of 10 filaments measures only 8 denier. One of its remarkable properties is flexibility. In one form Vinyon achieves 100% recovery after stretching; hence, it is not hard to visualize applications which call for that property.

Vinylidine chloride appears to have lost the coarseness which characterized its fabrics before the war. Those now manufactured for automobile upholstery are finer and softer, also stain resistant and durable. Vinylidine chloride filaments have tensile strength ranging from 40,000 to 20,000 pounds per square inch.

In the field of protein fibers, there is every justification to look for constant improvement in manufacturing properties. The casein product in the past has had one drawback—lack of strength. It possesses, however, the resilience and warmth of wool, and more recently a fiber has been developed that is finer than the natural product.

New exploratory work has been resumed in textile materials with some significant results. British research conducted in rayon from alginic acid, a product of dry seaweed, may provide us with another fiber of long-chain molecules. Three mills in China are manufacturing a cloth from grass with greater tensile strength and resiliency than cotton.

But what may prove the greatest textile development since the power loom is taking place in a plant in Milltown, N. J. There, textile technicians have succeeded in turning raw cotton into fabric cotton without spinning or weaving. It is not done with mirrors but with a resin binder. The resin holds the fibers in place instead of friction.

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

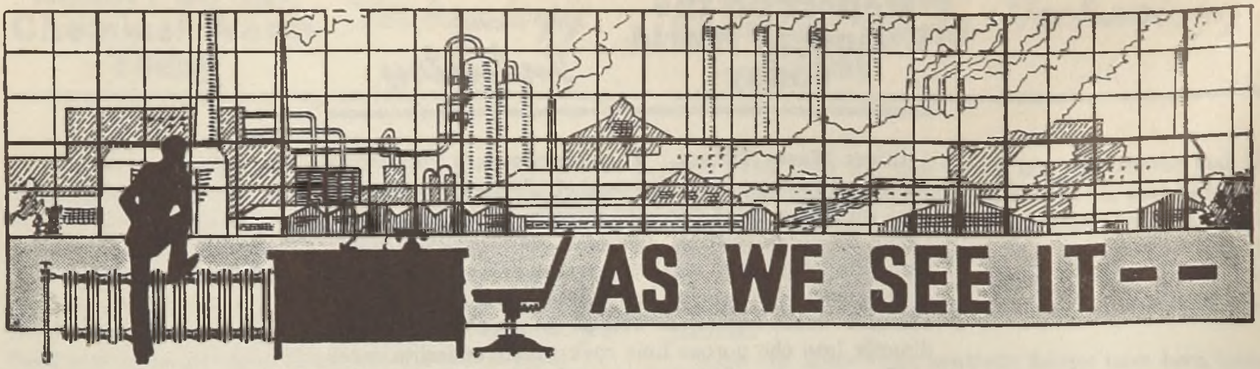
Commerce and Industry

Citrus Waste Waters. The waste waters from citrus canneries were originally disposed of, like any other industrial waste, by being run into streams or settling ponds. Odors of decomposition, however, soon caused trouble with the neighbors, and better disposal was required. Underground disposal has been employed in a few cases in Florida; waste waters (as well as sewage) were pumped directly into the porous lime rock which underlies most of the peninsula. But this was stopped when well water began to taste, and methane, formed by fermentation underground, ignited, blew out wells, and broke out from fissures at the surface. Even today, several years after this practice has been stopped, gas traps are utilized on certain wells in the citrus belt.

Controlled fermentation has since been used as a means of rendering the more dilute waste liquors safe for disposal, and the recovery of yeast solids is presently being considered as a protein supplement for stock feed. It has been found practical to concentrate the waste water containing the highest solids (8%), press liquor from rind dewatering, to a molasses containing 70–80% solids. Much of this molasses has been used for stock feed, but during the war when any source of carbohydrates was exploited, some of it was used by distilleries as the basis for neutral spirits. Although the price of about thirty dollars per ton for citrus waste molasses represents considerable inflation, it is expected that the inevitable drop in price will not materially affect its production because of its importance to waste disposal.

Swords and Plowshares. Despite the huge increase in catalytic cracking capacity during the war, peace found United States refiners, who represent 42% of the nation's crude capacity, with no catalytic processes at all. These were mostly operators who had a capacity of less than 10,000 barrels per day. As such they represented an uncertain market for the sale of most catalytic units which, as a rule, are not designed to handle less than this amount daily. During the war period, over a million barrels of daily capacity were installed, and, in the opinion of petroleum men, this represented an expansion which normally would have taken fifteen years. To those refiners having installed catalytic capacity, the postwar holds no specters, for they can make a high-premium motor fuel for competitive purposes. It is the smaller manufacturer who would have felt the pinch.

Knowing this, the Houdry Process Corporation and the Lummus Company have been working on a small TCC unit to meet the requirements of a small refiner and have recently come up with equipment that efficiently refines about two or three thousand barrels of crude per day at a cost comparable to the larger units. This was possible owing to savings in construction—integral elevator design for the spent and regenerated catalyst, elimination of vapor superheaters by increasing catalyst rates, and smaller structures for supporting the equipment. By utilizing equipment already available, costs of complete installation for high octane are said to be economical.



Materials of Construction. The war introduced a new catalyst to the petroleum industry—hydrofluoric acid—and at the same time brought corrosion headaches never before experienced either in rate of attack or in materials affected. Few data were available at the time, because, as the authors (M. E. Holmberg and F. A. Prange of Phillips Petroleum Company) point out, practically no commercial experience with the substance under pressure existed. Considerable pilot plant work was instigated, and data were obtained; naturally at the time the data were not circulated indiscriminately to the chemical engineers of the country. Now experience has been gained through the commercial units, and the article "Corrosion in Hydrofluoric Acid Alkylation" proves to be an exhausting survey of suitable and nonsuitable materials. We learn that carbon steel is the basic material for construction of pressure vessels when the acid is held at low temperatures. However when the B.t.u.'s are applied, alloys of copper and nickel are prescribed. Certain materials should not be used, and reading the article will add much to your knowledge of hydrofluoric acid attack. Then, too, there is the explanation of the peculiar fact that threaded pipe must be avoided.

Softwood Cellulose. Lovell, of Rayonier Incorporated, begins his paper on fibrous holocellulose from softwoods with the agreeable observation that, to understand the ultimate uses of cellulose from wood, fundamental knowledge is necessary. With that in mind he examines the problem of making wood cellulose in fibrous form from two representative American softwoods, hemlock and slash pine. For some time it has been considered much more difficult to do this than to make wood cellulose from hardwood. Lovell, however, describes a method of obtaining cellulose in close to theoretical amounts, and he concludes that such a material deserves further study.

Making Antimalarials. Quinacrine hydrochloride was required in huge quantities when the war demand for antimalarials got underway. One of the manufacturers, Eli Lilly and Company, report now on improvements in the manufacturing process for making it. When this paper was originally submitted to us, for reasons of national security the censor decided it would have to be held from publication. Now here it is, lock, stock, and ether extraction, from the acridine compound to the crystallization, with comments about hydrochloric corrosion of the equipment. See Jones, Shaw, and Waldo.

Exacting Extracting. Butadiene for use in synthetic rubber manufacture had a rather high purification specification, and two major methods were worked out during the war period to meet this requirement. However these procedures could be improved, and Smith and Braun, of the Blaw-Knox Company, wade right into the problem and examine several solvents to solve it. Economic laws, which are written in red and black inks, determine the problem in the last analysis. It is studies such as this that will keep our synthetic industry alive.

Plate, Mal, or Needle. Pressing and sweating to make an oil-free wax are, according to Ferris and Cowles of the Atlantic Refining Company, the two ancient and proved methods which give no indication of being displaced. Old as these methods are, trouble develops often in the manufacturing processes, and for years explanations for the peculiar behavior of wax have been made without correcting the difficulties. Basic to correcting the faults is knowledge of why a batch goes wrong. With the help of microscopes and photomicrographs, the authors arrive at a theory about the crystal behavior of waxes which, if methods of throwing down the proper form are developed, may solve the production headaches.

Catalytic Mathematics. The newer and more important catalytic processes have vast unexplored and unknown areas which experimental and mathematical techniques have yet to touch. Hulburt, of Hunter College, analyzes kinetically certain heterogeneous reactions in continuous flow systems and comes out with certain dimensionless ratios for estimating the effect of diffusivity on yield.

War Problem. Preventing the rotting of military materials became a major problem to manufacturing concerns which shipped supplies to the hot, steamy Pacific jungles. Impregnating certain parts with fungicidal waxes was standard technique, but was accompanied by various problems to be solved before it could be a commercial success. The way these barriers were scaled is told in "Mercurial Fungicide Wax Problems" which comes from the Belmont Radio and Biwax Corporations.

New Polymer. Cumene (isopropylbenzene) was an important addition to high-octane gasoline. Now, with the slackened demand for this powerful fuel, new processes are appearing for the utilization of installed capacity. One of these is described by Hersberger, Reid, and Heiligmann, of the Atlantic Refining Company, who, by dehydrogenating the cumene, obtain low-cost α-methylstyrene. The product promises to become an important plastic or elastomer. Its successful adoption required a new method of polymerization of α-methylstyrene and the authors trod new fields.

Alcohol from Wheat. It must startle our enemies to witness the efficiency which is carried out in every phase of our war production. We carry a study from Thorne, Emerson, Ilson, and Peterson, of the University of Wisconsin, on the evaluation of malts for the production of alcohol from wheat. They find that knowledge of the amylase content of a malt is necessary but not completely adequate for the accurate evaluation of its fermentation possibilities.

With the Departments. Instrumentation of commercial importance often develops from the adaptation of laboratory mechanisms, and this month Munch tells us about two of the most recent—an automatic recording gage for low pressures and an ionization gage. Murdock notes that in water-starved areas the effluent from trickling filters makes good process water for industrial uses. Von Pechmann finds that issuing company manuals is conducive to good will, and that they cause benefits to accrue in excess of those originally intended. Brown, tackling the problem of disposal of government plants, brings out several strong arguments for their retention.

INDUSTRIAL AND ENGINEERING CHEMISTRY
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Editorials

WALTER J. MURPHY, EDITOR

Adequate Funds Urgently Needed if Dissemination of German Scientific Data Is to Continue

THE machinery recently set up in Washington to disseminate technical and scientific data gathered by American intelligence groups in Germany urgently requires oiling in the form of an adequate appropriation by Congress. Otherwise the dissemination of this valuable information to industry will grind to a slow stop with the result that plans for helping both large and small business and the creation of new jobs for returning veterans and former war workers will be hampered to a considerable degree.

Executive Orders 9568 and 9604, the first issued on June 8 of this year, the second on August 25, by President Truman, set up the administrative machinery for the release of scientific information considered secret during the war. They provide not only for the release of domestic data, but also for those found and reported on in the occupied zones of Germany. The office of the Publication Board is composed of John W. Snyder, chairman, Henry A. Wallace, vice chairman, and John C. Green, executive secretary. The American Chemical Society, through the action of its Board of Directors, has fully approved the purposes of the Publication Board, and has appointed a committee to consult with its executive secretary and other officials.

To help disseminate the information, our Directors have instructed that "the Secretary cause to be published in existing journals of the Society or in supplements thereto or in separate pamphlets, as may be practicable or desirable, lists of all reports from those who have examined enemy industry or scientific developments, indexes thereto, and abstracts thereof, in so far as they are available through government agencies and to distribute this material at cost if it appears inadvisable or undesirable to disseminate such information through the journals of the American Chemical Society; that a sum not to exceed ten thousand dollars be and is hereby authorized for the purpose. . . ."

The preliminary meeting of the Society's committee with an official of the Publication Board showed that the administrative workings of such an agency would be vast and extended, and the Government, through an emergency appropriation, has allocated a small sum of money to begin the necessary operations. Charles L. Parsons, Secretary of the Society, sent to John W. Snyder, chairman of the Publication Board, a letter informing him of the action of the Board of Directors of the Society and urged immediate action so that all such scientific information would be opened to American industry at the earliest possible moment.

At the time the project was originally discussed with American Chemical Society officials, it was thought that the scientific documents and original data now scattered widely in London, Paris, and Germany could be transported to this country and reproduced in one of the many ways usually employed. It was felt that this particular phase of the work could be done most easily in cooperation with societies such as ours. However, certain obstacles have developed, one being that prior agreement with our Allies prevents any original documents from being taken out of the various zones of occupation. Of course, because of this agreement original research documents and data in occupied zones other than our own will be available to our scientists. This makes the problem much more difficult. Instead of using the facilities available in this country, we must set up complete reproduction equipment with the necessary expert staff, in British and American occupied zones and in England, France, and Germany.

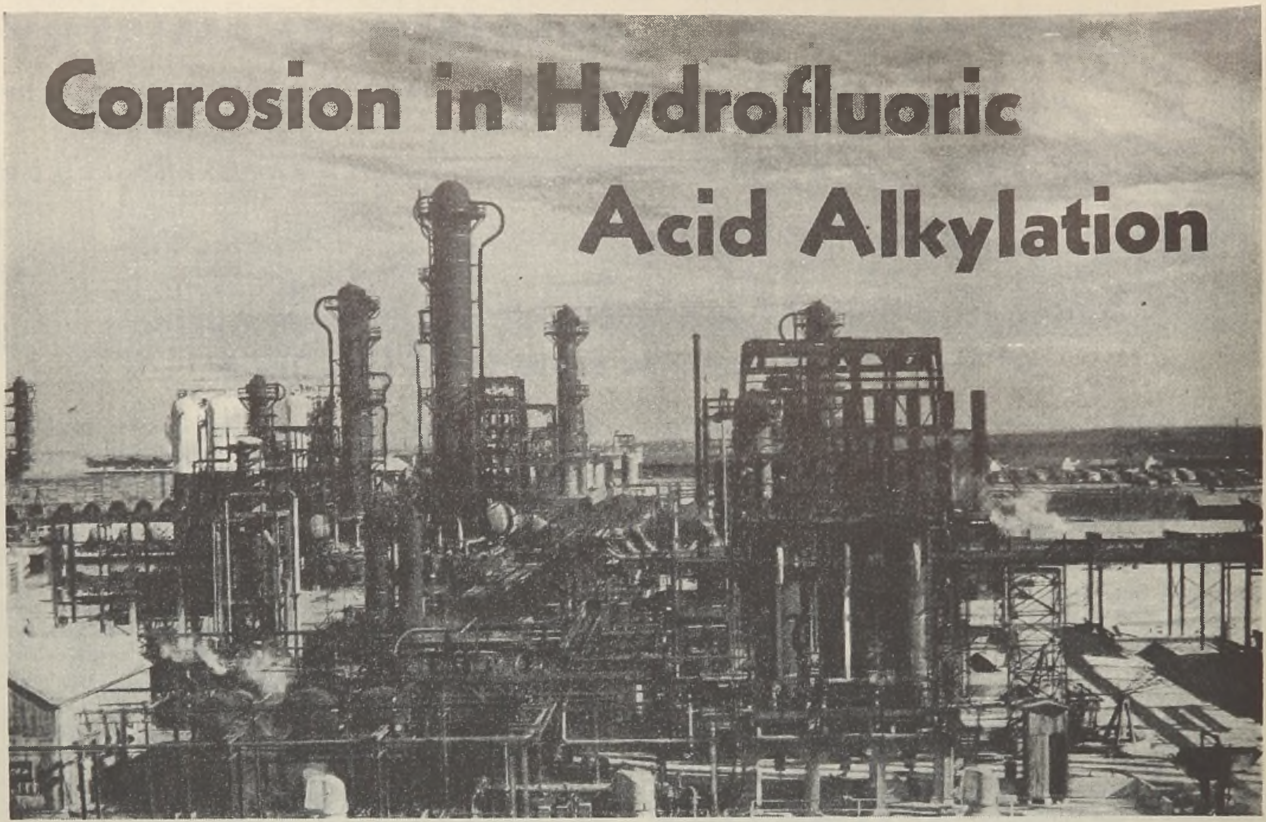
Consequently the original estimate of how much this program would cost is far too little, and soon to come before Congress is the request of the Publication Board for additional funds. This should be granted. American industry will gain much if the data of our enemies are made easy to procure, and it will be one of the few positive gains of the war of which we can be certain. Germany has advanced far in fields which were, to her, wartime necessities, and there is a vital need for our scientists to become cognizant of, and easily familiar with, these developments.

The necessity for funds can be understood better when it is realized that this same administrative board will dispense to industry all the data resulting from our domestic war efforts in scientific fields. This will be a prodigious undertaking, and if we are to guarantee that these research efforts are not lost we must record them for all posterity. To do this will require swift and positive implementation of the executive orders. If the board is to function, Congress must appropriate adequate funds and should recognize the necessity for their continuation as the war years recede.

This is probably one of the biggest publishing ventures of all time, and if carried out properly, it will make available to every company, large and small, and to every individual this huge block of crystallized knowledge which represents the investment of billions of dollars in research work. It would be most unfortunate if all the brilliant work of our scientists during the war years, and the tremendous investments of money and energy of the intelligence teams, were lost forever because Congress failed to make a generous appropriation.

We must have a positive program, the machinery and functioning of the executive orders must be smooth, and there should be no hesitancy or doubt about the paramount importance to our civilization of making these data freely available. We believe Congress, once it fully understands the importance of this work, will cheerfully appropriate adequate funds. Something in the neighborhood of two million dollars will be required for the next fiscal year. This is indeed a small expenditure when we remember what irreplaceable information of a scientific nature will be made available to American industry.

Corrosion in Hydrofluoric Acid Alkylation



Hydrofluoric Acid Alkylation Unit

M. E. Holmberg and F. A. Prange

PHILLIPS PETROLEUM COMPANY, BARTLESVILLE, OKLA.

The number of desirable materials of construction for anhydrous hydrofluoric acid service is comparatively small. Carbon steel is the basic material and is adequate for pressure vessels up to a temperature of approximately 150° F.; Monel metal or Monel-clad steel is the desirable material for higher temperatures. Cupronickel might be particularly suitable in heat exchanger tubes. Monel metal is the desired material for valve trim in severe service. Materials to be avoided can be divided into three classes. The first class is made up of straight chrome stainless steels and copper alloys (except cupronickel), which are velocity sensitive in anhydrous hydrofluoric acid and in high concentrations of the acid. The second class, materials which may be attacked by intergranular corrosion, includes Hastelloy A and Hastelloy B, cast iron, and high-zinc uninhibited brasses. The third class, materials used for piping and fittings that are brittle or notch sensitive, includes free-machining steel, high-phosphorus steel, and others of similar properties.

THE war, with its tremendous demands for aviation gasoline, was instrumental in adding a new corrosive agent to refinery problems—hydrofluoric acid. Because there was little commercial experience with hydrofluoric acid under pressure, considerable pilot plant work was done before the first commercial HF alkylation unit was built. As a result of both the pilot plant work and more than two years of experience in operation of commercial HF alkylation units, this company has accumulated extensive data on corrosion of metals in hydrofluoric acid. This article presents some of the metallurgical information gained from this experience.

Corrosion in hydrofluoric acid involves typical oxidation and reduction phenomena—hydrogen evolution, oxygen, and sometimes galvanic currents. In most cases the process seems to be reduction of hydrogen to molecular hydrogen, while the fluorine combines with the metal to form metallic fluorides. Hydrogen is observed by the increase in pressure of a closed bomb. Oxygen greatly increases the corrosion rate in aqueous hydrofluoric acid.

Corrosion testing in hydrofluoric acid is complicated by several factors. The duration of test plays a vital part in the measurements of corrosion rates. All metals tested in anhydrous acid, with the possible exception of silver, form protective films or scales that decrease the initially high rates to the low rates observed in commercial use. This means that short-time corrosion rates should be discounted unless the scale formed on the test sample is of appreciable thickness or unless the validity of short-time rates has been confirmed by longer tests. After a scale has formed, diffusion through the scale plays a larger part in the corrosion than the initial rate of reaction on clean metal. When the scale reaches a certain thickness, it begins to flake off, and the corrosion approaches a steady rate.

The effect of time is noticed in another way. Some materials such as aluminum and stainless steels form a very protective film under atmospheric conditions. When they are subjected to hydrofluoric acid, the film protects them for a short while. Not until the film has been completely penetrated does the true corrosion rate appear.

Temperature also plays an important part. As temperature increases, the reaction rate likewise increases. But, as pointed out above, diffusion may be a deciding factor in many cases. Steel and copper are particularly affected, and at very high temperatures (above 200° F.) neither material is satisfactory. The rate of corrosion of Monel metal and cupronickel also increases with temperature, but not nearly so rapidly as the corrosion of the above-mentioned materials.

Increase in velocity of hydrofluoric acid streams over the surface of some materials may increase their corrosion rate. The main material of construction—plain carbon steel—is comparatively insensitive to velocity, but materials such as 12-chrome stainless steel and copper are very sensitive. Under these circumstances, laboratory tests with quiet or low-velocity streams need confirmation from plant experience, such as may be obtained on pumps, bubble caps, and throttling valves.

CORROSION TESTS

Early experiments to determine corrosion resistance were made in the laboratory, using both agitated and unagitated bombs filled with anhydrous hydrofluoric acid or mixtures of various hydrocarbons with the acid. The laboratory work demonstrated that corrosion was not noticeably affected by the presence of moderate amounts of hydrocarbon. Hence, correlation with the hydrocarbon-acid ratio was not attempted. Some tests were made in laboratory reactors. While some of the low-temperature tests were made with samples insulated from one another by Saran and polystyrene, tests at elevated temperatures could not be made with insulated racks because of decomposition of insulating materials. In order to confirm data obtained with uninsulated racks, a few tests were made in which the acid dripped over the samples and was thus prevented from forming an electrically conducting continuous phase. No significant difference was found in corrosion rates in tests conducted with insulated or with uninsulated samples.

Field tests were made by circulating acid and acid-hydrocarbon mixtures through test chambers in which the samples were suspended on metal bars. This apparatus was used to determine simultaneously the operating characteristics of valves, pumps, pump packing, etc. Tests on aqueous acids were made in steel and copper reboilers. Since this field test equipment was not equipped to maintain a constant temperature, corrosion rates could be obtained only for a range of temperatures. The corrosion results can accordingly only be grouped; but within the range of error ordinarily experienced, the data are very consistent.

Table I shows the results of tests, lasting 6 to 40 days, on some of the materials tested in essentially anhydrous hydrofluoric acid and in acid-hydrocarbon mixtures. Where only a single temperature is given, the test temperature was closely controlled.

Tests were also made in aqueous hydrofluoric acid of approximately 40 to 50% concentration. Results on the various copper alloys were similar, and no particular alloy had a consistent advantage. The uniformity of results from one test to another indicates that bimetallic corrosion between the various metals exposed was not great. Eight to twenty-one day tests on copper, red brass, antimonial admiralty brass, cupronickel, phosphor bronze, and 444 bronze gave rates varying from 0.0125 to 0.0250 inch per year at 275–300° F. Monel showed a slightly greater corrosion rate, 0.0296 inch per year average. These data were confirmed by tensile-strip corrosion samples. In all, five tests were run in this range. Three others had to be eliminated because air, used to pressure in the acid, caused excessively high rates of corrosion.

At 185° F. two tests on copper, red brass, antimonial admiralty brass, 30% cupronickel, silicon bronze, Ambrac (70 copper–25 nickel–5 zinc), and 20% cupronickel gave rates varying from 0.0006 to 0.0040 inch per year in tests lasting 18 days. Two 11-day tests at 140° F. gave comparable results. Magnesium alloys (Dow metals E and J) had corrosion rates varying from 0.024 to 0.016 inch per year.

The corrosion rate obtained from weight loss does not always give a complete picture of the phenomena involved. Intergranular corrosion, for instance, may cause the material to lose all of its strength without perceptible weight loss. Further metallurgical examinations are often necessary.

GRAPHITIC CORROSION. Several samples of Ni-Resist cast iron exposed to anhydrous hydrofluoric acid showed graphitic corrosion, a manifestation of galvanic corrosion in which the graphite is unattacked while the iron is completely corroded. The specimens swelled and cracked but still maintained their identity, although the material could be cut with a knife.

DENICKELIZATION. This type of corrosion occurs on Monel, and to a lesser extent on cupronickel, upon exposure to aqueous hydrofluoric acid. Scaly layers of copper in severe cases and thin adherent films in milder cases form on the surface. Some pitting may be present. The most severe denickelization was observed on samples included in tests in which the acid was pressured into the vessel with air. This and other supporting observations lead to the belief that denickelization is caused by the presence of oxygen.

INTERGRANULAR CORROSION. Samples of Hastelloy A and Hastelloy B exposed to aqueous hydrofluoric acid for 3 days (pressured in with air) suffered severe intergranular corrosion; that is, the grain boundary material corroded away and left individual grains to drop out. After exposure these particular samples had the characteristics of a lump of sugar rather than of a piece of metal.

STRESS CORROSION. Tests were made to determine whether stress corrosion could be induced in low-carbon steel and in 18–8 stainless steel. Pieces pulled in two under tension and then

Cavitation Corrosion of a 12-Chrome Stainless Steel Impeller after Four Months of Service in Anhydrous Hydrofluoric Acid

Cracking of Hardened Steel in Anhydrous Hydrofluoric Acid; These Pieces Are the Fragments of a Valve Plug

Intergranular Corrosion of Hastelloy A in Aerated Aqueous Hydrofluoric Acid (X 250)

Peculiar Pitting Accompanying Denickelization of Monel by Aerated Aqueous Hydrofluoric Acid (X 200)

dented with a ball peen hammer were exposed to anhydrous hydrofluoric acid at 150° F. for one week. No intergranular corrosion resulted, nor was the rate of corrosion higher than on the unworked samples. However, in aqueous acid, cold-worked 18–8 did show stress corrosion.

CORROSION ON EQUIPMENT

Examination of equipment used in commercial hydrofluoric acid alkylation and pilot plant work added valuable information on corrosion. From such examinations it is possible to determine the extent of galvanic corrosion, the effect of velocity, etc. Frequent inspections were made on pilot plant equipment and any extraordinary occurrences followed in detail. Plant equipment, in particular, determines the validity of the corrosion tests.

EFFECT OF VELOCITY. The experimental pumping unit brought out the important fact that 12-chrome stainless steel was sensitive to the velocity of liquid flow. After 4 months of anhydrous service at atmospheric temperature, a 12-chrome stainless impeller was badly pitted by cavitation attack. The carbon steel impeller used to replace it was unattacked by cavitation after a longer period of use. This characteristic of 12-chrome material was further confirmed by the rapid corrosion and erosion of 12-chrome disks in gate valves and motor valves. Hence, it is concluded that 12-chrome stainless is unsatisfactory for hydrofluoric acid service because of its sensitivity to velocity.

Copper alloys are similarly unsuited for service in high-velocity streams of the anhydrous acid. Laboratory equipment demonstrated that yellow brass, copper, brazing bronzes, and low-silver silver solders were rapidly corroded away. An acid bubble tower, operating at approximately 150° F., contained experimental bubble caps of Monel, silicon bronze, and copper. In 4 months of operation the teeth of some of the copper caps were corroded off. Silicon bronze was also badly corroded but slightly less than the copper. Since the original thickness was 0.083 inch and the final thickness nil, the corrosion rate was more than 0.12 inch per year. The Monel caps were practically unattacked.

In another unit the acid bubble tower had one Everdur (silicon bronze) tray, 0.128 inch thick, with caps of the same material; after approximately 8 months of operation, the caps and trays were almost completely destroyed by corrosion. Still another instance of failure was on antimonial admiralty brass used in an acid preheater operating at approximately 190° F.; the tubing was badly pitted in only 2 months by what was probably a cavitation type of attack.

Cupronickel differs from the other copper alloys in that it is not similarly affected. This was noted when cupronickel was used in conjunction with copper and brazing bronzes. Experience has shown that most copper alloys, with the exception of cupronickel, are not satisfactory in high-velocity streams of anhydrous hydrofluoric acid.

CORROSION OF STEEL EQUIPMENT. Correlation between corrosion tests and corrosion observed on commercial plant and laboratory equipment has been good. On the low-temperature parts of the hydrofluoric acid equipment, thickness of scale, machining marks, and undulations on the welds all indicate a rate of corrosion not exceeding 0.01 inch per year. The acid bubble tower in the section handling nearly anhydrous hydrofluoric acid at about 150° F. shows corrosion on steel to be about 0.03–0.05 inch per year. In all of the equipment in use no instance of stress corrosion has yet appeared. None of the field welds in piping and vessels were stress-relieved, and it is believed that evidence of stress corrosion would have been detected over two years of operation had any been present. Pitting has been notably absent on the steel equipment.

SEASON CRACKING. Yellow brass copper tubing fittings, which are quite commonly used in laboratory work, are very susceptible to this type of intergranular corrosion. Cracks appear in a short

TABLE I. CORROSION RATES ON ALLOYS IN ANHYDROUS HYDROFLUORIC ACID

Temp., ° F.	Rate in Inches per Year: Plain Carbon Steel[a] High	Plain Carbon Steel[a] Av.	Monel Metal High	Monel Metal Av.	Phosphor Bronze[b] High	Phosphor Bronze[b] Av.	Antimonial Admiralty High	Antimonial Admiralty Av.	30% Cupronickel High	30% Cupronickel Av.	Mg (Dow Metals E & J) High	Mg (Dow Metals E & J) Av.	Aluminum High	Aluminum Av.
60–80	0.0048	0.0028	0.0036	0.0032	0.02	0.02	0.01	0.01	0.0070	0.0020	0.0199	0.0052	0.0228	0.0204
80–100	0.0083	0.0062	0.0018	0.0009	0.0188	0.0188	0.0188	0.0128	....	....	0.0234	0.0171	....	....
100–120	0.0267	0.0140	0.0047	....	....	....	....	....	....	....	....	....	....	....
130	0.0270	0.0140	....	....	....	....	....	....	....	....	0.0000	0.0000	....	....
150	0.0296	0.0247	....	....	....	....	....	....	....	....	....	....	....	....
175	0.048	....	....	....	....	....	....	....	....	....	....	....	....	....
180–190	0.129	0.089	....	....	0.06	0.06	0.02	0.02	0.01	0.01	....	....	0.976	....
250–300	0.120	0.105	....	....	....	....	....	....	....	....	....	....	....	....

[a] These rates are also true for low-alloy steels such as carbon-molybdenum and S.A.E. 4140.

[b] 4.75 tin–0.25 phosphorus–95 copper. This is representative of results on copper alloys with high copper content such as pure copper, aluminum bronze, silicon bronze, and 444-bronze. Red brass is intermediate between admiralty and bronze.

time after exposure to hydrofluoric acid and may appear in as little as one hour when the temperature is raised to 150° F. The remedy is to use tin bronze, aluminum bronze, silicon bronze, red brass, or 70 copper–29 zinc–1 tin type of brass, which are much less subject to stress cracking.

Monel Metal. This alloy is widely used in our laboratory work on hydrofluoric acid. Considerable experience has shown that corrosion is only slightly increased with increasing temperature in the range 100° to 200° F. The use of Monel in impellers, stators, shafts, and laboratory columns has been very satisfactory. The weldability of Monel makes it an easily fabricated nonferrous material. Plant experience has also been favorable. Monel bubble caps and linings operating at 150° F. are attacked only slightly. Some leaky welds are, however, experienced. Monel trim in various types of valves has been very satisfactory.

Cupronickel. Laboratory work with cupronickel at temperatures up to 200° F. indicates that it is satisfactory for use with hydrofluoric acid. Its good resistance to aqueous acid makes it a desirable material when the service conditions vary from aqueous to anhydrous acid.

Lead. This metal corrodes rapidly in the anhydrous acid. Its plastic properties, however, make lead gaskets convenient for laboratory equipment. Their use should be restricted to short-time runs, particularly until operators become familiar with their characteristics.

Silver Solders. In direct contact with anhydrous hydrofluoric acid, particularly when exposed to high velocity, low-silver silver solders corrode rapidly. For exposure to severe service in laboratory equipment, A.S.T.M. Grade No. 7 silver brazing alloy has proved satisfactory.

Blistering. Blisters, presumably caused by hydrogen, were found on the acid settler, stripper feed tank, stripper overhead accumulator, and inner contactor shell after 16 months of service. The blisters varied in size up to $^3/_4$ inch in diameter and were under high pressure. The inner contactor liner was most severely blistered. No blisters have been found in the seamless steel pipe, which is usually made of a fully killed steel. This indicates that the dirtiness of the semikilled pressure vessel plate is a large factor in blistering.

Embrittlement. Upon exposure to aqueous acids, such as hydrochloric or sulfuric, some steels, particularly hard spring steels, become so brittle that they crack instead of deforming when highly loaded. There is evidence that this is true also of hydrofluoric acid. Hardened alloy bolts, springs, lock washers, and plug valve plugs have cracked in a brittle manner when exposed to anhydrous and aqueous hydrofluoric acid. This type of failure has not been detected in the soft unhardened steels. Where strong alloy materials are required, materials like K-Monel and hardened nickel should serve well.

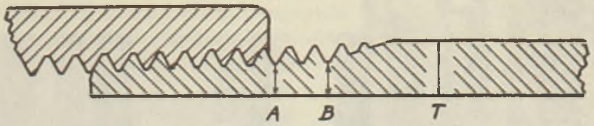
OTHER METALLURGICAL CONSIDERATIONS

Threaded Pipe. In early laboratory and pilot plant tests several failures were experienced at the threaded joints in small size pipe. Several factors were found to contribute to the failures. The first was the extremely thin metal section at the root of the last engaged thread in standard weight pipe. Table II gives a list of wall thicknesses. It is evident that very little metal is left to resist corrosion.

A second factor concerns the impact characteristics of threaded pipe. V-threads present a rather severe notch at their base. Combined with the thin wall of schedule-40 pipe, this factor makes it subject to failure under impact bending loads. Where the force moment is the greatest (at the last engaged thread), the pipe is the weakest.

A third cause of failure is the use of notch-sensitive material like high-phosphorus or Bessemer steels. They may be expected to give trouble, particularly on cold days.

Table II. Wall Thickness of Threaded Pipe Joints[a]



Nominal Pipe Size, Inches	Thickness[b] in Inches: Schedule 40 (Standard Weight) T	A	B	Schedule 80 (Extra Strong) T	A	B	Schedule 160 T	A	B
$^1/_8$	0.068	0.033	0.038	0.095	0.060	0.065	...	...	...
$^1/_4$	0.088	0.031	0.044	0.119	0.062	0.075	...	...	...
$^3/_8$	0.091	0.036	0.047	0.126	0.071	0.082	...	...	...
$^1/_2$	0.109	0.039	0.052	0.147	0.077	0.090	0.187	0.117	0.130
$^3/_4$	0.113	0.043	0.056	0.154	0.084	0.097	0.218	0.148	0.161
1	0.133	0.045	0.063	0.179	0.091	0.109	0.250	0.162	0.180
$1^1/_4$	0.140	0.052	0.070	0.191	0.103	0.121	0.250	0.162	0.180
$1^1/_2$	0.145	0.056	0.075	0.200	0.111	0.130	0.281	0.192	0.211
2	0.154	0.064	0.084	0.218	0.129	0.148	0.343	0.253	0.273

	Double Extra Strong		
$^1/_2$	0.294	0.217	0.237
$^3/_4$	0.308	0.230	0.251
1	0.358	0.263	0.288
$1^1/_4$	0.382	0.286	0.312
$1^1/_2$	0.400	0.304	0.330
2	0.436	0.346	0.366

[a] The calculations were made from the dimensions as given in Am. Standards Assoc. Standard B2.1—1942. Eccentricity and undercut weld (in lap-weld and butt-welded pipe) will still further reduce the effective thickness at the threaded joint. In practice, the minimum expected thickness should be somewhere between the *A* and *B* dimensions. Because of stress concentration, the resistance to impact of the small sizes is less than is indicated by comparison of wall thicknesses with pipe of larger diameter.

[b] *T* = wall thickness of unthreaded pipe; *A* = thickness at root of thread at the normal hand engagement; *B* = thickness at root of the last perfect thread.

To minimize failures, threaded joints should be avoided wherever possible; but if they are required, schedule-80 or schedule-160 pipe should be used. In addition, notch-sensitive metals should not be used.

Bull Plugs and Swage Nipples. A somewhat similar problem to that of the threaded pipe is found in connection with the ordinary bull plugs and swage nipples. These, however, are so brittle that failure is not confined to the threads. More than ten failures, only two of which were in hydrofluoric acid equipment, received attention. In all cases they were made of a high-phosphorus, high-sulfur, free-machining steel which has little ductility in the transverse direction. This has necessitated the use of special A.I.S.I. 1020 steel fittings. It should be pointed out that these brittle fittings are dangerous, not only in hydrofluoric acid equipment but elsewhere in a refinery.

A simple test will distinguish between good-quality and extremely bad fittings. A ring cut from the free-machining fitting will snap after only a small amount of flattening and practically no elongation. A good quality steel, such as is usually found in low-carbon seamless pipe, will crush almost completely, and the steel will tear rather than snap.

Butt-Welded Pipe. Two failures have occurred in butt-welded pipe in experimental work on hydrofluoric acid. One was in a 2-inch-diameter bomb which burst at moderate pressure. The second was in a $^1/_4$-inch standard-weight nipple. From this and other observations on the erratic quality of welded pipe, it was concluded that seamless pipe should be used exclusively in hydrofluoric acid service.

Copper Welds. Welds in deoxidized copper plate made with copper rod were not satisfactory. After exposure to aqueous acid, the inclusions in the weld metal were corroded out and, as a result, left a porous weld.

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FIBROUS HOLOCELLULOSE FROM SOFTWOODS

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A method utilizing acidified sodium chlorite is described for preparing relatively large batches of fibrous holocellulose from two representative American softwoods, western hemlock (*above*) and slash pine (*right*). Some of the important characteristic properties of the product are examined in detail.

TO UNDERSTAND the ultimate potential uses of the cellulose in wood, it is necessary to have a fundamental knowledge of the structure of wood cellulose fibers, especially the relation of the various chemical components to one another in the cell wall. A promising approach to this problem lies in the study of fibrous holocellulose, or wood cellulose in fibrous form, which contains the whole carbohydrate fraction of the wood after delignification. It is desirable to be able to prepare fibrous holocellulose conveniently and in moderately large quantities.

The preparation of holocellulose from wood (*5, 20*) was originally developed as an analytical determination, using small samples of solvent-extracted wood meal. The method is essentially a series of short chlorinations, with intermediate extractions of the chlorinated lignin by means of hot dilute monoethanolamine in alcohol, and is designed to minimize any hydrolysis during chlorination. The alcoholic extraction medium serves to leave behind all the carbohydrate material. However, it is difficult to apply this method to large samples of wood meal because there is local overheating and consequent degradation of the cellulose during chlorination (*9, 13*). For the same reason it is difficult (*31*) to use coarse forms of wood in which the fiber structure is retained. In general, the chlorination methods may be considered unsuitable for the preparation of fibrous holocellulose from woods.

For some time it has been known (*28*) that ordinary wood chips can be delignified by treatment with aqueous chlorite solutions at moderately high temperatures (100° C.). More recently Sohn and Reiff (*23*) made a systematic study of this method. They found that a wide variety of plant materials, including wood, could be reduced to lignin-free fibers having a high hemicellulose content and high viscosity. By extending the time, temperatures of 50–70° C. could be used, particularly in the presence of buffers such as sodium acetate or pyridine. About the same time Jayme (*11*) and others (*4, 14, 21*) described the preparation of holocellulose from spruce wood shavings with acidified sodium chlorite solutions.

PREPARATION OF HOLOCELLULOSE[1]

The two coniferous pulpwood species were western hemlock (*Tsuga heterophylla*) and slash pine (*Pinus caribaea*). The logs selected were sound wood, free of rot, blue stain, or other faults. The hemlock was 100 to 300 years old, and the pine, 16 to 20 years.

For relatively large batches of holocellulose (500 grams or more) wood chips of uniform thickness (4 mm.) were cut by hand from cross-sectional slabs of logs 2.5 cm. thick. Heartwood was omitted from the pine samples. The chips were not allowed to dry below a moisture content of about 50%. It was found unnecessary to solvent-extract the wood, despite the high extractive content in the case of slash pine. Wood dust, bark pieces, and other contaminants were carefully avoided.

The uniform wood chips (2.5 kg., 50% moisture) were placed in a stout 9-liter glass vessel, having a ground-glass standard-taper neck (₮ 45/50). The vessel was filled with a solution of 600 grams of commercial sodium chlorite in 8 liters of water containing about 12 ml. of glacial acetic acid (pH of chlorite solution, 5), and placed in a thermostatically controlled constant-level water bath at 65° C. Temperature was maintained at 60–65° C. for 6 hours. Evolution of gas, largely chlorine dioxide, caused much frothing, particularly with the slash pine; this froth was led away through all-glass connections to a small catch bottle.

At the end of 6 hours, the hot liquor was poured off, and the vessel immediately filled with a fresh chlorite solution of the same composition as the first. For the second stage the temperature was maintained at 65–68° C. for 7 hours. In a third stage with fresh liquor the temperature was kept at 70° C., again for 7 hours. Finally a fourth charge of chlorite solution was used at 70–74° C. for 1 hour only. At this point the soft white chips were carefully drained of liquor and covered with warm distilled water several times, to avoid loss of fiber.

Further washings were carried out in a large (20-liter) stone vacuum filter; by this time the chips had become thoroughly disintegrated into a white pulp. Prolonged soaking in changes of distilled water over a period of several days was necessary to free the gelatinous fibers of the last traces of reagent.

To evaluate the product obtained by digesting wood chips in chlorous acid, holocellulose was prepared from the same wood by the customary chlorination-extraction method. However, as the wood meal ordinarily used is not always representative of the whole wood (*2*), it was preferred to use thin shavings to ensure against loss of fiber fractions or chemical degradation of the wood substance during reduction to a finely divided form.

Shavings, 40 microns thick, were cut from rectangular wooden blocks (38 mm. along the grain, 32 mm. across the grain, and 25 mm. high) with a hand chisel blade and table microtome. The sample blocks were cut from the cross-sectional slabs used for making uniform chips, by sawing through these slabs at parallel distances 19 mm. on either side of the center, and cutting the resultant long piece at regular distances of 32 mm. across the grain.

The thickness of the shavings was chosen so that they could be readily penetrated by reagents and still retain sufficient strength to be handled without disintegration. The cutting was done in the direction of the fiber axis, to minimize severing of the fibers as far as possible with such thin sections. The blocks were kept moist while cutting, and the shavings were not dried until they had been solvent-extracted in the standard manner (*30*).

For delignifying 40μ wood shavings, a chlorination procedure was developed as suggested by the work of Storch (*27*). The moist wood shavings, in 1- to 10-gram lots, were placed in a glass chamber which could be evacuated to about 10 mm. pressure. Chlorine gas was admitted to the evacuated chamber at such a rate as to reach atmospheric pressure in 5 minutes. The chamber was then opened, and the shavings were quickly removed and covered with alcohol, followed by the usual sequence of hot 3% monoethanolamine in alcohol, alcohol, water, as used in the standard holocellulose determination (*29*). About eight or nine such chlorinations and extractions were necessary before the holocellulose gave a negative test for lignin.

Western hemlock shavings from the sapwood showed no significant difference in holocellulose yield, as isolated by the chlorination procedure, from shavings taken from the center of the bole or from a position between these two extremes:

Location of Wood Sample in Bole	% Yield on Basis of Extractive-Free Wood
Outer edge (sapwood)	68.9
Center	69.5
Midway to center	69.1

Hence the yield of holocellulose from chips, including all portions of the bole, may be expected to average about 69%. The actual yield of cellulosic fiber from hemlock by the chlorite method was found to be less (about 64%); similarly, the yield of slash-pine cellulosic fiber from chips was about 63%. This loss of yield is not surprising since there is an essential difference in the two methods of preparation—namely, the use of a hot aqueous medium rather than a hot alcohol medium. The solubility of chlorine-prepared holocellulose in hot water is considerable (about 10% in 1 hour at 100° C.); undoubtedly this very soluble part of the native wood carbohydrates cannot be retained without an alcoholic extraction medium. By the chlorite method of preparation, the free fibers of holocellulose prepared from undried wood chips have never been changed essentially from their natural aqueous environment. This may be an important advantage, particularly when it is considered that cellulose is likely to retain solvent molecules tenaciously (*24*), to form "inclusion cellulose". The use of an aqueous medium may be preferred in order to examine the advantages of producing commercially a wood cellulose fiber which more closely approaches the composition of native wood cellulose.

A further comparison of the two methods of delignification was made with respect to the effect on the average viscometric degree of polymerization (D.P.). A high-viscosity sulfite wood cellulose from western hemlock was subjected to the conditions of the wood chip delignification, and the result compared with a product obtained by chlorinating and extracting this same raw material in the standard manner (*29*).

After four chlorinations (total of 20 minutes) the product had an average D.P. of 930; after 4-hour digestion at 60° C. in acidified sodium chlorite, D.P. was 1100. In both cases delignification appeared to be substantially complete. A standard cellulose from cotton, with a D.P. of 940, was treated for 5 hours at 60° C. with 200% sodium chlorite at pH 4 and had a final D.P. of 900. These chain length data support the idea that the delignification conditions used have little degrading effect on cellulose.

SOLUBILITY IN ALKALINE SOLUTIONS

A characteristic of any cellulose preparation is its fractional solubility in alkaline solutions. This fractional solubility depends for the most part on the presence of hexosans or pentosans having a relatively low degree of polymerization. In addition, the molecular fine structure of cellulose fiber plays a part, so that the less highly oriented chains may have more ability to dissolve at a given chain length than those more highly oriented (*7*).

The determinations of alkaline solubility were made on samples washed in organic solvents (using the sequence, 70% ethanol, 95% ethanol, absolute ethanol, hexane) before being dried, in order to avoid the horniness found when fibers of such high hemicellulose content are dried from water. The moisture content was determined after thorough conditioning at 70% relative humidity and room temperature, by drying in an oven at 105° C. for 3 hours. Samples of about 250–300 mg. were weighed accurately into a 125-ml. conical flask. The flask with contents was flushed out with nitrogen for several minutes, tightly closed with a rubber stopper, and placed in a thermostat at 20° C. After at least 15 minutes 100 ml. of sodium hydroxide solution (also previously cooled to 20° C.) were added, and the resulting slurry

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[1] Since this work was completed, a method for the isolation of hemicelluloses from unextracted softwoods was reported in a preliminary communication by L. E. Wise [IND. ENG. CHEM., ANAL. ED., 17, 63–4 (1945)]. The wood was reduced in a Wiley mill, and then delignified with a strongly acid solution of sodium chlorite at 60° and 30° C.

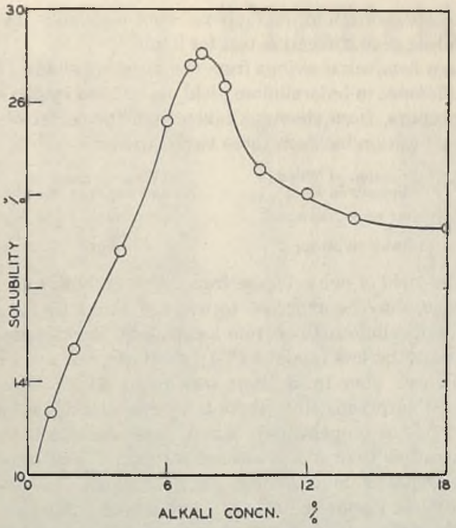

Figure 1. Fractional Solubility of Slash Pine Holocellulose in Aqueous Sodium Hydroxide Solutions at 20° C.

was kept under nitrogen for 30 hours. In some cases it was first necessary to break up clumps of fibers that did not disperse satisfactorily in the alkali; this was done simply by stirring for a minute with a glass rod. After extraction, the undissolved residue was collected on a C-porosity, fritted Pyrex filter crucible (60 ml. capacity) with suction but without drawing air into the mat. The mat was washed on the filter three times with fresh caustic solution at 20° C.; suction was then applied with full force to draw three 50-ml. portions of water rapidly through the alkali-cellulose mat. (This step was designed to avoid having the sample come into appreciable contact with caustic solutions of greater dissolving power than the one in which the solubility was being measured.) The mat was covered with 0.1 *N* sulfuric acid and washed five times with this reagent over a period of 5 minutes. The final wash was with distilled water (ten times). The residue was weighed in the crucible after drying at 105° C., and the result was calculated on the basis of dry weight of original sample.

This method of fractional solubility determination was found to be accurately reproducible and not dependent upon close standardization of the various manipulations involved.

In some instances with 18% caustic solution, the alkaline filtrate before the first aqueous wash was collected separately, neutralized with a slight excess of glacial acetic acid, and allowed to stand overnight. The amount of any precipitate which settled out (so-called beta-cellulose) could be determined by volumetric oxidation according to the method of Launer (*16*).

The so-called alpha-cellulose fraction, which is insoluble in 18% sodium hydroxide solution, forms the greater part of pine and hemlock holocelluloses; the remainder, however, is entirely the very soluble gamma fraction, which is not reprecipitated when the 18% caustic extract is neutralized:

	Western Hemlock	Slash Pine
Alpha fraction, %	76.1	79.5
Beta fraction, %	None	None
Gamma fraction, %	23.9	20.5

Different wood specimens, particularly of pine, gave values for the alpha and gamma fractions that varied within 1 or 2%, but in all cases the beta fraction was absent. This implies that the distribution of chain lengths is not continuous, and that the short-chain fraction probably is separated from the long-chain fraction by a region of intermediate chain lengths which are absent in the native wood cellulose. This characteristic of holocellulose is in agreement with the findings of others (*1*, *18*).

The effect of alkali concentration on the amount extracted is marked; a sharp peak of maximum solubility was found for slash pine holocellulose at an alkali concentration of 7.5% (Figure 1). It is well known (*6*) that wood celluloses isolated by the usual sulfite or sulfate processes, so that the original soluble fraction is removed and the residue more or less degraded, show a distinctly higher alkali concentration for maximum solubility than 7.5% (usually in the range 10 to 12%). Thus a high maximum fractional solubility at a relatively low alkali concentration evidently is characteristic of the holocellulose and, probably to a lesser degree, of other wood celluloses prepared so as to retain a large part of the very soluble polysaccharides of the native fiber.

It also appears from the low optimum concentration of alkali (below the concentration limit of mercerization for wood cellulose) that the large soluble fraction is present in the most accessible parts of the crystalline-amorphous structure of the fiber.

However, it may be expected (*19*) that appreciable amounts of nonglucosic hexosans or pentosans still remain in the insoluble fraction. Any such resistant nonglucosic constituents (cellulosans) may be regarded (*19*) as forming an integral part of the least soluble fraction of the wood cellulose, in some unexplained manner. The greatest part of such cellulosans, in the case of the softwoods, is probably mannan. This hexosan has a structure and configuration similar to that of cellulose, and isolated mannans (*10*) show an ability to form derivatives (regenerated films and threads) similar to that of cellulose. It is therefore not unreasonable to suppose that the total resistant fraction of holocellulose is potentially useful cellulose which should be retained as far as possible during the delignification and subsequent purification processes used for preparing commercial wood celluloses.

Slash pine holocellulose may be refined with cold alkaline solutions of medium concentration to give a high yield of cellulose insoluble in 18% caustic solution (Table I). In this series the extractions were carried out without, at any time, drying the fibers before the final product was obtained. Instead, the water remaining in the fibers was made part of each alkaline solution. The yield of resistant (insoluble) cellulose was not affected when the excess of very soluble carbohydrates was removed with weak sodium carbonate solution. However, stronger caustic solutions decreased this yield, although not so much as when a hot dilute alkaline treatment was used.

In the case of hemlock (Table I), using the same sequence but with an additional hot water extraction, similar results were found. Most of the short-chain fraction could be removed with the cold alkaline solutions while retaining the high yield of resistant cellulose that is a recognized characteristic of holocellulose.

AVERAGE CHAIN LENGTH

The value of the "average" viscometric chain length of holocellulose must be considered with due regard for the fact that the chain-length distribution function seems to be characterized by two widely separated peaks, corresponding to a long-chain and a short-chain fraction, respectively. The short-chain fraction should contribute very little to the total viscosity compared with

Table I. Alkaline Refining of Softwood Holocellulose

Softwood Used	Refining Treatment in Successive Steps	% Yield in Each Treatment	% of Product Insoluble in 18% NaOH	Yield of Insol. Part, % of: Holocellulose	Yield of Insol. Part, % of: Wood
Slash pine	None	100	82.8	82.8	51.7
	2% Na_2CO_3, 25° C.	92.2	89.9	82.8	51.7
	4% NaOH, 25° C.	87.5	94.6	76.3	47.7
	9% NaOH, 25° C.	82.5	100.0	66.5	41.6
	0.5% NaOH[a], 100° C.	79.4	91.7	67.1	42.0
	9% NaOH, 25° C.	80.8	100.0	59.1	37.0
Western hemlock	None	100.0	76.2	76.2	49.0
	H_2O, 100° C., 1 hr.	90.3	82.8	74.8	48.1
	2% Na_2CO_3, 25° C.	93.7	88.3	74.6	48.0
	4% NaOH, 25° C.	92.4	92.6	72.4	46.5
	9% NaOH, 25° C.	85.8	98.6	65.2	42.0

[a] 5 hr. at 5% consistency (followed 4% NaOH treat).

Table II. Average Degree of Polymerization of Extracted Holocelluloses

Holocellulose	Extraction Conditions	% of Product Insol. in 18% NaOH	Viscometric D.P.
Western hemlock	None	76.1	1150[a]
	2% Na_2CO_3, 15° C.	88.3	1200
	4% NaOH, 25° C.	92.6	1600
Slash pine	None	79.9	810
	H_2O, 100° C., 1 hr.	86.0	1005
	2% Na_2CO_3, 15° C.	91.0	955
	4% NaOH, 25° C.[b]	94.0	1095

[a] D.P. of holocellulose by chlorination extraction of hemlock shavings, 1170.

[b] After 1-hr. water boil and drying.

Table III. Valley Beater Physical Tests (Slash Pine)

	Holocellulose				Bleached Kraft		
Beating time, min.	0	5	10	15	30	60	75
Freeness	610	480	120	25	595	240	140
Burst	...	173	172	170	118	141	146
Tear	...	1.69	1.41	1.39	2.47	2.14	2.06
Fold	...	....	....	1913	....	....	813
Free shrinkage	...	6.9	9.4	32.8	....	....	13.5

the long-chain fraction; rather it should have the effect of decreasing the actual concentration at which the viscosity is being measured by an amount corresponding to the fraction of very short chains in the sample. Thus, more significant chain-length values are obtained after removal of most of the very short chains by extraction with weak alkaline solutions (Table II).

These D.P. values were measured (*17*) in the strongly alkaline solvent, dimethyldibenzylammonium hydroxide; hence the effect of the alkaline extraction process on any alkali-sensitive linkages (*3*) in the native wood cellulose is eliminated. It is possible that appreciably higher chain lengths would be found by measuring the viscosities of holocellulose nitrates in an organic solvent. The actually useful chain linkages are those that remain unaffected by treatment with alkaline solutions.

The average degree of polymerization found for both pine and hemlock celluloses is substantially in the range 1100–1600. This is similar to the values (1000–1500) found by Staudinger and Husemann (*25*) for a variety of woods digested in chlorine dioxide and extracted with cold alkali.

PHYSICAL PROPERTIES

The pine and hemlock chlorite holocellulose fibers before drying appeared round and straight under the microscope; when dried they collapsed and twisted, and were unable to regain their original appearance on rewetting. The undried mass of fiber had a gelatinous appearance, with a decidedly soapy texture. On drying, the sheets were tough and horny, with a high gloss.

The physical properties of slash-pine chlorite holocellulose were evaluated by the standard methods of this laboratory and compared with a moderately strong sample of bleached sulfate pulp from southern pine (Table III). Undried samples of holocellulose were beaten at 1.25% consistency in a Valley beater, with 5 pounds on the lever arm, for different periods of time. Sheets were formed at 40-pound basis weight on the British sheet mold. The physical properties of the sheets were determined, using the Canadian standard freeness tester, standard Mullen tester, M.I.T. fold tester, and Elmendorf tear tester. It is apparent that this holocellulose showed a characteristically rapid drop in freeness on beating and reached a very low value. Bursting strength was high initially and did not increase further.

This result does not agree with the findings of other investigators (*9*, *13*) who used holocellulose obtained from spruce shavings by the chlorination method, where the strength always developed rapidly on beating. Schenck and Kurth (*22*), however, found similar behavior in holocellulose from wheat straw. Jayme (*12*) and Klauditz (*15*) examined in considerable detail the relation between hemicellulose content and strength of sheets; they concluded that the maximum strength is to be found at a certain optimum hemicellulose content which is less than that in carefully prepared holocellulose.

CONCLUSION

The preparation of holocellulose from softwoods has always been regarded as more difficult than the corresponding preparation from hardwoods. This may be due in part to the greater proportion of lignin present within the secondary wall of softwood fibers (*26*). Holmberg and Jahn (*8*) stated that it is not possible to prepare a true holocellulose from softwoods, as the last part of the lignin is so difficult to remove that the carbohydrate part necessarily suffers some degradation. However, analytical determinations of pentosan and lignin during delignification, upon which such judgment is usually based, admittedly are subject to error. The recovery of cellulose from softwoods in high yield, with the greater portion of the associated short-chain polysaccharides (characteristic of the native wood cellulose) still remaining, is close to the theoretical ideal of wood cellulose isolation. When such a product is obtained in its native fibrous form, as in the present method of recovery, it provides a material deserving of study, both from the point of view of cell-wall chemistry and the matter of maximum utilization of wood substance for chemical conversion purposes.

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CATALYTIC CRACKING OF PURE HYDROCARBONS

Cracking of Naphthenes

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Cracking of eleven naphthenes containing 6 to 18 carbon atoms was studied over a silica-zirconia-alumina catalyst. It was found that naphthenes are quite susceptible to the action of the catalyst and that both the ring and any side chains contribute to the total cracking. The rate of cracking increases rapidly with increased molecular weight. Secondary reactions of isomerization and saturation play an important part in determining the final products. Catalyzed cracking at 500° C. proceeds at about one thousand times the rate of thermal cracking, and there are significant differences in the product distributions.

CRACKING of paraffins and olefins over a silica-zirconia-alumina catalyst under conditions similar to those employed in the commercial cracking of petroleum fractions was described in previous articles of this series (*4*, *5*). These studies gave a picture of some of the reactions favored by cracking catalysts, with far less ambiguity than would result from observation of the cracking of petroleum fractions comprising a mixture of hydrocarbons. This method has been extended to a study of the naphthenes or alicyclic hydrocarbons, which are prominent constituents in the majority of petroleum fractions employed for cracking. An effort was made to secure a wide variety of naphthenic hydrocarbons, covering carbon numbers (C No. = n in C_nH_m) from 6 to 18. These were cracked by the catalyst and procedure previously described (*4*); the definitions and terminology are the same.

The catalyst, obtained from Universal Oil Products Company, analyzed 86.2% silica, 9.4% zirconia, and 4.3% alumina by weight. This catalyst gives results similar to those obtained with the present commercial silica-alumina cracking catalysts. Properties and sources of hydrocarbons follow, with compounds arranged in the order of increasing molecular weight:

Cyclohexane from Eastman Kodak Company was washed with concentrated sulfuric acid to remove aromatics and distilled. The melting point was 6.1° C., boiling range 80.2–81.2° C., d_4^{20} 0.7785, n_D^{20} 1.4263.

Methylcyclopentane was isolated from a California petroleum by repeated fractionation. It had a boiling point of 72.0° C., d_4^{20} 0.7488, and n_D^{20} 1.4100.

Methylcyclohexane from the hydrogenation of toluene over nickel had a boiling point of 100.6° C., d_4^{20} 0.7688, n_D^{20} 1.4232, and an aromatic content of 0.6%.

Hydrindan (hexahydroindan) was prepared by hydrogenation over nickel of indan from Eastman. It was washed with sulfuric acid containing silver sulfate. The product contained 8.6% distilling below 160° C., chiefly methylcyclohexane, but this was not discovered until after the cracking experiment had been made. The rest of the material distilled at 160–168° C. Properties of the mixture used as a cracking stock were d_4^{20} 0.8568, n_D^{20} 1.4611, specific dispersion at 20° C. $[10^4 (n_F - n_C)/d]$ of 95.

Isopropylcyclohexane from the hydrogenation of isopropylbenzene (Dow Chemical Company) was washed with sulfuric acid–silver sulfate. It contained 4.8% lower-boiling material, chiefly methylcyclohexane, and the remainder distilled at 153–154° C. The mixture, as used, had d_4^{20} 0.7994, n_D^{20} 1.4396.

Decalin (decahydronaphthalene) from Eastman was washed with sulfuric acid–silver sulfate to remove aromatics. The boiling range was 190–193.5° C., d_4^{20} 0.8859, n_D^{20} 1.4763.

Cyclopentylcyclohexane was prepared by hydrogenating over nickel at 200° C. cyclopentylbenzene from the condensation of cyclopentene with benzene in the presence of aluminum chloride. The product was washed with sulfuric acid–silver sulfate and had a boiling point of 216° C., n_D^{20} 1.4721, d_4^{20} 0.8753.

Amylcyclohexanes were from hydrogenation of amylbenzenes from Sharples Chemicals Inc. The latter are stated by the manufacturer to contain at least 90% secondary amyl structures, with the rest tertiary. The hydrogenation product was washed with sulfuric acid–silver sulfate to remove aromatics. It was later found to contain 5% boiling below C_{11}, chiefly methylcyclohexane. The remainder distilled at 195–200° C. The mixture had d_4^{20} 0.8152 and n_D^{20} 1.4485.

Bicyclohexyl from Eastman was washed with sulfuric acid–silver sulfate and fractionally distilled to constant refractive index. Its boiling point was 239° C., d_4^{20} 0.8860, n_D^{20} 1.4795, melting point 3.4° C.

Amyl Decalins were prepared from Sharples amylnaphthalenes. The manufacturer states that the latter are entirely 2-substituted and that the amyl group is at least 90% secondary, with the rest tertiary. The amylnaphthalenes were fractionally distilled, and the center fraction was hydrogenated over nickel. The product was washed with sulfuric acid–silver sulfate and fractionally distilled. The central fraction, boiling from 142° to 144° C. at 15 mm., was used. It had d_4^{20} 0.8874, n_D^{20} 1.4814, and specific dispersion at 20° C. $[10^4 (n_F - n_C)/d]$ 97.2.

Abietanes were from the hydrogenation over nickel at 200–250° C. of abietenes from the G and A Laboratories (Savannah, Ga.). The abietenes are a mixture of unsaturated, partially hydrogenated phenanthrene homologs derived from rosin oil. The sample used, with n_D^{20} 1.5410, was hydrogenated twice over fresh catalyst until no more hydrogen was consumed. The product in a simple distillation from a flask started over at 250° C., and reached 307° C. at 5% and 357° C. at 95% over. It had d_4^{20} 0.9236, n_D^{20} 1.5035, specific dispersion at 20° C. $[10^4 (n_F - n_C)/d]$ 105, molecular weight in benzene 249, and bromine number 6.8.

Where hydrocarbons were found to contain small amounts of lower-boiling material, corrections were made in computing results.

CRACKING BEHAVIOR

The naphthenes were cracked over the silica-zirconia-alumina catalyst in the fixed-bed apparatus previously described. The usual catalyst volume was 50 cc., temperature 500° C., process period 1 hour, pressure atmospheric, and flow rate about 13.5 moles hydrocarbon per liter of catalyst per hour, unless otherwise noted. The general purpose of these experiments was to survey a number of compounds rather than to examine any one in extensive detail. With Decalin, however, a limited study of the effect of operating conditions was made. Results for monocyclics are given in Table I and for bicyclics in Table II.

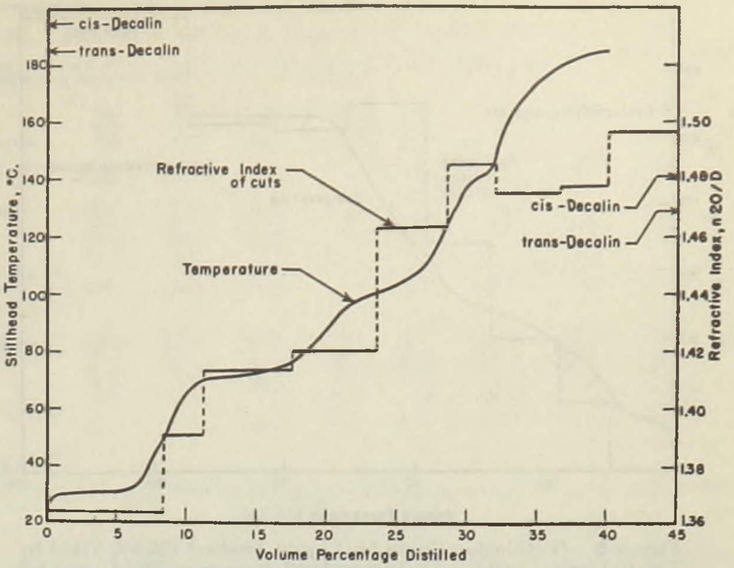


Figure 1. Distillation Curve for Liquid Product (78.0% Yield by Weight) from Cracking Decalin at 500° C. and 13.7 Moles per Liter per Hour

CYCLOHEXANE. The reactions of cyclohexane at 500° C. were slight. The little gas produced was about half hydrogen. The small amount of lower-boiling liquid product appeared to be a mixture of C_6 olefins and paraffins; it had an olefin content of about 8%, an aromatic content of about 4%, and may have contained some methylcyclopentane. The amount of isomerization to methylcyclopentane, however, could not have been more than 4% of the feed. When cyclohexene was treated under similar conditions, conversion to methylcyclopentane was over 30% (*5*). The liquid boiling at 80° C. from the cyclohexane run, plus the distillation bottoms, had a refractive index, n_D^{20} of 1.4271 (cyclohexane 1.4263, benzene 1.5012); hence it probably did not contain over 1% benzene.

METHYLCYCLOPENTANE. Cracking at 500° and 550° C., as with cyclohexane at 500°, gave a gas fairly high in hydrogen. Lower-boiling liquid product was chiefly C_6 material, although traces of cyclopentane appeared to be present. There was little or no isomerization to cyclohexane. The fairly saturated quality of the C_2–C_4 hydrocarbon gas is indicative of the occurrence of hydrogen transfer reactions, since simple cracking would give only olefins. Bottoms from the run at 550° C. were 5.6% by weight of the feed, and had n_D^{20} 1.4575, which signifies the presence of condensation products or aromatics.

METHYLCYCLOHEXANE. Cracking was somewhat greater than that of the C_6 naphthenes, but the products were varied and no single reaction predominated. The lower-boiling liquid contained a small amount of C_5 and some C_6 and C_7, with 11% olefins in the C_6–C_7 range. There was a little material of high refractive index (n_D^{20} 1.50) in the 6% bottoms above 100° C.

ISOPROPYLCYCLOHEXANE. Results from cracking this C_9 naphthene indicate that it was fractured in both the side chain and ring. The gas was rich in both C_3 and C_4 hydrocarbons, while the cracked liquid, judging from distillation temperatures, optical properties, and bromine numbers, was a mixture of naphthenes and aliphatics, with a relatively small aromatic content. Recovered C_9 material contained an appreciable amount of aromatics. Yields and properties of liquid fractions follow:

Boiling Range of Fraction, ° C.	Amount, Wt. % of Charge	Analysis of Fraction, Wt. %	
		Olefins	Aromatics
20–50	7.3	34	..
50–87	3.5[a]	25	..
87–145	1.7	...	..
145–158	62.6	3.5	12
Above 158	4.9	...	(n_D^{20} 1.4911)

[a] Corrected for lower-boiling material in charge.

AMYLCYCLOHEXANES. Results resembled those with isopropylcyclohexane. The cracked liquid was a complex mixture, with C_5–C_7 more prominent than C_8–C_{10} material. The fraction 30–85° C. contained 35% olefins, and the fraction 85–105° C., 20% olefins and 11% toluene; the latter suggested cracking in the side chain accompanied by ring dehydrogenation. Cracked material above 105° C. contained even more aromatics, judging from the refractive index which reached a maximum of 1.4798 for the 140–170° C. cut. The product within the charge boiling range, 195–200° C., was not much changed (n_D^{20} 1.4510 compared to 1.4497 for material of the same range in the charge). The bottoms, 3.5% by weight of the charge, had n_D^{20} 1.5285 and, thus, were quite aromatic. It should be noted that these aromatics did not necessarily all derive from the cyclohexane

TABLE I. CATALYTIC CRACKING OF MONOCYCLIC NAPHTHENES

Hydrocarbon	Cyclohexane	Methylcyclopentane		Methylcyclohexane	Isopropylcyclohexane	Amylcyclohexanes
Exptl. conditions						
Temp., ° C.	500	500	550	500	500	500
LHSV[a]	1.5	1.5	1.6	1.7	2.1	2.5
Flow rate, moles/l./hr.	13.8	13.2	14.0	13.6	13.3	13.4
Gaseous product						
Moles/mole charge	0.031	0.078	0.172	0.212	0.51	0.54
Volume %						
H_2	46.3	29.1	45.2	27.0	12.0	17.6
CH_4	...	...	14.0	7.8[c]	6.9	8.2
C_2H_4	...	...	4.7	4.2	3.7	4.3
C_2H_6	...	...	3.8	...	0.9	1.7
C_3H_6	...	...	14.9	14.0	19.5	19.5
C_3H_8	...	...	10.1	13.9	11.1	9.9
Iso-C_4H_8	...	...	1.2	1.1	4.8	4.4
n-C_4H_8	...	...	1.2	3.7	8.0	8.3
C_4H_{10}	...	...	4.9	28.3	33.1	26.1
Total olefins	21.6	32.2	22.0	23.0	36.0	36.5
Total saturates	32.1	38.7	32.8	50.0	52.0	45.9
C No. of saturates	2.8	2.8	...	...	...	...
Material balance, wt. % of charge						
Gas	0.9	2.9	4.2	7.4	17.2	13.5
Liquid below original b.p.	4.6	5.7	1.7	6.0	12.5[d]	21.2[d]
Remaining liquid	86.2	88.4	89.8	79.0	67.5	62.8
Carbon	0.1[b]	0.2[b]	0.7[b]	7.6	1.4	1.3
Loss	8.2	2.8	3.6		1.4	1.2

[a] Liquid hourly space velocity.
[b] CO from regeneration not included.
[c] Including C_2H_6.
[d] Corrected for lower-boiling material in charge.

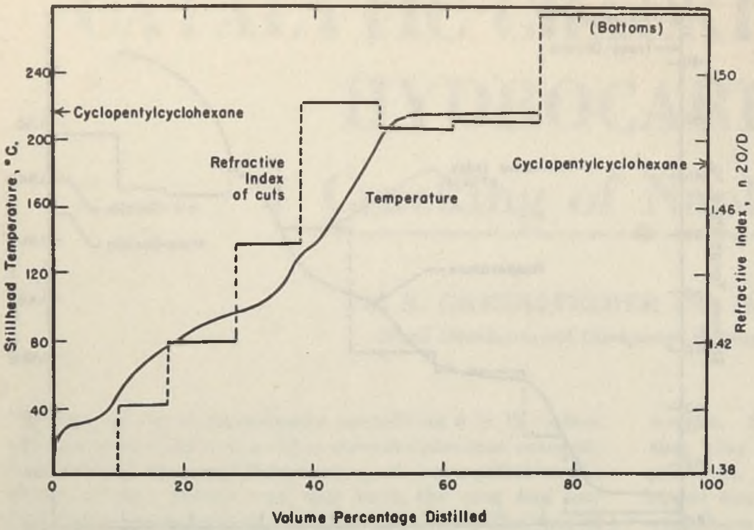


Figure 2. Distillation Curve for Liquid Product (75.6% Yield by Weight) from Cracking Cyclopentylcyclohexane at 500° C. and 6.8 Moles per Liter per Hour

ring, since pentenes alone, treated under even milder conditions, gave rise to considerable quantities of higher-boiling aromatics (*5*).

Hydrindan (Hexahydroindan, Bicyclo[4.3.0]nonane). Cracking was fairly extensive. The gas contained some hydrogen and much saturated hydrocarbon. The liquid was rich in isopentane and a C_7 fraction resembling methylcyclohexane, but also contained compounds not identified in the range of C_6, C_8, and C_9. Olefin contents of liquid fractions were: 20–50° C., 15%; 50–75° C., 20%. Aromatics were not prominent except in the bottoms; the fraction 75–110° C. contained only 7%. The bottoms above 168° C., 9.1% by weight of the charge, had n_D^{20} 1.5379.

Decalin (Decahydronaphthalene). Decalin was cracked over the catalyst at 450°, 500°, and 525° C., with the results outlined in Table II. Figure 1 shows a typical distillation curve for the liquid product. The cracking of Decalin gave rise to a variety of products, indicating fission at various places in the molecule and the occurrence of a number of secondary reactions. The gaseous product was rich in C_3 and C_4 hydrocarbons, which tended to be saturated, especially at low flow rates or low temperatures. The liquid product was composed of hydrocarbons from C_5 to C_{10}, with the C_6 range prominent. Identification of individual compounds was not attempted except for naphthalene, isolated by fractionation and crystallization from the combined bottoms of several runs at 500° C. in an amount corresponding to 0.5% by weight of the charge, which must have been less than the amount actually formed. Considerable amounts of methylcyclopentane were strongly indicated by the physical properties of the C_6 product. Very little or no benzene was formed, but there were appreciable amounts of aromatics in the higher boiling range. More detailed analyses of the products from cracking Decalin under similar conditions were given by Bloch and Thomas (*1*), who also showed substantial amounts of methylcyclopentane.

The A.S.T.M. motor-method octane number of the 20–180° C. product from cracking Decalin in a group of runs at 500° C. and 13.6 moles per liter per hour was 79.5 clear and 88.5 with 3 ml. of tetraethyllead per gallon.

The effect of cracking conditions with Decalin was further studied in the series of runs listed in Table III. The catalyst sample was the same type as that used for other runs, but was somewhat more active; consequently the depth of cracking under given conditions was appreciably greater. Results in Table III indicate that doubling the flow rate reduced the total depth of cracking about as much as did lowering the temperature by 50° C. Thus 450° C. and 13.6 moles per liter per hour gave the same cracking as 500° and 26.7 moles per liter per hour. The nature of the products was different, however, both in distribution and saturation. In general, low temperatures and low flow rates favor saturation by hydrogen transfer. Another feature strongly influencing saturation is the process period; shortening the process period so that the catalyst does not become too deactivated by carbonization leads to greater saturation under given conditions. A run at 400° C. for 15 minutes, included in Table III, shows the results from a combination of most of the conditions favoring saturation; the gas was 89% saturated and the C_6 liquid was 98% saturated. The amount of C_6 saturates produced in

Table II. Catalytic Cracking of Bicyclic Naphthenes

Hydrocarbon	Hydrindan	Decalin			Cyclopentyl-cyclohexane	Bicyclohexyl		Amyl Decalins	Abietanes
Exptl. conditions									
Temp., ° C.	500	450	500	525	500	500	500	500	500
LHSV	1.8	0.9	2.1	1.9	1.2	1.3	2.5	3.0	3.6
Flow rate, moles/l./hr.	12.5	5.7	13.7	12.0	6.8	6.8	13.3	12.8	12.9
Gaseous product									
Moles/mole charge	0.500	0.396	0.622	0.65	0.690	0.721	0.636	0.955	1.022
Volume %									
H_2	20.7	23.2	29.0	21.9	14.9	30.6	30.7	19.3	20.6
CH_4	....	0.0	7.0	14.0	3.7	15.5	....	7.3	7.9
C_2H_4	....	0.7	5.1	4.5	5.4	4.3	....	4.2	3.2
C_2H_6	....	0.0	2.1	0.9	4.4	2.1	....	2.1	3.4
C_3H_6	....	0.7	13.9	13.6	16.4	11.3	....	22.1	21.4
C_3H_8	....	8.6	8.8	13.3	11.4	7.8	....	7.2	6.7
Iso-C_4H_8	....	0.0	2.5	2.0	2.3	0.8	....	4.8	6.0
n-C_4H_8	....	9.3	2.3	5.0	6.0	3.0	....	9.6	9.5
C_4H_{10}	....	57.5	29.3	24.8	35.5	24.6	....	23.4	21.3
Total olefins	29.5	10.7	23.8	25.1	30.1	19.4	29.5	40.7	40.1
Total saturates	49.8	66.1	47.2	53.0	55.0	50.0	39.8	40.0	39.3
C No. of saturates	3.9	....	....	....	....	....	....	....	....
Material balance, wt. % of charge									
Gas	17.7	12.1	15.0	16.3	18.6	12.8	13.6	17.1	15.0
Liquid below original b.p.	17.3	29.8	25.3	25.6	35.2	44.5	30.4	48.2	59.0
Remaining liquid	69.1	52.8	52.7	47.4	40.4	29.7	48.1	26.8	20.3
Carbon	1.4	1.1[a]	1.4	10.7	0.8[a]	1.0[a]	1.0	1.2	1.6
Loss	4.5	4.2	5.6		5.0	12.0	6.9	6.7	4.1

[a] CO from regeneration not included.

Table III. Effect of Conditions in Catalytic Cracking of Decalin

(Atmospheric pressure; duration of runs, one hour, except 400° C. run which was 15 minutes; catalyst for these runs was of the same type but more active than that used for all other runs)

Exptl. conditions								
Temp., ° C.	500	500	500	400	450	500	550	550
LHSV	1.1	2.1	4.2	1.1	2.1	2.1	2.1	4.2
Flow rate, moles/l./hr.	6.8	13.6	26.7	6.8	13.6	13.6	13.6	26.7
Gaseous product								
Moles/mole charge	0.885	0.675	0.520	0.344	0.410	0.675	1.494	0.880
Volume %								
H_2	35.8	27.5	25.8	2	22.6	27.5	51.5	35.3
Olefins	17.5	26.3	33.2	11	17.6	26.3	24.8	34.2
Saturates	46.7	46.2	41.0	87	59.8	46.2	23.7	30.5
Mol. weight	31.8	37.6	38.4	35.6	40.9	37.6	26.2	31.8
Olefins in C_6 fraction, wt. %	9	14	25	2	9	14	24	36
n_D^{20} of remaining liquid[a]	1.5271	1.5060	1.4930	..	1.4910	1.5060	1.5258	1.5034
Material balance, wt. % of charge								
Gas	20.4	18.4	14.5	8.9	12.1	18.4	28.4	20.2
Liquid below original b.p.	33.0	27.2	21.6	18.0	23.9	27.2	24.2	24.8
Remaining liquid	39.1	50.6	61.6	68.9	63.0	50.6	40.7	52.8
Carbon	1.2	1.0	0.5	2.8	0.6	1.0	2.6	0.7
Loss	6.3	2.8	1.8	1.4	0.4	2.8	4.1	1.5
Total cracked (no-loss basis), wt. %	58.3	47.9	37.3	30.1	36.7	47.9	57.5	46.4

[a] n_D^{20} for Decalin is 1.4763.

this run was 0.38 mole per mole of Decalin cracked, which is higher than in any other run.

Dehydrogenation of Decalin was appreciable, especially at the higher temperatures, and was reflected in both the high hydrogen content of the gas and the high refractive index of the material remaining above 180° C.

To test the thermal stability of Decalin under the conditions of the more severe runs, an experiment was made at 525° C. and a flow rate of 6 moles per liter per hour, with glass beads replacing the catalyst. No gas was obtained and only 0.5% of lower-boiling liquid. Thermal and catalytic reactions will be more fully compared in a later section.

Cyclopentylcyclohexane. Catalytic cracking gave a variety of products, and no reaction could be singled out as especially prominent, although C_6 to C_7 material predominated in the liquid, and C_3 and C_4 in the gas. Data are given in Table II, and a distillation curve is reproduced in Figure 2. Olefin contents of all fractions were rather low, varying from 6 to 16% over the range 50–125° C. Considerable amounts of aromatics were present in the material boiling above 100° C. and in the distillation bottoms.

Bicyclohexyl. Results (Table II and Figure 3) show that bicyclohexyl cracks readily over the catalyst with the formation of a variety of products. The gas is rather saturated. C_6 hydrocarbons are especially prominent in the liquid, and their presence indicates a tendency of the two rings to split apart at the connecting link. The properties of the C_6 plateau fraction (boiling range 70–73° C., n_D^{20} 1.4130) agree with those of methylcyclopentane (71.8° C., 1.4098), but the cut may contain mixed aliphatic and alicyclic hexanes. The olefin content of this cut was 10% for the run at 6.8 moles per liter per hour. Aromatic hydrocarbons were present in the C_8–C_{11} fractions, but analysis of the C_6 fraction showed none.

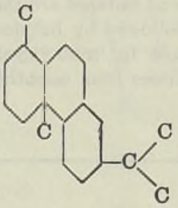
The gas from bicyclohexyl contained hydrogen, and the bottoms from the distillation had a refractive index indicating the presence of biphenyl or other highly aromatic compounds. Formation of aromatics by dehydrogenation and possibly by other reactions thus takes place concurrently with cracking, as it does with other naphthenes examined that contain a cyclohexane ring and, have a total of 9 or more carbon atoms.

Amyl Decalins. These naphthenes cracked readily at 500° C. The amount of lower-boiling liquid, including that recovered in a vacuum distillation of the bottoms, exceeded 48%. Distillation showed a wide distribution of products over the boiling range and the presence of many different compounds. Analyses of fractions were:

Boiling Range, ° C.	Wt. % of Charge	Composition, Wt. % Olefins	Aromatics	Satd. naphthenes
20–40	7.5	44	...	...
50–80	8.0	39	<5	21
80–111	7.1	38	8	...

There was little Decalin (boiling at 185–195° C.) in the product; hence exclusive removal of the side chain was not an important reaction here any more than with the other alkyl naphthenes.

Abietanes. The sample was a mixture obtained by hydrogenating neutral rosin oil and, presumably, consisted of alkylated perhydrophenanthrenes such as



The average number of carbon atoms per mole was 18.0. The mixture cracked extensively and gave a high yield of lower-boiling liquid which was evenly distributed over the range 20° to 250° C. The C_6 cut contained 40% by weight olefins.

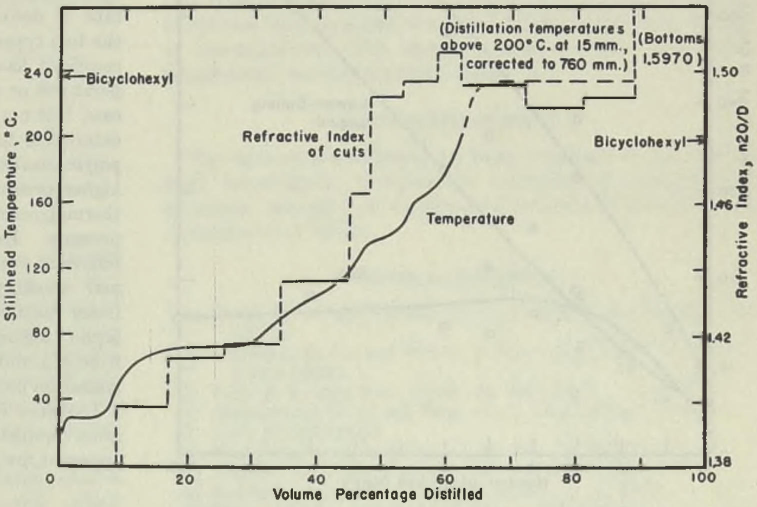


Figure 3. Distillation Curve for Liquid Product (74.2% Yield by Weight) from Cracking Bicyclohexyl at 500° C. and 6.8 Moles per Liter per Hour

CATALYTIC CRACKING

Figure 4 summarizes the results with naphthenes. At fixed conditions the total decomposition increases rapidly with molecular weight and rises from 7% for C_6 to 79% for C_{18}. It should be noted that the total decomposed includes gas, lower-boiling liquid, and carbon, but not products of the same or increased boiling point, so that primary dehydrogenation and condensation reactions are not considered except to the extent of the weight of hydrogen released. As the molecular weight of the naphthene increases, gas formation increases rapidly at first but soon levels off and becomes relatively less important, while formation of lower-boiling liquid increases continuously.

The various types of naphthenes tested, including cyclopentane and cyclohexane types, mono- and bicyclic, condensed and linked ring, display similar rates of decomposition at a given molecular weight; that is, the rate of cracking generally depends on the molecular weight and not on the structure. There is some evidence, upon close examination of the data, that the bicyclic naphthenes crack a little more readily than the alkylmonocyclic naphthenes of the same molecular weight, but this effect, if real, is still of minor importance. In general, the product analyses show that the length of any alkyl side chains does not affect the product distribution noticeably; it is concluded that cracking in a side chain of sufficient length obeys the rule of preferentially forming C_3 or larger fragments without selecting any linkage of otherwise specified situation with respect to the ring. Because of alternative reactions which may occur in the system, a more precise statement cannot now be made.

Gas compositions for all the naphthenes are similar in that hydrogen, propylene, and butanes are the most prominent constituents by volume, followed by butylenes and propane. Exception should be made for methylcyclopentane, which gave very little butanes. Gases from naphthenes tend to be rather saturated compared to the gases obtained from paraffins and aliphatic olefins (*4*, *5*). Higher saturation was also observed in the products from cracking the cyclo-olefins, cyclopentene and cyclohexene, which were reported previously (*5*).

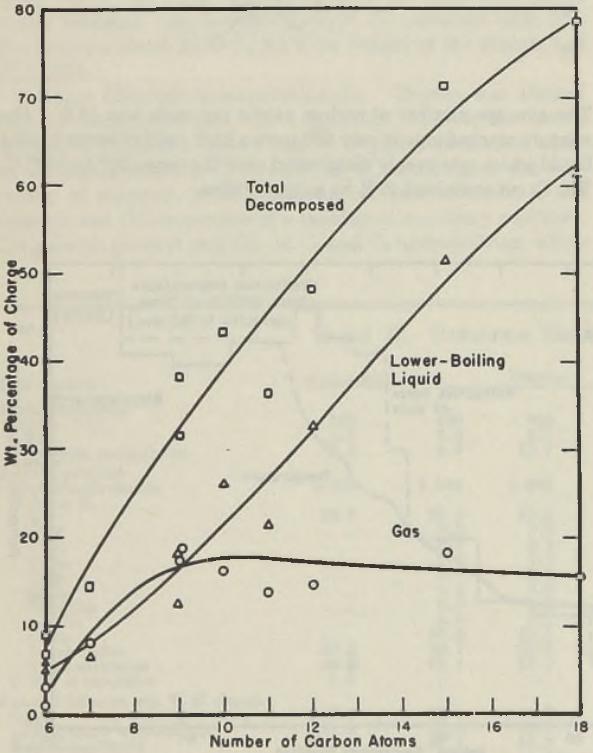


Figure 4. Results from Catalytic Cracking of Naphthenes at 500° C. with Flow Rate of 13.7 Moles per Liter per Hour

Naphthenes, like paraffins (*4*), do not appear to isomerize directly according to the results with methylcyclopentane and cyclohexane. Therefore, the substantial amounts of methylcyclopentane indicated from the catalytic cracking of Decalin and bicyclohexyl are ascribed to isomerization of intermediate cyclo-olefins or to isomerization occurring concomitantly with cracking. Thus, cyclohexene was isomerized extensively and then saturated to methylcyclopentane (*1*, *5*); however, in spite of this the mechanism of the production of methylcyclopentane from Decalin is not so clear, since Bloch and Thomas (*1*) state that isomerized forms of Decalin were found in their products of cracking at 400° C. In the latter case it cannot be said whether or not an olefinic intermediate derived from Decalin entered into the reaction. At present there seems to be no means of further clarifying the mechanism involved in the reported isomerization of bicyclic naphthenes.

The reactions of naphthenes over the cracking catalyst may be summarized as follows:

1. Both the ring and any side chains contribute to the total cracking observed.
2. Hydrocarbon fragments of 3 or more carbon atoms are preferentially produced.
3. Products from naphthenes are more saturated than those from paraffins or aliphatic olefins. This is ascribed to an increased rate of "hydrogen transfer" (*5*, *9*).
4. Isomerization of C_6 to C_5 rings occurs, presumably via the corresponding cyclo-olefins, or concomitantly with cracking of the parent hydrocarbon.
5. There is considerable dehydrogenation of C_9 or higher cyclohexane-type naphthenes to aromatics.

It is evident from the series of experiments with Decalin that the relative amounts of various products obtained depend considerably on the conditions under which catalytic cracking is effected. This dependency results from the number of primary and secondary reactions involved. Because of the complexity of the reactions, it must be recognized that generalizations regarding product distribution in catalytic cracking are related to the particular conditions employed.

COMPARISON WITH THERMAL REACTIONS

When catalytic and thermal cracking of naphthenes are compared, it is seen that the catalyst greatly accelerates the rate of decomposition. This fact makes exact comparison of the two types of cracking difficult, for because of it the thermal reactions have usually been carried out either at higher temperatures or at higher pressures than the catalytic. In the first case, it is not certain whether observed differences are due to the catalyst or to the difference of temperature; in the second case polymerization and condensation reactions are favored by the higher pressure in the thermal treatment. The catalytic and thermal reactions have been compared chiefly at atmospheric pressure. Keeping the disparity of temperature in mind, the following conclusions have been reached. Compared to thermal cracking, the catalytic treatment gives: Considerably faster reaction (factors of 500 to 4000), more saturated gas and liquid, higher ratio of liquid to gas, less hydrogen formation from C_{10} and higher naphthenes, and smaller amounts of condensation products.

Evidence for these points follows. The data for Decalin are most complete. Reaction rates are compared by calculating the apparent first-order rate constants:

$$k_1 = (1/t) \ln (100/100 - C)$$

where C = percentage decomposed
t = contact time, seconds

TABLE IV. CATALYTIC AND THERMAL CRACKING OF DECALIN

Type	Catalytic			Thermal				
Source	This work			Sundgrén (*8*)		Dyakova and Petrov (*2*)[a]		
Temp., ° C.	450	500	525	580	600	500	550	600
Flow rate, moles/l./hr.	5.7	13.7	12.0	0.48	0.48	0.25	0.25	0.25
Time, sec.[b]	8.7	3.4	3.7	99	95	220[a]	195[a]	170[a]
% decomposed (no-loss basis)	44.8	44.1	48.0	13.8	20.5	6.3	15	35
k_1, sec.$^{-1}$ × 10^3	69	170	180	1.5	2.4	0.3[a]	0.82[a]	25[a]
Material balance, wt. %								
Gas	12.1	15.0	16.3	3.3	7.8	3.6[c]	8.1[c]	18[c]
Liquid below original b.p.	29.8	25.3	25.6	9.3	11.0	2.7	6.9	16
Remaining liquid	52.8	52.7	47.4	80.8	73.8	90	85	49
Carbon	1.1	1.4	10.7	1.2	1.7	3.7[c]	0[c]	17[c]
Loss	4.2	5.6		5.4	5.7			
Gas analysis, vol. %								
H_2	23.2	29.0	21.9	69.8	61.3	72	59	60
Olefins	10.7	23.8	25.1	14.3	15.3	20	21	26
Saturates	66.1	47.2	53.0	15.9	23.4	8	20	14
Moles/mole decomposed								
H_2	0.20	0.40	0.30	1.61	1.98	3.22	2.46	2.32
Hydrocarbon gas	0.68	1.00	1.06	0.70	1.24	1.25	1.73	1.56

[a] Size of apparatus and gas densities were estimated.
[b] Corrected for expansion; assumes catalyst 100% void.
[c] Estimated.

Limitations of this method of comparison were previously noted (*4, 5*).

METHYLCYCLOPENTANE. Thermal cracking studies (*6, 7*) show that C_3 is a prominent product, as in catalytic cracking. The catalytic reaction is much faster and gives more hydrogen, less ethylene, and more saturated hydrocarbons:

Type	Catalytic	Thermal
Reference	This work	(*6*)
Temp., ° C.	550	600
% decomposed	6.8	about 27
Gas analysis, vol. %		
Hydrogen	45.2	22
Olefins	22.0	53
Saturates	32.8	25
Ethylene	4.7	19

CYCLOHEXANE. Compared to thermal cracking (*3, 6, 7*), the catalytic reaction is about a thousand times as fast, and gives more hydrogen and more saturated hydrocarbons:

Type	Catalytic	Thermal
Reference	This work	(*7*)
Temp., ° C.	500	540
% decomposed	6.1	about 13
Gas analysis, vol. %		
Hydrogen	46.3	18
Olefins	21.6	58
Saturates	32.1	24

AMYLCYCLOHEXANES. Estimated thermal (*2*) and catalytic data are outlined below. The catalytic rate is five hundred to a thousand times as fast, corrected to the same temperature. From the gas yields and analyses it is estimated that the moles of hydrogen per mole of amylcyclohexanes cracked is four times as great in thermal as in catalytic treatment:

Type	Catalytic	Thermal
Reference	This work	(*2*)
Temp., ° C.	500	550
Material balance, wt. %		
Gas	13.5	25
Lower-boiling liquid	21.2	11
Remaining liquid	62.8	60
Loss + carbon	2.5	4
Gas analysis, vol. %		
H_2	17.6	46
Olefins	36.5	30
Saturates	45.9	24

DECALIN. When Decalin was passed through the catalytic cracking apparatus at 525° C. and a flow rate of 6 moles per liter per hour, with glass beads replacing the catalyst, the amount of cracking was negligible. Thermal cracking of Decalin under more severe conditions has been reported for atmospheric pressure (*2, 8*) and for high pressure (*10*). From the calculated rate constants, the catalytic rate is of the order of four thousand times the thermal rate. Representative data from catalytic and thermal cracking are given in Table IV.

Other important characteristics of the catalytic decomposition of Decalin, compared to the thermal decomposition, are: much less hydrogen, lower ratio of olefin to saturates in the gas, lower ratio of olefin to saturates in the liquid, more uniform distribution of liquid products, much smaller percentage of benzene in the 75–95° C. C_6 fraction, and relatively less naphthalene and condensation products. The differences in distribution of products are shown in Tables IV and V. Amounts decomposed in the thermal experiments were less than in the catalytic, but it is believed that with greater thermal conversion these comparisons would hold or be even more pronounced.

The more uniform distribution of products in the catalytic product is notable. In thermal cracking of Decalin at 500° C. and 60 atmospheres (*10*), as at 580° C. and 1 atmosphere, large amounts of C_7 and higher-boiling material are formed. Although complete data are not available for tabulation, olefin analyses show even higher thermal olefin contents, and even lower catalytic, for the fractions above C_6.

TABLE V. AMOUNTS AND ANALYSES OF FRACTIONS FROM CRACKING DECALIN

Type and reference	Catalytic, This Work		Thermal	
Temp., ° C.	500	525	580	600
Flow rate, moles/l./hr.	13.7	12	0.5	0.5
% decomposed	44	48	14	20
Fraction as wt. % of liquid boiling 25-185° C.				
25–55° C.	17	13	7	8
55–75° C.	26	27	2	2
75–95° C.	11	10	26	24
95–115° C.	15	18	47	44
115–145° C.	12	10	11	14
145–175° C.	11	10	4	5
175–185° C.	8	12	3	3
Above Decalin	36	about 30	103	73
Olefin content, wt. of fraction				
25–55° C.	25	...	21	22
55–75° C.	20	20	...	...
75–95° C.	...	...	46	44
Aromatic conten , wt. % of fraction (75–95° C.)	<15	<20	47	54

BICYCLOHEXYL. Thermal cracking was investigated (*2*) at 500°, 550°, and 600° C. The rate of decomposition was about one thousandth of that observed catalytically. Formation of gas and higher-boiling residue was more extensive relative to the 10–200° C. fraction than with the catalyst. As with Decalin, the thermal production of hydrogen was pronounced, being about four times as plentiful as the catalytic for the same amount of decomposition. The thermally cracked liquid was highly unsaturated, but the catalytic was not.

ACKNOWLEDGMENT

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QUINACRINE HYDROCHLORIDE . . .

Improvements in Manufacturing Processes[1]

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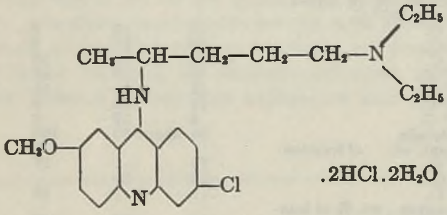
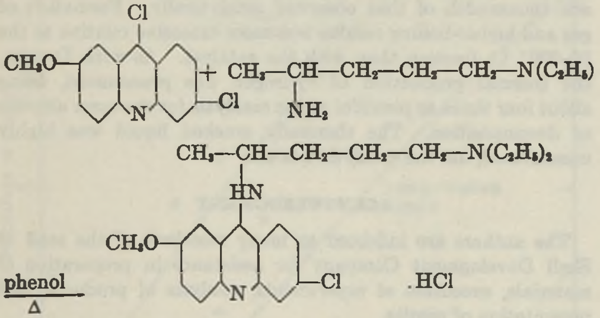
A number of improvements have been made in the process for manufacturing quinacrine hydrochloride. The quantity of phenol used in the initial reaction has been substantially reduced. The phenol has been removed from the reaction mixture by aqueous sodium hydroxide. The concentration of hydrochloric acid from which quinacrine hydrochloride is precipitated has been reduced to 1%. Water-insoluble impurities have been removed from the crystallized product by washing with warm acetone.

THE wartime need for vast quantities of antimalarial drugs made the large-scale manufacture of quinacrine hydrochloride (*1*) a problem of prime importance. This paper deals only with the last stage of the complete manufacturing process—that is, the condensation of 2-methoxy-6,9-dichloroacridine with 1-diethylamino-4-aminopentane and the purification of the resulting quinacrine after conversion to the dihydrochloride (dihydrate):



(1)

The condensation of the two intermediates is best effected by heating them together in the presence of phenol, and previous investigators (*1*) recommended that a large quantity of phenol be used:



The resulting reaction mixture is a viscous liquid at 100° C. and a hard resinous mass at room temperature. From this mixture the quinacrine must be separated and converted to the dihydrochloride dihydrate (formula 1) in a high state of purity.

The process as disclosed in the patent literature (*2*) is, briefly, as follows: A mixture of 1 mole of 2-methoxy-6,9-dichloroacridine, 1 mole of 1-diethylamino-4-aminopentane, and 5 or 6 moles of phenol is heated at 130° C. for 1 hour. The melt is shaken with 2 *N* sodium hydroxide solution, and the quinacrine free-base is extracted with ether. The quinacrine is removed from the ether solution by agitation with aqueous acetic acid. Upon treatment of the acetic acid solution with sodium hydroxide, the quinacrine is released as the free-base which is taken up in ether. Finally, the ether solution is dried and treated with hydrogen chloride to precipitate quinacrine hydrochloride.

Obviously this process would have to be modified for operation on any commercial scale. In practice, quite a different procedure has been employed. The hot phenol reaction mixture is transferred into a large volume of acetone, and the resulting solution is treated with an excess of 36% hydrochloric acid to precipitate quinacrine dihydrochloride. The product is collected and washed twice by suspension in acetone to remove all of the phenol. The crude dihydrochloride is recrystallized by solution in warm water followed by treatment of the filtered solution with concentrated hydrochloric acid until the solution contains 5% of free acid. This brings about almost complete precipitation. The crystals are collected and washed twice by slurrying with acetone. Finally the product is dried at 50° to 60° C.

There are a number of serious drawbacks to the process as just outlined. The first precipitation from acetone by the addition of concentrated hydrochloric acid must be conducted carefully, and the mixture must be cooled slowly in order to obtain crystals which can be easily filtered. Even with the most careful control, extremely fine crystals are sometimes obtained which are difficult to handle. The process is wasteful of acetone. Experience has indicated that, for every pound of quinacrine produced, about 2.5 pounds of acetone are lost, even though a fairly efficient acetone recovery system is employed. The several washings of the product with acetone and subsequent filtrations require an excessive amount of handling of the product and the use of much equipment. Both the acetone-hydrochloric acid solution and the 5% aqueous hydrochloric acid solution, from which the crystallizations are made, are highly corrosive to equipment.

REMOVAL OF PHENOL

In improving the process, our approach was to remove the phenol from the reaction mixture by treatment with sodium hydroxide solution. This would eliminate the use of the large volumes of acetone. It would also greatly reduce the amount of equipment needed, because the reaction, the removal of phenol, and the conversion of the quinacrine to the dihydrochloride could all be carried out in the same vessel. When the reaction mixture is treated with sodium hydroxide solution, the phenol is taken into the aqueous phase as sodium phenate, and the quinacrine free-base remains as a gummy, water-insoluble mass. As mentioned, this can be taken up in ether and separated from the water solution, but the use of ether would introduce objectionable problems of handling and solvent recovery.

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[1] Publication of this paper was withheld, at the time of its original submission, by the government censor for reasons of national security.

It was found that the gummy, quinacrine free-base becomes a mobile liquid at 80° to 90° C. Further, when the reaction mixture containing phenol was treated with hot aqueous sodium hydroxide solution and then cooled to about 40° C., the quinacrine base could be sharply separated from the water solution, provided the density differential between the two was great enough. If the specific gravity of the water solution was 1.13 or greater, the quinacrine base separated to the top, whereas if the specific gravity of the water solution was 1.06 or lower, the base separated to the bottom. When the specific gravity of the aqueous solution was between these two values, separation was not satisfactory. In practice it was advantageous to use sufficient water so that the resulting water solution had a specific gravity of about 1.04. If 5 moles of phenol had been used with each mole of the reactants as specified, the large volume of water required would have presented a handling problem. Thus, for each 100 pounds of resultant quinacrine about 250 gallons of water solution were necessary to remove the phenol. This difficulty was overcome when it was found that a large excess of phenol was not necessary in the reaction. In fact, the yield of quinacrine was slightly improved if only 1.25 to 1.5 moles of phenol were used with each mole of intermediates.

To obtain optimum yields and a final product having the desired color, it was necessary to control the reaction temperature closely. The reaction proceeded spontaneously with heat evolution at 110° to 115° C., and it was necessary to resort to efficient cooling to hold the temperature below 115° C. The adverse effect of higher reaction temperatures on yield is indicated by the following figures:

Reaction Temp., ° C.	Reaction Time, Hr.	% Yield of Quinacrine Dihydrochloride Dihydrate
115	1	85
130	1	77
145	1	67
160	1	55
175	3/4	50
175	2	0

Reaction temperatures above 115° C. also led to a product containing colored impurities which were difficult to remove in order to meet the desired color standard.

The removal of phenol from the reaction mixture by stirring for an hour with hot 1.2 *N* sodium hydroxide solution introduced the question as to whether the quinacrine decomposed appreciably under these conditions. Laboratory tests indicated that not more than 0.5 to 1% decomposition occurred when it was heated for 1 hour at 100° C. with 1.2 *N* sodium hydroxide. After the treatment with sodium hydroxide solution, the quinacrine base was washed twice by agitation with hot distilled water.

HYDROCHLORIC ACID CONCENTRATION

The conversion of the base to the dihydrochloride and its final purification involved dissolving it in hydrochloric acid, treating the resulting aqueous solution with carbon, filtering, crystallizing, and washing the crystalline dihydrochloride with acetone.

The quinacrine base was taken into solution by heating and agitating it with four or five volumes of water containing approximately the theoretical quantity of hydrochloric acid necessary to form the dihydrochloride. The pH of the solution was adjusted to 3.5–4.5, in which range the solubility of quinacrine hydrochloride is at a maximum. A quantity of activated carbon equal to 2.5% of the total weight of the solution was added, and the resulting mixture agitated and heated to 80° C. for an hour. Adsorption isotherm studies indicated a grade of activated carbon known as Darco G 60 gave best results. Other studies indicated that the decomposition of quinacrine hydrochloride in water solution (pH 4.5) at 80° to 100° C. was less than 0.6% per hour.

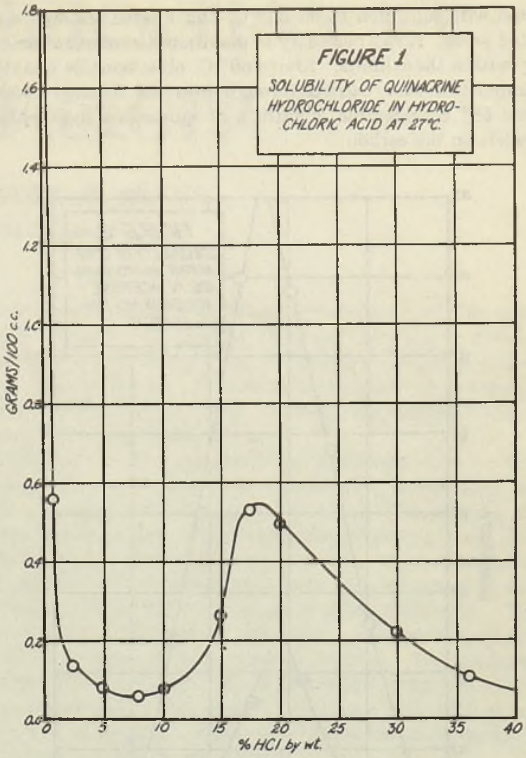

FIGURE 1
SOLUBILITY OF QUINACRINE HYDROCHLORIDE IN HYDROCHLORIC ACID AT 27°C.

After heating for 1 hour with carbon, the solution was cooled to below 40° C. and allowed to stand for 2 hours or longer. This period of standing was found to be necessary in order to allow the precipitation of difficultly soluble impurities which otherwise appeared in the finished product. The mixture was then rapidly

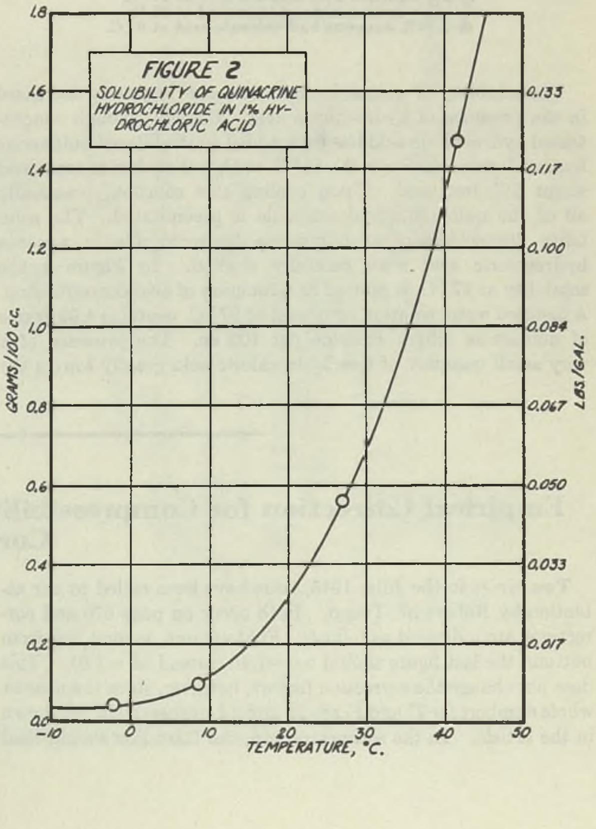

FIGURE 2
SOLUBILITY OF QUINACRINE HYDROCHLORIDE IN 1% HYDROCHLORIC ACID

heated with agitation to 58–60° C. and filtered through a preheated press. It was necessary to maintain the temperature carefully within these limits. Above 60° C. objectionable quantities of impurities were carried through into the finished product. Below 58° considerable quantities of quinacrine hydrochloride were left on the carbon.

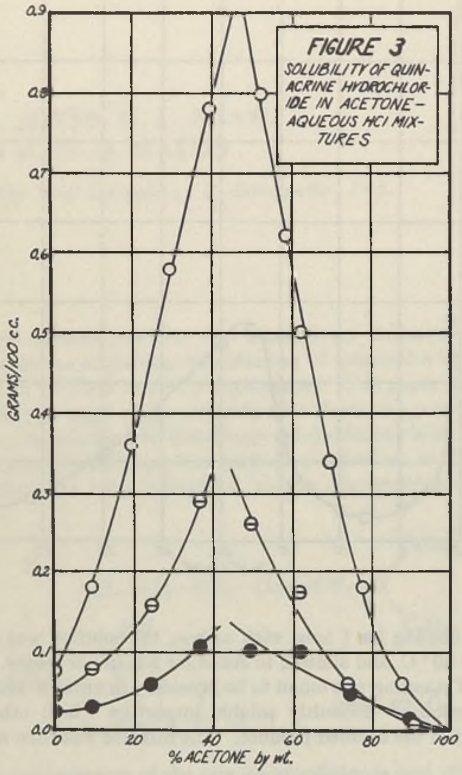

FIGURE 3
SOLUBILITY OF QUINACRINE HYDROCHLORIDE IN ACETONE–AQUEOUS HCl MIXTURES

○ 5% aqueous hydrochloric acid at 27° C.
⊖ 1% aqueous hydrochloric acid at 0° C.
● 2.54% aqueous hydrochloric acid at 0° C.

The solubility of quinacrine hydrochloride is greatly decreased in the presence of hydrochloric acid. Usually, enough concentrated hydrochloric acid has been added to the filtered quinacrine hydrochloride solution at 50–55° C. so that the solution contained about 5% free acid. Upon cooling this solution, practically all of the quinacrine hydrochloride is precipitated. The solubility characteristics of quinacrine hydrochloride in aqueous hydrochloric acid were carefully studied. In Figure 1 the solubility at 27° C. is plotted as a function of acid concentration. A distilled water solution saturated at 27° C. contains 4.92 grams of quinacrine dihydrochloride per 100 cc. The presence of a very small quantity of free hydrochloric acid greatly lowers the solubility, and the minimum solubility is reached in approximately 8% acid solution. The use of 8% hydrochloric acid was objectionable, however, because of its corrosive action on the process equipment, and also because it created numerous difficulties in drying the final product. Figure 2 presents the effect of temperature on the solubility of quinacrine hydrochloride in 1% acid. This curve shows that effective precipitation is obtained at 0° to 5° C. In this temperature range the solubility in 1% hydrochloric acid is less than 0.006 pound per gallon.

CRYSTALLIZATION

The characteristics of the crystals obtained in the precipitation from acid solution were highly important from the standpoint of both filtration and of the disintegration rate of tablets made from the quinacrine dihydrochloride dihydrate. Agitation during precipitation brought about the formation of extremely small crystals which were difficult to handle. It was found highly important to avoid any agitation until the temperature throughout the entire mixture was below 20° C.

Following filtration at 5° C., the wet cake of quinacrine hydrochloride crystals was slurried with acetone to facilitate removal of the remaining hydrochloric acid solution and colored impurities. The solubility of quinacrine hydrochloride in mixtures of acetone and aqueous hydrochloric acid solutions of various concentrations was investigated. Figure 3 discloses that, in mixtures containing 40 to 45% acetone, the solubility reaches a sharp maximum. To avoid appreciable loss of quinacrine hydrochloride in the acetone slurry stage, it was therefore advantageous to use sufficient acetone so that the resulting solution contained more than 80% acetone. A second acetone slurry at 30° to 35° C. removed any residual water-insoluble impurities.

The product was dried to the dihydrate (formula 1) in a hot air dryer for 13 hours at 50° C.

The process outlined here has a number of advantages over the former one. The yields have been 85% of theoretical, or higher, of a product of consistently high purity. Maximum yields by the old process were about 77%. A 33% increase in the volume of production has been achieved with only 60% of the original equipment, which was relatively easily adapted to the present process. The consumption of acetone has been reduced by approximately 40%, phenol by 65%, and hydrochloric acid by 55%. The reduction in the quantity of phenol, removed in the present process as sodium phenate, simplifies the problem of recovery or disposal of phenol residues. Corrosion of equipment by hydrochloric acid has been reduced to a minimum. Simplification of the process and equipment has reduced labor requirements as well as maintenance.

LITERATURE CITED

(1) Drosdov and Cherntzov, *J. Gen. Chem.* (U.S.S.R), 5, 1576, 1736 (1935); Magidson and Grigorovskiĭ, *Khim. Farm. Prom.*, 1933, 187; Jensch and Eisleb, U. S. Patent 1,782,727 (1930); Schulemann, Mietzsch, and Wingler, U. S. Patent 1,889,704 (1932).
(2) Mietzsch and Mauss, U. S. Patent 2,113,357 (1938).

Empirical Correction for Compressibility Factor and Activity Coefficient Curves—Correction

Two errors in the July, 1945, issue have been called to our attention by Robert M. Trapp. Both occur on page 670 and corrections are indicated as follows: First column, second line from bottom, the last figure should be −1.46 instead of −1.61. This does not change the correction factors, however, since the nearest whole numbers for T_r and P_r are 28 and 14, respectively, as shown in the article. In the second column, the third line should read $f/p = 1.16$ instead of 1.15. It should be pointed out that these correction factors should not be considered accurate to better than 1%. If these curves approximate actual conditions to within 1 or 2%, their use will be justified.

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BUTADIENE PURIFICATION BY SOLVENT EXTRACTION

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Apparatus and method used to investigate solubility and distribution in C_4 olefin-solvent systems are described. Mixtures of components were used to obtain solvents of desirable characteristics. Data are presented for three types of solvent mixtures: miscible, immiscible, and a miscible mixture containing complex-forming salts. The inherently small differences in physical properties between butadiene and the C_4 mono-olefins preclude the possibility of an ideal solvent. The choice of solvent must be made on an economic basis. The applications of extraction processes in general and of quaternary systems are discussed.

BUTADIENE used for copolymerization to synthetic elastomers should have a purity of 98.5% and be free, particularly, from acetylenic derivatives. Initial purification and repurification of the gas recycled in the process have been obstacles to the commercial use of butadiene. A survey of purification processes was made at the beginning of the synthetic rubber program in connection with current activities in plant construction. Experimental work was then undertaken to supplement available published information on the process of liquid-liquid extraction. The work was limited to a study of the removal of butene isomers in initial purification of butadiene by measurement of solubility and equilibrium in C_4 olefin-solvent systems. This paper presents the experimental method and data for several solvent mixtures. The field of usefulness of extraction is rapidly expanding, but the theory is not so clearly understood as it is in other unit operations. A pertinent discussion of extraction is therefore included in the paper, and some observations on the use of quaternary diagrams are given.

Butadiene can be concentrated by distillation from a mixture of butane and butene homologs with which it is commonly associated, but cannot be purified in this way. The presence of 1-butene and isobutene, which have normal boiling point differences only 1.7° and 2.2° C. from butadiene, make this operation impracticable. Several methods have been proposed to effect purification which take advantage of other differences. These are adsorption, absorption, extraction, azeotropic distillation, extractive distillation, and chemical reaction. The conjugated double bond of butadiene, which makes the compound of value for polymerization, also imparts resonance. In consequence, differences in properties between the diene and mono-olefins are not so great as might be anticipated.

The purification of butadiene by extraction is an important example of the application of this operation to close-boiling compounds. The limitations in distillation caused by similar vapor pressures of the components or deviations from ideal solution resulting in azeotropes are not operative in extraction. On the contrary, a deviation from Raoult's law is essential to extraction, usually between the components to be separated, and always

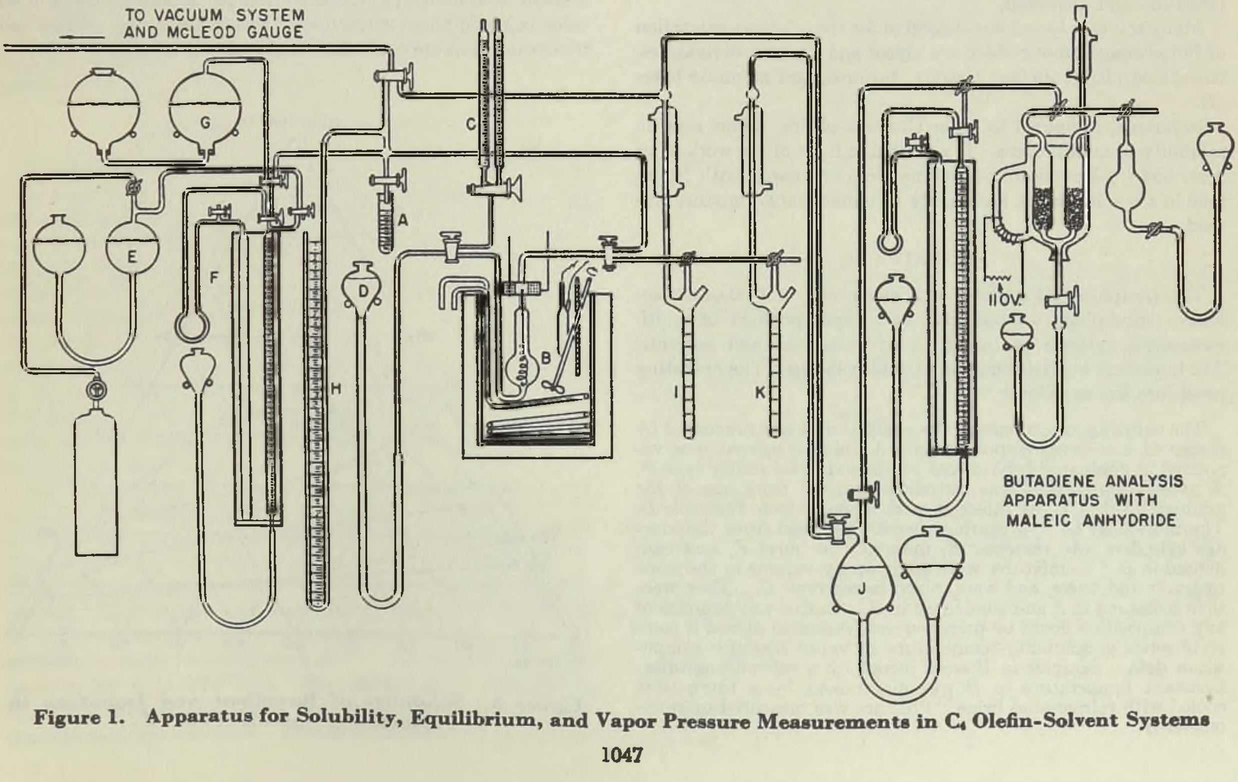

Figure 1. Apparatus for Solubility, Equilibrium, and Vapor Pressure Measurements in C_4 Olefin-Solvent Systems

between the solvent and one component where the deviation must be large enough to cause partial miscibility. Immiscibility of two components indicates a large positive deviation. A third component will be distributed between the other two if it deviates from Raoult's law to a different degree in each.

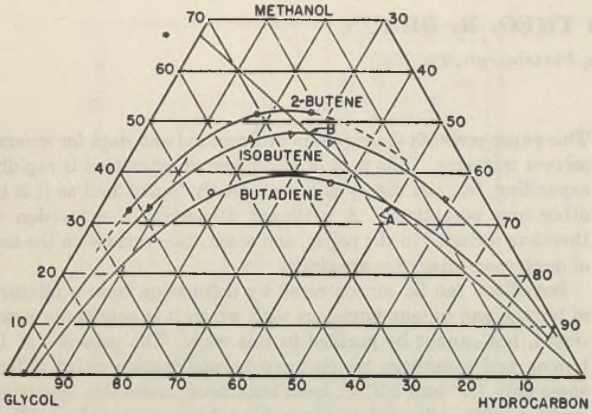

Figure 2. Solubility of C_4 Olefins in Methanol and Glycol at 20° F.

The most important application of extraction is to the difficult separations encountered in resolving azeotropes or mixtures with similar vapor pressure as in petroleum or fatty acid fractions. Butadiene-butene mixtures are similar to *n*-heptane–methylcyclohexane or C_{18} fatty acid mixtures in that the components of each mixture form nearly ideal solutions, and each component exhibits positive deviations in solvents which are effective in the separation of the mixture. There is a difference in the degree of deviation, and separations can be obtained in efficient multicontacting equipment. The deviation, and therefore solubility, differences which effect separation in the case of butadiene mixtures are the result of small differences in the forces of polarization and dispersion.

Many solvents have been suggested for the selective extraction of butadiene. Among these are glycol and glycerol derivatives, lactic acid nitrile, diethyl tartrate, furfural, and aromatic bases (*2*).

Isobutene, compared to other C_4 mono-olefins, differs least in solubility from butadiene. It was used in most of the work to be described. 1-Butene and 2-butene were compared with isobutene in a few instances, and finally a commercial C_4 mixture was used.

APPARATUS

The equipment (Figure 1) was assembled to evaluate solubility, liquid-phase compositions, and vapor pressure of multicomponent systems of liquid C_4 hydrocarbons and solvents. The butadiene analysis equipment is also shown. The operating procedure was as follows:

The entire apparatus except the analysis unit was evacuated by means of a mercury vapor pump. A volatile solvent was vaporized in graduated tube *A* and condensed in solubility tube *B*. A nonvolatile solvent was introduced into *B* from one of the graduated tubes, *C*, by injection with mercury from reservoir *D*. The individual C_4 hydrocarbons were vaporized from the storage cylinders into reservoir *E*, measured in buret *F*, and condensed in *B*. C_4 mixtures were made up by volume in the same reservoir and buret, and were mixed in reservoir *G*. They were then measured in *F* and condensed in *B*. In this way samples of any composition could be prepared and varied to obtain a complete series of solubility-temperature or vapor pressure–composition data. Samples in *B* were mixed by a solenoid agitator. Constant temperature in *B* was maintained by a thermostat cooled with refrigerated brine. Pressure was measured on manometer *H*.

Liquid-phase separation was accomplished by mixing the components in *B* in proportions to produce two phases, and adding mercury from *D* to discharge the top phase into graduated tube *I* which was cooled with ice and salt. The volume of the phase was measured, and the C_4 hydrocarbons were stripped from the liquid by heating *I*. The residual liquid volume was measured in *I*. The evolved gas was collected in reservoir *J*, measured in the buret of the butadiene analysis apparatus, and finally analyzed. The lower phase was discharged into graduated tube *K* and measured in the same way. Density-temperature-composition relations were determined for the solvents and solvent mixtures used. Tie lines were determined in weight or volume units from the lever arm principle, knowing the relative proportions of the two phases; or by actual analysis for solvent content and hydrocarbon composition of each phase as described.

MATERIALS. Isobutene was prepared by dehydration of *tert*-butanol over alumina at 400° C. A middle fraction was obtained for use by simple distillation. 1-Butene and 2-butene were obtained from The Matheson Company, Inc., with a stated purity of 99%. Butadiene from The Matheson Company was 98% pure. The Firestone Tire and Rubber Company kindly furnished butadiene for preliminary work. A C_4 hydrocarbon fraction containing 35% butadiene was supplied by the Petroleum Conversion Corporation. The solvents were C.P. chemicals.

SELECTION OF SOLVENTS

Solvents were selected for trial by analogy from known solubility properties of hydrocarbons. Furfural, alcohols, and amines are compounds which give positive deviations from Raoult's law in hydrocarbon solutions. Figures 2 and 3 present three types of typical solubility behavior of C_4 hydrocarbons with methanol, glycol, and furfural at 20° F. Little use was made of vapor pressure measurements in comparing solvents, as solubility was more quickly determined. This type of information is necessary, however, in solvent recovery. The order of the deviation in total measured pressure from the calculated value is shown in Figure 4 for ethylene glycol solutions.

Both components of a mixture must be incompletely miscible with a solvent if each is required to be separated in a pure state. Ethylene glycol would fulfill this requirement for butadiene-butene separation. The amount of this solvent which would be necessary is too great for practical use, however, because of the limited solubility shown in Figure 2. Methanol is completely miscible with both C_4 hydrocarbons at 20° F. and would be of no value in liquid-phase extraction at this temperature. Water and triethanolamine are equivalent to glycol.

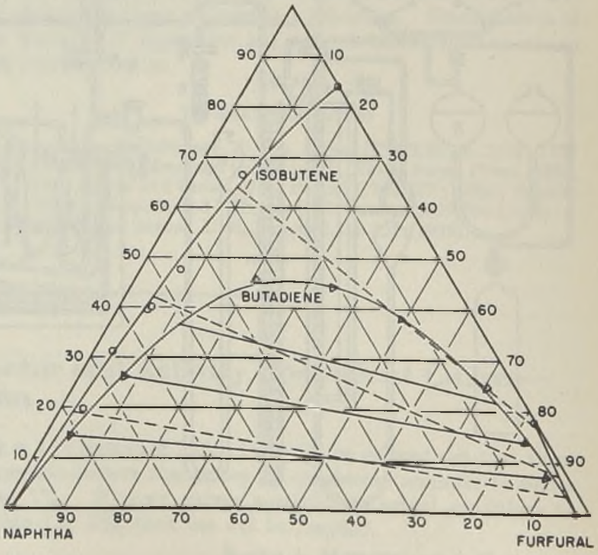

Figure 3. Solubility of Butadiene and Isobutene in Furfural and Naphtha at 20° F.

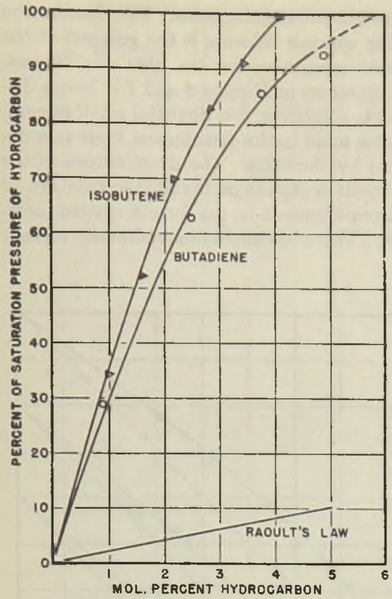

Figure 4. Deviation from Ideal Solution of Butadiene and Isobutene in Glycol at 20° F.

The selectivity of chemically similar solvents for a given component in a mixture is, in general, inversely proportional to the mutual solubility in the system. Solvent requirements and selectivity can be altered, but not independently, by mixing solvents. Compounds have been blended to obtain a solvent mixture of ideal characteristics for lubricating oil extraction (*7*). Solvents blended from alcohols and glycols were determined to be selective essentially for hydrocarbon structure by Smith and Funk (*8*). Since the preliminary work indicated that no single solvent was likely to fulfill all requirements for butadiene purification in liquid-liquid extraction, mixed solvents were investigated.

Solubility measurements, similar to those shown in Figure 2, were made with five miscible solvent pairs: methanol-water, methanol-glycol, glycol-acetone, glycol-isopropanol, and triethanolamine-methanol. One immiscible solvent pair was investigated—furfural-naphtha. Finally a miscible solvent system containing cuprous chloride was studied. The latter system was intended to combine the effect of chemical reaction with solubility difference to enhance the distribution of butadiene and butenes between two liquid phases.

MISCIBLE SOLVENT SYSTEMS

The choice of a solvent or solvent mixture must be made with regard to both solvent requirements and distribution, other things being equal, for practical use. The selectivity of five solvent pairs was compared at equal solubilities from data illustrated by Figure 2. This is an approximation which would not be justified if the two components did not form nearly ideal solutions. The comparison is shown in Figure 5, where the ratio of the amount of mixed solvent to the amount of butadiene is plotted against the ratio of butadiene and isobutene, solvent-free, in the two ternary mixtures at constant solvent composition. For example, point *A* in Figure 2, representing a solvent/butadiene ratio of 1, is plotted against the butadiene/butene ratio at points *A* and *B*, of 1.72.

The solvent pair triethanolamine-methanol shows the best apparent distribution at low solvent ratios. At a solvent ratio of 1, the solvent composition is 57% triethanolamine by weight. This composition was used in measurements of equilibrium and solubility in ternary systems of the mixed solvent, butadiene-isobutene. A C_4 fraction analyzing 35% butadiene was substituted for the two pure hydrocarbons in two measurements. The data are given in Table I and Figures 6 and 7. All measurements were made at 20° F. (−6.67° C.). The raffinate phase contained no solvent; therefore, the use of rectangular coordinates to represent the data was adequate. Extraction column calculations can be made by the method exemplified by Maloney and Shubert (*6*) for the four-component system.

TABLE I. PHASE RELATIONS IN THE SYSTEM BUTADIENE-ISOBUTENE-SOLVENT[a] AT 20° F.

Equilibrium, Wt. % Butadiene (Solvent-Free) in: Solvent phase	Hydrocarbon phase	Solvent Content: Wt. % Butadiene (Solvent-Free)	Lb. Solvent/Lb. Hydrocarbons in: Solvent phase	Hydrocarbon phase
79.2	77.6	0	4.79	0
56.4	51.2	65.2	1.64	..
50.9	44.6	79.2	1.28	..
40.2	32.2	79.6	1.27	..
54.6	47.4 (C_4 fraction)	93.2	0.94	..
37.2	25.5 (C_4 fraction)	100.0	..	0

[a] Solvent = 57% triethanolamine + 43% methanol.

IMMISCIBLE SOLVENT SYSTEM

Furfural and a hydrocarbon such as iso-octane have been used to separate fatty acids by extraction (*3*). Furfural is a selective solvent for the more polar components of a fatty acid mixture and also of their glycerol esters. Its use in lubricating oil extraction is common. It becomes miscible with low-molecular-weight hydrocarbons, as it is with fatty acids, at normal temperature and cannot be used as a single solvent. The use of furfural for these extractions is made possible by the addition of a paraffin hydrocarbon of sufficiently great molecular weight to be insoluble in it. There is, then, a distribution of the components of the mixture to be separated between the furfural and paraffin hydrocarbon phases.

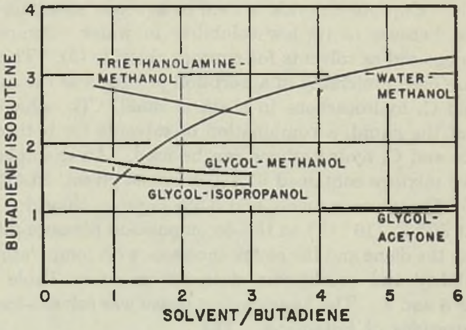

Figure 5. Selectivity of Solvent Mixtures

Solubility and equilibrium data for the systems butadiene-isobutene-furfural, butadiene-naphtha-furfural, and isobutene-naphtha-furfural are given in Tables II and III and Figures 3 and 8. The four-component system furfural-butadiene-isobutene-naphtha is plotted in part in Figure 9; data are given in Table IV. Tie line data which do not permit interpolation are not included

TABLE II. FURFURAL-HYDROCARBON SOLUBILITY AT 20° F. (WEIGHT PER CENT)

Butadiene[a]	Isobutene	Furfural	Isobutene	Furfural	Naphtha	Butadiene[a]	Furfural	Naphtha
7.0	20.7	72.3	19.8	3.7	76.5	14.4	3.8	81.8
22.0	26.5	51.5	31.2	3.0	65.8	26.3	7.5	66.2
22.7	49.8	27.5	39.5	5.0	55.5	45.9	20.6	33.5
13.6	65.3	21.1	40.2	5.5	54.3	44.1	34.8	21.1
6.4	78.6	15.0	47.5	6.9	45.6	37.9	49.3	12.8
0	84.1	15.9	55.9	9.6	34.5	24.8	70.3	4.9
0	17.9	82.1	66.6	7.0	26.4	13.8	82.7	3.5
						7.0	89.2	3.8

[a] 98% pure.

Table III. Furfural-Hydrocarbon Equilibrium at 20° F. (Weight Per Cent)

	Hydrocarbon Phase			Furfural Phase		
Butadiene	14.4	26.3	36.5	7.0	13.8	21.7
Naphtha	81.8	66.2	51.0	3.8	3.5	4.0
Furfural	3.8	7.5	12.5	89.2	82.7	74.3
Isobutene	19.2	64.0		3.0	16.2	
Naphtha	78.3	26.5		2.0	0.3	
Furfural	2.5	9.5		95.0	83.5	
Butadiene	7.1			17.0		
Isobutene	20.6			61.0		
Furfural	72.3			22.0		

in the tables, and only experimental values have been used. Equilibrium in the four-component system can be represented by a single curve (Figure 6) on rectangular coordinates. Solvent content, however, must be plotted at fixed ratios of solvent/hydrocarbons and furfural/naphtha when rectangular coordinates are used, as with ternary systems. Figure 7 shows this for two furfural/naphtha ratios. The points at 0 and 100% butadiene were obtained from the ternary diagrams. The naphtha used was Stoddard solvent with the following properties: specific gravity, 0.7668 at 60° F.; bromine number, 1.47; A.S.T.M. distillation, initial point 316°, end point 376° F.

CHEMICAL REACTION IN SOLUTION

The use of cuprous halides in butadiene purification is one of the oldest methods. The halide, used either as a solid, in suspension, or in solution, forms complex compounds with olefins. The butadiene complex has a higher decomposition pressure than that of the mono-olefins at the same temperature, and separation is possible. Cuprous chloride is used in aqueous ammonia or acid solution because of its low solubility in water. Amines have been suggested as solvents for cuprous chloride (*5*). These solutions are used preferably in absorption processes as the solubility of liquid C_4 hydrocarbons in them is small. To enhance solubility of the liquid, a combination of solvents for both cuprous chloride and C_4 hydrocarbons can be used. An example of one effective mixture contained 61.5% ethylene glycol, 26.4% methanol, 6.6% sodium cyanide, and 5.5% cuprous chloride. It was used at 50° F. (10° C.) as the decomposition pressure difference between the diene and the olefins increases with temperature.

Solubility and equilibrium data are given in Table V and Figures 6 and 7. The hydrocarbon phase was solvent-free at all concentrations of butadiene. The solvent mixture was stable, after precipitation of sodium chloride formed from reaction of the salts, and could be re-used after being freed from the hydrocarbons by heating and flashing. Some data with re-used solvent are included. Vapor pressure measurements made with the solvent mixture before addition of the salts were believed to indicate that chemical reaction was contributing to the equilibrium distribution between the two phases.

DISCUSSION OF SYSTEMS

Each of the three solvent types for which data have been given will effect a separation of butadiene from C_4 olefins. As each is stable and easily recovered, the choice lies in a consideration of equilibrium compared to solvent requirements. The distribution in the solvent containing cuprous chloride is the greatest of the three. However, solvent requirements are also the largest. (These conclusions are apparent in Figures 6 and 7.) Since distribution is proportional to solubility, it is doubtful whether complex formation contributes more to the distribution than does decreased solubility caused by the salts. The distributions in the furfural-naphtha and triethanolamine-methanol solvents are of similar order. Solvent requirements in the former system, however, are much greater. The triethanolamine-methanol solvent

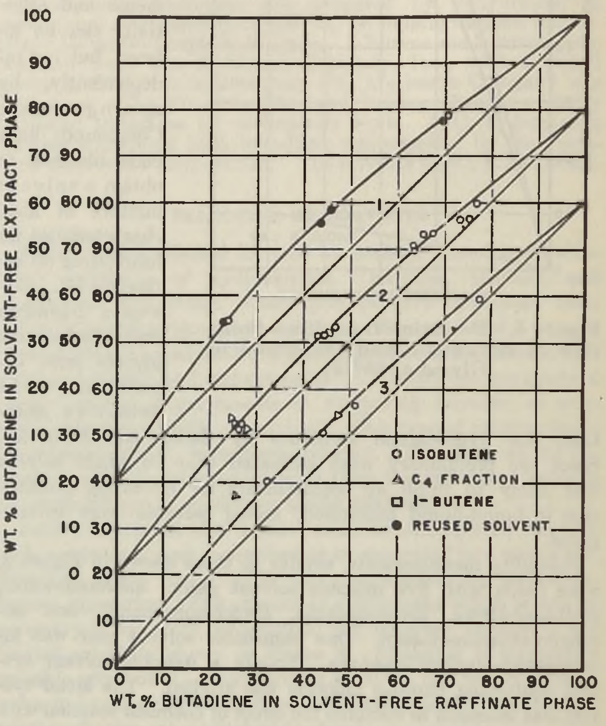

Figure 6. Butadiene–Mono-olefin Equilibrium in Solvent Mixtures

1. **61.5% glycol, 26.4% methanol, 12.1% $Na_3Cu(CN)_4$ at 50° F.**
2. **Furfural-naphtha at 20° F.**
3. **43% methanol, 57% triethanolamine at 20° F.**

Table IV. Equilibrium and Solubility in the System Butadiene-Isobutene-Furfural-Naphtha at 20° F.

	Original Mixt.		Solvent Phase			Hydrocarbon Phase		
No.	Lb. furfural / Lb. naphtha	Lb. solvent / Lb. C_4 HC	Wt. % naphtha (free of C_4 HC)	Wt. % butadiene (solvent-free)	Lb. solvent / Lb. C_4 HC	Wt. % naphtha (free of C_4 HC)	Wt. % butadiene (solvent-free)	Lb. solvent / Lb. C_4 HC
1	0.54	1.54	17.5	48.7	2.26	89.1	46.5	1.35
2	1.53	1.56	5.0	31.4	4.58	88.2	26.4	0.88
3[a]	1.45	1.58[b]	8.6	31.4	3.66	85.4	27.9	0.96
4	1.51	1.76[c]	8.8	52.0	4.70	84.2	45.6	0.99
5[a]	1.47	1.81	8.4	73.2	3.56	81.5	67.7	1.17
6	1.57	1.71	4.9	73.2	3.63	75.4	65.4	1.09
7[a]	4.30	1.89	6.0	32.1	4.60	75.8	25.1	0.63
8	4.62	1.82[b]	4.5	33.9	4.94	74.6	24.8	0.61
9	4.30	3.17	7.2	51.2	5.58	88.1	43.0	0.95
10[a]	4.15	1.93	6.6	51.6	3.58	76.2	44.6	0.74
11[a]	4.72	1.96	5.7	69.8	3.03	61.8	63.8	0.83
12[a]	4.35	1.82	5.2	76.6	2.83	62.8	75.2	0.83
13	4.35	1.94	9.3	79.1	3.23	59.4	77.0	0.75
14	8.00	1.88	4.7	32.5	3.86	66.8	27.0	0.49
15	8.50	1.84	4.7	70.8	2.59	54.4	63.1	0.60
16	8.42	2.13[b]	4.2	32.4	5.69	71.7	25.3	0.48
17	9.55	2.10	6.9	48.7	3.09	28.6	45.1	0.65
18	10.90	0.93	3.8	27.3	3.77	35.3	25.3	0.25
19	11.92	0.89	4.7	53.1	2.06	18.0	46.6	0.40
20	11.50	1.11	...	76.3	1.88	31.1	73.2	0.78

[a] Projected on quaternary diagram in Figure 9.
[b] C_4 hydrocarbon mixture (HC = hydrocarbon).
[c] 1-Butene.

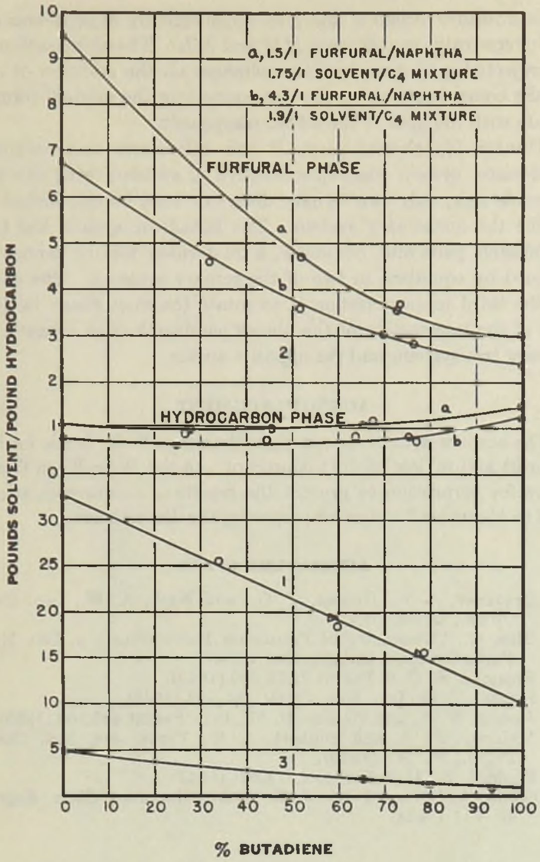

Figure 7. Solubility of Butadiene-Mono-olefin-Solvent Mixtures

1. 61.5% glycol, 26.4% methanol, 12.1% $Na_3Cu(CN)_4$ at 50° F.
2. Furfural-naphtha at 20° F.
3. 43% methanol, 57% triethanolamine at 20° F.

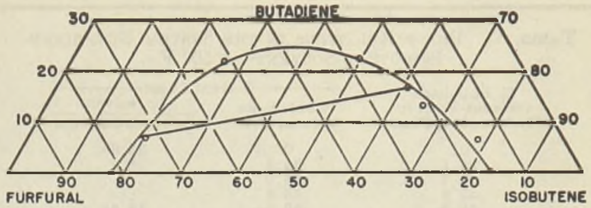

Figure 8. Solubility in the System Butadiene-Isobutene-Furfural at 20° F.

system, therefore, indicates the best distribution consistent with low solvent ratio. The minimum reflux and solvent ratios for this system are 20.5 and 6.8 with a feed containing 35 weight % butadiene, a product containing 98%, and a recovery of 99%. About sixty theoretical extraction units are required for this separation with 1.5 times the minimum reflux.

When two components, such as butadiene and C_4 olefin, do not form hydrogen bonds or complexes with a series of solvents, distribution between two liquid phases will be independent of the particular solvent at equal solubility. No immiscible solvent mixture can be equal to a miscible solvent system because only one of the solvents can show appreciable selectivity. Solvent requirements will, accordingly, be greater in the former system in proportion to which the inactive solvent (naphtha) is used. The preceding conclusions are based on data which have not yet been published. These conclusions and the number of theoretical extraction units which have been computed for separation appear to be in line with processes in commercial use. Some of the longest columns ever constructed are used in butadiene purification.

The four-component system of furfural-butadiene-isobutene-naphtha is of additional interest because few quaternary data are given in the literature. A quaternary system at constant temperature is commonly represented by a tetrahedral diagram in which each of the four apexes corresponds to 100% of one of the four components. The system can be graphically represented more easily by projection onto one triangle of the tetrahedron. Brackner, Hunter, and Nash (*1*) described the method. Figure 9 shows a projection onto the butadiene-naphtha-furfural triangle. A point on the triangle is located by adding one third of the percentage of isobutene in a mixture to the percentage of each of the other components of the mixture. The isobutene apex is thus located at $33^1/_3\%$ of butadiene, furfural, and naphtha, since $^1/_3 \times 100\%$ isobutene = $33^1/_3\%$, and $33^1/_3\% + 0\%$ butadiene = $33^1/_3\%$ butadiene, etc. The solubility diagrams of the three ternary systems were located in this way in Figure 9. Six pairs of quaternary equilibrium points are projected also. Tie lines 3

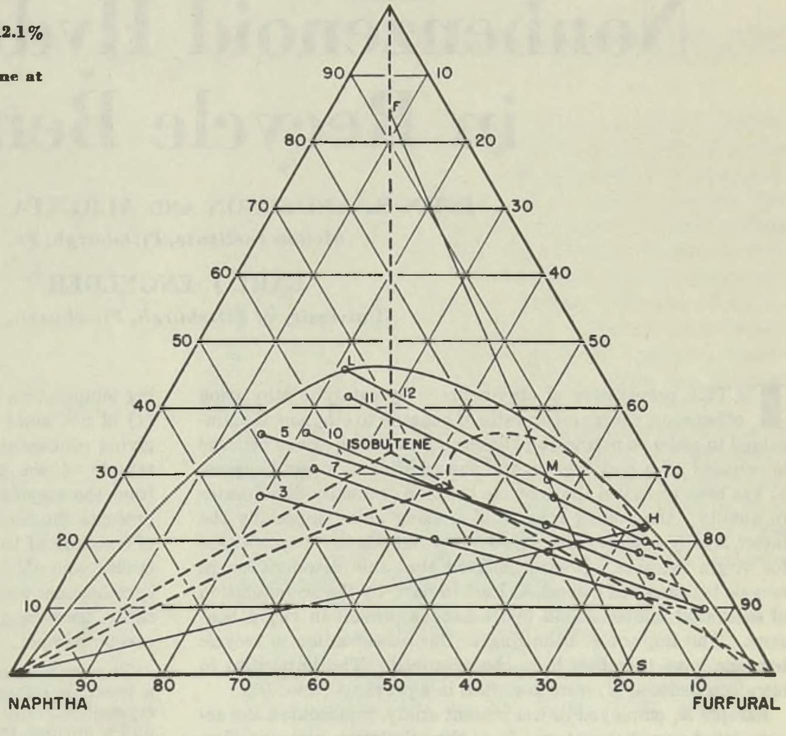

Figure 9. Projection of Quaternary System on Butadiene-Naphtha-Furfural Plane

Numbered tie lines refer to data in Table IV.

TABLE V. PHASE RELATIONS IN THE SYSTEM BUTADIENE-ISOBUTENE-SOLVENT[a] AT 50° F.

% Butadiene (Solvent-Free) in Hydrocarbon Phase	Solvent Phase	
	% butadiene (solvent-free)	Lb. solvent / Lb. hydrocarbons
0	0	32.6[b]
24.1	34.3	25.5
24.7	35.0	..
43.8	55.5	..
45.6	58.1	19.6[b]
46.6	59.7	18.6
69.3	77.5	15.6[b]
70.5	78.3	15.6
100	100	10.1[b]

[a] Solvent = 61.5% ethylene glycol + 26.4% methanol + 6.6% sodium cyanide + 5.5% cuprous chloride.
[b] Re-used solvent.

and 5 were obtained with a ratio of furfural to naphtha in the original mixture of about 1.5; the other tie lines represent a ratio of about 4.5. The three ternary solubility curves define the heterogeneous region on three sides of the tetrahedron. The solid section outlined by these curves and by the surfaces joining them on which the quaternary equilibrium points lie define the complete heterogeneous region. The equilibrium phases of tie lines 7 and 12 lie on the surfaces, but the compositions of the furfural-rich phase of the other lines plotted are apparently in error. Material balances are shown by the tie lines if the projected composition of the original mixture lies on the line, as in ternary systems.

The projected diagram has other properties equivalent to the ternary diagram. The mixture *M* resulting from the addition of naphtha and furfural of ratio *S* in Figure 9 to isobutene and butadiene in the projected ratio *F* lies on line *FS*. Its position on the line is in inverse ratio to the quantities of hydrocarbons and solvents mixed: pounds S/pounds $F = MF/MS$. The weights of equilibrium phases *H* and *L* in which mixture *M* separates are in inverse ratio to distances *MH* and *ML*. The composition of a projected quaternary mixture changes on the addition of one of the components along the line connecting the original composition with the apex of the added component.

Hunter (*4*) showed that, if the chloroform-acetone-acetic acid-water system was representative of systems with one immiscible pair, only two ternary diagrams need be established to define the quaternary system. The butadiene system has two immiscible pairs and, obviously, a quaternary tie line cannot be defined by equilibria in two of the ternary systems. The effect of the third ternary system is to rotate the quaternary tie line out of the intersection of the planes passing through ternary tie lines of two systems and the opposite apexes.

ACKNOWLEDGMENT

The authors wish to express their thanks to E. H. Leslie for his interest and review of the manuscript; to the Blaw-Knox Company for permission to present the results of this investigation; and to Mercedes Zimmer for preparing the illustrations.

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Nonbenzenoid Hydrocarbons in Recycle Benzene

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IN THE preparation of ethylbenzene by catalytic ethylation of benzene, a large molar ratio of benzene to ethylene is maintained in order to minimize polyethylation. The excess benzene is recycled after rectification and the addition of virgin benzene. It has been observed that recycle benzene gradually deteriorates in quality; the boiling range and freezing point, especially the latter, finally reach values considerably outside the specifications for virgin benzene. It was believed that this deterioration in recycle benzene was caused, at least in part, by the accumulation of saturated nonbenzenoid hydrocarbons present in virgin benzene. The impurities belonging to this classification in recycle benzene have therefore been characterized. The impurities in nitration benzene (*1*) were described in a previous paper (*2*).

Sample *A*, employed in the present study, represented the accumulated recycled material from the ethylation of a considerable volume of refined coke-oven benzene from a large number of sources. The virgin benzene entering the reaction had a solidifying temperature (*1*) of not less than 4.85° C. and a boiling range (*1*) of not more than 1.0° C. Figure 1 is a distillation curve, giving condensation temperatures of distillate at 760 mm., of a sample of the saturated nonbenzenoid hydrocarbons secured from the recycle benzene, plus some *n*-pentane. Figure 1 also presents the results of determinations of refractive indices (n_D^{20}) of fractions of the distillate, and the normal boiling points (solid circles) and n_D^{20} (open circles) of the paraffins, cyclopentanes, and cyclohexanes whose normal boiling points are within the condensation temperature range of the bulk of the nonbenzenoid hydrocarbon sample.

The methods and reagents used in this work were discussed in a previous paper (*2*). Sample *A* (35.5 liters) was fractionally crystallized until 1005 ml. of a highly contaminated product, *B*, and a purified fraction, *C*, were obtained. The solidifying temperatures (*1*) were as follows: *A*, 1.95° C.; *B*, approximately −52° C.; *C*, 3.00° C. Fraction *B* was separated into two fractions by adsorption on silica gel, using *n*-pentane to displace the

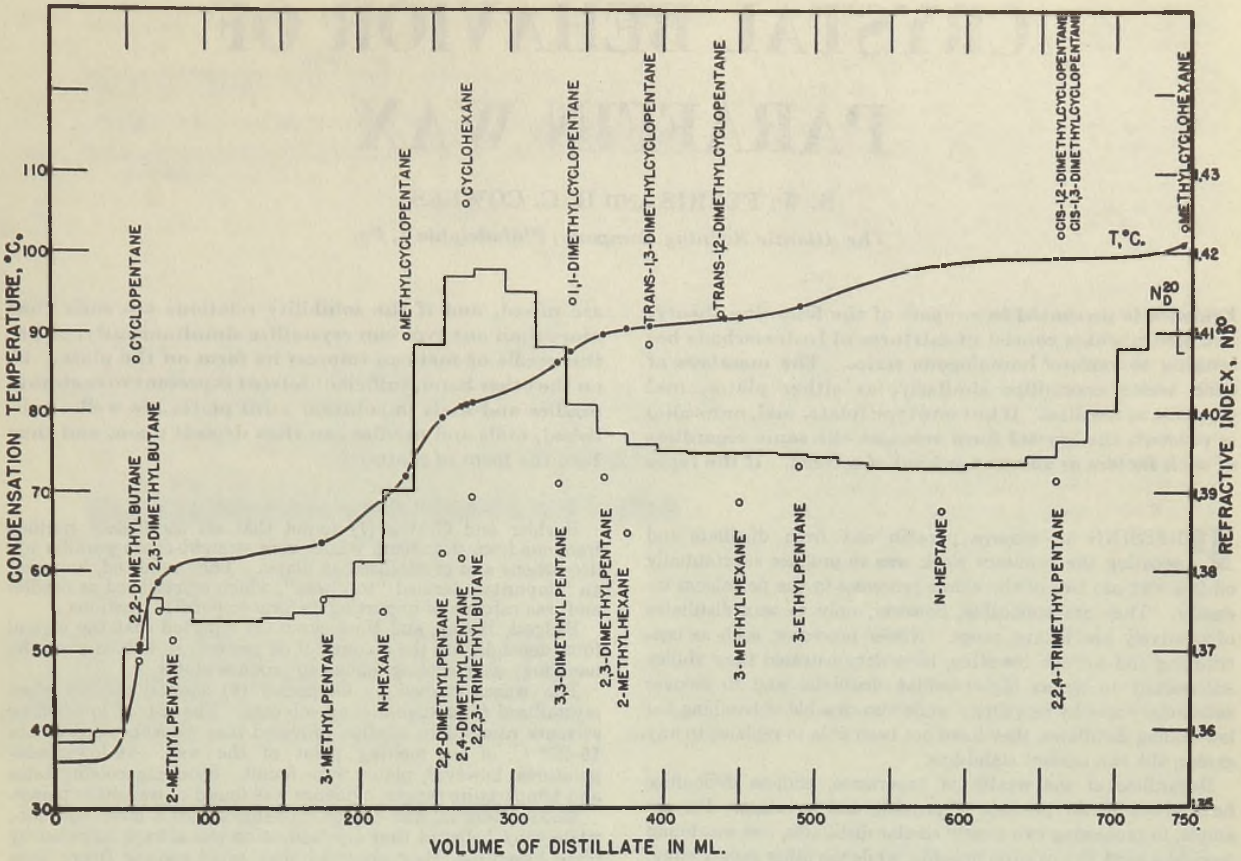

Figure 1. Condensation Temperature and Refractive Index as a Function of Volume for Saturated Nonbenzenoid Hydrocarbons Secured from Recycle Benzene Plus Some *n*-Pentane

Solid circles and open circles give the normal boiling points and refractive indices, respectively, of the indicated pure hydrocarbons known to have boiling points within the condensation temperature range. Data on the pure hydrocarbons taken from reports of A.P.I. Research Project 44 at the National Bureau of Standards.

paraffins and cycloparaffins, and methanol to displace the aromatic fraction. The paraffins and cycloparaffins, together with some of the *n*-pentane, were fractionated under high reflux in a still with a jacketed and heated column, 2000 mm. high and 26 mm. in internal diameter, made of Pyrex and packed to a height of 1960 mm. with single-turn 4-mm. (approximately) Pyrex helices. After the bulk of the displacing liquid (*n*-pentane) had been distilled, the distillation data shown in Figure 1 were obtained. A total of 600 ml. of the distillate (indicated in Figure 1) was distilled from the column, after which the remainder (140 ml.) was distilled using the still with the column of smaller diameter described in the previous paper (*2*). The last two fractions (indicated in the refractive index data of Figure 1) were obtained after Tetralin had been added to the contents of the still.

Fifteen milliliters of ethylbenzene and 125 ml. of benzene were recovered from the aromatic fraction from the separation by adsorption.

Fraction *B* (1005 ml.), obtained from 35.5 liters of recycle benzene by purification of the latter through a change of solidifying point of 1.05° C., consisted of approximately 680 ml. of saturated nonbenzenoid hydrocarbons (Figure 1), 125 ml. of benzene, 15 ml. of ethylbenzene, and 185 ml. of material unaccounted for in the analysis. These data show that the recycle benzene contained several volume per cent of saturated nonbenzenoid hydrocarbons, and that the bulk of the impurities in recycle benzene belong to this classification. However, the compositions of the nonbenzenoid hydrocarbon samples secured from recycle benzene and from virgin benzene, shown in the previous paper (*2*), are, in some respects, strikingly different.

In general, the present sample is preponderantly paraffinic, while the previous sample was preponderantly naphthenic. The data for the previous sample indicated the presence of a considerable quantity of methylcyclohexane, while its presence in the present sample in as large an amount has not been demonstrated.

The condensation temperatures (Figure 1) point to the fact that about 25% of the sample of saturated nonbenzenoid hydrocarbon impurities in the present study is composed of compounds with boiling points below 80° C.; in contrast, the previous sample (*2*) was composed almost entirely of compounds boiling above 80° C. For the present sample, for the fractions of distillate in the boiling range above 80° C., the refractive indices are, in general, considerably lower than corresponding fractions from the previous sample.

These comparisons suggest that the gradual deterioration in the quality of the recycle benzene is attributable to the preferential accumulation of paraffins. Some lower-boiling paraffins (2-methylpentane, 3-methylpentane, and *n*-hexane) seem to have been introduced during the ethylation process; most of the naphthenes (except cyclohexane) present in the original benzene appear to have been removed to a large extent.

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CRYSTAL BEHAVIOR OF PARAFFIN WAX

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Evidence is presented in support of the following theory: Petroleum waxes consist of mixtures of hydrocarbons belonging to various homologous series. The members of each series crystallize similarly, as either plates, mal crystals, or needles. If but one type (plate, mal, or needle) is present, the crystal form remains the same regardless of such factors as amount or kind of solvent. If the types are mixed, and if the solubility relations are such that more than one type can crystallize simultaneously, either the needle or mal can impress its form on the plate. If, on the other hand, sufficient solvent is present to maintain needles and mals in solution until plates are well established, mals and needles can then deposit upon, and thus take the form of plates.

PRESSING to remove paraffin wax from distillate and sweating the resultant slack wax to produce substantially oil-free wax are two of the oldest processes in the petroleum industry. They are applicable, however, only to wax distillates of relatively low boiling range. Newer processes, such as centrifuging and solvent dewaxing, have demonstrated their ability successfully to dewax higher-boiling distillates and to recover satisfactory wax by recycling; while also capable of handling the low-boiling distillates, they have not been able to replace, to any extent, the two ancient stand-bys.

Regardless of the wealth of experience, endless difficulties have arisen in the practice of pressing and sweating. For example, in processing two closely similar distillates, one was found to yield a hard, dry cake on pressing, while the other gave a salvy, mushy cake. Furthermore, the slack wax from the latter type of cake almost invariably behaved in an unsatisfactory manner when sweated.

When the microscope was brought into play, it was found that the pressing operation was successful if the wax crystallized in well-formed plates. After pressing has been completed, the cake is removed from the press, melted, and transferred to the sweating pans, where it is slowly cooled to form a new cake. Here the microscope shows that satisfactory sweating occurs only when the wax forms needle crystals. Yet the wax originally crystallized from the distillate for pressing was the same wax chilled to cake form for sweating.

Centrifuging, particularly from naphtha solution, seemed to be at its best when the wax assumed no definite crystalline form except that so long referred to as amorphous.

Several investigators have determined the chemical composition of petroleum waxes and almost unanimously report them as composed solely of straight-chain paraffin hydrocarbons. A multitude of theories were advanced to explain the Jekyll-Hyde character of wax, and, with composition accepted as constant, this factor was largely ignored. Without attempting to present a complete review of the subject, the following theories, all accepted in some quarters, may be noted:

Buchler and Graves (*1*) found that all completely purified fractions from petroleum waxes were straight-chain paraffin hydrocarbons and crystallized as plates. They reported, however, an "impurity" termed "soft wax", which crystallized as needles and was capable of imparting its form to purified fractions.

Padgett, Hefley, and Henricksen (*9*) reported that the crystal form depended on the amount of oil present, as well as upon the handling; slow cooling tended to produce plates.

The waxes studied by Carpenter (*2*) showed needles when crystallized from high-boiling solvents. The use of low-boiling solvents resulted in needles, provided they were obtained within 15–20° C. of the melting point of the wax. At lower temperatures, however, plates were found. Studying cooling rates and temperature ranges, evidence was found of transition points.

Rhodes, Mason, and Sutton (*10*) introduced a novel solution; while they believed that crystallization was always initiated by plate formation, they observed that rapid cooling (more than 0.1° C. per minute) caused the plates to curl at the edges. Needles, then, were merely rolled plates.

Tanaka and co-workers (*13*) found the habitual form to be needles but considered the viscosity of the distillate to be the controlling factor, with high viscosity fostering needles.

Katz (*6*), partially confirming Rhodes and co-workers, deemed plate formation a necessary precursor to needle formation and con-

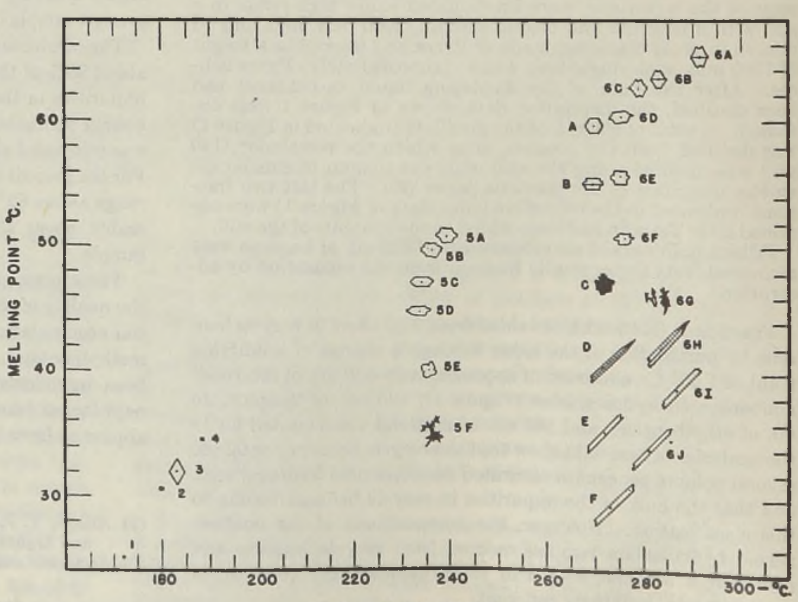


Figure 1. Crystal Types of Purified Paraffin Waxes

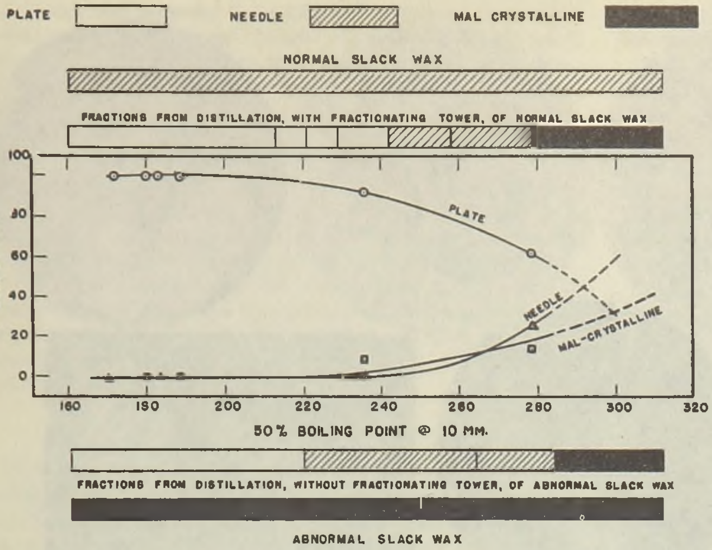


Figure 2. Comparison of Slack Waxes

sidered needles to consist of plates characteristically formed in layers. Later, amplifying the suggestions of Carpenter, Katz (7) introduced the concepts of "concentration of change C_c" and "temperature of change T_c"; both "changes" were from plate to needles, and the reverse change was held to be impossible. He found that T_c is constant for any given wax, substantially independent of solvent, and 5–10° C. below the melting point. C_c is influenced by both wax and solvent; it is the concentration of wax in any given solvent at which the transformation from plate to needle takes place. Wax concentrations above C_c produce needles, and concentrations below C_c, plates. Therefore, according to Katz' theory, a wax which crystallizes as a needle in dilute solution is an impossibility.

Ivanovszky (5) came to a conclusion diametrically opposed to that of Rhodes and co-workers, showing that the removal of amorphous matter from paraffin wax permits the growth of very large needles whch pass or grow into plates.

When a number of partially confirmatory, partially contradictory explanations are advanced on the basis of good observations for the same phenomenon, either an erroneous assumption has been made or some important variable has been uncontrolled. In this instance the present writers believe the erroneous assumption is that petroleum waxes are chemically homogeneous; the uncontrolled variable is actually a rather wide variation in chemical composition of the various fractions chosen for crystal study.

Two previous publications (3, 4) were devoted principally to the presentation of evidence that the composition of wax is, in fact, complex. While the authors did not demonstrate the actual structure of those constitutents which were not straight chain, they reported nine oil-free waxes, each of substantially the same molecular weight, but varying in melting point from 63.6° to 34.0° C.

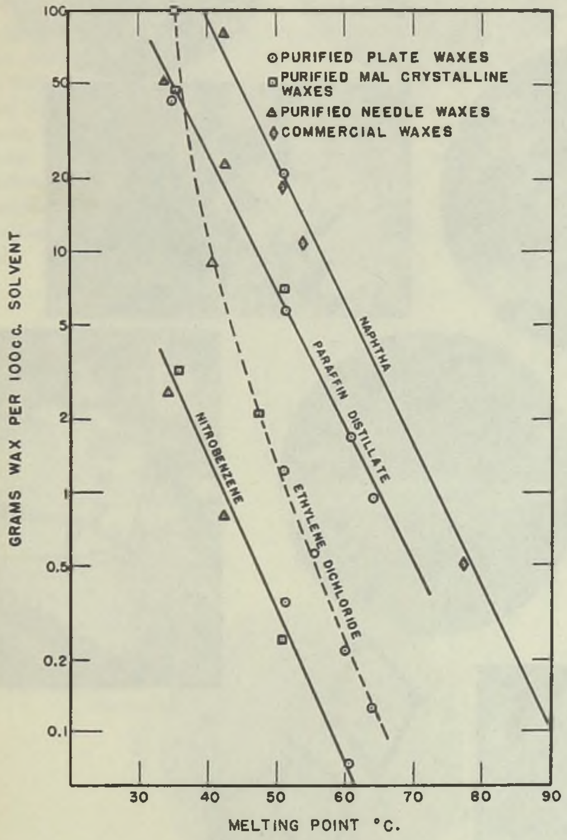


Figure 3. Solubility at 20° C. of Paraffin Waxes in Various Solvents

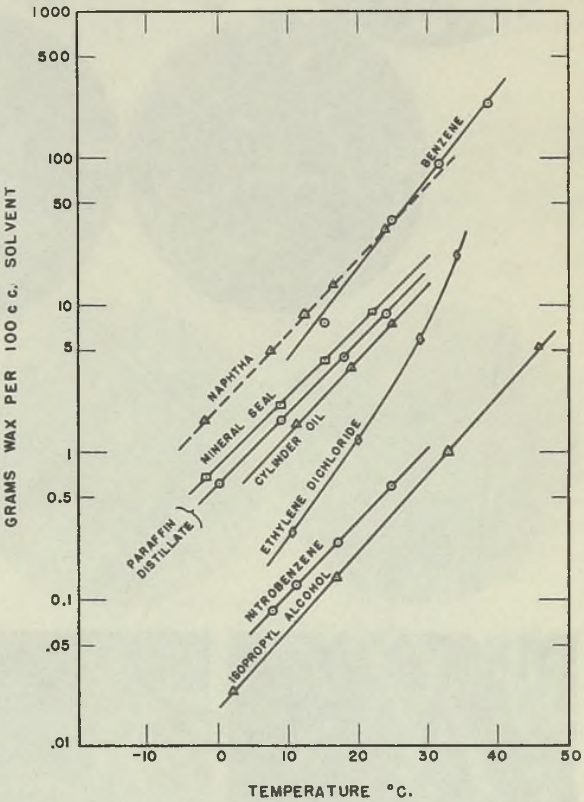
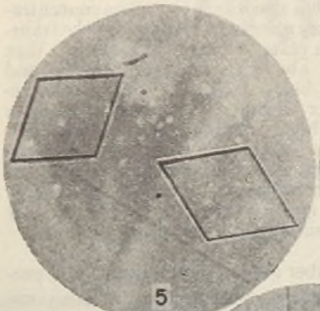


Figure 4. Solubility of Purified Plate Wax (Melting Point 51° C.) in Various Solvents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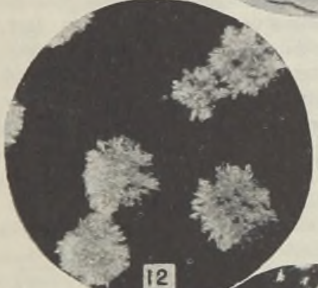
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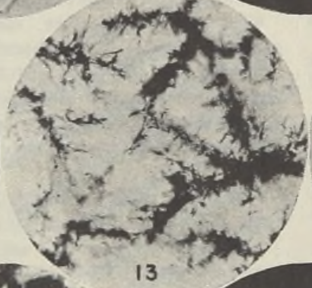
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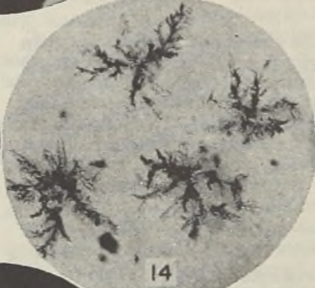
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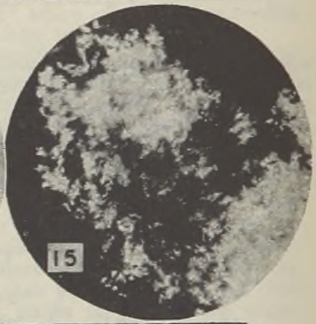
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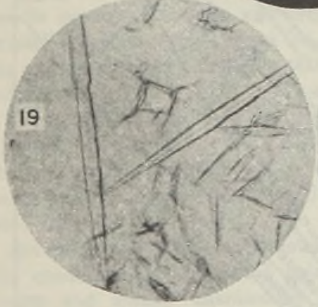
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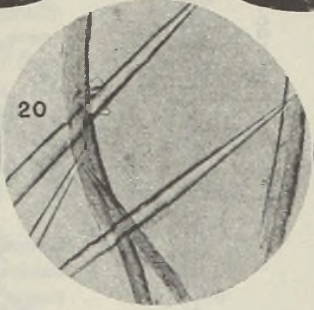
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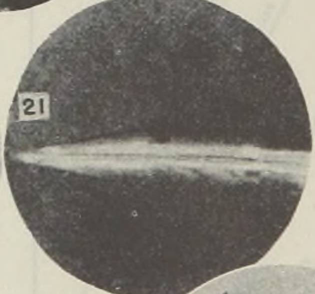
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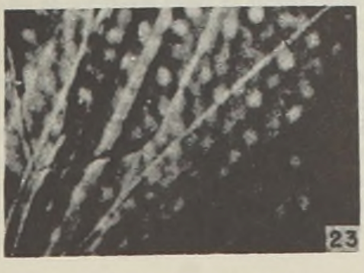
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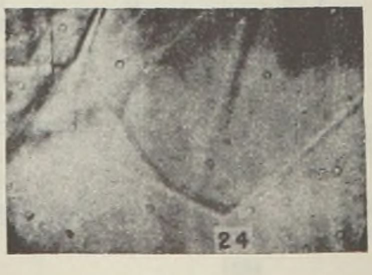
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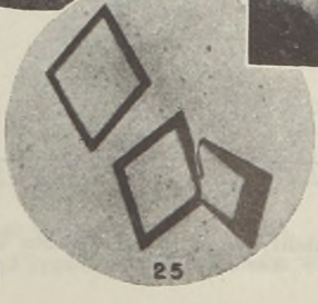
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A theory was proposed to explain the occurrence of at least three types of wax crystals. In brief, the theory depended upon the assertion that there were three classes of wax; each class, when pure, exhibited one of the three well-known types of crystal form. That the theory did not receive wide acceptance has been demonstrated by subsequent publications of other investigators. There was one rather adequate basis for lack of credence; all but one of the photomicrographs presented were of waxes crystallized from dilute solutions. Still more pertinent was the fact that the vast majority of the crystals were obtained from nonpetroleum solvents such as nitrobenzene and ethylene dichloride.

Since proposing the theory the authors have been able to test it more rigorously, and have found it helpful in the study of a wide variety of problems related to wax refining. The purpose of the present communication is to restate the theory and to present additional evidence in its support.

COMPOSITION

Figure 1, reproduced from a previous publication (*4*), presents boiling point and melting point data on a number of highly purified fractions obtained from a mid-continent slack wax. Methods of purification and physical properties have already been presented (*3*, *4*); suffice it to say here that each fraction is narrow with respect both to distillation range and to melting range. Samples 6*B* and 6*J*, for example, have substantially the same boiling points and molecular weights; yet their melting points differ widely, and there are considerable differences between their refractive indices and specific gravities (liquid), respectively. The only reasonable explanation is that their structures differ markedly. Samples 6*I* and 6*J* were subjected to careful combustion analyses by Mair and Schicktanz (*8*), who reported them to be composed chiefly of cyclic hydrocarbons.

Figure 1 was drawn by representing, in lieu of the customary points, the crystal form of each fraction as obtained from ethylene dichloride. (Fractions 1, 2, and 4 were not studied in this particular solvent.) Three general types appear—plate, needle, and (for want of a better term) "mal-formed crystal". Furthermore, these three types fall into bands. For a given boiling range, those of highest melting points (straight-chain paraffin hydrocarbons) crystallize as plates; those of the lowest melting points (cyclic hydrocarbons), as needles; those of intermediate melting point (possibly branched-chain paraffins) form mal crystals. The most persistent efforts to resolve mal crystalline fractions, such as 5F, C, and 6G, into plates and needles have been unavailing.

That the waxes other than straight-chain (plate) do not occur as impurities, is shown by the central portion of Figure 2, also taken from the previous paper (*4*). In the "front end" of paraffin distillate all the crystallizable materials appear to be of the plate type, but in the "back end" the sum of needle and mal crystal types is greater than 50%. These curves indicate that in higher-boiling distillates the percentage of plate waxes would be small, and this is borne out both by rough observation of their crystal habit and by careful experimentation.

The proportions of the various types of waxes probably vary to some extent from crude to crude; nevertheless the authors believe that the generalities covered by Figure 2 will be found applicable to the vast majority of the wax-bearing petroleums.

SOLUBILITY

Both needle and mal crystalline waxes have marked powers, under the proper conditions, of impressing their own form on plate waxes. The most important factor appears to be the relative solubilities of the various types of waxes in whatever solvent may be present.

Figure 3 shows the solubility, at a single temperature, of samples embracing pure plate, needle, mal crystalline, and commercial waxes, respectively, in four solvents. Figure 3 leads to the generalization that the solubility of a wax in a given solvent is substantially independent of type, but varies with melting point. In other words, waxes 4, 5F, E, and 6J (Figure 1) would be soluble to substantially the same extent in any solvent which the authors have investigated.

Figure 4 shows the solubility of a purified plate wax at various temperatures in a number of solvents. This information is similar to that found for commercial waxes by Sachanen (*11*), and by Sullivan, McGill, and French (*12*); that is, solubility is high in naphtha or benzene, lower in oils of higher boiling ranges, and very low in nitrobenzene and isopropyl alcohol.

BASIS FOR THE THEORY

The theory, as stated in the synopsis at the beginning of this article, rests upon the behavior of wax crystals as observed under the microscope. The authors, as well as many others, have recorded their findings by means of photomicrographs. It is extremely difficult, however, to obtain significant photomicro-

Figures 5 to 11. Crystallization of Purified Plate Waxes

Figure No.	Melting Point, ° C.	Wax Concn., G./100 Ml. Solvent	Solvent Used
5	65.5	0.05	Nitrobenzene (cloud point, 25° C.)
6	51.0	77.6	Nitrobenzene (cloud point, 25° C.)
7	62.8	0.05	Acetic acid
8	55.2	2.0	Ethylene dichloride
9	47.1	35	Oil of 100 Saybolt Universal sec. viscosity at 100° F.
10	62.8	1.8	Oil of 8000-sec. viscosity at 100° F.
11	51.0	(From its own melt)	

Figures 12 to 18. Crystallization of Purified Mal Waxes

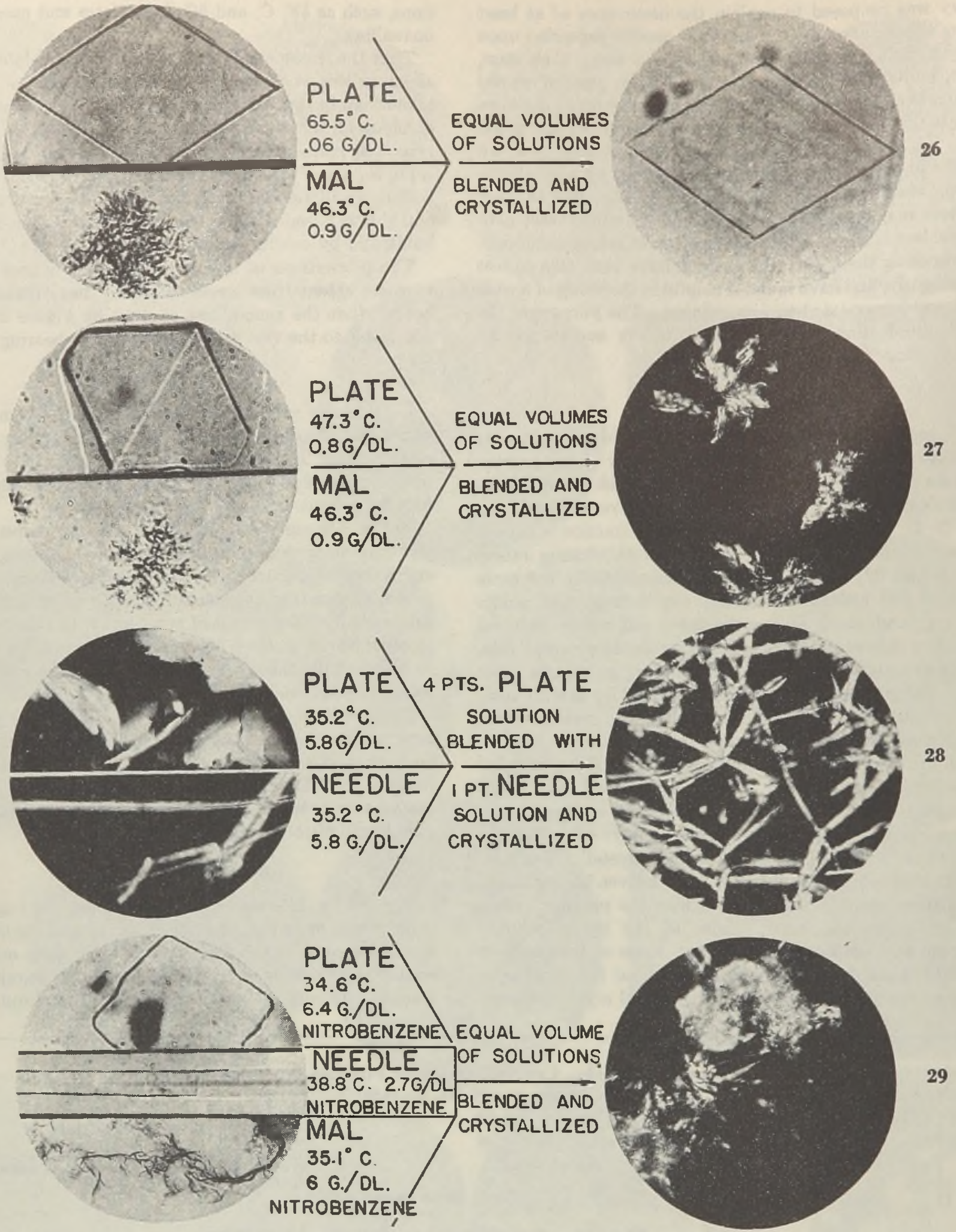
Figure No.	Melting Point, ° C.	Wax Concn., G./100 Ml. Solvent	Solvent Used
12	42.8	1.8	Nitrobenzene
13	46.3	10	Ethylene dichloride
14	50.9	0.6	Nitrobenzene
15	54.2	0.3	Nitrobenzene
16	47.1	0.7	Acetic acid
17	60.3	0.1	Nitrobenzene
18	46.3	(From its own melt)	

Figures 19 to 22. Crystallization of Purified Needle Waxes

Figure No.	Melting Point, ° C.	Wax Concn., G./100 Ml. Solvent	Solvent Used
19	42.1	20	Ethylene dichloride
20	40.5	1.8	Nitrobenzene
21	34.4	(From its own melt)	
22	42.1	(From its own melt)	

Figures 23 to 25. Crystallization of Pure Paraffins (from Their Own Melts)

Figure No.	Paraffin	Melting Point, ° C.
23	Dodecane	−9.6
24	Tetradecane	5.5
25	2,2,3,3-Tetramethylbutane	101.6



Figures 26 to 29. Influence of Certain Types on Crystal Form of Other Types (in Nitrobenzene Solution)

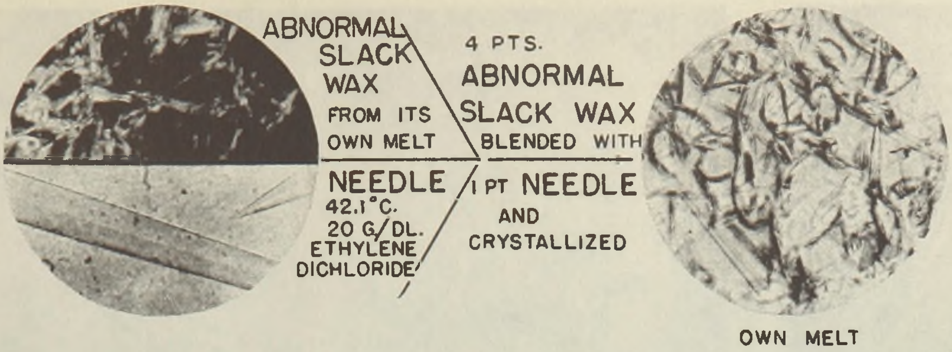
Melting points are given in ° C.; concentrations of wax, in grams per 100 ml. of solvent.

graphs of crystals forming in concentrated solutions or in their own melts, because changes normally occur far too rapidly to be properly recorded by ordinary "stills". Since it was necessary to extend the studies to concentrated wax solutions and pure waxes, the moving picture camera was utilized to obtain pictures while crystallization was proceeding at normal rates. Individual frames have been enlarged and given a rectangular form to distinguish them from the ordinary stills or photomicrographs which are circular.

Magnifications are not reported because they appear to have no bearing on the proposed theory; also, particularly with plate and needle crystals, the size is dependent on the rate of crystallization, with slow rates favoring large crystals. This is much less pronounced with mal waxes. At no time, however, were the authors able to secure evidence that the rate of crystallization exerted any influence on the type (plate, needle, or mal) of crystal appearing.

CRYSTALLIZATION OF FRACTIONS

Purified Fractions. Figures 5 to 11 present the crystals formed by plate-type waxes, of various melting points. Experiments were chosen to test other theories; thus concentration was varied from very dilute solutions (Figures 5 and 7), through



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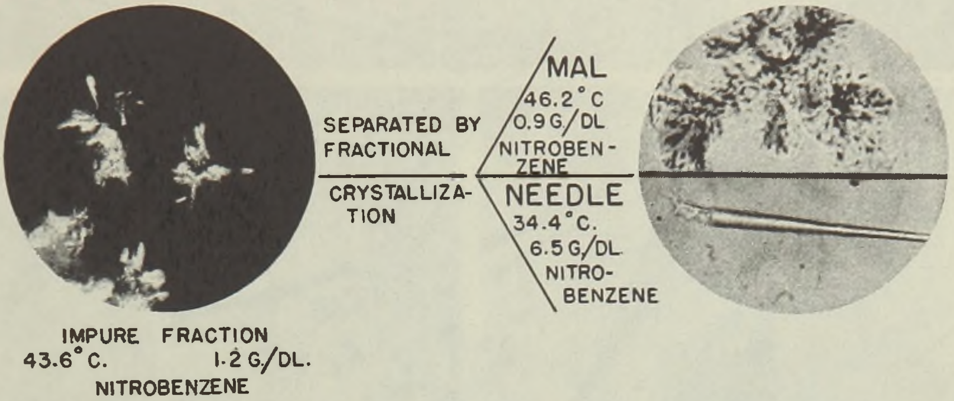

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Figures 30 and 31. Influence of Certain Types of Crystal Form of Other Types

Melting points in ° C.; concentrations of wax, in grams per 100 ml. of solvent.

concentrated solutions (6 and 9), and finally to the absence of solvent (Figure 11). Viscosity varied from the very low values of the ethylene dichloride solution to that indicated for Figure 10. The actual viscosity during crystallization was far higher than the value given, inasmuch as the crystals formed at about 77° F. In spite of these drastic variations, the plate waxes remained true to type.

The cinemicrograph (Figure 11) shows an outstanding characteristic of plate wax in concentrated solution—namely, the tendency for the crystals to pile one upon the other. Crossing the field diagonally are crystals which might be taken for needles. The motion picture itself demonstrates unequivocally that they are plates on edge.

Figures 12 to 18 offer similar evidence for mal crystalline waxes, and Figures 19 to 22, for needle waxes. Figures 23, 24, and 25 show the crystal form of three pure paraffin hydrocarbons; 23 and 24 offer good confirmation of the suggestions already made, since the substances studied are straight-chain hydrocarbons and form plates. The subject material of Figure 25, however, is certainly branched. Study of Figure 1 suggests that branching may become rather pronounced before the plate habit is destroyed. Although tetramethylbutane (Figure 25) is highly branched, there are no long branches. A guess may be hazarded, therefore, that sample 5C or 5D (Figure 1) is made up of chains carrying short side chains, whereas in 5E or 5F the side chains are longer.

FRACTIONS CONTAINING MORE THAN ONE TYPE. Figures 26 to 31 show the effect of one type of wax upon another. In the first test (26) a dilute solution of plate wax, which crystallized as shown in the upper portion of the left-hand circle, was mixed with a dilute solution of a mal crystalline wax, whose crystal is also shown. When crystals were obtained from the mixture, they were perfect plates; that is, the mal crystal wax had no effect. The same mal crystal wax, however, completely destroyed the plate crystals in the next trial (27).

The difference is in the solubilities. Figure 3 indicates that solubility of a wax in a given solvent is largely a function of the melting point of the wax. The mal shown in Figure 26 was, therefore, much more soluble than the plate; it could not crystallize while the high-melting plates were forming. In Figure 27, however, its solubility was much the same as that of the plate wax, and it therefore impressed its own form on the plate. A similar ability on the part of needle wax to cast plate wax into its own mold when solubility relations are favorable is demonstrated by Figures 28.

When waxes of all three types (29) were present, the crystal was mal. Poorly formed needles from "abnormal" slack wax were changed to clean needles by adding a pure needle wax (30). The impure fraction shown in Figure 31 exhibits the typical mal crystal form, but that needle crystals had lost their normal form is demonstrated by the results of fractional crystallization.

Coexisting crystals of more than one type are almost never encountered. Whichever type is able firmly to establish itself appears to dominate. Thus, while it has not been rigorously proved, the mal crystalline wax shown in Figure 26 appears to have deposited on the preformed plates and thus taken up their habit. In other words, either needles or mal crystals can impress their form on plates during simultaneous crystallization; plates require conditions where they can crystallize alone and appear to take up the other types.

On this basis the wax in paraffin distillate sheds its chameleon behavior. The highest-melting (least-soluble) waxes in the distillate are plates, but the total wax concentration is relatively low. When, therefore, the distillate is chilled prior to pressing, needles and mals are held in solution while the plates form. In slack wax, on the other hand, there is insufficient oil to hold the needles and mals in solution; hence one or the other will prevail. If however, the boiling range of the distillate be extended (Figures 1 and 2), the proportion of plates tends to decrease while the


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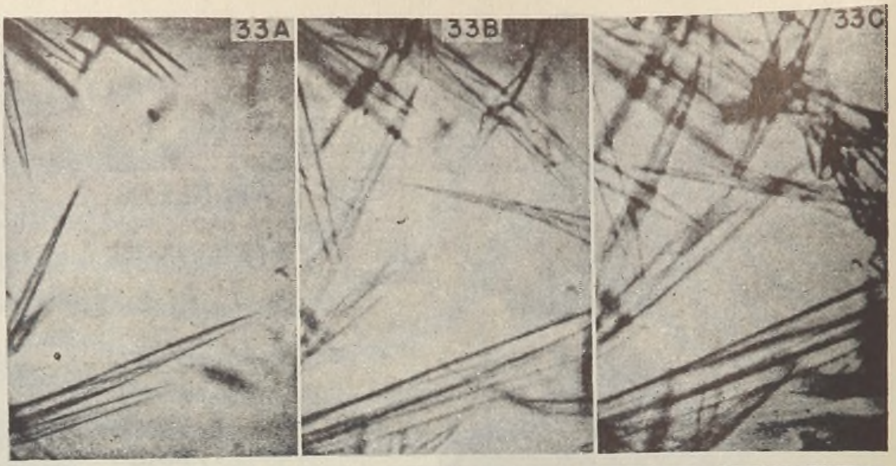


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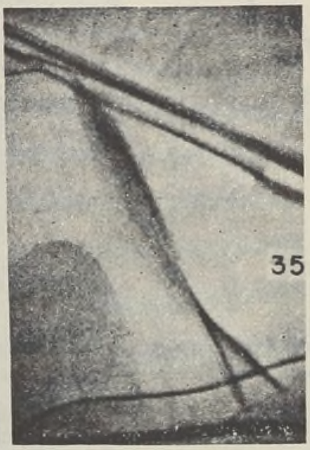
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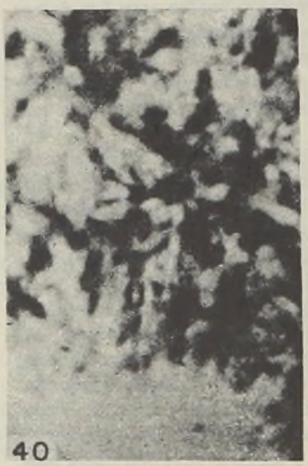
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Figure 32. Normal Slack Wax

Figure 33. Normal Slack Wax after Removal of Oil

Figure 34. 12.5–25% (Fractionated) Overhead from Normal Slack Wax

Figure 35. 25–37.5% (Fractionated) Overhead from Normal Slack Wax

Figure 36. 37.5–50% (Fractionated) Overhead from Normal Slack Wax

Figure 37. 50–62.5% (Fractionated) Overhead from Normal Slack Wax

Figure 38. 62.5–75% (Fractionated) Overhead from Normal Slack Wax

Figure 39. 75–87.5% (Fractionated) Overhead from Normal Slack Wax

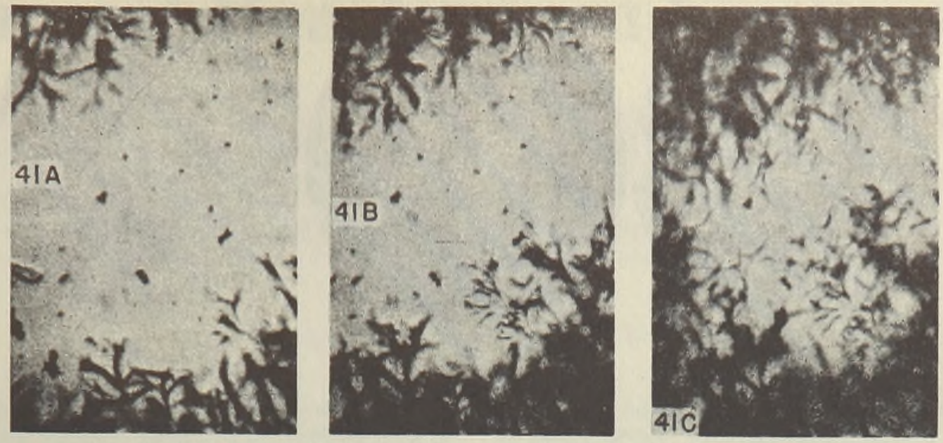
Figure 40. 12.5% Residual from Fractional Distillation of Normal Slack Wax

proportion of high-melting mals increases. As a result the plate crystals do not become established; mal crystals predominate, and the distillate fails to press.

SLACK WAXES

Figures 32 to 45 (obtained by own-melt crystallization) illustrate the application of the plate-needle-mal theories to the study of the behavior of two slack waxes; one was "normal" in that it sweated well, the other "abnormal", in that it failed to sweat properly. Figure 32 shows the appearance of the normal slack wax, the crystals being typical of the interlacing needles most suitable for sweating. Figure 33 demonstrates that the crystallization is not altered by removal of oil.

The normal slack wax was separated into fractions by vacuum distillation in a fractionating tower. The 12.5–25% cut (Figure 34) exhibited unmistakable plate crystals, as did the three fractions which followed (35, 36, and 37). The approximate boiling range of each cut is indicated in the upper portion of Figure 2, which reveals that the first four fractions of the normal slack wax should contain little except plate waxes; the microscope verifies this. In the next cut, however, the needle waxes are increasing in proportion and impress their form on the plates (Figure 38). The next cut also gives needles (39). The still residue, however, contains enough of the mal crystalline type to destroy both plates and needles (40), although not enough to influence the crystals of the entire slack wax.



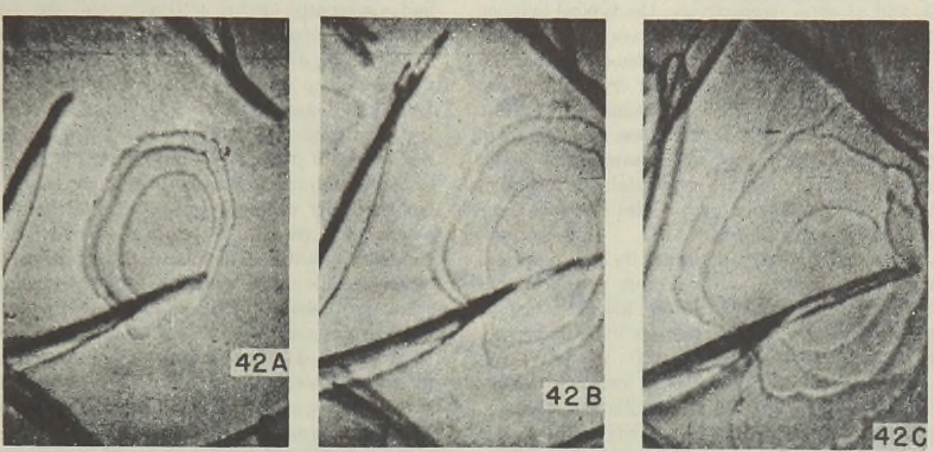


Figure 41. Abnormal Slack Wax

Figure 42. 15–30% Overhead from Abnormal Slack Wax

Figure 43. 30–70% Overhead from Abnormal Slack Wax

Figure 44. 70–85% Overhead from Abnormal Slack Wax

Figure 45. 15% Residual from Abnormal Slack Wax

Figure 41 shows why the slack wax is abnormal in operation; such a structure is better adapted to holding oil than to releasing it. When, however, this material is cut into fractions by simple vacuum distillation, the low-boiling 15–30% cut (Figure 34) again exhibits plates as it should, since neither needle nor mal crystal waxes occur within this boiling range (Figure 2). The next long (30–70%) cut includes enough needle wax (Figure 43) so that the plates are suppressed, and the same is true of the 70–85% fraction (44). The residue, however (45), exhibits especially poor structure, even though its percentage is higher than that from the normal slack wax. An indication of the powerful effect of the mal crystal waxes may be secured by noting how little difference there is in the crystal form of the 15% residue and the entire slack wax (41), even though the great bulk of the slack wax is composed of materials which, when pure, form plates or needles. If the paraffin distillate, from which the abnormal slack was pressed, had been cut a little "shorter", the proportion of mals would have been decreased, and the slack would have been entirely normal.

46 47 48

Figures 46 to 48

Figures 42, 33, and 41 show, respectively, the typical manner of growth of plates, needles, and mals. Plates are very thin and frequently pile one upon the other; needles "shoot" across the field, and in either case the size of individual crystals may be varied between wide limits by control of the cooling rate. Mals seem always to be relatively small, and differences in cooling rate have little effect. Instead of single crystals, growing gradually, small crystals appear suddenly, and more crystals appear until the field is obscured. Indeed, they act as if the lattice is too complicated to permit large crystals to form.

That either needle or mal crystal can impress its form on plates seems clear; it is not so definite as to whether needle or mal crystal is more powerful. Evidence indicates, however, that in the middle ranges of paraffin distillate there is little difference, the needles being possibly a bit more powerful. As the boiling range climbs, however, the power of the mals increases rapidly and completely controls all the heavier wax distillates.

These findings are rather consistent with the suggestions made earlier in the paper for the molecular configuration of the three crystal types of wax: that plates are either straight chain or chains with short branches, that compounds crystallizing as needles contain cyclic structures, and that the mals have long branches. One would expect the crystal lattice of straight-chain substances to be relatively simple, and able to accommodate the more irregular compounds only with some difficulty or after the plate crystal has already attained considerable size. On the other hand, the straight or slightly branched molecule could probably adapt itself rather readily to the lattice of a crystal more complex than its own.

STRUCTURE OF NEEDLES

An outstanding peculiarity of needles is what appears as a line or "rib" extending along the crystal and always equidistant from the sides; it is apparent in some of the crystals of Figures 19 to 22, 29, 30, 33, 43, and 44, and can always be seen by adjusting the focus. It is quite different from the lines appearing at the edges of plate crystals, as in Figure 5 or 9; the latter is the result of optical phenomena depending on the focus and the refractive indices of the solvent and crystal, respectively.

This needle with a central rib has been a puzzling phenomenon. It manifestly cannot be the kind of rib which would result from a rectangular or triangular cross section, for then it would not always be seen at the center of the crystal. The only explanation which seemed to fit the facts (or appearances) was the existence of a hole through the center of each needle. This seemed so improbable, however, that the authors were accustomed to offering it as a joke. Then on one occasion (when the idiosyncracies of needles was not the subject under investigation), a slack wax was crystallized very slowly on the stage of a microscope (Figures 46, 47, and 48). This slack wax was known (as were all "normal" slack waxes) to crystallize in needles; in this instance the crystals had apparently grown vertically, and the microscope, focused at a plane along the crystal axis, accomplished optical sectioning.

Figures 46, 47, and 48 lend some credence to the idea of a drilled needle. They could also be used to support the contention of Rhodes and co-workers (*10*) that crystals are rolled plates. This is particularly true of Figure 47. If, however, we assume that needles result from the rolling of thin plates, the growing process of a needle should be largely that of increasing its diameter without markedly changing its length, and the sides should be approximately parallel. Countless observations have convinced the present authors that needles do not grow in this manner; they merely lengthen, thicken, and taper toward the growing tip. Thus they behave exactly as one would expect them to if the deposited material were all coming from the surrounding solution (Figure 33). It is not necessary to assume that any of the crystal surface is actually curved. The cross section of the needle may be polygonal, with the number of sides too large to be resolved by the microscope.

Unexpected support for the unlikely hypothesis of a "crystal with a hole" was offered by A. R. Thompson of the University of Pennsylvania, during the discussion which followed the oral presentation of this paper. The authors appreciate his permission to quote him as follows: "In the course of a study of the solubilities of inorganic salts in aqueous alcohol solutions, it was found that if such a solution of ammonium nitrate were cooled slowly, the salt crystallized in the form of needles with a hole through the center." The authors do not believe that they have offered definite proof of the existence of drilled wax needles, but have no other explanation for the ever-present median line, and present the evidence with the hope that others can propose a better solution.

ACKNOWLEDGMENT

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Chemical Reactions in Continuous-Flow Systems

HETEROGENEOUS REACTIONS

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General kinetic equations governing reacting, flowing mixtures are applied to reactions catalyzed at the walls of a cylinder. Dimensionless ratios for correlating yields, diffusivity, and process variables are presented. Simple formulas for estimating the influence of diffusivity on yield are given and extended to turbulent flow in tubes for which the ratio, *L/D*, of length to diameter exceeds 60. Extension to pelleted catalysts and to catalysts poisoned by products is discussed.

HETEROGENEOUS reactions in continuous-flow reactors fall into two classes. Type A reactions, in which one or more products accumulate in the reactor, are exemplified by "coke" production in catalytic cracking of petroleum fractions, chromatographic analysis, and zeolitic ion exchange reactions. Type B reactions are those in which all reactants and products are continuously removed. Most catalytic processes fall in this class, since the products are usually readily and completely desorbed from the catalyst into the stream of unchanged reactants and products. In countercurrent extraction there is a transfer of material from one phase to another, each of which is removed at independent rates.

Both classes of reactions can be analyzed kinetically as special cases of the general differential equations for flow systems presented in a previous paper (*5*). These may be recapitulated briefly for isothermal systems:

$$\frac{Dm}{Dt} = -m\nabla . \mathbf{V} \tag{1}$$

$$\frac{\partial mc_k}{\partial t} = m\Gamma_k - \nabla . mc_k\mathbf{V}_k \tag{2}$$

where c_k = concentration of kth component of fluid mixture, (moles gm.$^{-1}$)
m = mean density of flowing mixture, grams cm.$^{-3}$
$\mathbf{V}_k$ = vector velocity of kth component, cm. sec.$^{-1}$
$\mathbf{V}$ = mean vector velocity of mixture, cm. sec.$^{-1}$
t = time, sec.
Γ_k = rate of production of kth component in fluid stream, moles gram^{-1} sec.$^{-1}$
$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{V}.\nabla$
$\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z}$

In homogeneous phases, Equation 2 can be simplified further by defining a diffusion velocity,

$$\mathbf{U}_k = \mathbf{V}_k - \mathbf{V} \tag{3}$$

and using Fick's law of diffusion,

$$-mc_k\mathbf{U}_k = \nabla D_k mc_k \tag{4}$$

where D_k = diffusivity of kth component, cm.^{2} sec.$^{-1}$

Substituting Equations 3 and 4 into Equation 2, expanding the divergence operator, and using Equation 1,

$$m\frac{Dc_k}{Dt} = m\Gamma_k + \nabla . \nabla D_k mc_k \tag{5}$$

There is thus one equation for each component of the mixture.

In type A reactions the velocity of any component which accumulates in the reactor is zero. For such components Equation 2 replaces Equation 5 and reads:

$$\frac{\partial mc_k}{\partial t} = m\Gamma_k \tag{2A}$$

In this case the density, m, refers to the mean density of matter in the reaction space, whether actually flowing or not. Thus catalytic packing may be considered as a fluid component of zero velocity. In countercurrent absorption towers, the velocities, $\mathbf{V}_k$, of absorbent fluid are not zero but are set as independent design variables at predetermined values. In this way all possible cases are formally included.

Mathematically type A reactions result in problems in which the concentrations are functions of time, increasing continually for accumulating components. In type B reactions, however, concentrations reach a steady state in which time is not an explicit variable. This paper considers in detail the application of these equations to heterogeneous catalyzed reactions.

SURFACE REACTIONS IN A CYLINDER

One of the simplest heterogeneous reactors consists of a cylinder into which reactants are passed; the cylinder wall has catalytic action. Although it presents too little surface to serve as a practical reactor, the unpacked cylinder deserves consideration as an approximate model for the tortuous passages to be found in actual pelleted catalytic packing. A careful analysis of this case should indicate at least the qualitative kinetic behavior of more complex packings and the significant dimensionless variables, in terms of which more complex cases can be analyzed empirically.

Consider first a reaction in which all products and reactants concerned in the kinetic rate expression are continuously removed from the reactor. A steady state will be reached in the reactor for which $\partial C_k/\partial t = 0$ everywhere in the interior of the cylinder. Let it be further assumed that the flow is adequately represented by a mean axial velocity, $\mathbf{V}$, uniform in any cross section of the reactor. At the surface, however, the velocity is zero, in accordance with known facts. This introduces the approximation of an infinite velocity gradient at the surface but alters no essential features of the chemical behavior of the system. Concentrations now depend upon two space variables: z, the axial distance from entrance to the reactor, and r, the radial distance from the axis. Equation 5 becomes for this two-dimensional case:

$$\frac{mu}{r}\frac{\partial c_k}{\partial r} + mw\frac{\partial c_k}{\partial z} = D_k\left[\frac{\partial^2 mc_k}{\partial r^2} + \frac{1}{r}\frac{\partial mc_k}{\partial r} + \frac{\partial^2 mc_k}{\partial z^2}\right] + m\Gamma_k \quad (6)$$

where u = radial component of mean velocity **V**
w = axial component of mean velocity **V**

However, since the mean velocity is purely axial, $u = 0$ and reactants reach the walls by diffusion. Moreover, a previous paper (*5*) showed that almost all practicable conditions result in negligible axial diffusion in comparison with the mean axial velocity. Hence

$$D_k\frac{\partial^2 mc_k}{\partial z^2} << mw\frac{\partial c_k}{\partial z}$$

Since there is no reaction in the bulk phase ($m\Gamma_k = 0$), Equation 6 becomes:

$$mw\frac{\partial c_k}{\partial z} = D_k\left[\frac{\partial^2 mc_k}{\partial r^2} + \frac{1}{r}\frac{\partial mc_k}{\partial r}\right] \quad (7)$$

From Equation 1 under these conditions,

$$w\frac{\partial m}{\partial z} = -m\frac{\partial w}{\partial z} \quad (8)$$

At the surface $r = R$, the velocity $w = 0$, and

$$-D_k\frac{\partial mc_k}{\partial r} = -m\Gamma_k \quad (9)$$

As an initial condition, let us choose

$$mc_k = m_0 c_{k_0} \quad (z = 0) \quad (10)$$

i.e., uniform concentration over the entire entry cross section.

Equations 7 to 10 form a determinate system of partial differential equations, boundary and initial conditions. Before integrating them, however, it will be instructive to transform to dimensionless variables:

$$\zeta = z/L;\ \eta = r/R;\ f = c_k/c_{k0} \quad (11)$$

Noting that Equation 8 can be integrated at once to give $mw = G$, where G = mass velocity (grams cm.^{2} sec.$^{-1}$), a constant,

$$\frac{G}{L}\frac{\partial f}{\partial \zeta} = \frac{D_k}{R^2}\left[\frac{\partial^2 mf}{\partial \eta^2} + \frac{1}{\eta}\frac{\partial mf}{\partial \eta}\right] \quad (12)$$

$$-\frac{D_k c_{k0}}{R}\frac{\partial mf}{\partial \eta} = -m\Gamma_k \quad (\eta = 1) \quad (13)$$

$$\frac{\partial mf}{\partial \eta} = 0 \quad (\eta = 0) \quad (14)$$

$$mf = m_0 \quad (\zeta = 0) \quad (15)$$

If the net reaction which occurs is

$$\Sigma a_j A_j \longrightarrow \Sigma b_m B_m$$

we define

$$\nu = \frac{\Sigma b_m - \Sigma a_j}{a_\alpha} \quad (16)$$

where α refers to any chosen reference reactant A_α. The density m can be expressed in terms of f, since

$$m = m_0/[1 + \beta(1 - f)] \quad (17)$$

where m_0 = density of feed mixture
β = $\nu M_0 c_{\alpha 0}$
M_0 = mean molecular weight of feed mixture

The factor $M_0 c_{\alpha 0}$ is the mole fraction of the αth component in the feed mixture. Since the mean molecular weight of mixture M is given by

$$1/M = \sum_{k=1}^{N} c_k = m/V$$

where V = molar volume of mixture

the presence of inert components is accounted for. The previous paper (*5*) gave a more complete discussion of Equation 17.

The assumption that the mass velocity is constant in any cross section is partially justified by proper choice of G and D_k. If the constant velocity is taken as the mean velocity of the cross section, mass velocity G gives the mean flow per unit cross-sectional area in the tube and is easily measured experimentally. If the flow is laminar, D_k is independent of the mean velocity, but this case is seldom of practical importance. In turbulent flow, D_k is given by the usual mass transfer coefficient as a function of Reynolds number and mean velocity. Any of the usual approximations (*7*) may be used to estimate its value. Since these may be defined to reproduce the radial mass transfer from a turbulent stream in the form

$$N_k = -D_k\frac{dc_k}{dr}$$

it is not necessary to consider the radial velocity gradients further. Hence, if mass transfer coefficients are used as defined, the approximation of constant velocity in any cross section would be expected to cause negligible error in the kinetic equations.

Equations 12 to 15 are mathematically tractable only for the case in which the mean fluid density is unchanging throughout the reactor. For gas reactions with no increase in the total number of moles ($\nu = 0$), for most liquid reactions, for reactions in dilute streams ($M_0 c_{\alpha 0} << 1$), and in the initial stages of any reaction ($f \approx 1$), this condition will be satisfied. Taking $m = m_0$, and defining the space velocity as $S = G/m_0 L$ (in sec.$^{-1}$), Equations 12 to 15 become:

$$\frac{\partial f}{\partial \zeta} = \frac{D_k}{SR^2}\left[\frac{\partial^2 f}{\partial \eta^2} + \frac{1}{\eta}\frac{\partial f}{\partial \eta}\right] \quad (12A)$$

$$f_\eta(\zeta, 1) = \frac{R}{D_k m_0 c_{k0}} m\Gamma_k \quad (13A)$$

$$f_\eta(\zeta, 0) = 0 \quad (14A)$$

$$f(0, \eta) = 1 \quad (15A)$$

The various possibilities for $m\Gamma_k$ have been extensively discussed (*4*). Let us suppose, by way of example, that the surface is only sparsely covered with adsorbate and that the reaction on the surface is much slower than the rate of adsorption. The surface concentration is then given effectively by the adsorption isotherm in the absence of reaction. For a first-order reaction on the surface, under these conditions,

$$m\Gamma_k = -k_1'\Omega\theta_k \quad (18)$$

where Ω = moles adsorption sites per cm.^{2} of surface
θ_k = fraction of sites occupied by the kth sort of molecules
k_1' = fraction of molecules adsorbed which react per second

When reaction occurs between adsorbed molecules and impinging molecules in the gaseous phase,

$$m\Gamma_k = -k_2\Omega\theta_k mc_j \quad (19)$$

When reaction occurs bimolecularly between adjacent molecules absorbed on the surface,

$$m\Gamma_k = -k'_2\Omega^2\theta_j\theta_k \quad (20)$$

For a sparsely covered surface,

$$\theta_k = \frac{k_a}{k_d} m_0 c_{k0} f \quad (21)$$

where k_a, k_d = specific rates per cm.^{2} for adsorption and desorption, respectively.

For the first-order case, which also includes a bimolecular reaction with one component in large excess, Equations 18 and 21 give:

$$m\Gamma_k = -k_1 m_0 c_{k0}\Omega f$$

where $k_1 = k_1'k_a/k_d$

and Equation 13A becomes

$$f_\eta(\zeta, 1) = -\frac{Rk_1\Omega}{D_k} f \tag{22}$$

The set of Equations 12A, 22, 14A, and 15A is identical with that considered by Paneth and Herzfeld in the kinetic analysis of the removal of metallic mirrors by free radicals (*6*). It is readily solved by standard methods. Writing

$$\kappa = D_k/SR^2; \quad \alpha = Rk_1\Omega/D_k; \quad f = Z(\zeta).R(\eta)$$

Equation 13A reduces to two ordinary differential equations:

$$\frac{dZ}{d\zeta} + \lambda\kappa Z = 0 \tag{23}$$

$$\frac{d^2R}{d\eta^2} + \frac{1}{\eta}\frac{dR}{d\eta} + \lambda R = 0 \tag{24}$$

where λ is a separation constant with values to be determined. Equation 23 has the solution

$$Z = e^{-\lambda\kappa\zeta} \tag{25}$$

while Equation 24 has the general solution

$$R = AJ_0(\sqrt{\lambda}\eta) + BY_0(\sqrt{\lambda}\eta) \tag{26}$$

where J_0 and Y_0 are the Bessel functions of zero order. Equation 14A becomes:

$$R_\eta(0) = 0 = AJ_0'(0) + BY_0'(0)$$

But Y_0' is infinite at the origin whereas J_0' is zero at the origin; hence $B = 0$. Equation 22 indicates that λ must satisfy the relationship,

$$\alpha J_0(\sqrt{\lambda}) = -\sqrt{\lambda}J_0'(\sqrt{\lambda}) = +\sqrt{\lambda}J_1(\sqrt{\lambda}) \tag{27}$$

Suppose Equation 27 to be satisfied for the series of values $\lambda = \lambda_j$, deferring their evaluation for the moment. Equation 24 then has the solution,

$$R_j = A_jJ_0(\sqrt{\lambda_j}\eta) \tag{28}$$

and Equation 15A becomes

$$1 = \sum_{j=0}^{\infty} A_j\, J_0(\sqrt{\lambda_j}\, \eta) \tag{29}$$

which may be solved for A_j as will be seen.

The complete solution is, then,

$$f = \sum_{j=0}^{\infty} A_je^{-\kappa\lambda_j\zeta}\, J_0(\sqrt{\lambda_j}\, \eta) \tag{30}$$

The mean conversion over the entire cross section of the reactor is $1 - \bar{f}$, where

$$\bar{f} = 2\int_0^1 f\eta d\eta = 2\sum_{j=0}^{\infty}A_je^{-\kappa\lambda_j\zeta}\int_0^1 \eta J_0(\sqrt{\lambda_j}\eta)d\eta \tag{31}$$

Constant A_j may be determined from Equation 29 by applying the relations,

$$\int_0^1 \eta[J_0(\sqrt{\lambda_j}\eta)]^2d\eta = \frac{1}{2}\{J_0^2(\sqrt{\lambda_j}) + J_1^2(\sqrt{\lambda_j})\} \tag{32}$$

$$\int_0^1 \eta J_0(\sqrt{\lambda_j}\eta)J_0(\sqrt{\lambda_k}\eta)d\eta = 0 \quad (k \neq j) \tag{33}$$

$$\int_0^1 \eta J_0(\sqrt{\lambda_j}\eta)d\eta = J_1(\sqrt{\lambda_j})/\sqrt{\lambda_j} \tag{34}$$

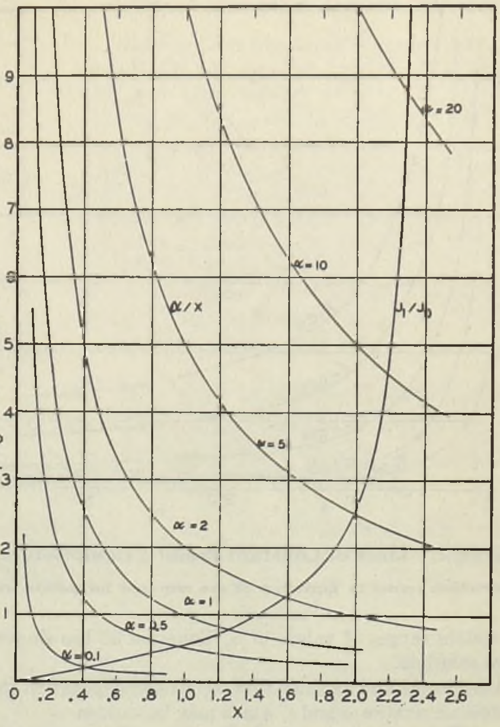

Figure 1. Chart for Determining λ_0, the First Root of $J_1(x)/J_0(x) = \alpha/x$

Thus, from Equation 29,

$$A_j = \frac{2\, J_1(\sqrt{\lambda_j})}{\sqrt{\lambda_j}[J_1^2(\sqrt{\lambda_j}) + J_0^2(\sqrt{\lambda_j})]} \tag{35}$$

and from Equation 31,

$$\bar{f} = 4\sum_{j=0}^{\infty}\frac{J_1^2(\sqrt{\lambda_j})e^{-\kappa\lambda_j\zeta}}{\lambda_j[J_1^2(\sqrt{\lambda_j}) + J_0^2(\sqrt{\lambda_j})]} \tag{36}$$

Substituting for $J_1\,(\sqrt{\lambda_j})$ from Equation 27

$$\bar{f} = 4\sum_{j=0}^{\infty}\frac{\alpha^2}{(\alpha^2 + \lambda_j)}\cdot\frac{e^{-\kappa\lambda_j\zeta}}{\lambda_j} \tag{37}$$

$$\bar{f} = \frac{4\alpha^2e^{-\kappa\lambda_0\zeta}}{\lambda_0(\lambda_0 + \alpha^2)}\,[1 + \Delta_1 + \ldots + \Delta_j + \ldots] \tag{38}$$

$$\text{where } \Delta_j = \frac{\lambda_0(\lambda_0 + \alpha^2)}{\lambda_j(\lambda_j + \alpha^2)}\, e^{-\kappa(\lambda_j - \lambda_0)\zeta}$$

There remains only the evaluation of λ_j from Equation 27. This may be done graphically in any case, as shown in Figure 1, where $1/\sqrt{\lambda}$ is plotted against $J_1(\sqrt{\lambda})/J_0(\sqrt{\lambda})$. Writing $x = \sqrt{\lambda}$, Equation 27 becomes:

$$\frac{\alpha}{x} = \frac{J_1(x)}{J_0(x)} \tag{39}$$

The roots are given by the intersection of the rectangular hyperbola, α/x, with the Bessel-function analog of tan x, $J_1(x)/J_0(x)$. The latter has poles at the roots of $J_0(x)$ and the same zeros, x_j, as $J_1(x)$:

$$x_j = (1 + 4j)\frac{\pi}{4} - \frac{3}{2\pi(1 + 4j)}\left[1 - \frac{8}{\pi^2(1 + 4j)^2} + \ldots\right] \tag{40}$$

$$\text{or } x_1 = 3.8317; \quad x_2 = 7.0156; \quad x_3 = 10.1735$$

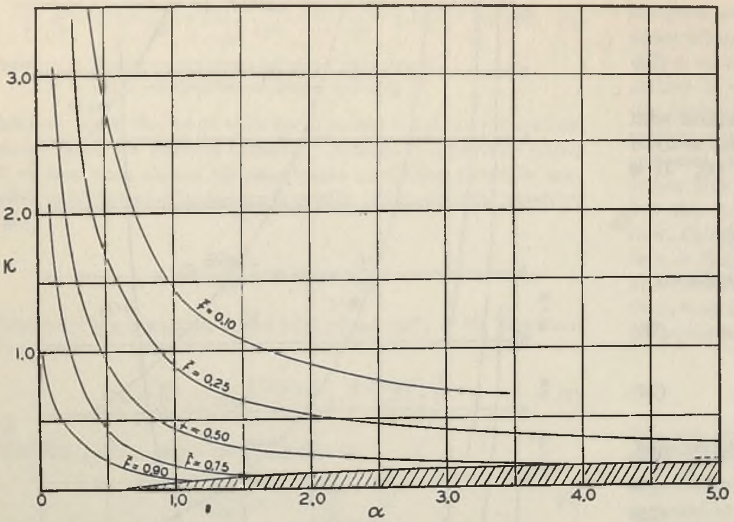

Figure 2. Lines of Constant Product Composition, $\bar{f}$, showing κ vs. α

Correction terms to Equation 38 are required for points within the shaded area.

For certain ranges of values of α, Equation 39 has simple analytical solutions.

Equations 38 and 39 show that conversion depends on the two dimensionless ratios α and κ, which may be written

$$\alpha = \frac{R^2}{D_k} \cdot \frac{k_1\Omega}{R} = \frac{2t_D}{t_{1/2}} \tag{41}$$

$$\kappa = \frac{D\kappa}{R^2} \cdot \frac{1}{S} = \frac{\tau}{2t_D}$$

where $t_D = R^2/2D_k$ = average time required for a molecule to diffuse a distance R

$t_{1/2} = R/k_1\Omega$ = half life, in seconds, for reaction on given amount of surface per unit volume

$\tau = 1/S$ = nominal contact time based on space velocity of feed

The orders of magnitude of α and κ likely to be met in practice can now be estimated easily. Diffusivities in gases range from $D \approx 10$ cm.^{2} sec.$^{-1}$ for turbulent diffusion down to $D \approx 10^{-2}$ cm.^{2} sec.$^{-1}$ for diffusion in laminar flow. If the tube radii range from $R = 10^{-2}$ to $R = 10$ cm., t_D will range from 10^4 to 10^{-3} second. Any reasonably fast reaction has a half life ranging from $t_{1/2} = 10^2$ to 10^4 seconds. Hence α will range from 10^{-7} to 10^2.

In turbulent flow the diffusivity, D_k, should be defined in terms of a mass transfer coefficient, defined by

$$N_k = -D_k \Delta mc_k/R$$

where N_k = moles of component A_k transferred per cm.^{2} per sec.

Δmc_k = difference in concentration between midstream and wall

All of the theories for estimating N_k agree (7) that it is nearly proportional to the mean velocity. Thus, Sherwood finds that $V\Delta mc/N = 650$ in air and carbon dioxide for Reynolds numbers greater than 15,000. Putting $V = SL$ gives $D_k = N_kR/\Delta mc_k = RSL/650$ and $\kappa = L/650\ R$. This result implies that, since the ratio κ of contact time to diffusion time is constant at all space velocities in a given reactor, an increase in space velocity brings about an exactly compensating increase in diffusivity by turbulence. One may expect, therefore, that when diffusion is exclusively rate controlling (in the limit of very high space velocities), conversion will become independent of space velocity. It will be shown that diffusion is a modifying factor in conversion only for κ greater than 0.186. This gives a lower limit of 120 for L/R. Thus, if reaction occurs in a tube more than 60 diameters in length, diffusion will have no significant effect on conversion. The number 60, based on measurements of Sherwood and Woertz (*8*) on air and carbon dioxide, would be less for denser fluids. The importance of this limitation in the use of "differential reactors", recommended by Hougen and Watson (*4*), should be emphasized, for if the catalytic bed is too short, the diffusivity of reactants and products must be considered in analyzing the resulting data. In pelleted catalysts the appropriate value of R is of the same order of magnitude as the mean pellet radius; therefore it is not surprising that diffusion is found to be of only minor importance in many catalytic reactions (*1*). Two cases now need to be considered:

CASE I. Diffusion to the wall is rapid in comparison with the half life of the reaction on the surface. α is then very small. The first root of Equation 39 will also be very small. For small x, $J_1(x)/J_0(x) \approx x/2$. Hence $x_0 = \sqrt{2\alpha}$ and $\lambda_0 = 2\alpha$. When κ is large enough so that Δ_j may be neglected in Equation 38,

$$\bar{f} = \frac{e^{-\tau/t_{1/2}}}{1 + \alpha/2} = \frac{e^{-2\kappa\alpha}}{1 + \alpha/2} \tag{42}$$

As $\alpha \rightarrow 0$, this approaches the value to be expected for a nonflow system.

Figure 2 shows the relation between parameters κ and α when conversion is kept constant, calculated from Equations 38 and 39, and neglecting all terms but the first. Small values of α require large values of κ to maintain conversion. That is, slow reactions require long contact times, diffusion rates being equal. But large values of κ are just those for which higher terms in the series of Equation 38 are negligible. Figure 1 shows that $\lambda_0 = 2\alpha$ with sufficient accuracy as long as $\alpha \leqq 0.1$. Under these conditions, $\lambda_1 \approx 14.5$ and the second term in Equation 38 becomes, at most, $\Delta_1 = 0.001$ (for $\kappa = 0$).

For larger values of α a more accurate evaluation of κ is required. Graphical and numerical solutions of Equation 39 were used in computing Figure 3. The higher terms of Equation 38 do not have to be considered for values of κ greater than 0.186. But the correspondingly short contact times occur in practice

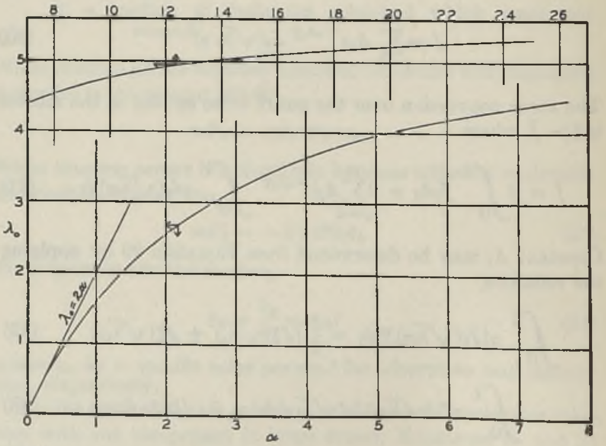

Figure 3. λ₀ vs. α, Where α = (Mean Diffusion Time)/ (Reaction Half Life)

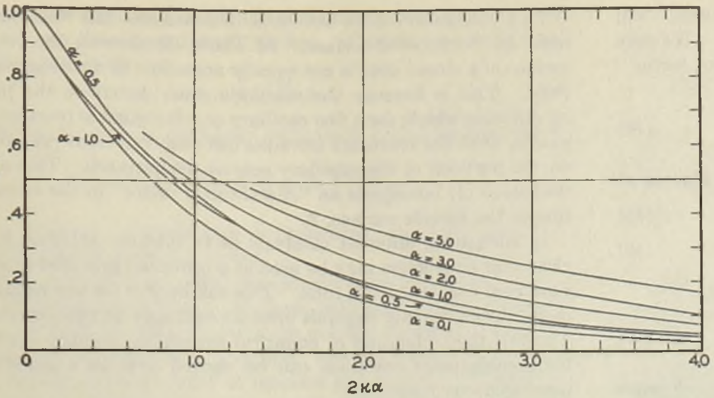

Figure 4. Fraction Unconverted, $\bar{f}$, vs. Time-Temperature Factor, $2\kappa\alpha$, Where $2\kappa\alpha$ = (Contact Time)/(Reaction Half Life)

only for very fast reactions, in which case α is so large that the controlling influence of diffusion rate must be considered in more detail.

Case II. Diffusion to the wall is slow in comparison to the half life of reaction on the surface. Parameter α is then large and diffusion is rate controlling. Inspection of Figures 1 and 3 shows that, for this case, large variations in α give relatively small changes in λ_0. Hence the qualitative behavior of Equation 38 can be observed by holding λ_0 constant as α varies. As α approaches infinity, $\lambda_0 \rightarrow 5.783$ and $\lambda_1 \rightarrow 30.471$. The term Δ_1 in Equation 38 then becomes exp. $(-24.688\,\kappa)$. This is less than 0.01 for κ greater than 0.186. Hence for infinitely fast diffusion the correction terms Δ_j are unimportant if κ is greater than 0.186. It has already been pointed out that this condition is automatically satisfied by turbulent flow at Reynolds numbers above 15,000 in a tube more than 60 diameters in length.

At lower Reynolds numbers the diffusivity is effectively a constant of the flowing mixture, independent of mean velocity. Consequently, there will be a maximum space velocity above which higher terms in Equation 38 must be taken into account. In short contact times, reaction will be reasonably complete only for the larger values of α (Figure 2). The shaded area in Figure 2 includes the values of κ for which Δ_1 in Equation 38 exceeds 0.01. The limiting value $\kappa = 0.186$ at $\alpha \rightarrow \infty$ is much reduced for smaller values of α. This chart serves as a useful guide to the validity of the simple rate law of Equation 38.

Intermediate cases, in which diffusion is a modifying but not the exclusive rate-controlling influence, are depicted in Figures 4 and 5. In Figure 4 the fraction of unconverted reactant is plotted against the "time-temperature" factor, $2\kappa\alpha$, for several values of κ and α. Figure 5 shows the ratio of these fractions to those to be expected for infinitely rapid diffusion ($\alpha = 0$) at the same value of $\kappa\alpha$. Graphically and numerically determined values of λ_0 have been used. These charts provide a quantitative evaluation of the importance of diffusion as a rate-modifying process.

Since previous treatment of this problem (*3*) was confined to just those conditions in which higher terms in Equation 38 must be considered, it has seemed worth while to discuss the present case in some detail. Without extensive numerical integration it is impossible to say just what modifications must be introduced when the mean density of the reacting fluid is not constant. However, analogy with the homogeneous case, where exact solutions are possible, suggests that the results would be only slightly modified. No doubt the percentage correction to the yield would be about the same. Figure 5 should be a useful chart even when there is an increase in the total number of moles as reaction proceeds.

APPLICATION TO PELLETED CATALYST

The extent to which the foregoing results are applicable to reactors packed with pelleted catalyst needs further consideration. Qualitatively at least, the interstices between the pellets might be considered as "cylindrical" reactors. Radius R in the previous equations would then be an effective one for the packing. Parameters κ and α may be rewritten in terms of the surface area per gram of catalyst and the pellet diameter as follows.

It is required that Equation 13A give the moles of reactant converted per cm.^{2} nominal surface per second. Let

W = grams catalyst per cm.^{3} reactor space
ρ = pellet density
d = pellet diameter
Σ = actual surface area per gram catalyst
N = number pellets per cm.^{3}

For cubic packing, $N = 1/d^3$, but this expression will be somewhat different for other types of packing or for irregular pellets (*2*). Hence,

$$N = N_0(1/d^3)$$

where $N_0 = 6W/\pi\rho$ is a packing factor, equal to unity for cubic packing. The amount converted per cm.^{3} reactor space is $W\Sigma\Omega k_1 m_0 c_{k0} f$, in moles cm.$^{-3}$ sec.$^{-1}$. The nominal surface—i.e., that calculated assuming perfectly smooth spherical pellets—is $\pi d^2 . N_0/d^3 = \pi N_0/d$. Hence the equivalent of Equation 22 is:

$$f_\eta(\zeta, 1) = -\frac{R}{D_k}\,\frac{W\Sigma d\Omega k_1 f}{\pi N_0} \tag{43}$$

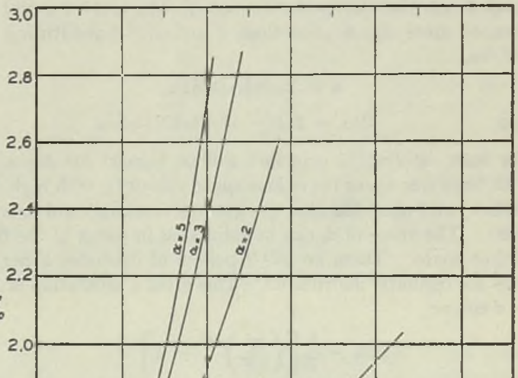

Figure 5. Correction Factor for Influence of Diffusivity on Yield, Where $\bar{f}_0$ = Exp.$(-2\kappa\alpha)$, $2\kappa\alpha$ = (Contact Time)/(Reaction Half-Life), α = (Mean Diffusion Time)/(Reaction Half-Life)

The distance, R, a molecule must diffuse to reach the surface will be of the order of magnitude of the pellet diameter, d. We may put $R = d_0 d$, leaving d_0 as an empirical "diffusion radius factor". We have then

$$\alpha = \frac{W \Sigma d^2 d_0 \Omega k_1}{D_k \pi N_0} \tag{44}$$

The nominal space velocity, S_0, based on an empty reactor is:

$$S_0 = S(1 - W/\rho) \tag{45}$$

hence

$$\kappa = D_k/R^2S = D_k(1 - W/\rho)/S_0 d_0^2 d^2 \tag{46}$$

When α is small, conversion depends only upon:

$$2\kappa\alpha = 2\,\frac{W\Sigma\Omega k_1(1 - W/\rho)}{S_0 \pi d_0^2 N_0} \tag{47}$$

When diffusion is not rate controlling, conversion is independent of pellet diameter, d, and varies only with the amount of catalytic surface per unit volume of reactor. The factor $(1 - W/\rho)$ is the fraction of free space. As it increases, space velocity decreases and increases conversion. On the other hand, free space can be increased for a given catalyst only at the expense of the total amount of surface in the reactor. This results in a maximum value of $2\kappa\alpha$ when $W/\rho = {}^1/_2$, other factors than W being held constant. This is close to the value (0.52) for regular cubic packing. One may conclude, therefore, that the more regularly the pellets can be packed, the more efficient the catalyst.

When diffusion plays a dominant role, κ is the most important parameter. The largest values of κ will be had with a large free space (to decrease space velocity) and a small pellet diameter (to shorten diffusion time). As is to be expected, the intrinsic activity of the surface is of minor importance when diffusion is rate controlling. Small dense pellets thus provide the most effective catalyst for a given weight of packing.

When the pellets are too far apart to touch one another—for example, in "fluidized" catalysts—the effective value of R will be much larger than the pellet diameter. The factors d_0 and N_0 are then of more significance than d and N. Substituting $N_0 = 6W/\pi\rho$,

$$\alpha = \Sigma\rho d^2 d_0 k_1 \Omega/6D_k \tag{48}$$

and

$$2\kappa\alpha = \Sigma(1 - W/\rho)\rho k_1 \Omega/3d_0 S_0 \tag{49}$$

For such catalysts, conversion will be highest for dense pellets with large free-space (to reduce space velocity), with high specific surface, and close together (to get the maximum aid from diffusion). The value of d_0 can be estimated in terms of the fraction of free space. There are $N^{1/3}$ pellets of diameter d per cm. if they are regularly distributed. This gives a separation of $1/N^{1/3} - d$ cm. or

$$d_0 = \frac{1}{2}\left[\left(\frac{\pi\rho}{6W}\right)^{1/3} - 1\right] \tag{50}$$

since $N = 6W/\pi d^3\rho$ for spheres. Again there is an optimum value of W/ρ which gives maximum conversion for other parameters held constant. However, since in practice, W/ρ in a fluidized bed is decreased by increasing the space velocity, this maximum may not be observed.

Thus, the qualitative conclusions are not seriously modified in passing from the highly idealized unpacked cylinder to a real bed of pellets. The significant dimensionless variables for empirical analysis are the same, and the qualitative dependence of conversion upon them should be similar.

Analysis of more complex reaction mechanisms than that attempted here unfortunately leads to great mathematical difficulties when a general treatment is desired. Numerical integration for specific values of κ and α would afford a solution in particular cases. However, it is likely that rational empirical analysis of experimental results in terms of these parameters would be a more satisfactory procedure.

This calculation does not take into account the "effectiveness" of the pelleted surface. As Thiele (*9*) showed, the entire surface of a closed pore is not equally accessible to reacting molecules. This is because the reactants must penetrate the pore by diffusion which, for a fine capillary or a fast surface reaction, is so slow that the reactants are adsorbed and converted primarily on the portions of the capillary nearest the entrance. This consideration (*4*) introduces an "effectiveness factor" in the estimation of the specific surface, Σ.

In comparing different catalysts as to intrinsic activity, it is clear that conversion may be used as a criterion, provided t_D and κ are kept constant in all runs. This will be true for any reaction in which the velocity depends upon a single specific reaction rate. Thus all the techniques of empirical correlation pointed out (*5*) for homogeneous reactions can be carried over to a study of heterogeneous reactions.

ONE PRODUCT ACCUMULATES

In many catalytic systems catalyst activity declines because the surface becomes coated with a nondesorbed reaction product as reaction proceeds. In this case the preceding analysis must be modified, since a steady state is not reached. The analysis of the fluid stream proceeds just as before. However, the specific surface activity, Ω, is now a variable, decreasing with time and giving a problem of type A.

Let us suppose as before that the reaction occurring is $\Sigma a_j A_j \rightarrow \Sigma b_m B_m$, but that now one of the products, B_β, deposits on the catalytic surface and poisons it. For this component the velocity is zero, and Equation 2 becomes:

$$\frac{\partial mc_\beta}{\partial t} = m\Gamma_\beta \quad (r = R)$$

As an example, let B_β be formed unimolecularly from A_α and let A_α disappear unimolecularly, but with a different rate constant. Further, suppose the active surface to decrease in area at the same rate at which B_β is formed. Then on the surface,

$$\frac{\partial\Omega}{\partial t} = -k_2'\Omega m_0 c_{\alpha 0} f \tag{51}$$

Equations 12A to 15A hold as before for this case, so that f depends upon time only implicitly through Ω. Hence, putting $\eta = 1$, Equation 29 may be substituted into Equation 51 and the integration performed. Putting $\Omega = \alpha D_k/Rk_1$ and $\gamma = k_2' m_0 C_{\alpha 0}$,

$$\frac{d\alpha}{\alpha f} = -\gamma dt$$

$$-\gamma t = \int_{\alpha_0}^{\alpha} d\alpha/\alpha f \tag{52}$$

To complete the integration we need to know $f(\alpha)$. We have seen that most practical cases are covered by

$$f = e^{-\kappa\alpha}/(1 + \alpha/2) \quad (\alpha \leqq 0.1) \tag{53}$$

The integration may be performed in series to give

$$-\gamma t = \ln(\alpha/\alpha_0) + \Phi(\alpha/\alpha_0) + Q \tag{54}$$

where

$$-\Phi(\alpha/\alpha_0) = 2\kappa\alpha_0\left(1 - \frac{\alpha}{\alpha_0}\right) + \frac{(2\kappa\alpha_0)^2}{2.2!}\left[1 - \left(\frac{\alpha}{\alpha_0}\right)^2\right] + \dots + \frac{(2\kappa\alpha_0)^n}{n.n!}\left[1 - \left(\frac{\alpha}{\alpha_0}\right)^n\right] + \dots \tag{55}$$

$$-Q = (e^{2\kappa\alpha_0} - e^{2\kappa\alpha})/4\kappa$$

hence

$$\alpha = \alpha_0 e^{-\gamma t - \Phi - Q} \tag{56}$$

When conversion is low ($2\kappa\alpha_0 << 1$), $Q \approx 0$, $-\Phi \approx 2\kappa\alpha_0 - 2\kappa\alpha$, and

$$\alpha = \alpha_0 e^{-\gamma t - 2\kappa\alpha + 2\kappa\alpha_0} = \frac{\alpha_0 f}{f_0}\, e^{-\gamma t} \tag{57}$$

where $f_0 = \exp. (-2 \kappa\alpha_0)$ is the conversion under given reaction conditions on an unpoisoned surface. This may be substituted into Equation 53:

$$f = f_0^{e^{-\gamma t} f/f_0} \tag{58}$$

The factor γ can be evaluated empirically by taking logarithms:

$$-\gamma t = -\ln(f/f_0) + \ln\left(\frac{\ln f}{\ln f_0}\right) \tag{59}$$

This equation is remarkable in presenting one of the few theoretically justified log-log curves.

Equation 57 shows that the effectiveness of the surface, at constant process period t, decreases with increasing conversion; i.e., more active catalysts are more quickly poisoned. Near the beginning of the process period, activity falls off in exact proportion to the decrease in reactant and linearly with increasing process period. Thus one would expect the poisoning deposit to build up in inverse proportion to the concentration of reactant and to increase exponentially with time when conversion is low. Other mechanisms of poisoning will, of course, give different kinetic behavior.

The case in which diffusion is rate controlling is not so easily treated since there is no analytical expression for λ under these conditions. The limiting case, λ_0 = constant, is not of practical importance, since the large values of α for which it holds are soon reduced by poisoning. For the experimental determination of rate constants, very fast reactions for which α_0 is large may be studied best on almost completely poisoned surfaces, to which Equation 59 will apply. In the converse problem, given the rate constants and specific surface area, a numerical integration of Equation 52 will serve in calculating the conversion to be expected.

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Mercurial Fungicide Wax Problems

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Fungus growth closely parallels the fungicide concentration in microcrystalline waxes. High temperatures rapidly deplete the fungicide concentration in microcrystalline waxes. At 105° C. mercurial fungicides afford best protection in the following order: phenylmercuric stearate, phenylmercuric salicylate, pyridylmercuric stearate. At 125° C. the order of protection is: phenylmercuric stearate, phenylmercuric salicylate, pyridylmercuric stearate. The minimum amount of fungicide in waxes necessary to provide protection against fungus growth is as follows: pyridylmercuric stearate, about 0.35%; phenylmercuric salicylate, about 0.10%; phenylmercuric stearate, about 0.08%.

TO PREVENT the deterioration and complete failure of certain military equipment, moisture- and fungus-proofing has become an accepted part of the manufacturing process. Many of the component parts and assemblies requiring this treatment are processed with a fungicidal microcrystalline wax in either an open or vacuum impregnating tank. Immediately after the introduction of such processes, it was noted that this procedure involved problems which had not been fully anticipated. After a short period of use, crystals of the fungicide were observed on the covers of the wax tanks. This suggested that the fungicide was subliming, and, as a result, its concentration in the wax was decreasing. Thus, the fungicide concentration would eventually reach a point where protection against fungus growth would no longer exist.

Our laboratories were confronted with the problems of determining the rate of decrease of the fungicide in the wax during processing, the effect of the temperature of the wax bath upon rate of sublimation, the effect (and possible revision) of vacuum during cycling, and the determination of a minimum fungicide concentration necessary to provide protection against fungus growth.

One per cent of phenylmercuric salicylate (as a fungicide) incorporated in a microcrystalline wax was used in production. Many parts, previous to the introduction of the tropicalization program, had been processed in open wax tanks. Fear of toxicity of fungicide to personnel engaged in processing resulted from the lack of clear-cut scientific data as to the toxicity of the compounds being used. As a result, open-tank processing was quickly abandoned.

Vacuum impregnation was based upon a 40-minute cycle consisting of: (*a*) baking parts to be impregnated 20 minutes at 230° F. (110° C.) at vacuum of not less than 20 inches of mercury; (*b*) running hot wax into the tank to cover parts and retaining the vacuum 5 minutes; (*c*) releasing the vacuum and allowing the parts to soak in wax at 230° F. for an additional 5-minute period; (*d*) draining the wax from the tank and allowing the excess wax to drain from the parts for 10 minutes at 230° F.; and (*e*) removing the parts from the tank and allowing them to cool in the open air.

A SAMPLE of the original wax was taken, and samples were also removed from the vacuum tank daily; all were submitted to chemical and biological tests. The conventional method of titrating mercuric salts with a standard thiocyanate solution[1]

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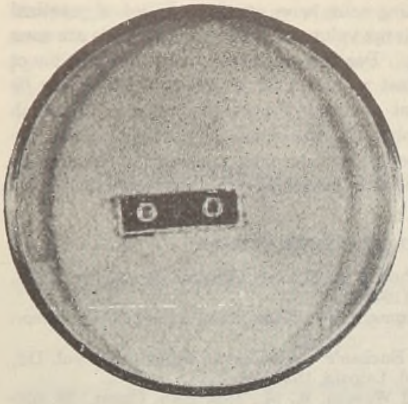

Canvas-Base Bakelite Coated with Wax Containing No Fungicide, Showing Heavy Growth; Tested with *A. niger* 6277

Canvas-Base Bakelite Treated with Mercurial Wax, Showing No Growth and a Zone of Inhibition; Tested with *T. köningi*

was used to determine the fungicidal content of the waxes. A 2-gram sample of wax was weighed into an Erlenmeyer flask and dissolved in 50 cc. of warm benzene. When a clear solution resulted, 50 cc. of acetone followed by 10 cc. of distilled water were added. The sample was titrated with a standard solution of 0.01 *N* potassium thiocyanate using 2 cc. of ferric ammonium sulfate as indicator. After each addition of the potassium thiocyanate the samples were thoroughly shaken. The end point was the characteristic orange-pink coloration observed in the aqueous portion which separated upon standing[2]. The thiocyanate solution was standardized using weighed quantities of the fungicide.

The wax samples for chemical tests were also used for mycological tests. The procedure consisted of impregnating 3-cm. disks of Whatman 41 H filter paper with the wax and then leaching for 8 hours in running tap water at 25° C. (77° F.). The samples were placed on a nutrient-agar medium in Petri dishes and inoculated with spore suspensions of pure and mixed fungus cultures. Pure cultures of *Aspergillus niger* 6277 and *Trichoderma köningi*, and a mixed culture of *Chaetomium globosum* 6205, *Penicillium luteum* 9644, and *Aspergillus niger* 6277 were used. Ten-day incubation at a relative humidity greater than 95% and a temperature of 30° C. (86° F.) followed.

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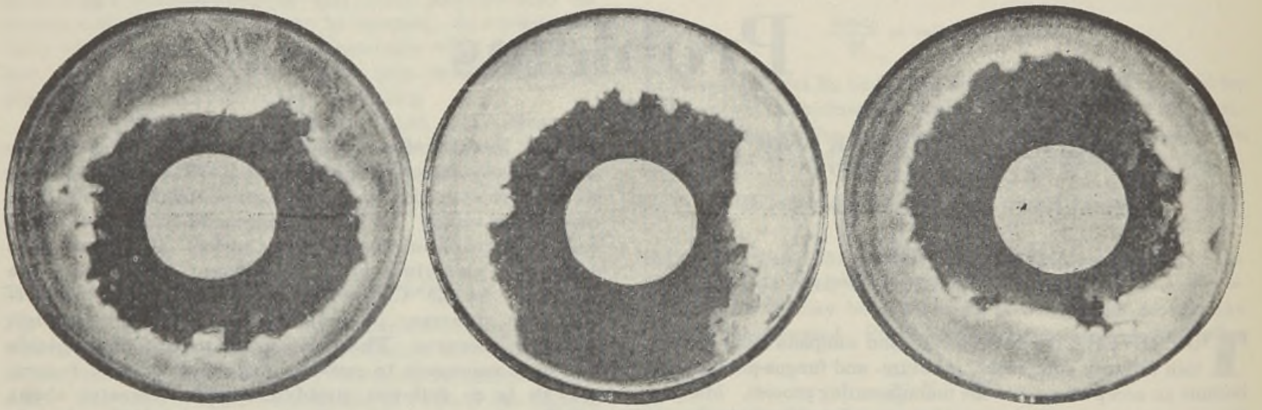
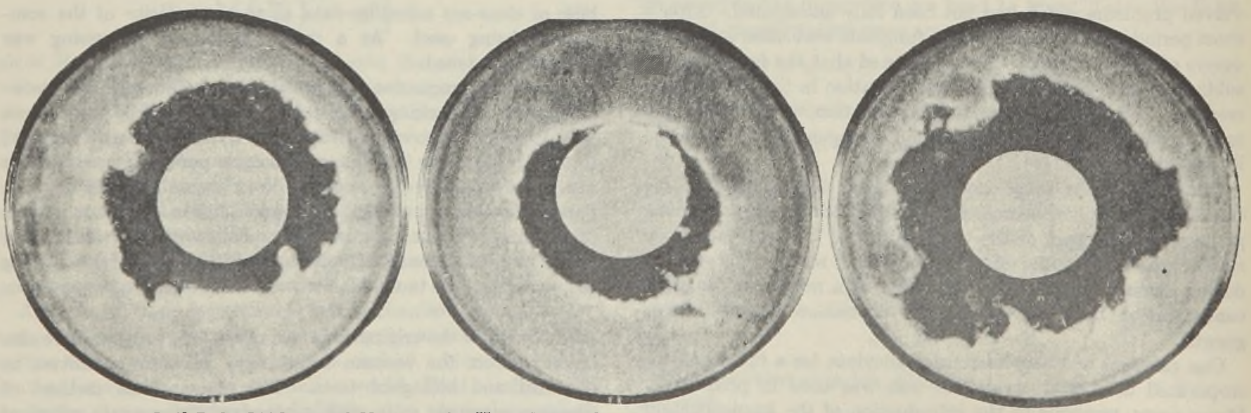
[2] Cl^- interferes with this test. The Cl^- was precipitated as AgCl. Comparison with standard solutions indicated that the Cl^- content of the waxes utilized in the tests was less than that of a standard solution containing 1 mg. of Cl^- per liter in a 1:9 HNO_3 solution.



Original. Unheated sample; 0.90% phenylmercuric stearate in a microcrystalline wax

1. Heated at 105° C. for 24 hours; 0.89 % phenylmercuric stearate remaining

2. Heated at 105° C. for 72 hours; 0.86 % phenylmercuric stearate remaining



3. Heated at 105° C. for 144 hours; 0.83 % phenylmercuric stearate remaining

4. Heated at 105° C. for 264 hours; 0.75 % phenylmercuric stearate remaining

5. Heated at 105° C. for 360 hours; 0.70 % phenylmercuric stearate remaining

Typical Set Used in Making Data for a Mycological Graph (*Trichoderma köningi*)

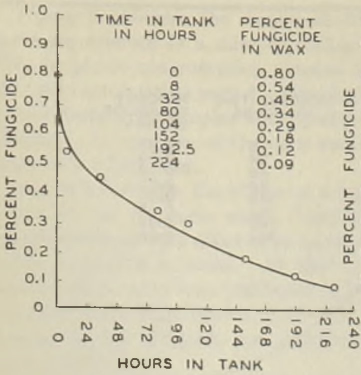


Figure 1. Original-Production Vacuum Cycling

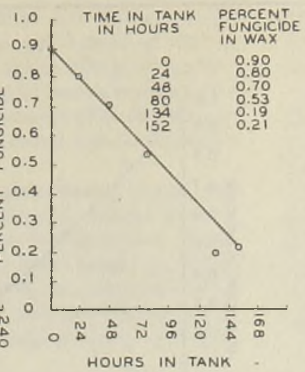


Figure 2. Revised-Production Vacuum Cycling

Where results were difficult to interpret, observations were made with a 30× magnification.

Similar chemical and mycological tests were performed on waxes containing 1% of several mercurial fungicides; these fungicidal waxes were heated in the laboratory in a thermostated and well-ventilated oven for 360 hours. At various intervals in the heating period, samples were taken for testing.

FIGURE 1 indicates results obtained with the original vacuum cycle. Heating was continuous. As a result of the initial rapid decrease in fungicide concentration during processing, the cycling was revised.

Figure 2 indicates results when a revised vacuum cycle was used. The abscissa is given as hours in the tank and does not indicate a period of continuous heating. Heating (by steam) of the production tank was begun about one hour before use; at the end of each production day, heating was discontinued and the tank allowed to cool. Figure 2, then, shows the total time the wax remained in the tank. Step 2 of the original vacuum cycle was changed so that the vacuum was released immediately after the hot wax covered the component parts. As a result of this revised heating and vacuum cycling, the sudden initial decrease in fungicide concentration was eliminated.

In Figures 3 to 8 the "zone of inhibition" may be defined as the clear area around a test sample in which the spores from the inoculation did not germinate and mycelial growth was absent. The zone of inhibition was determined by measuring the distance of clear area around the test sample. Petri dishes 10 cm. in diameter were used, and the test samples were 3 cm. in diameter.

If fungus growth did not occur in the region 0.5 cm. or less from the sample, the zone of inhibition was classified as narrow. The zone of inhibition was classified as medium if no growth occurred in the region 0.5 to 1.5 cm. from the test sample, as wide if from 1.5 to 2.5 cm. from the sample, and as very wide if 2.5 to 3.5 cm. from the sample. On the mycological graphs the ordinate (growth) axis refers to fungus growth on the test sample itself.

Figure 3 indicates the results obtained with a microcrystalline wax containing 1% of phenylmercuric salicylate heated at 105° C. (221° F.). The quantity of fungicide (0.13%) present after heating for 360 hours was sufficient to provide fungus protection (narrow zone of inhibition). There was a slow, uniform decrease in the fungicide concentration. The solid line represents the results obtained with *Aspergillus niger* 6277, the broken line *Trichoderma kōningi*, and the dashed line the mixed culture (*A. niger*, *Penicillium luteum* 9644, and *Chaetomium globosum* 6205). The same code system is used throughout.

Figure 4 indicates the results obtained with the same wax heated at 125° C. (257° F.). The initial decrease in the concentration of the fungicide is rapid. When compared with Figure 3, it is evident that heating at 105° C. is preferable to that at 125° C. However, even after heating for 360 hours at 125° C., fungus protection was still present. At 168 hours (0.10%) fungus growth occurred up to but not on the test sample (no zone of inhibition). This condition prevailed through the remainder of the 360-hour heating period.

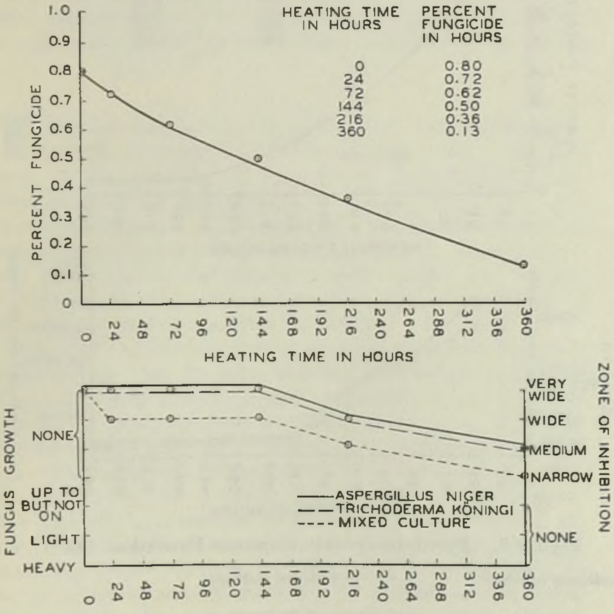


Figure 3. Phenylmercuric Salicylate Heated at 105° C.

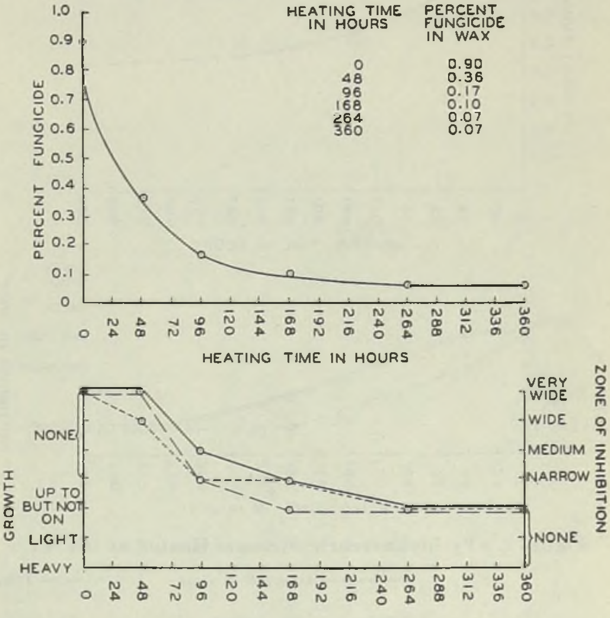


Figure 4. Phenylmercuric Salicylate Heated at 125° C.

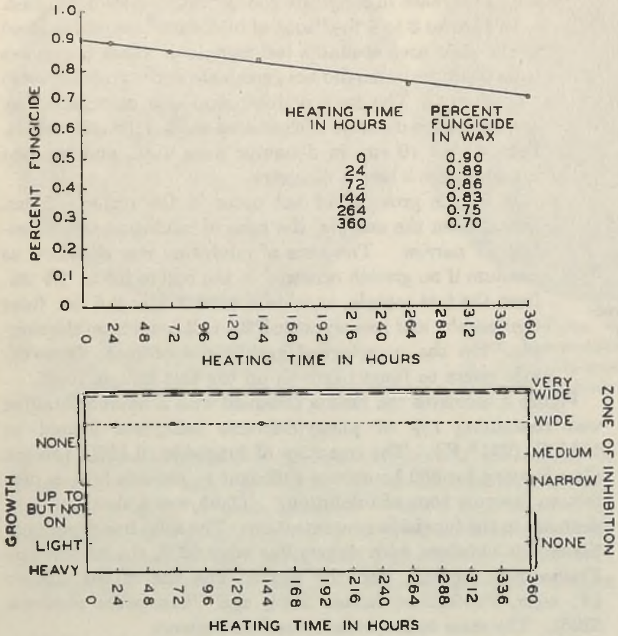


Figure 5. Phenylmercuric Stearate Heated at 105° C.

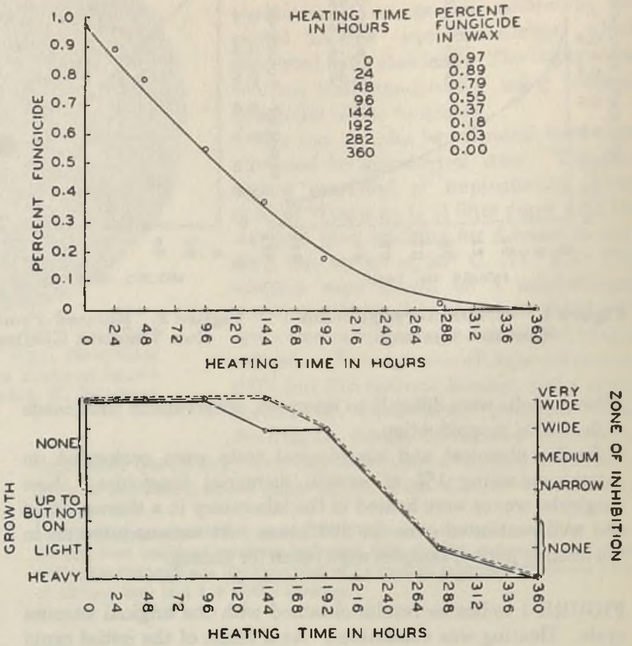


Figure 6. Phenylmercuric Stearate Heated at 125° C.

——— *Aspergillus niger* — — — *Trichoderma köningi* - - - - - - Mixed culture

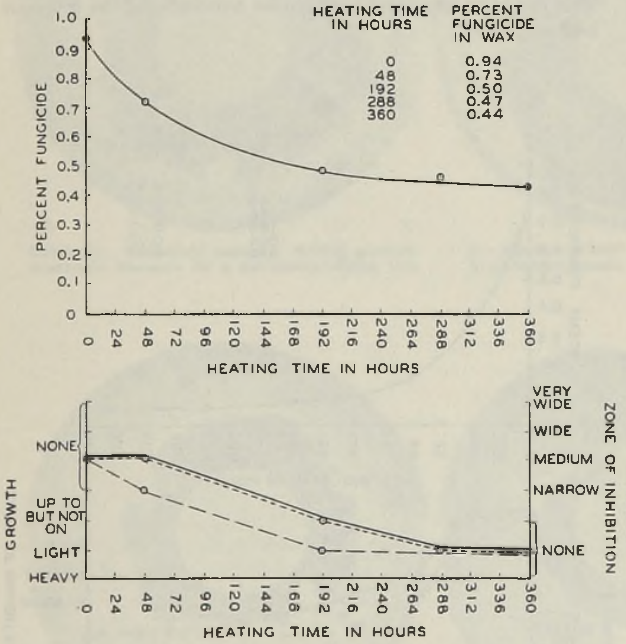


Figure 7. Pyridylmercuric Stearate Heated at 105° C.

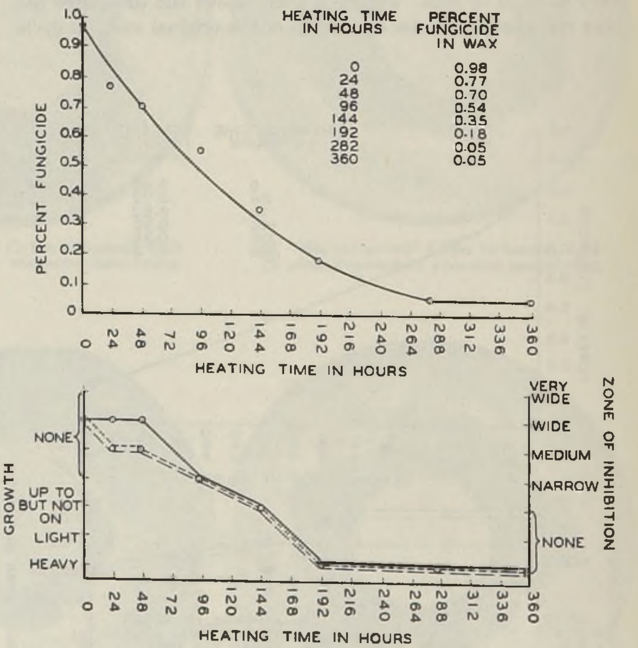


Figure 8. Pyridylmercuric Stearate Heated at 125° C.

——— *Aspergillus niger* — — — *Trichoderma köningi* - - - - - - Mixed culture

Figure 5 indicates the results obtained with 1% of phenylmercuric stearate in a microcrystalline wax heated at 105° C. The fungicide concentration remains above 0.70% throughout the 360-hour heating period. Mycological results similar to the initial (unheated) samples were obtained even after 360 hours of heating. All samples of the pure and mixed cultures showed a wide zone of inhibition.

Figure 6 indicates the effects of a higher heating temperature (125° C.) on the same wax. Comparison of Figures 5 and 6 clearly illustrates the effect of an increase in temperature on mercurial fungicides in waxes. At 125° C. good fungus protection was obtained for at least 192 hours (0.18%) as compared to more than 360 hours when heated at 105° C. The decrease in the percentage of the fungicide was considerably more rapid at 125° than at 105° C.

Figure 7 indicates the results obtained with 1% of pyridylmercuric stearate in a microcrystalline wax heated at 105° C. Proper fungus protection was present only up to 192 hours (0.50%) for *A. niger* and *P. luteum* and up to 96 hours for *T. köningi*. Although heating for 360 hours had only reduced the fungicide concentration to 0.44%, fungus protection had been lost.

Figure 8 indicates the effects of the same wax heated at 125° C. Proper fungus protection was present only up to 144 hours (0.35%). The decrease in fungicide concentration continued for a longer period when heated at 125° than at 105° C.

Mycological tests indicate a minimum concentration of fungicide necessary to provide protection against fungus growth. When the fungicide concentration in production has decreased to this minimum level, the concentration must again be increased by the addition of a "fungicide concentrate" (either a true solution or a colloidal dispersion of the fungicide in the wax).

ACKNOWLEDGMENT

The authors are indebted to Helen Conlon for assistance in performing mycological tests. Photographs were taken by Bert Cannon.

POLYMERIZATION OF ALPHA-METHYLSTYRENE

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α-Methylstyrene has been homopolymerized by solutions of Friedel-Crafts catalysts in organic solvents at temperatures as low as −130° C. to molecular weights as high as 84,000. The highly polymerized product includes a wide range of molecular weights as shown by distribution curves based on fractional precipitation. This polymer is not distorted in boiling water and has a higher fusion point than polystyrene but is inferior in strength to the latter. A copolymer of isobutylene and α-methylstyrene which can be formed into thin, strong, flexible sheets has been made by the same polymerization technique. The emulsion copolymerization of butadiene and α-methylstyrene yields an elastomer comparable to that now obtained from butadiene and styrene; the optimum ratio of butadiene to α-methylstyrene contains a greater proportion of butadiene than is used with styrene. In this copolymerization α-methylstyrene has advantages of stability and ease of handling when compared to styrene.

THE large-scale manufacture of low-cost cumene (isopropylbenzene) perfected for aviation gasoline is also a potential basis for the manufacture of low-cost alpha-methylstyrene. Good yields of this monomer can be obtained from cumene by dehydrogenation (*1*). Unlike styrene, α-methylstyrene does not undergo spontaneous polymerization on heating. It can, therefore, be distilled at atmospheric pressure, stored, and handled without loss due to polymer formation. Its properties along with those of styrene are given in Table I.

The many published studies of the homopolymerization of α-methylstyrene fail to give high-molecular-weight polymers. Klages (*7*), using phosphoric acid as catalyst, obtained an unsaturated polymeric product of low molecular weight. Tiffeneau (*21*) reported that the use of concentrated sulfuric acid as catalyst yielded a saturated dimer, which he concluded was diphenyldimethylcyclobutane. Later investigators (*2*) proposed the structure 3-phenyl-1,1,3-trimethylhydrindene for this saturated dimer. The formation of a polymer (molecular weight 4200) by contacting α-methylstyrene with activated bleaching earth or clay is claimed by Stanley and Salt (*14*); Lebedev and Filonenko (*9*) also disclosed an unsaturated low-molecular-weight polymer upon contacting with Florida earth. Sapiro *et al.* (*12*) investigated the high-pressure polymerization of α-methylstyrene and reported that polymers having a molecular weight of 5600 to 6100 are produced at pressures greater than 3000 atmospheres at about 100° C. in the absence of any catalyst. Hydrochloric acid, benzoyl peroxide, and zinc chloride failed to accelerate this reaction. Staudinger and Breusch (*16*), in a rather extensive treatise on the polymerization of α-methylstyrene, claimed that it does not polymerize on long standing, either with or without exposure to light in the cold; they stated that with heat and catalysts it is much more difficult to polymerize than is unsubstituted styrene. Treatment with stannic chloride yielded saturated polymerization products from the dimer to the octamer, whereas vigorous action yielding unsaturated polymeric materials was observed with titanium tetrachloride and boron trichloride catalysts. The unsaturated dimer found in the foregoing products was reported (*2*) to be 2,4-diphenyl-4-methyl-1-pentene.

Several copolymers with alpha-substituted styrene are also reported in the literature. Palmer (*10, 11*) stated that alpha-substituted styrenes are not polymerizable alone by means of heat, but that a clear, colorless resin was readily formed by copolymerizing α-methyl-*p*-methylstyrene with styrene. Kropa (*8*) achieved copolymerization of this same monomer with acrylonitrile. Copolymers of α-methylstyrene with maleic anhydride (*4*) and with butadiene (*22*) are recorded in the patent literature.

Table I. Properties of α-Methylstyrene

	Sp. Gr., 20/4 d_4^{20}	M.P., ° C.	B.P., ° C.	Refractive Index, n_D^{20}
Styrene (*2A*)	0.9056	−30.6	145.2	1.5470
α-Methylstyrene (*2A*)	0.9134	<−20	161–162	1.5384
α-Methylstyrene (exptl.)	0.9106	−23	159–164	1.5359

Table II. Polymerization of α-Methylstyrene by Ionic Catalysts

Run No.	Dilution		Reaction Temp., ° C.	Yields		Polymer			
	Solvent	Ratio		% monomer converted	G. polymer/g. catalyst	Intrinsic viscosity [η]	Mol. wt.	Fusion, ° C.	Catalyst Soln.
1	EtCl	14/1	−130	86	210	2.56	58,900	215–227	1% $AlCl_3$ in EtCl
2	EtCl	14/1	−130	85	200	2.64	61,300	219–227	1% $AlCl_3$ in EtCl
3	EtCl	14/1	−130	80	...	3.62	84,000	.....	1% $AlCl_3$ in EtCl
4	EtCl	6/1	−100	..	...	0.68	15,600	196–228	1% $AlCl_3$ in EtCl
5	EtCl	6/1	−100	..	...	0.62	14,200[a]	196–226	1% $AlCl_3$ in EtCl
6	EtCl	2/1	− 77	..	...	0.50	11,500	206–211	0.5% $AlCl_3$ in EtCl
7	EtCl	1/1	− 50	73	230	0.19	4,400	157–166	1% $AlCl_3$ in EtCl
8	EtCl	1/1	− 50	35	410	0.19	4,400	172–185	1% $AlCl_3$ in EtCl[b]
9	EtCl	1/1	− 50	45	350	0.21	4,900	145–162	1% $AlCl_3$ in EtCl
10	EtCl	4/1	− 50	85	200	0.26	6,100	163–189	1% $AlCl_3$ in EtCl
11	EtCl	14/1	− 50	84	110	0.25	5,700	204–213	1% $AlCl_3$ in EtCl
12	EtCl	14/1	− 20	..	...	0.036	840	63–76	1% $AlCl_3$ in EtCl
13	EtCl	1/1	− 19	..	...	0.093	2,140	127–137	1% $AlCl_3$ in EtCl
14	EtCl	1/1	− 15	..	...	0.099	2,280	166–177	0.5% $AlCl_3$ in EtCl
15	EtCl	1/1	0	..	...	0.098	2,260	171–181	0.5% $AlCl_3$ in EtCl
16	EtCl	1/1	23	..	...	0.033	770	86–98	0.5% $AlCl_3$ in EtCl
17	CS_2	14/1	− 91	91	150	1.30	30,200	217–223	1% $AlCl_3$ in EtCl
18	CS_2	14/1	− 92	70	390	1.04	24,100	175–199	1% $TiCl_4$ in CS_2
19	CS_2	1/1	− 50	75	150	0.35	8,050	171–196	1% $AlCl_3$ in CS_2 (slurry)
20	*n*-BuCl	1/1	− 50	0	...	..	....	.....	1% $AlCl_3$ in BuCl
21	Liquid SO_2	1/1	− 50	10	20	..	Low	.....	1% $AlCl_3$ in liq. SO_2

[a] α-Methylstyrene 99% pure instead of 96–97% as normally used.
[b] Catalyst injected over a period of one hour.

IONIC-CATALYZED POLYMERIZATION

Previous experience in this laboratory on low-temperature polymerization, such as that reported by Thomas *et al.* (*18*, *20*) on isobutylene and on isobutylene-diene copolymers (*17*, *19*), prompted the thought that α-methylstyrene might respond to ionic catalysts at low temperatures; it was considered probable that side reactions resulting in low-molecular-weight polymers would be suppressed at these temperatures. A series of experiments with ethyl chloride as a diluent for α-methylstyrene and as a catalyst solvent for aluminum chloride yielded a series of high-molecular-weight polymers not previously reported. The spray method of catalyst addition was employed as advanced by Thomas *et al.* (*17*, *19*) for Butyl rubber synthesis. The experimental technique follows:

The reaction system made of copper is shown in Figure 1. The catalyst chamber is attached to a nitrogen cylinder equipped with a pressure-reducing valve. The catalyst solution flows through a lagged copper capillary fitted with a valve near the injection orifice. A constant pressure (5 pounds per square inch), maintained on the catalyst solution, gives a uniform spray from the jet. The reactor has been kept as free as possible from internal appliances so that the formation of polymer does not clog the apparatus. The amount of catalyst added is obtained by weighing the catalyst chamber and assembly before and after use.

A mixture of α-methylstyrene and diluent is charged to the reactor equipped with a stirrer and thermocouple or toluene thermometer. The reaction mixture is then cooled to the desired reaction temperature by adding powdered solid carbon dioxide (in these experiments, down to −78° C.) or by pumping liquid nitrogen into the expansion chamber jacket around the reaction vessel. A previously prepared solution of catalyst is then cooled to reaction temperature, or to −60° to −65° C. when lower reaction temperatures are used, and injected into the rapidly agitated reaction mixture by forcing it through a 0.012-inch-diameter glass orifice by pressure. The outlet of the orifice is held about one inch above the surface of the reaction mixture. The catalyst addition is regulated, along with further cooling of the reaction mixture, so that a range of temperature of ±5° C. is maintained. After completion of the reaction, the activity of the catalyst is stopped at the reaction temperature by the addition of precooled ethyl alcohol to the reaction mixture. When the polymer forms in discrete particles (lowest temperatures), as much of the free liquid as possible is removed and the polymer is further washed with cooled alcohol. The polymer is finally broken up into small pieces, steam-distilled to remove remaining unreacted α-methylstyrene and solvents, and dried. When the polymer forms a viscous gel with the diluent and unreacted monomer, alcohol is added and the solvent evaporated until coagulation results. The polymer is then thoroughly washed with alcohol and finally steam-distilled.

The catalyst solution is best prepared by adding the catalyst to a small portion of slightly cooled dry solvent, agitating to cause solution, adding the remaining solvent to bring to the desired concentration, and chilling to final temperature in the catalyst chamber.

HOMOPOLYMERIZATION

Table II gives data on experiments run according to the technique just described; they were carried out to about 80% conversion of the monomer in most cases. In a few instances where low-molecular-weight polymers were formed, the viscosity of the system became so great that agitation and, consequently, heat dissipation became poor and necessitated stopping the experiment. Several experiments run to determine the effect of the extent of the reaction on molecular weight showed that this was negligible in the range studied. Runs 7 and 9, made under identical conditions, show that polymer of substantially the same molecular weight was obtained at both 45 and 73% conversion of monomer to polymer. The average yield was 2 grams of polymer per gram of catalyst solution added. The catalyst solution used in most cases contained 1% by weight of aluminum chloride; thus the polymer yield was 200 grams per gram of aluminum chloride added.

Since the freezing point of α-methylstyrene is about −23° C., the technique of using high dilutions of reaction solvent (ethyl

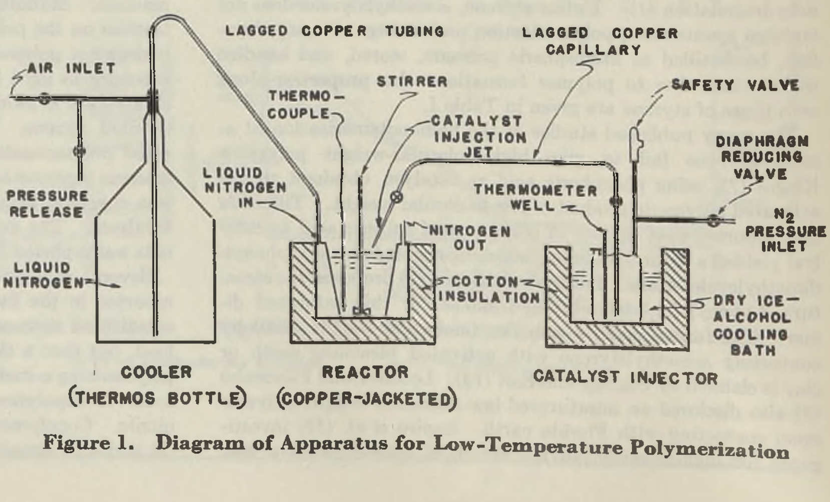


Figure 1. Diagram of Apparatus for Low-Temperature Polymerization

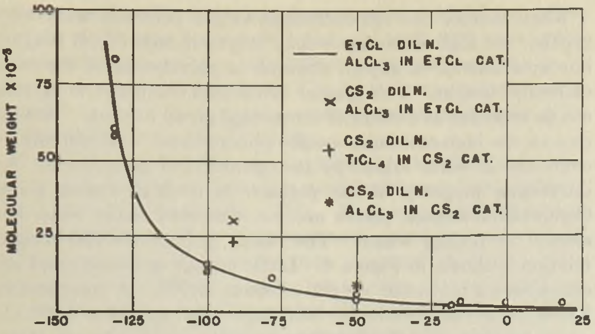


Figure 2. Effect of Temperature on α-Methylstyrene Polymerization

chloride in most cases) was employed in order that experiments could be conducted below this temperature. In the limits used, dilution ratio of 1/1 and higher (Table II), there was no apparent relation between this factor and molecular weight and yield of polymer. Actually the dilution ratio given represents the condition at the start of the experiment, since the ratio of monomer to solvent changes as the reaction proceeds as a result of the addition of extra solvent and consumption of the monomer. The reaction is carried out in a solvent primarily to facilitate better heat removal and to have a common solvent for catalyst and monomer. As will be shown later, the nature of this solvent is important.

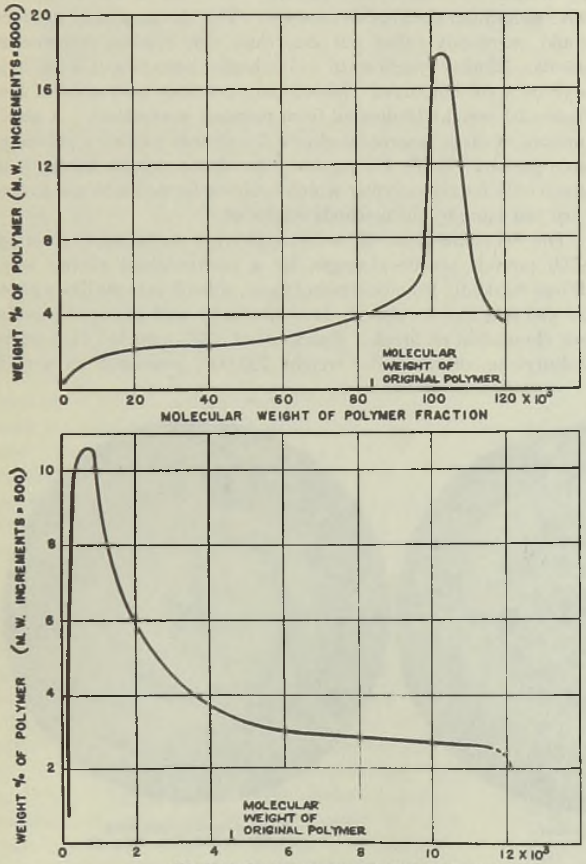


Figure 3. Differential Distribution Curves for Poly-α-methylstyrene of High Molecular Weight (*above*) and Low Molecular Weight (*below*)

Figure 2 gives data plotted from Table II which show the relation between temperature of reaction and molecular weight of polymer. The curve is for the system ethyl chloride–aluminum chloride. Polymers having average molecular weights from 770 (at 23° C.) to 84,000 (at −130° C.) were obtained. The molecular weights were calculated from intrinsic viscosities in benzene, using Kemp and Peters' constant (*6*) for styrene which, although probably not exactly correct for α-methylstyrene, is felt to provide a good relative measure of the degree of polymerization. The samples used for these determinations were subjected to rigorous steam distillation and drying to remove traces of solvents and unreacted monomer.

$$\text{molecular weight} = [\eta]K$$

$$[\eta]_{C \to 0} = \frac{\ln \eta_r}{C}$$

Staudinger's constant (*15*) gives values approximately three times greater, which presumably should be used when patent literature values are compared. A sharp break in the molecular weight–temperature curve occurs at approximately −100° C. The molecular weight distribution curve (Figure 3, upper graph, and Table III), obtained on a polymer with an average molecular weight of 84,000, is interpreted in the light of this sharp dependence of molecular weight on reaction temperature. The distribution curve shows a long tail of low-molecular-weight polymers. This may be explained on the basis of the reaction being exothermic. As reaction occurs there is a local-temperature rise in the reaction zone which markedly decreases molecular weight. The reaction is extremely rapid, similar to that of isobutylene (*20*), and the heat release can be momentarily greater than can be dissipated. This is the reason for injecting a dilute solution of the catalyst and having violent agitation. These facts suggest that the shape of the distribution curve can be controlled to some degree by variations in catalyst concentration, rate of addition, and heat dissipation methods. A low-molecular-weight polymer (average 4500) was also fractionated, and the result is shown in Figure 3 and Table III.

The differential distribution curves were plotted from values obtained from the integral distribution curves of the fractional precipitation data on the polymers. These integral distribution curves showed, in the normal manner, the cumulative percentage of polymer up to any given molecular weight, the molecular weight of the various fractions being considered as the molecular weight at the mid-percentage of the fraction. The distribution curve of the high-molecular-weight polymer was obtained by precipitation of the polymer from toluene by the addition of acetone; the curve of the low-molecular-weight polymer was obtained by

Table III. Fractional Precipitation of Poly-α-methylstyrene

Sample No.	Mol. Wt.	Fraction No.	Fraction Wt.%	[η]	Mol. Wt.	% × Mol. Wt.
1	4,500	1	6.0	0.50	11,500	690
		2	6.4	0.46	10,600	680
		3	8.2	0.42	9,600	790
		4	13.1	0.31	7,100	930
		5	8.2	0.24	5,600	460
		6	7.5	0.19	4,500	340
		7	7.5	0.14	3,300	250
		8	9.4	0.10	2,300	220
		9	6.0	0.074	1,700	100
		10	27.7	0.030	700	190
						4,650
2	84,000	1	8.6	4.92	114,000	9,800
		2	25.9	4.38	102,000	26,400
		3	9.3	4.31	100,000	9,300
		4	26.9	3.31	77,000	20,700
		5	10.7	2.39	56,000	6,000
		6	6.2	1.56	36,000	2,200
		7	7.6	1.15	27,000	2,100
		8	4.8	0.38	9,000	400
						76,900

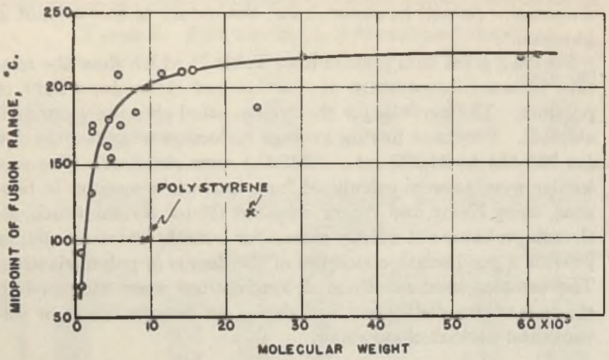


Figure 4. Effect of Molecular Weight on Fusion of Poly-α-methylstyrene

precipitating the polymer from benzene by the addition of methyl alcohol.

The reaction was found to be sensitive to various materials. When sulfur dioxide was substituted for ethyl chloride as a reaction medium, poor yields and lower-molecular-weight polymers were obtained. Solvents such as butyl chloride inhibited polymer formation entirely. One system, in which both the catalyst solvent and reaction medium were carbon disulfide, produced a marked increase in molecular weight at a given temperature. Two such experiments are plotted in Figure 2. This effect of carbon disulfide was obtained with either aluminum chloride or titanium tetrachloride as catalyst. Another experiment was run at −90° C. in which the reaction medium was carbon disulfide, but the aluminum chloride was added in ethyl chloride solution. The molecular weight increase in the polymer, previously noted in the case of the carbon disulfide system, was also observed in this experiment. Unfortunately, the freezing point of carbon disulfide did not permit its use at temperatures below −100° C.

All factors bearing on the reaction have not yet been thoroughly investigated. It was determined, however, that the temperature of the catalyst solution was not critical, just so long as it was kept at the reaction temperature or, in the cases of extremely low reaction temperature, at −60° to −65° C. Orifices other than the 0.012-inch size can also be employed, although the maximum orifice size will depend to some extent on how rapidly heat can be dissipated and on the heat capacity of the system. The reaction is rapid, and approximately equal molecular weight polymers were obtained in one set of experiments where the catalyst was added over a period of 5 minutes in one case and over a period of 1 hour in the other.

The α-methylstyrene employed was approximately 97% pure, the other 3% being primarily cumene. Its properties are listed in Table I. Reactions made with 99.9% pure α-methylstyrene did not increase the molecular weight of the polymers although improved yields per unit of catalyst might result.

α-Methylstyrene oxidizes on standing in contact with air; the products of oxidation are formaldehyde and acetophenone. The α-methylstyrene used in the experiments was freshly prepared. Oxidation products can be removed by steam distillation in the presence of reactive phenolic compounds such as resorcinol, followed by a second steam distillation in the presence of sodium hydroxide.

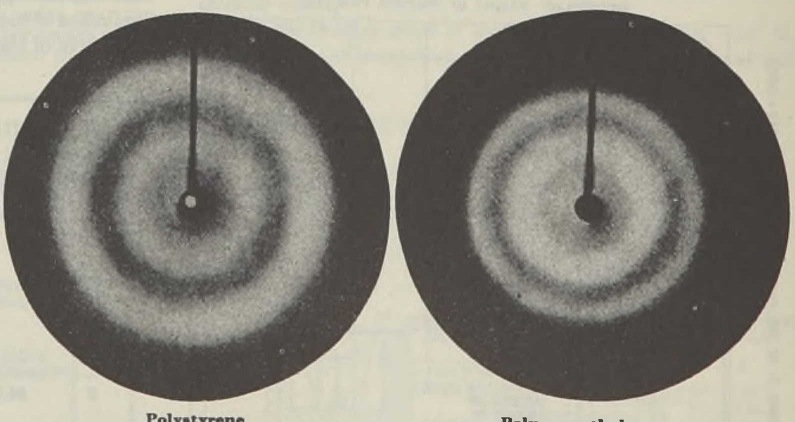
When molded the low-molecular-weight polymers were very brittle; the high-molecular-weight polymers were much tougher but were inferior in impact strength to polystyrene of the same molecular weight. This greater brittleness compared to styrene can be expected as a result of the methyl group loading. Brittleness in the high-molecular-weight polymers can undoubtedly be overcome to some extent by incorporation of plasticizers. An interesting property of the polymer is its high fusion point. Compression-molded pieces are not distorted easily when immersed in boiling water. The fusion point–molecular weight relation is shown in Figure 4. Little change in fusion point occurs above a molecular weight of about 10,000. A comparative fusion point for styrene of 9000 molecular weight is 100° C., which is about 100° C. lower than that of α-methylstyrene of the same molecular weight. The figures given are the mid-temperatures between the start of fusion and complete fusion when the powdered polymer was placed on a metal surface heated at the rate of 4° C. per minute.

Figure 5 shows the Laue x-ray diffraction patterns for poly-α-methylstyrene and for polystyrene. If anything, the rings are more distinct in the poly-α-methylstyrene pattern; the measured distances for the monomer unit and the distance between chains indicated by the patterns are not considered absolute. The values for polystyrene check closely those reported by Katz (*5*).

COPOLYMERIZATION

With Isobutylene. The ionic catalyst procedure was used to prepare a copolymer from 80 parts of isobutylene- and 20 parts by weight of α-methylstyrene at −108° C. in ethyl chloride with aluminum chloride as catalyst. The thermoplastic product could be readily rolled out into thin, dry, pliable, translucent sheets. Similar reactions in which higher amounts of α-methylstyrene were employed yielded only crumbly polymers of low molecular weight (indicated from intrinsic viscosities). A small amount of diene incorporated into the system yielded a vulcanizable plastic. Table IV presents the data; tensile strength is given only for the polymer which could be formed into a satisfactory test piece by the methods employed.

The 80 isobutylene–20 α-methylstyrene copolymer, showing 1500 pounds tensile strength by a conventional rubber test, differs markedly from polyisobutylene, since it is more like a plastic and less like a rubber. It is nontacky and shows relatively low elongation at break. Sparks *et al.* (*13*) reported that polyisobutylene, of molecular weight 200,000, processed on a cold



Polystyrene

Poly-α-methylstyrene (84,000 molecular weight)

Figure 5. X-Ray Diffraction Patterns

	Structural Distances, Å.	
Polystyrene (5)	4.8	10.0
Polystyrene (this work)	4.66	9.52
Poly-α-methylstyrene (this work)	5.24	9.19

mill as was the above-mentioned copolymer, exhibited a tensile strength of 680 pounds per square inch although 1900 pounds was observed for the same polyisobutylene when processed in a Banbury at elevated temperatures. The Laue x-ray pattern for the unstretched 80 isobutylene–20 α-methylstyrene polymer is quite diffused, only one ring being visible.

WITH BUTADIENE. The use of α-methylstyrene for copolymerization with butadiene to produce a rubberlike product was mentioned in the patent literature (*22*). However, no comparison is made between the effects of styrene and α-methylstyrene on the physical properties of the elastomers prepared by their copolymerization with butadiene. In view of this, it was deemed of interest to study copolymers of butadiene and α-methylstyrene as well as polymers of butadiene, α-methylsteyrne, and styrene.

Small-scale polymerizations were carried out in the laboratory in capped 12-ounce bottles which were maintained at constant temperature by immersion in an automatically controlled thermostat. This thermostat consisted of a water bath heated by hot water flowing through a copper coil; the hot water flow was controlled by an open-and-shut solenoid valve which was operated through an electronic relay regulated by a thermoregulator. Continuous agitation was provided by placing the thermostat on a shaking machine.

Since the formula of the emulsion used for comparative laboratory studies need not exactly duplicate that employed in commercial operations, a working emulsion formula similar to that reported by Fryling (*3*) was used without change throughout this portion of the investigation. The selection of this formula does not imply that it is the best for all of the polymerizations examined; it does, however, eliminate one set of variables from the experiments:

	G./100 G. Soap Soln.	Parts
Butadiene	39.2–56	70–100
α-Methylstyrene and/or styrene	16.8–0	30–0
Mercaptan of high mol. wt.	0.31	0.55
$(NH_4)_2S_2O_8$	0.17	0.30
Soap (sodium oleate)	5.9	10.5
Water	94.1	168

Upon the completion of polymerization, the latex in each case was coagulated by the addition of a water solution of sodium chloride and sulfuric acid. The coagulated polymer was then thoroughly washed with hot water and dried. For testing purposes the dry polymer was compounded as a tire tread stock and examined in accordance with normal rubber test procedures.

In the first series of experiments (Table V) the ratio of butadiene to mono-olefin was held constant, and the effect of substituting α-methylstyrene for styrene was studied. In general, partial substitution of styrene by α-methylstyrene seems to result in a somewhat inferior rubber. On the other hand, complete substitution of α-methylstyrene for styrene, in the ratio of 25 parts to 75 parts of butadiene, ultimately yields a vulcanizate which is comparable with one obtained through the copolymerization of butadiene and styrene.

If, however, as was the case in the second series of experiments, the ratio of butadiene to α-methylstyrene is varied, the optimum ratio of reactants (80 parts butadiene, 20 parts α-methylstyrene) yields a vulcanizate which seems superior to the best butadiene-styrene vulcanizate prepared.

These data indicate that α-methylstyrene may prove economically and technically advantageous for use in preparing vulcanizable elastomers. One factor that should not be overlooked is that a retardation in rate of reaction was noted in cases where α-methylstyrene was used as a comonomer. It is possible that this sluggishness can be overcome, at least to some extent, by changes in the emulsion formula or modification of the reaction conditions.

TABLE IV. COPOLYMERIZATION OF ISOBUTYLENE AND α-METHYLSTYRENE AT A REACTION TEMPERATURE OF −105° C.

Isobutylene, %	α-Me-styrene, %	Appearance of Polymer after Milling	Flexibility	Tensile Strength, Lb./Sq. In.	Elongation at Break, %
60	40	Stiff, boardlike	Poor	..	...
70	30	Boardlike	Poor	..	...
75	25	Boardlike	Poor	..	...
80	20	Flexible thin sheets	Good	1500	110
77 (+3% isoprene)	20	Vulcanized sheet[a] was relatively hard but brittle, had some flexibility			
85	15	Rubberlike	Good	..	...

[a] 100 parts polymer, 1 sulfur, 2 zinc oxide, 1 stearic acid, 1 Tuads; cured 45 minutes at 307° F.

WITH MALEIC ANHYDRIDE. The copolymer of α-methylstyrene and maleic anhydride reported in the literature (*4*) was confirmed in this laboratory. Equal parts of the two compounds, heated for 4 hours at 80–90° C., yielded a clear, hard, brittle resin with a fusion range of 230–261° F. (110–127° C.). In conjunction with these experiments, it was further found that the unsaturated dimer of α-methylstyrene formed a copolymer when heated with an equal weight of maleic anhydride at 200° C. for several days. The product in the latter case was solid at room temperature but fluid in boiling water; it could not be steam-distilled.

CONCLUSIONS

Alpha-substituted ethylenic compounds containing an aromatic residue are generally reported to be weak in their tendency to polymerize. The basis for this opinion is a comparison with the unsubstituted monomers which are easily polymerized at normal temperatures and sometimes without the addition of catalysts. The result has been that such alpha-substituted monomers have attracted only minor attention in polymerization studies. The work reported here shows that, although α-methylstyrene is not susceptible to polymerization to high-molecular-

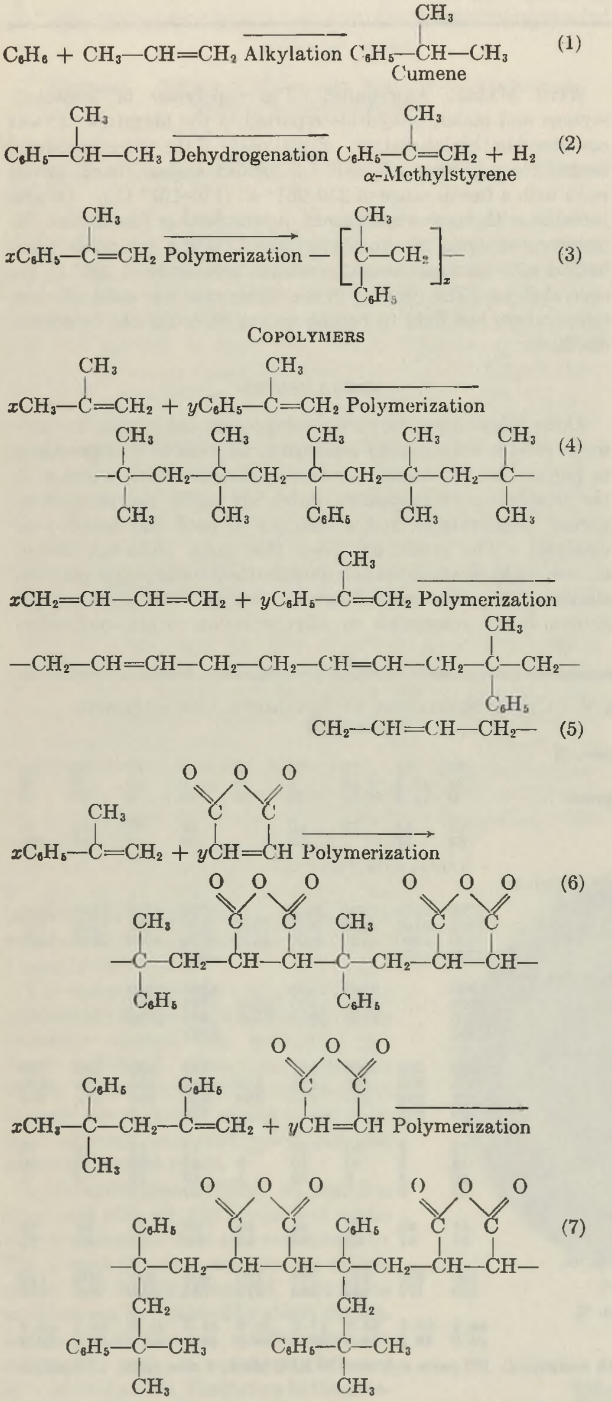
TABLE V. COPOLYMERIZATION OF BUTADIENE AND α-METHYLSTYRENE

Reaction mixture, %									
Butadiene	75	75	75	75	70	80	80	90	100
Styrene	25	12.5	6.25	0	0	0	20	0	0
α-Methylstyrene	0	12.5	18.75	25	30	20	0	10	0
Reaction, %									
Yield	70	83	79	69	..	81	87	78	82
Gel	63	47	..	28	..	14	44	57	78
VULCANIZATE TESTS[a]									
Ultimate tensile, lb./sq. in. (cured at 292° F.)									
30 min.	2760	2270	2530	3300	..	3250	3220	1580	1300
45 min.	2630	2160	2500	2670	2370	3130	2620	1920	790
75 min.	2920	2350	2750	2700	2970	2970	3050	2010	1180
150 min.	2760	2100	..	..	..	3200	..	..	..
300% modulus, lb./sq. in.									
30 min.	1780	..	2160	1400	..	1500	1860	..	..
45 min.	1970	..	2370	1950	2250	1780	2340	..	..
75 min.	2330	..	2700	2200	2430	1870	2700	..	..
150 min.	2480	..	..	..	..	2300	..	..	..
Elongation at break, %									
30 min.	420	260	360	540	..	490	430	280	180
45 min.	375	230	320	385	315	430	330	290	120
75 min.	355	235	305	365	365	400	340	275	185
150 min.	325	215	..	..	..	370	..	..	..
Immediate set, %									
30 min.	15	5	10	20	..	15	15	10	10
45 min.	13	5	10	10	5	15	10	10	10
75 min.	10	3	8	10	1	10	10	5	5
150 min.	10	3	..	..	..	10	..	..	..
Shore hardness									
30 min.	67	65	63	59	65	62	64	64	70
45 min.	68	67	65	63	65	62	65	66	71
Crescent tear, lb./in.									
30 min.	300	205	210	265	290	300	225	200	110
45 min.	285	175	185	245	275	235	200	210	120
Lüpke rebound, %									
30 min.	44.2	45.2	42.8	41.0	40.6	44.5	41.8	46.1	48.2
45 min.	44.0	45.0	44.2	42.0	39.8	43.1	43.5	47.5	48.0

[a] Tread stock compound: 100 parts polymer, 50 EPC black, 5 zinc oxide, 1.75 sulfur, 1 Santocure.

weight materials by more common methods, it can be converted to high-molecular-weight polymers by a different approach. The method involving low-temperature polymerization (below the freezing point of α-methylstyrene) with ionic catalysts yields a polymer of very high molecular weight. The reaction is rapid and is influenced by added materials. Reactions carried out in carbon disulfide give polymers of highest molecular weight. In addition, copolymers with other hydrocarbons (isobutylene) can be formed by the same technique. The reactions involved in the preparation of α-methylstyrene and in the polymerizations reported here are summarized in Table VI.

TABLE VI. REACTIONS INVOLVED IN PREPARING AND POLYMERIZING α-METHYLSTYRENE



$$C_6H_6 + CH_3{-}CH{=}CH_2 \xrightarrow{\qquad} \text{Alkylation}\ \underset{\text{Cumene}}{C_6H_5{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3} \tag{1}$$

$$C_6H_5{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3 \xrightarrow{\qquad} \text{Dehydrogenation}\ \underset{\alpha\text{-Methylstyrene}}{C_6H_5{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2} + H_2 \tag{2}$$

$$xC_6H_5{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 \xrightarrow{\qquad} \text{Polymerization}\ {-}\left[\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2\right]_x{-} \tag{3}$$

COPOLYMERS

$$xCH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 + yC_6H_5{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 \xrightarrow{\qquad} \text{Polymerization}$$

$$-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-} \tag{4}$$

$$xCH_2{=}CH{-}CH{=}CH_2 + yC_6H_5{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 \xrightarrow{\qquad} \text{Polymerization}$$

$$-CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}$$

$$CH_2{-}CH{=}CH{-}CH_2{-} \tag{5}$$

$$xC_6H_5{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 + y\overset{\overset{O\quad O\quad O}{\diagdown\!\!\diagup\;\diagdown\!\!\diagup}}{\overset{C\qquad C}{\overset{|\qquad |}{CH{=}CH}}} \xrightarrow{\qquad} \text{Polymerization}$$

$$-\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\overset{\overset{O\quad O\quad O}{C\qquad C}}{\overset{|\qquad |}{CH{-}CH}}{-}\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\overset{\overset{O\quad O\quad O}{C\qquad C}}{\overset{|\qquad |}{CH{-}CH}}{-} \tag{6}$$

$$xCH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{C_6H_5}{|}}{C}}{-}CH_2{-}\overset{\overset{C_6H_5}{|}}{C}{=}CH_2 + y\overset{\overset{O\quad O\quad O}{C\qquad C}}{\overset{|\qquad |}{CH{=}CH}} \xrightarrow{\qquad} \text{Polymerization}$$

$$-\underset{\underset{C_6H_5{-}\underset{\underset{CH_3}{|}}{C}{-}CH_3}{\underset{|}{CH_2}}}{\overset{\overset{C_6H_5}{|}}{C}}{-}CH_2{-}\overset{\overset{O\quad O\quad O}{C\qquad C}}{\overset{|\qquad |}{CH{-}CH}}{-}\underset{\underset{C_6H_5{-}\underset{\underset{CH_3}{|}}{C}{-}CH_3}{\underset{|}{CH_2}}}{\overset{\overset{C_6H_5}{|}}{C}}{-}CH_2{-}\overset{\overset{O\quad O\quad O}{C\qquad C}}{\overset{|\qquad |}{CH{-}CH}}{-} \tag{7}$$

Although α-methylstyrene cannot alone be polymerized by emulsion under the conditions studied, it does copolymerize with butadiene to give a series of vulcanizable elastomers comparable to butadiene-styrene copolymers. The work indicates that the optimum copolymer contains more butadiene when α-methylstyrene is used as the comonomer in place of styrene. Advantages of greater monomer stability from the point of view of handling as well as some quality advantages are indicated for the α-methylstyrene rubbers.

The formation of copolymers from α-methylstyrene and polymerizable hydrocarbons in the presence of peroxide catalysts provides interesting material for the study of copolymers in the light of the theory advanced by Wall (*23*). Copolymerization with butadiene, styrene, or acrylonitrile involves one monomer with a finite reaction velocity and a second monomer, α-methylstyrene, which exhibits no tendency to polymerize under the reaction conditions employed. The copolymers formed from α-methylstyrene or its unsaturated dimer and maleic anhydride are unique cases in which no one of the monomers by itself is polymerizable under the given reaction conditions.

ACKNOWLEDGMENT

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Properties of Granular and Monocrystalline Ammonium Nitrate

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Such inherent properties of ammonium nitrate as hygroscopicity, melting point, solubility, and absolute density are independent of its method of manufacture. Other properties, such as its capacity to hold moisture, caking tendency, crushing strength, and apparent density vary with the size, shape, and porosity of its particles; the latter, in turn, vary with the process used in its preparation. This paper presents experimental data on the relation of porosity, size, and shape of ammonium nitrate to its behavior in storage and its drillability in the field. The results show that ammonium nitrate in the form of porous granules of uniform size and shape is more free flowing, exhibits less tendency to cake, and has a greater capacity to hold moisture before becoming undrillable than other types of the material which are less porous and more irregular in particle size and shape.

CAPACITY for producing synthetic ammonia and nitric acid in the United States and Canada has been greatly expanded during the war. Postwar utilization of part of these facilities is planned for production of ammonium nitrate for the fertilizer trade. The marked tendency of this material to cake and to absorb moisture under humid conditions interferes considerably with its use for this purpose. The first synthetic ammonium nitrate on the market was made in the form of monocrystals of relatively small particle size. Since then spraying and graining methods have been developed for producing this material in the form of granules. The ammonium nitrate prepared by these different methods differs considerably in certain physical properties. Observations are reported here on the properties of these different types of ammonium nitrate that affect particularly its behavior in storage and its drillability in the field. (The data presented in this paper relates only to the particular material submitted by the producers. Subsequent improvements in manufacture may alter greatly the physical properties of the recovered products.)

In the spraying method, a spray of molten ammonium nitrate containing 4–5% of moisture is allowed to fall in a tower through a countercurrent flow of cool air. The liquid droplets congeal in their fall through the tower to form sphere-shaped granules of approximately 8–20 mesh size. As the congealed granules reach the bottom of the tower, they are collected in a hopper with an open bottom and are conveyed on an endless belt to the drying equipment (*3*, *4*, *5*, *13*).

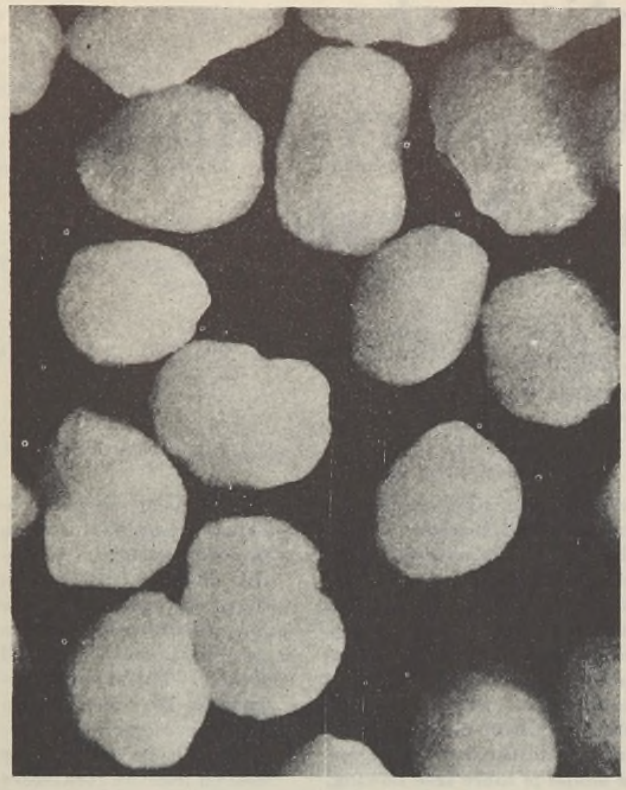
In the graining process a melt of ammonium nitrate containing 1–2% of moisture is run into a circular shallow vessel equipped with mechanical plows and jacketed for cooling with water or heating with steam. The rotation of the plows agitates the material during the graining process. It thus prevents the formation of a solid mass as the rest of the moisture is being eliminated by the heat first developed by the crystallization of the material from a state of fusion, and later supplied by steam or hot water in the jacket of the graining apparatus (*7*, *11*). The product prepared in this way is satisfactory with respect to the shape of particles, but the average particle size of the material now on the market is smaller than is desired in a fertilizer intended for separate application in the field.

Ammonium nitrate containing synthetic nitrogen was first produced at Notodden, Norway, in 1910. In the process used at that time the product was recovered in the form of relatively small crystals. The latest development in the crystallization method is known as the Oslo-Krystal process (*10*, *14*). The solution from neutralizers containing 80–85% of ammonium nitrate at 75–80° C. is mixed with mother liquor of 65% concentration and pumped to a vacuum evaporator. The discharge from this evaporator is passed at 58–60° C. to a second evaporator operating at lower pressure. The bottom of this evaporator communicates with a crystallizing tank. The supersaturated solution entering this crystallizing tank from the second evaporator is uniformly conducted upward through a dense suspension of crystals. The classifying action in the crystallizing tank keeps the fully grown crystals suspended in the bottom layer, and the smallest crystals in the top layer with the intermediate sizes suspended between. The saturated solution leaving the crystallizing tank is mixed continuously with the solution from the neutralizers, the mixture is again supersaturated to the desired extent, and the cycle is repeated.

PROPERTIES OF THREE TYPES

Table I gives mechanical analyses of these three types of ammonium nitrate. The sprayed and grained materials represent commercial production. The monocrystalline product was produced on a pilot plant scale. A microscopic examination of the three types showed that each particle of Krystal ammonium nitrate consists of a single crystal, whereas the granules of the sprayed and grained materials are aggregates of crystals. Determination of refractive indices with the petrographic microscope showed that the particles of Krystal ammonium nitrate were the orthorhombic form stable below 32° C., and had not passed through that transition (*9*). Differences in the physical properties of the three types of ammonium nitrate are illustrated in Figures 1 to 6.

The apparent density of the particles of each type of ammonium nitrate in bulk (Table II) represents the ratio of the weight of material required to fill a liter cylinder to the weight of the same volume of water at room temperature. The cylinder was filled



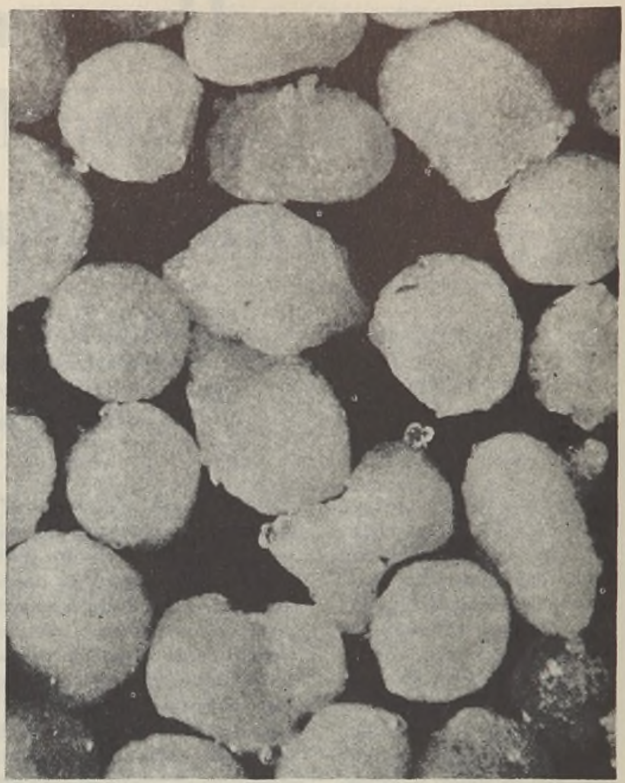


Figure 1 (*Left*). Sprayed Ammonium Nitrate, Old Production, 14–16 Mesh (× 16)
Figure 2 (*Right*). Sprayed Ammonium Nitrate, Current Production, 14–16 Mesh (× 16)

Table I. Screen Analysis of Typical Samples of Sprayed, Grained, and Monocrystalline Ammonium Nitrate

Type of Material	Screen Fractions, %				
	+10 mesh	10–14 mesh	14–20 mesh	20–40 mesh	−40 mesh
Sprayed[a]	14	38	26	17	5
Sprayed[b]	21	52	23	4	0
Grained	1	4	26	58	11
Monocrystals	22	57	14	6	1

[a] Old production.
[b] Current production.

by adding small increments of the material to the cylinder while it was gently tapped. Each value represents the mean of five determinations.

The apparent density of the average particle was determined by noting the density of an organic liquid that will hold the greater part of the particles in suspension. The absolute density of ammonium nitrate is 1.72 (*6*). The values obtained for the apparent density of the average particle of sprayed, grained, and monocrystalline ammonium nitrate are 1.56, 1.65, and 1.69, respectively. These data indicate that the sprayed particles contain an average of about 10% of voids, the grained particles about 4%, and the monocrystalline particles less than 2%. It was found that the particles of monocrystalline ammonium nitrate of 10-mesh size contain more voids than do those of 16-mesh size, an indication that the voids in this material increase with increase in crystal size.

Inasmuch as the granules of sprayed ammonium nitrate consist of aggregates of crystals while the particles of the monocrystalline material consist of only single crystals or crystal fragments, it would be expected that the apparent density of the crystals would be higher than that of the granules. The results obtained in the density determinations show that this is the case.

MOISTURE IN AMMONIUM NITRATE

Moisture was determined in the different types of ammonium nitrate by the following methods:

1. Drying in an air oven at 70° C. for 20 hours.
2. Drawing air at 70° C. through the sample for 2 hours.
3. Drying in a vacuum at room temperature over Anhydrone (anhydrous magnesium perchlorate) for 20 hours.

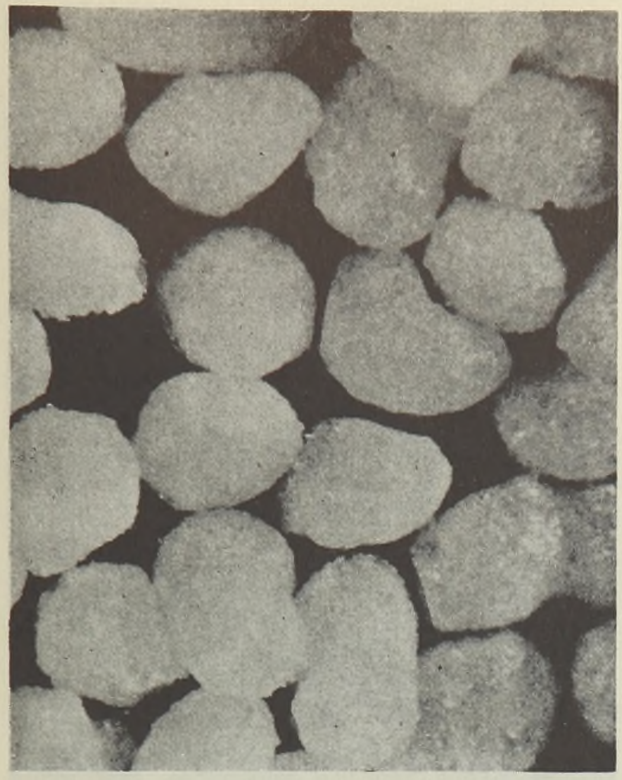
Moisture by these three methods was determined in (*a*) sprayed ammonium nitrate that had not been dried, (*b*) sprayed nitrate that had been dried and then treated with a fine mist of water while being rolled in a drum, (*c*) grained ammonium nitrate that had absorbed moisture after being dried, and (*d*) monocrystalline ammonium nitrate that had not been dried.

The results obtained (Table III) show that the three methods agree quite closely in the determination of absorbed moisture in all four types of ammonium nitrate, and that the vacuum method gives lower results than the other two methods for the determination of original moisture in ammonium nitrate. The data indicate that a portion of the original moisture in ammonium nitrate is present as occluded moisture and that this moisture is more difficult to remove than absorbed moisture.

Table II. Apparent Density of Different Types of Ammonium Nitrate

Type of Material	Apparent Density of:	
	Particles in bulk	Av. particle
Sprayed[a]	0.883	..
Sprayed[b]	0.859	1.56
Grained	0.978	1.65
Monocrystals	0.973	1.69

[a] Old production.
[b] Current production.



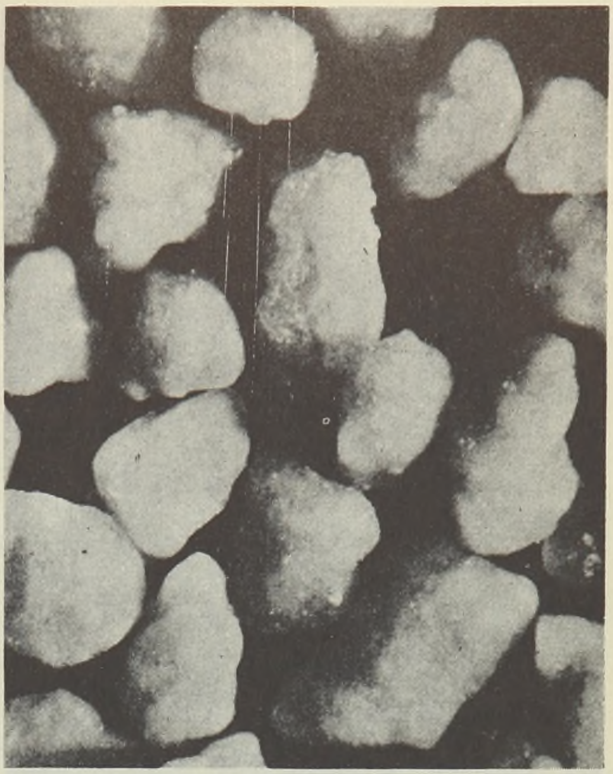


Figure 3 (*Left*). Sprayed Ammonium Nitrate, Showing Effect of Drying Following Slight Absorption of Moisture (× 16)
Figure 4 (*Right*). Grained Ammonium Nitrate, 14–16 Mesh (× 16)

The moisture in monocrystalline ammonium nitrate, which the vacuum method over Anhydrone fails to remove, amounts to about 0.35% of the weight of the sample. The data in Table II indicate that nearly 2% of the volume of the crystals is void. It must follow, therefore, that the greater part of the void space in the crystals is filled with air rather than mother liquor.

ABSORPTION OF MOISTURE. Saturated solutions of all three types of ammonium nitrate have the same vapor pressure at a given temperature (*16*), and all absorb moisture at essentially the same rate when exposed under the same conditions in a humid atmosphere (Table IV). The particles of granular ammonium nitrate, as already explained, are somewhat porous for the reason that they are made up of aggregates of crystals. The particles of monocrystalline ammonium nitrate, on the other hand, are nonporous and are incapable of holding any moisture except on their surface. A difference, therefore, exists in the quantity of moisture which the granular and monocrystalline materials will absorb before they become dripping wet. Thus the solution phase in a sample of monocrystalline ammonium nitrate containing 1.5% moisture will tend to settle out in the bottom of its container on standing. This quantity of moisture will not separate out as a solution phase from granular ammonium nitrate.

TABLE III. MOISTURE IN AMMONIUM NITRATE

Method			% Moisture in Ammonium Nitrate[a]			
			Sprayed[b]			
Type	Temp., ° C.	Time, hr.	Absorbed	Original	Grained absorbed	Monocrystalline original
Air oven	70	20	2.90	0.74	0.75	0.65
Air flow	70	2	2.87	0.72	0.77	0.57
Vacuum	25	20	2.82	0.38	0.71	0.28

[a] Determinations by Katharine S. Love.
[b] Old production.

TABLE IV. RATE OF MOISTURE ABSORPTION BY AMMONIUM NITRATE AT 30° C. AND A RELATIVE HUMIDITY OF 72.4%

		% Moisture Absorbed in:		
Type of Material	Treatment	2 hr.	4 hr.	6 hr.
Sprayed	None	11.86	23.68	34.16
Grained	None	10.91	20.20	29.22
Monocrystals	None	11.59	22.18	32.26
Sprayed	1% PRP[a]	0.15	0.23	0.29
Grained	1% PRP	0.17	0.27	0.38
Monocrystals	1% PAP[b]	0.14	0.27	0.37

[a] Petrolatum-rosin-paraffin.
[b] Petrolatum-asphalt-paraffin.

This difference in the water-holding capacity of granular and monocrystalline ammonium nitrate has a marked effect on their drilling properties. Thus the results of Whittaker and co-workers (*15*) indicate that untreated sprayed ammonium nitrate (old production) having the screen analysis shown in Table I does not become completely undrillable in a "rotating plate" distributor until its moisture content exceeds 4%. The drillability of a material decreases not only with increase in moisture content but also with decrease in size of particles. The average particle size of the monocrystalline ammonium nitrate used in the drillability tests was somewhat greater than that of the sprayed material as shown in Table I; in spite of this fact it became completely undrillable at a moisture content of only about 1.5%.

RELATIVE CAKING TENDENCY

The solubility of ammonium nitrate in water and the change in its solubility with temperature exceeds that of any other fertilizer material now on the market. A decrease in the moisture content or a lowering of the temperature will, therefore, result in a greater deposition of crystals than occurs after a similar

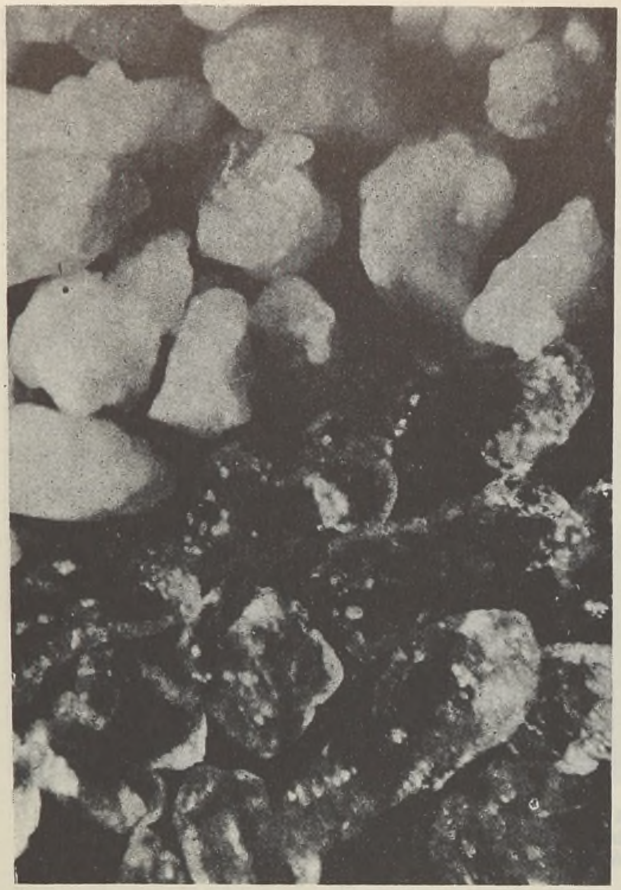


Figure 5. Monocrystalline Ammonium Nitrate, 14–16 Mesh (× 16); Clear Crystals Dried below 32° C., Opaque Crystals above 32° C.

Compare irregular shape of particles with granules in Figure 2 and numerous sharp points of contact between particles.

Figure 6. Sprayed Granules (Current Production), *above*, and Monocrystalline Ammonium Nitrate, *below* (× 16)

A greater volume of surface solution joins the monocrystalline material than the sprayed granules after both have been exposed to the same humidity for the same length of time.

change in any other fertilizer. Other factors, such as pressure, particle size, and time of storage, have also an independent effect on the caking of ammonium nitrate, but it has been shown that a slight change in moisture content has a greater effect on the caking of this material than a corresponding small change in any of the other factors that affect its tendency to cake (*2*).

When a limited quantity of water (1% or less) is sprayed onto granular ammonium nitrate while it is being rolled in a drum, a considerable proportion of the water is absorbed and held within the granules. A subsequent lowering of the temperature will cause deposition of crystals within as well as outside of the granules. This deposition of crystals to the extent that it takes place on the surface of the granules will induce caking, but to the extent that it occurs within the granule, it tends to increase the hardness of the granule. However, the crushing strength of a granule or crystal is weakened by a repeated gain and loss of moisture or by drying at a temperature above its transition point.

In the case of the nonporous monocrystalline ammonium nitrate, all absorbed moisture must remain on the surface of the particle and any deposition of crystals, as a result of lowering the temperature or loss of moisture, will be limited to the surface of the particles. This is indicated by the behavior of the sprayed granules (current production) and the monocrystalline product after being exposed to the same relative humidity for the same time. This exposure, as shown in Figure 6, causes the monocrystalline product to be joined together by a greater volume of surface solution than that joining the sprayed granules. Climatic changes following the absorption of a limited amount of moisture is, therefore, likely to cause a greater degree of caking in the monocrystalline than in the granular ammonium nitrate of the same particle size (*1*).

The caking of a soluble material is also governed by other factors. Thus the tendency of the particles of a material to knit together into a solid mass decreases with decrease in the area of contact between them. A material in the form of large particles will, therefore, cake less than when the particles are small, and when the particles are spherical than when they are irregular in shape. The monocrystalline ammonium nitrate used in this study (Figure 5) was not so uniform in shape as the sprayed material (Figure 2). Having, therefore, a larger area of contact between its particles, it exhibited a greater tendency to cake than was true of the granular material of similar particle size.

The sprayed ammonium nitrate first used in this investigation was prepared as already explained by spraying a melt of the material containing about 4.5% of moisture. In the subsequent drying of this sprayed material, small crystals were deposited on the surface of the granules as shown in Figure 1. These projections on the granules increased the points of contact between them, with the result that the product prepared in this way exhibited a greater tendency to cake than the current production represented in Figure 2. The granules of this latest production are not only more uniform and spherical than those of the earlier product, but the material as a whole shows less tendency to cake and is more free flowing.

Table V. Relative Crushing Strength of Dry Ammonium Nitrate Granules and Monocrystals

Type of Material	Crushing Strength of 8–10 Mesh Particles, Lb.	% of Particles with Definite Crushing Point	% Breakdown in Tumbling Test
Sprayed, old production	1.39	80	3.95
Sprayed, current production	2.47	90	0.95
Monocrystals, dried below 32° C.	3.78	39	7.65
Monocrystals, dried above 32° C.	1.93	43	9.15

Conditioning. The caking tendency of ammonium nitrate can be greatly reduced by treatment with 3–5% of a suitable conditioning agent such as kaolin or one of the varieties of kieselguhr (*12*). Storage tests indicate that, when the conditioning agent is properly applied, it is effective in reducing the caking of all types of ammonium nitrate. A conditioning agent, such as kieselguhr or kaolin, seems to adhere equally well to granular or monocrystalline ammonium nitrate although the distribution of the coating agent is likely to be more uniform on spherical particles than on irregular-shaped ones. The quantity of conditioning agent usually applied to sprayed or grained ammonium nitrate is in the neighborhood of 3–4%. Applications in excess of 5% are likely to undergo segregation. This was indicated in laboratory tests in which sprayed and monocrystalline ammonium nitrate samples of 8–14 mesh were coated with 6% of Kittitas (a type of kieselguhr) and then shaken for 15 minutes on a 60-mesh screen. The quantity of the conditioning agent that remained on each material at the end of the test amounted to approximately 3.5% of the weight of the sample. Slight agitation quickly reduced the conditioning agent adhering to the samples from 6 to 5%, but the agitation required to reduce the conditioning agent to 3.5% exceeded that to which the materials would normally be subjected under ordinary conditions of handling and storage.

CRUSHING STRENGTH OF PARTICLES

The crushing strength of sprayed granules and monocrystalline ammonium nitrate was determined in the apparatus described by Hardesty and Ross (*8*). It consists of a rack and pinion, similar to those used in adjusting the elevation of the barrel of a microscope, mounted directly over an anvil which rests on the platform of a spring scale. A single granule is placed on the anvil under the rack, and pressure is applied by lowering the rack until the granule breaks. A telltale on the face of the scale records the maximum stress required to crush the granule.

With this method of testing it was found that the granules of nonplastic materials, such as superphosphate and mixed fertilizers, showed a definite crushing strength which varied with their size, shape, and moisture content. All crushing-strength tests with ammonium nitrate were accordingly made with perfectly dry samples of known particle size. The granules and monocrystals of ammonium nitrate were found to differ from those of the other materials tested in that they exhibited plastic properties and frequently failed to show a definite crushing point. Crushing-strength tests were made with old and current sprayed granules and with monocrystals dried below and above 32° C. The number of particles of each of these four samples that had to be tested in order to obtain fifty with a definite crushing strength were 64, 55, 128, and 117, respectively. These tests indicate that the monocrystals are more plastic than the sprayed granules.

The results obtained in these crushing-strength tests are given in Table V. The values indicate that the sprayed granules of current production are considerably harder than the old-production granules, and that monocrystals dried below 32° C. are harder than those dried at a temperature above the transition point. Accurate data with the monocrystals were hard to obtain, however, owing to their plasticity, to their irregular shape, and to the fact that their resistance to crushing is less in the direction of their longitudinal axis than in the transverse direction. No crushing-strength tests were made with the grained material owing to the relatively small size of its particles.

The percentage breakdown that occurred when the materials were subjected to a tumbling test is shown in the last column of Table V. The test consisted in tumbling 200 grams of 8–14 mesh samples in 16-ounce bottles end over end for 48 hours, and then determining the proportion of each material that passed a 14-mesh sieve. The test indicates that the monocrystals have the greatest tendency to break down under the conditions of the test, and the current production of sprayed granules, the least.

SUMMARY

Each particle of monocrystalline ammonium nitrate as obtained in the Krystal process consists of a single crystal whereas the granules of the sprayed or grained material consist of aggregates of crystals. The grained ammonium nitrate is about twice as porous, and the sprayed ammonium nitrate about five times as porous as the monocrystalline material. The percentage of voids in monocrystalline ammonium nitrate increases with increase in the size of the crystals.

Sprayed, grained, and monocrystalline ammonium nitrate absorbs moisture at approximately the same rate under the same conditions. The capacity of these different types to hold moisture before starting to drip differ greatly, however, because of the difference in the porosity of their particles. A drop in temperature or humidity following absorption of moisture will deposit crystals within as well as outside of porous granules, but only on the surface of nonporous particles. This deposition of crystals to the extent that it takes place on the surface of the particles will induce caking, but to the extent that it occurs within the granules, it tends to increase the hardness of the granule. Differences in the porosity of the different types of ammonium nitrate thus have a marked effect on their capacity to hold absorbed moisture and on their tendency to cake under varying climatic conditions.

The apparent density of monocrystalline ammonium nitrate is greater than that of the sprayed material. The method of drying in a vacuum over Anhydrone removes absorbed moisture but not the occluded moisture from monocrystalline ammonium nitrate.

Monocrystals that have been dried above 32° C. and then cooled have a lower crushing strength than those dried below 32° C.; monocrystalline ammonium nitrate, whether dried above or below 32° C., shows a higher breakdown when subjected to a tumbling test than the latest type of sprayed ammonium nitrate. The sprayed material as currently produced is more free flowing and more uniform in size and shape than any other type of ammonium nitrate.

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Structural Changes in Vulcanization of Buna S

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The relations existing among combination of sulfur, loss of unsaturation, and development of physical properties have been determined for four related Buna S stocks over a range of cures at two temperatures. The data indicate two types of chemical change to be occurring during vulcanization: (*a*) a reaction involving combination of the polymer with sulfur, which is primarily responsible for the development of physical strength, and (*b*) a reaction involving loss of double bonds in the polymer, presumably a polymerization reaction, which is related to the first reaction and continues on overcure. A modification of the Kemp-Peters procedure for measurement of unsaturation of Buna S vulcanizates is based upon the use of a phthalate-dichlorobenzene solvent mixture.

THE development and production on a commercial scale of the synthetic rubberlike materials, particularly the butadiene copolymers, during the wartime emergency focused attention on phenomena associated with their vulcanization. These copolymers, particularly the synthetic tire copolymer known as Buna S (GR-S in the United States), lend themselves to vulcanization with sulfur and the same types of accelerators used with natural rubber; the vulcanizates possess many points of similarity to those derived from the natural elastomer.

The literature on the vulcanization of natural rubber is quite extensive. Several reviews are available (*3*, *4*, *11*, *14*, *23*), although most of these are not entirely up to date. Among the more recent publications of direct interest in this connection are those of Farmer and co-workers (*9*) and of Armstrong, Little, and Doak (*2*).

The government general-purpose rubber known as GR-S is a copolymer of 3 parts by weight of butadiene and 1 part of styrene (*17*). The polymerization is carried out in aqueous emulsion, and the final polymer may contain (*a*) unreacted monomer, which is usually well removed by "stripping", (*b*) low-molecular-weight polymers, (*c*) catalyst or its degradation products, (*d*) residual emulsifier or its conversion products (e.g., soap and/or fatty acids), (*e*) coagulants or their reaction products, (*f*) buffers, (*g*) auxiliary materials usually termed "modifiers", which influence the degree of cross linking or branch chaining in the polymer, (*h*) stopping agents for the polymerization, (*i*) antioxidants such as phenyl-β-naphthylamine which are added to prevent further polymerization in storage or transit. Thus, the so-called hydrocarbon polymer is not entirely pure hydrocarbon, and many of the variations in quality of the commercial product have been due in no small part to variations in number and quantity of these "nonrubber" impurities.

The concentrated research carried out on Buna S to date has produced a considerable body of information, even though much of the data has not been published for reasons of national security. Buna S possesses certain points of similarity to and certain differences from the natural polymer:

1. It is possible for polymerization to occur in the 1,2 as well as in the 1,4 position; branched chains and "pendant" vinyl groups result, which would be expected to affect chemical behavior as well as physical characteristics (*1*, *18*). Another contributing fact is the probability that both *cis* and *trans* structures exist in the same synthetic polymer. The natural polymer is believed to exist entirely in the *cis* modification.
2. Mathematical considerations and certain evidence (*1*) indicate styrene units to be randomly distributed throughout the chains. This, together with the presence of branched chains produced by 1,2 polymerization, leads to a high degree of nonsymmetry in the polymer; it probably accounts for the fact that this polymer, unlike natural rubber, does not crystallize on stretching and the probably related fact that pure gum stocks have relatively poor strength. Kemp and Straitiff (*18*) believe that this lack of structural symmetry may be responsible for inability to cross link and form a desirable structure in the vulcanizate.
3. The molecular weight is, in general, lower than that of natural rubber (*19*), and its distribution is quite broad (*18*). It has been indicated (*18*) that the presence of the lowest molecular weight polymers is detrimental to the quality of the vulcanizates. High-molecular-weight fractions, which compare favorably with natural rubber on the basis of molecular weight, tensile, and modulus, are tough and hard to handle on a mill. This difference may be due to the activating influence of the side-chain methyl group in the natural polymer on reaction with oxygen and resultant degradation during milling. This activating effect has been noted in a number of other instances—e.g., reactions with halogens, hydrogen halides, isomerizing agents, etc. It is well known that oxidative degradation accompanies the plasticization of natural rubber by milling (*5*, *8*, *12*).
4. Extension of the curing period of natural rubber stocks beyond the so-called optimum results in the phenomenon known as reversion. It is possible in certain cases to minimize this by the proper choice of accelerators (*13*). Such reversion does not occur with Buna S; instead, this polymer becomes progressively stiffer as cure progresses. It is worth noting that Hauser and Brown (*14*) believe the phenomenon of reversion to be associated with the action of oxygen. If this is true, the difference between the two types of polymers is probably associated with the type of activating effect noted above.
5. Hysteresis properties of the two types of vulcanizates are markedly different. The detrimental effect of heat build-up on the physical properties of the synthetic vulcanizates has been highly publicized. However, it should be noted that the action of heat alone (in the presence of air) is to cause further polymerization of the synthetic elastomer whereas, in the case of the natural polymer, heating in the presence of air causes oxidative degradation. Thus the difference in the action of heat may be oxidative in character and be associated with the activating influence of the methyl group in the isoprene unit.

UNSATURATION OF NATURAL RUBBER VULCANIZATES

Several investigators have attempted to measure the chemical unsaturation of natural rubber (*3*, *10*, *15*, *16*). Of the various methods proposed, the iodine chloride titration method of Kemp (*16*) has proved most valuable. It was modified by Blake and Bruce (*3*) for the analysis of vulcanized stocks. Brown and Hauser (*4*, *14*) reported extensive work and certain generalizations utilizing this method with various rubber stocks.

In the case of rubber-sulfur vulcanizates, the loss of one double bond was found to accompany the combination of one atom of sulfur, whereas in accelerated stocks the combination was in a definite ratio of atoms of sulfur combined to number of double bonds lost during the early part of the cure, and in excess of the one atom/double bond ratio. After combination of most of the sulfur, additional loss of double bonds was due apparently to polymerization by heat under the influence of accelerators or some similar effect due to oxygen.

Explanation of the evident combination of sulfur in excess of one atom per double bond saturated was explained by these authors in terms of several possible reactions: (*a*) addition, (*b*) bridging, (*c*) dehydrogenation, (*d*) polymerization. The first two types of reaction would produce a ratio of one atom of sulfur per double bond lost, as found in the simple rubber-sulfur compound. Reaction *a* is not in accord with observed properties of solubility, etc. If the ratio is greater than 1, an additional reaction must be taking place where sulfur can combine without loss of double bonds. Such a possibility might be reaction *c*. Excess loss of unsaturation may be a polymerization reaction, *d*, after most of the sulfur has combined.

Recent work of Farmer and Michael (*9*) led them to believe that the primary reaction of vulcanization is a substitution reaction on the alpha carbon atom. This corresponds somewhat to the dehydrogenation reaction suggested by Brown and Hauser, but with the cross linkage taking place at the carbon atom alpha to the double bond rather than on the doubly bonded one.

More positive evidence of sulfur substitution on the alpha carbon was presented recently by Armstrong, Little, and Doak (*2*), who studied the reactions with vulcanizing agents of certain olefins which have structures similar to rubber. The chief products of reaction of these simple aliphatic mono-olefins with sulfur, zinc oxide, and soluble zinc soap in the presence of accelerators consisted of the olefin bridged by sulfur at the alpha carbon atom. It was also observed that the degree of cross linking of rubber vulcanizates is closely related to the amount of zinc sulfide formed during the reaction, which is evidence in favor of a dehydrogenation type of reaction.

Selker and Kemp (*20*) recently presented evidence indicating that part of the combined sulfur in soft vulcanized natural rubber was attached to the alpha carbon atom.

EXPERIMENTAL PROCEDURE

Four related Buna S stocks were employed for this study. They were selected from the group studied by Cheyney and Duncan (*6*) in determining the temperature coefficient of the Buna S vulcanization reaction. They represented pure gum and channel black reinforced stocks, respectively, containing in each case 1 and 5% added sulfur. Cures were made at 270° and 300° F. Recipes are given in Table I.

TABLE I. RECIPES OF STOCKS

Stock No.	I	II	III	IV
Crude Buna S	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
Dibenzothiazyl disulfide	1.5	1.5	1.5	1.5
Bardol (softener)	5	5	5	5
Channel black	.	.	50	50
Sulfur	1	5	1	5

Physical tests were run by A.S.T.M. procedures. Sulfur determinations were made as outlined by Cheyney and Duncan (*6*). Attempts were made to measure unsaturation of these stocks by the Kemp-Peters procedure (*17*). This method was inapplicable to these samples for two reasons: *p*-Dichlorobenzene, the solvent they used, was not sufficiently active for some of these samples; and the use of acetone for purification of the sample before determination of unsaturation is believed unwise in general. In the latter connection, Cheyney and Robinson (*7*) and Kemp and Straitiff (*18*) noted that significant amounts of vulcanizate are extracted out of various Buna S stocks by acetone. This is not surprising in view of the fractions of extremely low molecular weight reported in this polymer by the latter authors and by Sebrell (*19*).

The use of acetone for extraction is open to the further objection that it fails to remove soap which may be present in the crude polymer; this fact was noted by Kemp and Peters (*17*). This is not a serious objection in a series where a given sample of polymer is used throughout. To compare samples of differing degrees of purity, it is desirable to use a solvent which removes as completely as possible nonpolymer material without removing polymer fractions. The writers have found that acetone is completely untrustworthy for this purpose; they have substituted ethanol, which is a solvent for the usual nonpolymer materials found in Buna S, including soap, and is a complete nonsolvent for the polymer fractions themselves.

Whereas Kemp and Peters stated that *p*-dichlorobenzene will usually dissolve vulcanized Buna S tread stocks within 3 hours, the channel black stocks investigated here did not dissolve even after 10 hours of continuous boiling in *p*-dichlorobenzene. When the samples were cut into paper-thin shavings with a razor blade, they would dissolve after several hours of boiling in *p*-dichlorobenzene. Uncured and pure gum stocks dissolved without too much difficulty.

The method of solution finally adopted utilizes a phthalate plasticizer in combination with *p*-dichlorobenzene. Most of the determinations were made with either dibutyl phthalate or dioctyl phthalate, which were used interchangeably. Other ester plasticizers would probably be satisfactory. These phthalates aid in peptizing the vulcanized rubber sample without affecting the unsaturation of the latter and show only a slight tendency to react with the iodine chloride reagent under the experimental conditions.

UNSATURATION MEASUREMENTS

The samples were passed through a cold, tight mill about thirty times to facilitate solution. This is believed to have no significant effect on iodine number, and Fisher (*10*) found that there is only a slight loss in unsaturation of pale crepe which had been milled 2 hours in air. The weighed sample (0.075 gram) was then extracted with alcohol for 16 hours, dried at 50° C. under high vacuum, and kept in vacuum prior to analysis. The analysis was carried out within 24 hours after extraction in order to minimize any oxidative effects.

The sample was placed in a 250-ml., Pyrex, stoppered iodine flask together with 5 ml. of phthalate, and 10 grams of *p*-dichlorobenzene were added. The flask was heated on a hot plate at about 180° C. with the stopper loosened. The sample swelled at first and then began to dissolve rapidly. In the case of the carbon black samples this preliminary swelling period was about 30 minutes. During the succeeding 10 minutes the solution changed from colorless to black, and the sample became well dispersed.

To ensure complete solution, 35 additional grams of *p*-dichlorobenzene were added during this period of rapid solution, and heating was continued for another 30 minutes. Solution was facilitated by whirling the flask from time to time, with care to avoid allowing particles to stick to the sides. When the sample was in solution, the flask was slowly cooled to room temperature; 30 ml. of chloroform were then added, followed by exactly 25 ml. of standard iodine chloride (0.2 *N*) solution in carbon tetrachloride. The glass stopper of the flask was closed, and a thin film of 15% potassium iodide solution was placed on it. The reaction solution was allowed to stand for one hour at room temperature. At the end of this time, 25 ml. of fresh 15% potassium iodide were added, followed by 25 ml. of ethanol for the pure gum stocks and 50 ml. for the carbon black stocks. Excess iodine was immediately titrated with standard 0.1 *N* sodium thiosulfate. Another 25 ml. of ethanol were added near the end of the titration to aid in breaking up the emulsions.

A blank containing identical quantities of all reagents was taken through the same procedure. The iodine value is obtained by the calculation:

$$\text{Iodine No.} = \frac{\text{ml. thiosulfate (blank} - \text{sample)} \times 1.269}{\text{sample wt. in grams}}$$

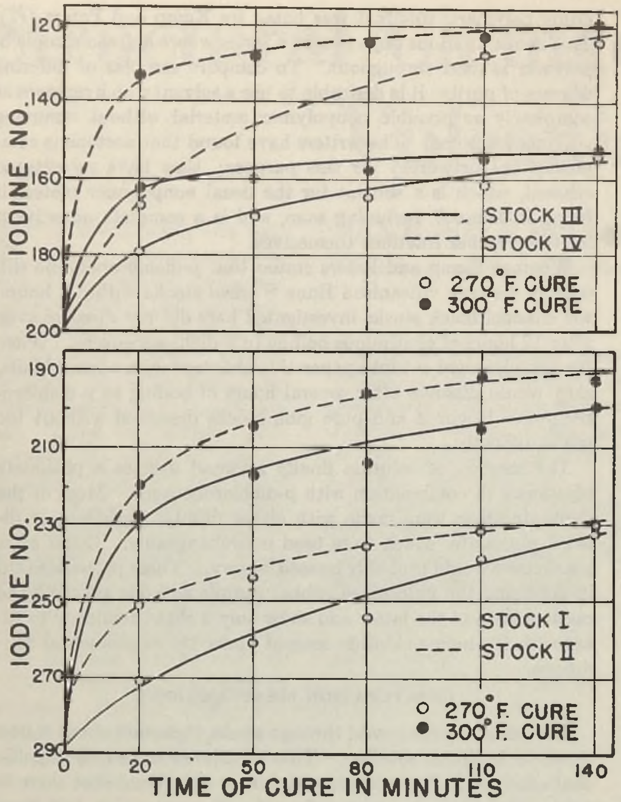

Figure 1. Curing Time *vs.* Unsaturation for Channel Black and Pure Gum Stocks

All determinations were made in duplicate. The iodine numbers in Table II were the averages of these duplicate determinations. Theoretical unsaturation for each stock was calculated on the basis of a 75% butadiene–25% styrene content for the hydrocarbon portion of the crude polymer. The iodine number is thus three fourths of that of polybutadiene, or 352. For each of the four stocks the percentage unsaturation was then obtained by multiplying this figure by the percentage polymer in the stocks. The theoretical values of iodine number for the four stocks are thus 310, 300, 215, and 210, respectively.

Each value of iodine number was converted to per cent unsaturation by a simple calculation (Table II). The four uncured stocks show excellent agreement at about 93% of theoretical. The remainder is presumably nonrubber material, with perhaps some diminution due to branch chaining, etc. This value is in excellent agreement with that of Kemp and Peters, who used an average value of 93% hydrocarbon content in the crude polymer.

EFFECTS OF VULCANIZATION

The experimental data in Table II are recorded graphically in Figures 1, 2, and 3. Temperature relations are what might be expected from previous data. Higher temperature results in a more rapid decrease in unsaturation, just as it results in a more rapid combination of sulfur and a more rapid increase of tensile strength. The reaction is most rapid in the first part of the cure and then tapers off. Unsaturation appears to approach a limiting value, although it had not positively reached this limit in any of the samples studied. There is some indication that this limit might be the same for the 270° and 300° F. stocks, at least for the reinforced stocks.

In the channel black stocks the rapid part of the reaction is considerably faster than in the pure gum stocks. Two factors may be involved: (*a*) The heat requirement for a given state of reaction may be largely required for the rubber-sulfur-accelerator system; a loaded stock containing only two thirds as much rubber as the corresponding pure gum stock would thus be expected to require roughly two thirds as much heat to reach a given state of cure. (*b*) The large amount of pigment in the loaded stock makes possible a rapid transfer of heat through the stock and thus facilitates a much more rapid cure. It should be noted that this effect is different from that usually reported for natural rubber systems, where carbon black exerts a retarding action on cure.

The 5% sulfur stock at a given temperature approaches a limiting iodine value lower than that of the corresponding 1% sulfur stock. Since the combined sulfur is greater in the 5% stock, some relation between combined sulfur and iodine value is indicated.

The matter of "equivalent cures" is indicated in Figure 2 for stocks III and IV. Here it is apparently possible to obtain an equivalent state of cure for the same stock at two different temperatures, as shown by both combined sulfur and unsaturation. There is, however, no such simple relation with tensile strength. Furthermore, this relation holds true over a limited range and, apparently, only for the reinforced stocks.

Elongation data are included in Table II. No curves are shown because the graphical character of this property was shown previously (*6*). The elongation goes through a maximum in the early stages of the cure, then decreases rapidly, and levels off at a fairly constant value. Significantly, the maximum elongation is reached more rapidly in the channel black stocks. However, this maximum seems to bear no simple relation to any

Table II. Properties of Buna S Vulcanizates

Stock No.	Curing Temp., ° F.	Curing Time, Min.	G. Combined S per 100 G. Polymer	Iodine No.	Unsaturation, %	Tensile Strength, Lb./Sq. In.	300% Modulus, Lb./Sq. In.	Elongation, %
I	...	0	0.000	288	92.9	..	..	..
	270	20	0.176	271	87.5	75	..	775
		50	0.220	261	84.3	100	..	1000
		80	0.264	254	82.0	100	..	1125
		110	0.264	239	77.1	100	..	800
		140	0.264	232	74.9	100	..	500
	300	20	0.264	228	73.7	50	..	900
		50	0.352	217	70.0	150	..	350
		80	0.484	214	69.0	175	..	300
		110	0.564	205	66.2	200	..	250
		140	0.617	199	64.1	225	..	250
II	...	0	0.000	278	92.7	..	..	..
	270	20	0.766	251	83.7	100	..	1000
		50	1.617	244	81.3	175	..	600
		80	2.466	236	78.7	200	..	300
		110	3.148	232	77.3	225	..	250
		140	3.744	230	76.7	250	..	175
	300	20	1.786	220	73.3	150	..	300
		50	3.659	205	68.4	200	..	250
		80	3.957	196	66.4	200	..	200
		110	4.000	192	64.0	275	..	200
		140	4.000	194	64.7	200	..	175
III	...	0	0.000	199	92.7	..	..	..
	270	20	0.092	179	83.3	300	200	625
		50	0.182	170	79.0	1050	300	575
		80	0.245	165	76.8	1950	650	550
		110	0.275	162	75.3	2300	700	550
		140	0.335	152	70.7	2300	850	525
	300	20	0.366	162	76.3	1100	400	750
		50	0.488	160	74.4	2250	950	700
		80	0.488	158	73.5	2300	1250	650
		110	0.488	155	72.1	2300	1350	600
		140	0.488	153	71.1	2300	1400	575
IV	...	0	0.000	195	92.9	..	..	..
	270	20	1.195	167	79.5	800	750	325
		50	1.671	147	70.0	2700	1650	225
		80	2.030	110	66.6	2450	2400	200
		110	2.268	127	60.4	2250	..	200
		140	2.507	124	59.1	2000	..	200
	300	20	2.089	133	63.4	2300	..	700
		50	2.567	128	60.9	2500	..	450
		80	2.806	124	59.1	2450	..	300
		110	2.885	123	58.6	2400	..	250
		140	2.885	119	56.6	2350	..	200

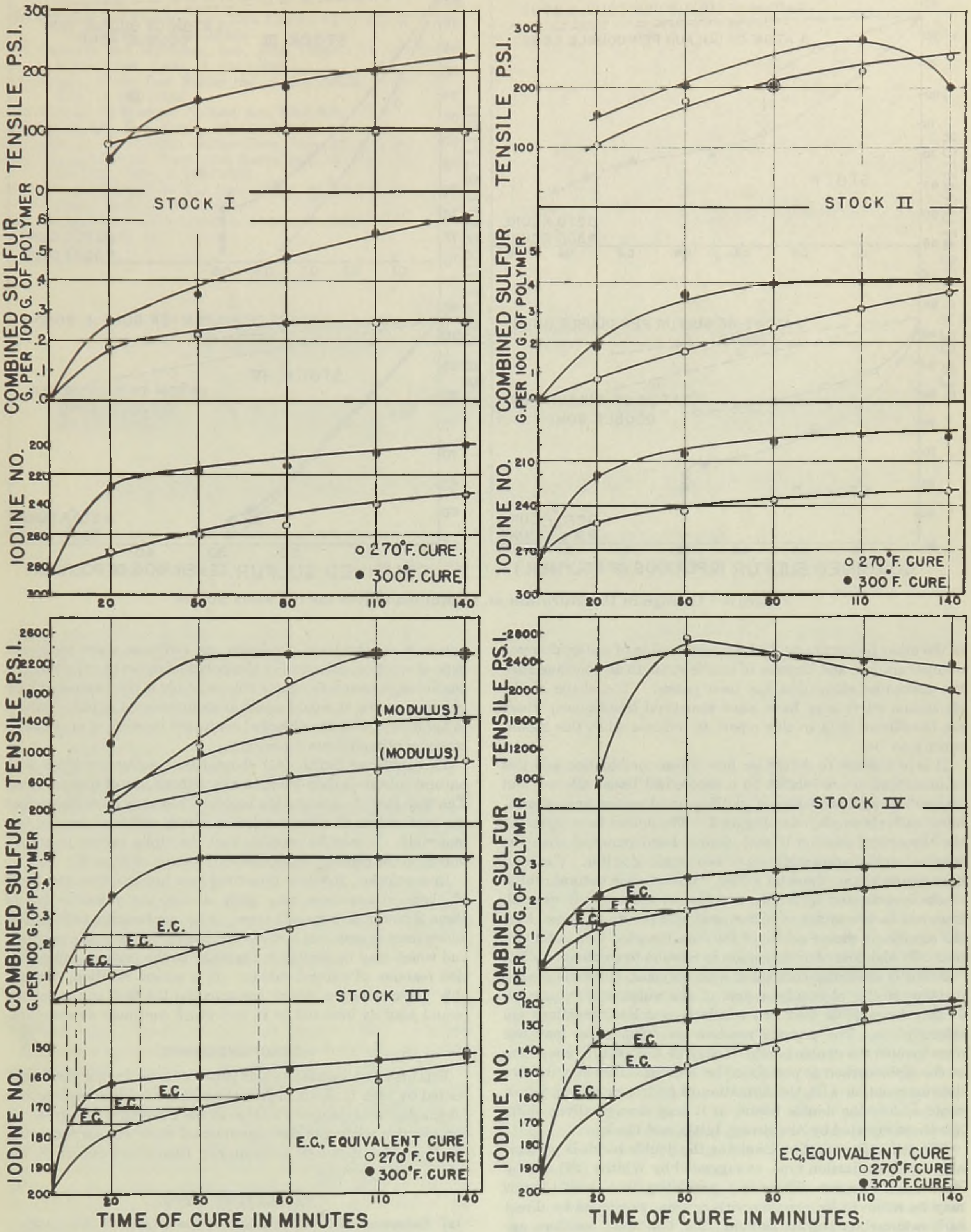

Figure 2. Effect of Cure on Properties of the Four Stocks

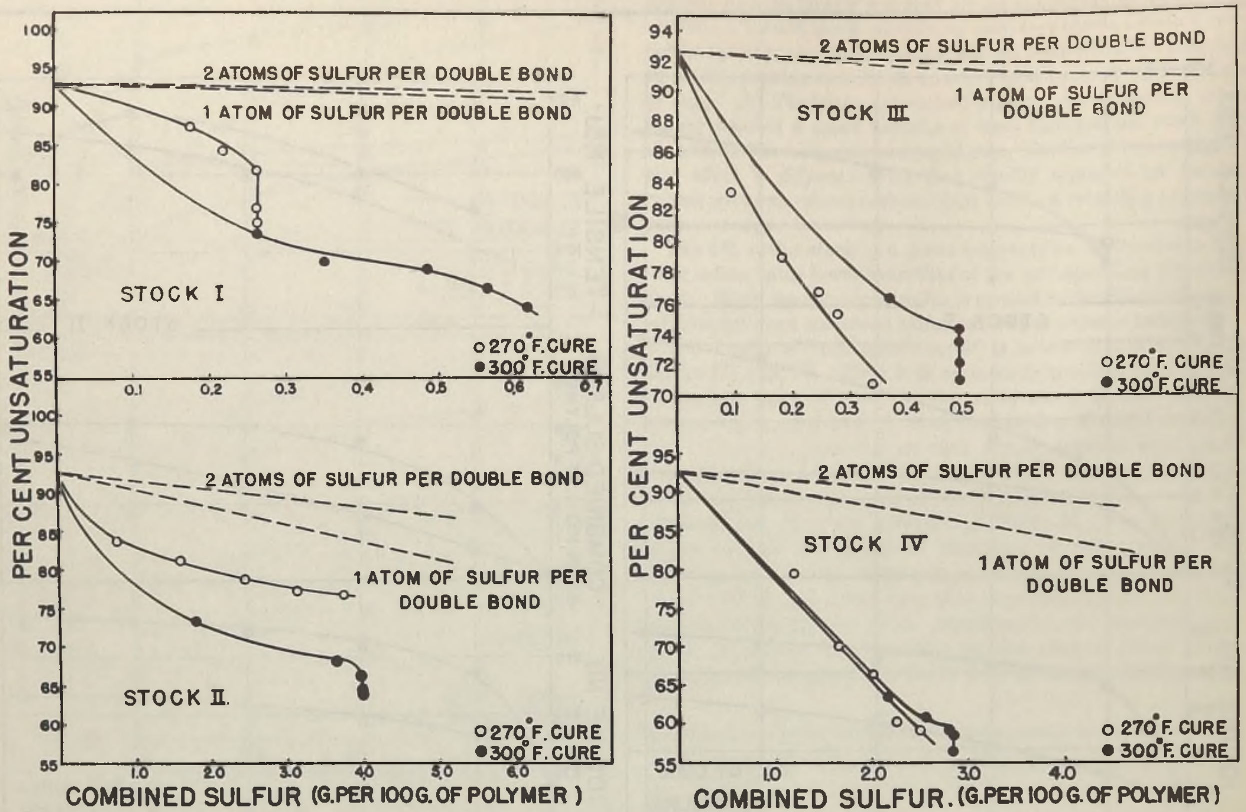

Figure 3. Change in Unsaturation *vs.* Combined Sulfur for the Four Stocks

of the other properties studied, as combination of sulfur, decrease of unsaturation, and increase of tensile strength all continue after the maximum elongation has been passed. The shape of the elongation curve may have some structural significance; there are insufficient data in this report to indicate what this significance may be.

It is of interest to determine how sulfur combination and loss of unsaturation are related on a theoretical basis. Brown and Hauser's general procedure of plotting unsaturation against combined sulfur is employed in Figure 3. The dotted lines represent the theoretical relation if each double bond removed were the result of combination with one or two atoms of sulfur. The solid lines represent experimental values. Whereas the natural rubber stocks investigated by Brown and Hauser indicated, in general, from one to two atoms of sulfur combined per double bond lost, the significant characteristic of the data reported here is the abnormally high loss of unsaturation in relation to combined sulfur.

Sulfur is obviously combining with polymer, but some second reaction is also obviously a part of the vulcanization process. It may be possible that two relatively unrelated reactions are taking place. The primary reaction involving sulfur may not even involve the double bond. It may be a substitutive reaction at the alpha carbon as postulated by Farmer. This may involve dehydrogenation with the formation of hydrogen sulfide, which could add to the double bonds, or it may involve allylic shifts like those reported by Armstrong, Little, and Doak.

The remaining reaction involving the double bonds is presumably a polymerization type, as suggested by Whitby (*22*) and by Brown and Hauser. There is a possibility that double bonds may be removed by reaction with oxygen, as well as by direct carbon-to-carbon polymerization. The two main reactions apparently bear a relatively constant relation, as evidenced by the linear relation between combined sulfur and loss of unsaturation in Figure 3. When the sulfur combination is complete, the decrease in unsaturation continues and indicates some additional type of reaction, presumably also polymerization in nature, which continues on overcure. Since this probably involves cross linkage between chains, it would result in an increase of rigidity; this is in agreement with the observed continued increase of modulus on overcure of such Buna S stocks.

Thornhill and Smith (*21*) showed that sulfur combines with natural rubber–carbon black stocks without loss of unsaturation. The high loss of unsaturation reported here may be evidence that the mechanism of vulcanization is totally different for the two materials. It may be possible that the alpha carbon is not involved in the primary vulcanization reaction of Buna S.

In conclusion, the data presented here indicate that two types of chemical reactions take place during the vulcanization of Buna S stocks of a specific type: (*a*) a combination with sulfur, which may or may not involve the double bonds in the polymer, and which may be similar in character to the primary vulcanization reaction of natural rubber; (*b*) a second reaction, presumably polymerization, which accompanies the first and is related to and possibly initiated by it, and which continues on overcure.

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Octane Number and Lead Susceptibility of Gasoline

EFFECT OF ORGANIC CHLORINE AND SULFUR

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Small quantities of organic sulfur are instrumental in lowering the octane number and decreasing the lead susceptibility of gasolines. In order to ascertain whether organic chlorine in gasoline would have a similar effect, synthetic samples containing from 0 to 1.0 weight % chlorine as organic chlorides were prepared and tested for motor-method octane number, lead susceptibility, corrosion, and gum. The gum and corrosion tests were negative at chlorine concentrations of 0.1 weight % and lower; the effect of organic chlorides on lead susceptibility was so great as to indicate that, above 0.001 weight %, chlorine should not be tolerated in gasoline, although this limit might be raised somewhat, depending on whether the particular chlorides present are normal, secondary, or tertiary. Work with another gasoline, and using 1-C aviation-method octane ratings indicated about the same permissible concentration, both for organic chlorides and for a number of organic sulfur compounds.

THE very deleterious effects of organic sulfur on octane number and lead susceptibility are well known and have been quantitatively reported (*1*, *2*). Similarly, A. M. McAfee, of Gulf Oil Corporation, observed that small quantities of organic chlorine introduced into gasoline in the use of an aluminum chloride catalyst decreased the lead susceptibility. This paper presents data showing the effect of six organic chlorides on leaded and unleaded motor-method octane number (A.S.T.M. D–357) as well as on gasoline corrosion and gum tests, together with information on the effects of organic chlorine and sulfur on the aviation 1-C octane number (A.S.T.M. Tentative Method D–614).

Three C.F.R. standard secondary reference fuels were used; they boil in the aviation gasoline range and have the following octane numbers:

Fuel	A.S.T.M. Octane No.
C-12	78.9
M-3	19.5
S-2	100.0

The tetraethyllead was the standard automotive type "red" fluid where A.S.T.M. octane numbers are reported and the standard aviation type "blue" fluid where 1-C octane numbers are given, both from the Ethyl Corporation. With the exception of the ethyl chloride which was a c.p. grade by the Du Pont Company, the organic chlorides and all of the sulfur compounds were obtained from Eastman Kodak Company and were better than 95% pure. After the respective chlorides were added to the C-12 fuel, the gasoline samples were analyzed for chlorine by burning in an atmosphere of oxygen and carbon dioxide. The combustion products were absorbed in sodium carbonate solution, and the chlorine was precipitated as silver chloride with standard silver nitrate solution, using potassium chromate as indicator. Errors in the analyses by this method were no more than 3% at chloride concentrations of 0.01 weight % and greater, and were only 13% at concentrations as low as 0.002 weight %. This method of analysis is a modification of one previously described (*4*), with equipment similar to that used in the determination of small quantities of sulfur (*3*). Since good checks were obtained with the compositions as made up by weighing, analyses were not carried out on samples used in the 1-C determinations.

In addition to the octane number study, four standard corrosion and gum tests were made on the C-12 gasoline samples: copper strip (A.S.T.M. D–130–30), corrosion and residue (FSB 530.11), gum (AN-VV-F-781; F-5d), and acidity of distillation residue [AN-VV-F-781; F-5e(7)]. Data for this gasoline are

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[1] Present address, Gulf Oil Corporation, Port Arthur, Texas.

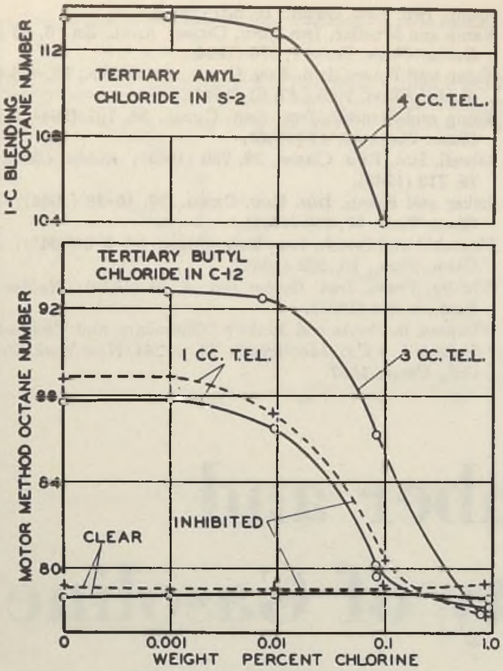


Figure 1. Effect of Organic Chloride Concentration on Octane Number

compiled in Table I. The only failure to meet aviation gasoline requirements was in the case of the gum test. When a sample containing 0.106 weight % chlorine as ethylene chloride was subjected to this test, 5.8 mg. of gum per 100 ml. of sample were obtained, whereas a maximum of 5 mg. per 100 ml. is allowable. Uninhibited and inhibited samples containing 1 weight % chlorine as *tert*-butyl chloride produced 13 and 11 mg. of gum per 100 ml. of sample, respectively. According to these results, no trouble will be encountered in meeting corrosion and gum specifications because of organic chlorides, provided the chlorine concentration is 0.1 weight % or less.

EFFECT OF CHLORIDES

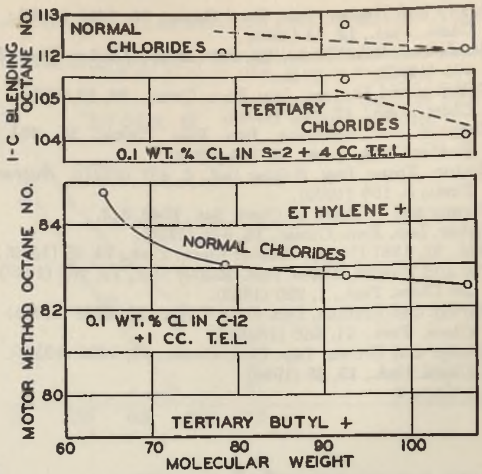


Figure 2. Effect of Various Chlorides on Octane Number

The octane numbers of unleaded samples containing up to 1.0 weight % chloride as *tert*-butyl chloride were not affected by the chlorine content. The octane numbers of samples containing tetraethyllead fluid, however, were appreciably reduced in the presence of minute amount of organic chlorine. This octane number depression began to occur between about 0.001 and 0.01 weight % chlorine when the chloride used was the *tert*-butyl compound. Figure 1 shows the effect of various amounts of *tert*-butyl chloride. Curves are presented for inhibited and uninhibited samples containing 0 and 1 cc. of tetraethyllead per gallon, and one curve represents an uninhibited sample containing 3 cc. per gallon.

In a homologous chloride series, increasing the molecular weight progressively decreases the lead susceptibility of the gasoline. The octane numbers obtained with samples containing about 0.1 weight % organic chlorine, using four primary chlorides and ethylene chloride, are plotted on Figure 2; 1 cc. of tetraethyllead per gallon was present in each sample of the homologous series. The octane numbers obtained in the presence of *n*-butyl and *tert*-butyl chlorides indicate that equal concentrations of isomeric chlorides act differently upon lead susceptibility; a tertiary decreases it more than a primary chloride.

None of the chlorine concentrations mentioned in this work include halides added with the tetraethyllead in the form of ethylene chloride and ethylene bromide. These are present

TABLE I. SUMMARY OF CORROSION TESTS AND OCTANE NUMBER RATINGS FOR GASOLINE CONTAINING ORGANIC CHLORIDES

Chloride added	tert-Butyl									
Chlorine, wt. %	0	0.0010	0.0093	0.0836	0.962	0	0.0010	0.0091	0.100	0.849
Inhibitor added, lb.[a]	0	0	0	0	0	1	1	1	1	1
Copper strip test	Negative									
Corrosion & residue, mg./100 ml.	0	0	0	0	1	0	0	0	0	1
Gum, mg./100 ml.	0	0	0	2	13	0	4	0	1	11
Acidity of distn. residue	Neutral									
A.S.T.M. motor-method octane No.										
Clear	78.6	78.7	78.8	79.6	78.6	79.2	79.0	79.0	79.2	79.3
+1 cc. T.E.L. (red)	87.7	87.8	86.5	80.2	78.2	88.8	88.9	87.2	80.4	77.8
Chloride added	tert-Butyl					*n*-Amyl	*n*-Butyl	*n*-Propyl	Ethylene	Ethyl
Chlorine, wt. %	0	0.0009	0.0073	0.084	0.780	0.1030	0.1019	0.1029	0.106	0.1003
Inhibitor added, lb.[a]	0	0	0	0	0	0	0	0	0	0
Copper strip test	..	..	..	..	..	Negative				
Corrosion & residue, mg./100 ml.	..	..	..	..	..	1.8	0.8	2.0	2.0	1.2
Gum, mg./100 ml.	..	..	..	..	..	1.8	1.3	2.0	5.8	3.0
Acidity of distn. residue	..	..	..	..	..	Neutral				
A.S.T.M. motor-method octane No.										
+1 cc. T.E.L. (red)	..	..	..	..	..	82.5	82.8	83.1	84.3	84.8
+3 cc. T.E.L. (red)	92.8	92.8	92.5	86.2	77.9	..	..	..	..	..

[a] Pounds of monobenzyl-*p*-aminophenol per 5000 gallons.

about 15% in excess of the stoichiometric quantity required for complete conversion of the lead to lead halides. Thus, with the "red" fluid used, the concentrations of chlorine and bromine are 0.006 and 0.021 weight % of the gasoline, respectively, for each cubic centimeter of T.E.L. added per gallon.

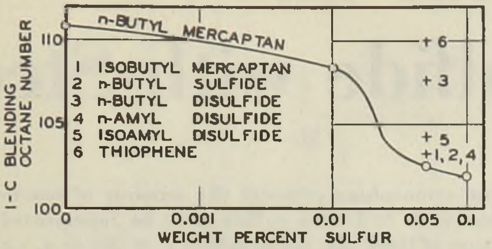


Figure 3. Effect of Organic Sulfur Compounds on 1-C Octane Rating

Tests were also conducted to determine the effect of organic chlorine and sulfur on 1-C ratings. Table II summarizes the data for leaded S-2 reference fuel containing various concentrations of organic chlorides, and the 1-C ratings of these samples are plotted against chlorine concentration and molecular weight in Figures 1 and 2. The trends shown are considered accurate, although it is generally recognized that the accuracy of single 1-C ratings is only about ±0.5 unit. *tert*-Amyl chloride was evaluated at chlorine concentrations of approximately 0.001, 0.01, and 0.1 weight %, and the effect of four other chlorides was determined at 0.1 weight % chlorine. With *tert*-amyl chloride, the 1-C rating of leaded S-2 reference fuel started to decrease when more than 0.001 weight % chlorine was present, although the rate of decrease was not rapid until 0.01 weight % chlorine had been exceeded.

EFFECT OF SULFUR

Table III summarizes the data for leaded 95% S-2 fuel in M-3 reference fuel containing various concentrations of organic sulfur compounds, and the 1-C ratings of these samples are plotted against sulfur concentration in Figure 3. The comment on accuracy of 1-C ratings should again be kept in mind. *n*-Butyl mercaptan was evaluated at sulfur concentrations of 0.01, 0.05, and 0.1 weight %, and the effect of six other sulfur compounds was determined at 0.05 weight % sulfur. Unfortunately, a 1-C rating of a sample containing 0.001 weight % sulfur as *n*-butyl mercaptan was not obtained. Since 0.01 weight % sulfur decreased the rating by 2.4 octane numbers, it is probable that at 0.001 weight % sulfur the 1-C rating would start to decrease.

In this investigation no attempt was made to determine the influence of type of fuel or octane number level. As indicated above, some information was obtained at 0.1 weight % chlorine and at 0.05 weight % sulfur on the effect of different types of organic chloride or organic sulfur compounds. For constant chlorine concentration, branched-chain chlorides had a more deleterious effect than straight-chain isomers; in general, increasing the number of carbon atoms in a homologous series decreased the 1-C ratings. These observations are in agreement with the data on the effect of organic chlorides on A.S.T.M. motor-method octane number.

The data on the effect of various types of organic sulfur compounds are not very conclusive. The decrease in 1-C ratings resulting from the addition of 0.05 weight % sulfur as *n*-butyl mercaptan, isobutyl mercaptan, *n*-butyl sulfide, *n*-amyl disulfide, or isoamyl disulfide was about the same; thiophene and *n*-butyl disulfide had considerably less effect. Ryan (*2*) observed that increasing the number of branched chains in an isomeric series or increasing the number of carbon atoms for a homologous series decreased the A.S.T.M. motor-method octane number of samples containing 0.05 weight % sulfur. In our work there was no consistent difference between the two sets of isomers, normal and isobutyl mercaptan or normal and isoamyl disulfide; however, the amyl disulfides were more detrimental than *n*-butyl disulfide.

Table II. Effect of Organic Chlorides on 1-C Octane Rating

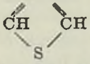
(S-2 reference fuel plus 4 cc. tetraethyllead)

Added Chloride	Boiling Range of Chloride, ° F.	Wt. % Added as Organic Cl	Aviation Method 1-C Rating: Cc. of T.E.L. in iso-octane	Aviation Method 1-C Rating: Equiv. blending octane No.
None	....	0.0	4.06[a]	113.5[a]
tert-$C_5H_{11}Cl$	181.4–185.0	0.0009	4.16	113.6
tert-$C_5H_{11}Cl$	181.4–185.0	0.0092	3.62	112.9
tert-$C_5H_{11}Cl$	181.4–185.0	0.0922	0.39	104.0
n-$C_5H_{11}Cl$	222.8–226.4	0.10	2.96	112.0
tert-C_4H_9Cl	122.0–123.8	0.10	0.61	105.4
n-C_4H_9Cl	170.6–172.4	0.10	3.42	112.7
n-C_3H_7Cl	113.0–116.6	0.10	2.99	112.1

[a] Average of two ratings.

Table III. Effect of Organic Sulfur Compounds on 1-C Octane Rating

(95% S-2 reference fuel + 5% M-3 reference fuel + 4 cc. tetraethyllead)

Added Sulfur Compound	Boiling Range of Sulfur Compound, ° F.	Wt. % S Added as Organic Sulfur	Aviation Method 1-C Rating: Cc. of T.E.L. in iso-octane	Aviation Method 1-C Rating: Equiv. blending octane No.
None	....	0.0	2.31[a]	110.8[a]
n-C_4H_9SH	204.8–208.4	0.01	1.29	108.4
n-C_4H_9SH	204.8–208.4	0.05	0.20	102.5
n-C_4H_9SH	204.8–208.4	0.1	0.15	101.9
iso-C_4H_9SH	188.6–192.2	0.05	0.30	103.3
(*n*-$C_4H_9)_2S$	366.8–272.2	0.05	0.30	103.3
(*n*-$C_4H_9)_2S_2$	212–217.4 (15 mm.)	0.05	1.07	107.7
(*n*-$C_5H_{11})_2S_2$	262.4–266(12 mm.)	0.05	0.30	103.3
(iso-$C_5H_{11})_2S_2$	251.6–257(10 mm.)	0.05	0.42	104.3
	183.2	0.05	1.90	110.0

[a] Average of two ratings.

In agreement with the work on motor-method octane numbers, and again depending upon the type of compounds present, not more than approximately 0.001 to 0.01 weight % chlorine or sulfur can be tolerated without decreasing the 1-C ratings. The copper-dish and gum tests were run on the samples containing up to 0.01 weight % chlorine or sulfur, and the samples passed specifications.

In this investigation, the 1-C ratings were converted to octane numbers from the values in Report No. 3 of the Subcommittee on Blending Octane Numbers of the Aviation Gasoline Advisory Committee. In the "blue" leading fluid used in the 1-C octane ratings there is no chloride. Bromine as ethylene bromide is present to the extent of 0.125 weight % of the gasoline when it is leaded to 4 cc. per gallon.

ACKNOWLEDGMENT

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Reaction Rate of Hydrogen Chloride and Sulfide with Steel

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At one atmosphere pressure the amount of reaction, y, of iron with hydrogen sulfide may be represented as a function of time t by the equation $y^2 = Kt + A$, where K is a constant dependent upon temperature and pressure, and A is a constant which may be zero or assume a positive value depending upon the type of iron. K may be represented as a function of temperature by an equation of the type: $\log_{10} K = B/T + C$. Addition of oxygen to hydrogen sulfide greatly accelerates its reaction rate with iron, but its reaction with an oxide-coated iron surface is substantially slower than with a clean iron surface. Hydrogen chloride reacts with iron or steel much less rapidly than does hydrogen sulfide under comparable conditions; the extent of its reaction with steel may be represented by the following type of equation: $y = k \log_{10} (bt + 1)$. When a 1 to 1 mixture of hydrogen chloride and hydrogen sulfide reacts with steel, the rate of formation of iron chloride is about the same as though hydrogen sulfide were absent. However, iron sulfide forms in the gas mixture at a rate only one third to one tenth as fast as it forms in pure hydrogen sulfide. "Inhibition" of iron sulfide formation is attributed to interspersion of iron chloride microcrystals in the mixed film.

DURING an investigation of the cooperative action of organic sulfur and chlorine compounds in extreme-pressure lubrication, it became of interest to study the rate of attack of iron and steel by hydrogen chloride, hydrogen sulfide, and mixtures of the two. One of the possible modes of action of such compounds was to decompose at the contact points of the gear teeth and liberate hydrogen chloride or sulfide, which would then react with the iron to form an inorganic lubricant film, such as iron chloride or sulfide. It was therefore considered important to investigate the reaction of these gases and mixtures of the two with iron at temperatures which might reasonably be expected to prevail at the contact points (*1*) after short contact periods. This might indicate whether or not films of iron sulfide or chloride could form with sufficient rapidity to provide effective lubrication, what substance predominated in the film formed by a mixture of the additives, and whether the additive mixture caused more rapid film formation than the additives acting singly.

Although subsequent work rendered it doubtful that hydrogen chloride or sulfide was actually intermediate in the reaction of organic chlorine and sulfur additives with steel, it did indicate that iron chloride or sulfide was formed at 150° to 300° C. From the lubrication standpoint, therefore, the principal interest in the work reported in this investigation lies in a study of the growth characteristics of sulfide and chloride films on iron and of the effect which one constituent of the mixed film (sulfide and chloride) exerts on the growth rate of the other.

Apart from the significance attaching to this study from a lubrication standpoint, it is also important from a corrosion standpoint. In many industrial processes involving the preparation of chlorinated compounds from anhydrous hydrogen chloride at high temperatures or the use of chlorinated compounds which crack at high temperatures to give hydrogen chloride, iron pipes and reactors are used. Consequently, information on the reaction rate of iron with anhydrous hydrogen chloride would be of considerable value in this connection. In the distillation of petroleum and in the cracking of petroleum hydrocarbons, hydrogen sulfide, sulfur, and hydrogen chloride are formed, and the reaction between these compounds and the iron in the equipment in which the processes are carried out is of practical interest.

Several investigators (*2*, *4*, *16*, *17*, *18*) have studied the rate of reaction of hydrogen sulfide with steel. In most cases the rates were measured over comparatively long periods, and the mechanism of film growth was not discussed. Wilson and Balke (*18*) measured the rate of reaction at two temperatures between 300° and 400° C. up to 4 hours of reaction time by measuring the volume of hydrogen evolved when hydrogen sulfide passed through a steel tube. They obtained a rapid initial rate followed by a slow rate at long periods. White and Marek (*17*) studied the reaction over long time intervals and observed that film scaling invariably occurred, with the result that the reaction rate was accelerated as time increased.

Anhydrous hydrogen chloride is known to react with steel only slowly at 200° to 300° C. Hofmann and Hartmann (*7*) compared the rate of reaction of several metals, including iron, with hydrogen chloride gas and with ammonium chloride vapor, and found that the latter attacks metals more rapidly than hydrogen chloride. No kinetic studies seem to have been undertaken for the purpose of ascertaining the mechanism of iron chloride film formation, however.

CORROSION TESTING

PREPARATION OF METALS. Three types of iron were used in this investigation. The Mallinckrodt electrolytic iron wire samples were 0.015 inch in diameter and assayed 99.8% iron and 0.023% sulfur. Immediately before use, they were rinsed with ether and dried.

Cold-drawn S.A.E. 1112 steel rods, $^1/_4$ inch in diameter and 1 inch long, were prepared by dry surface grinding with a fine alundum wheel (No. WGOKH-4). The final cut was made at a uniform rate of 0.25 inch per minute with a 0.004-inch depth of cut. Ends of the samples were finished by grinding on an emery wheel. No oil, grease, or other lubricant was used in preparing the samples, and they were always handled with clean forceps. Analysis revealed 0.22% sulfur by weight.

Cold-drawn, S.A.E. 1113 steel samples were the same size and prepared in the same manner as were the S.A.E. 1112 samples. This steel differed from S.A.E. 1112 in sulfur content which was 0.29% by weight, in machinability which was rated 30% higher, and in hardness which was about 20% greater on the Rockwell C scale.

APPARATUS. Figure 1 is a schematic diagram of the apparatus in which the corrosion tests were run. It was constructed entirely from Pyrex. Stopcocks appear at points 1, 2, 3, etc.; A_1, A_2, and A_3 show storage tubes for condensed gases; T_1, T_2, and T_3 indicate cold traps for condensing out moisture and any

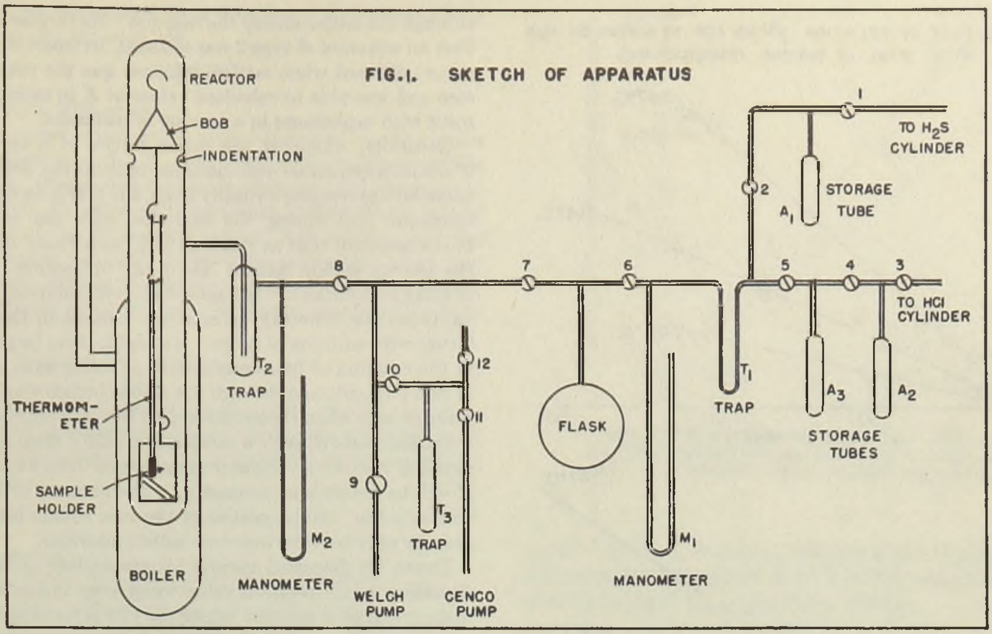


FIG. I. SKETCH OF APPARATUS

traces of other condensable impurities in the gases. Pressures were read on manometers M_1 and M_2. A large flask (2-liter capacity) was used for storing the gases. Constant temperature was maintained in the reactor by a boiling liquid, such as mercury or hexachlorodiphenyl oxide in the boiler surrounding the reactor.

PURIFICATION OF GASES. Hydrogen sulfide was introduced into the system from a commercial cylinder at 1 and condensed in A_1, which was cooled by a dry ice–naphtha bath. About one third of the sample was distilled off in order to remove volatile impurities. Prior to reaction, a sufficient amount of hydrogen sulfide was vaporized into the storage flask, which was kept at −55° C., and kept until the reaction was begun.

When hydrogen chloride was used, it was introduced into the system at 3 from a commercial cylinder and condensed in A_2 which was cooled by liquid nitrogen. About one third was then distilled off. Gas samples for reaction were collected and stored in the 2-liter flask as for hydrogen sulfide. When only hydrogen chloride was used, all cold traps except the storage tube were maintained at −75° C. When hydrogen sulfide or a mixture of hydrogen sulfide and chloride were used, however, they could be cooled no lower than −55° C. in order to avoid condensation of hydrogen sulfide.

To obtain a mixture of hydrogen chloride and sulfide of known composition, hydrogen chloride was first introduced into the storage flask to a definite pressure read on M_1. This was then entirely condensed in A_3 from which hydrogen chloride had been previously removed by condensation into A_2. Hydrogen sulfide was introduced into the storage flask to a definite pressure and condensed with the hydrogen chloride in A_3. This whole condensate was then distilled back into the storage flask where it was retained until ready for reaction.

REACTION PROCEDURE. Two steel samples were placed in the sample holder and suspended from the glass bob by means of glass hooks. A calibrated mercury thermometer was also suspended from the bob so that the thermometer bulb was opposite the middle of the steel samples. Indentations in the reactor tube served to support the bob and articles suspended from it. After the top of the reactor was sealed off, the system was evacuated to less than 0.01 mm. of mercury by the Welch pump. An electrical heating element, manually controlled by means of a variable transformer, brought the liquid in the outer jacket to boiling. Temperatures in the reactor bulb varied about 1° C. per inch of height in the neighborhood of the samples. During the reaction the maximum temperature variation was ±0.5° C.

When the reactor had reached constant temperature, the gas in the flask was quickly admitted until the desired pressure was obtained. After the desired reaction time had elapsed, the gas was removed by condensation in T_3, which was cooled by liquid nitrogen. When the samples had cooled under vacuum to room temperature, they were removed for analysis.

ANALYSIS OF SAMPLES. Analysis for sulfide on the electrolytic iron was made by the hydrogen sulfide evolution method described in the A.S.T.M. procedures. For the steel samples, however, it was necessary to modify this procedure so that little more than the sulfide film was dissolved in the determination in order to avoid a large blank. Loss in weight of the samples by the action of acid was determined in order to apply a blank correction for the sulfur originally present in the dissolved steel. In duplicate sulfide determinations on separate samples of equal area subjected to the same reaction condition, the deviations from the mean averaged about 3%.

Chlorides were determined potentiometrically using a silver electrode and a calomel reference electrode connected to the solution through an agar-agar-potassium nitrate bridge. Analyses made on duplicate test samples generally deviated ±1% from the mean.

REACTIONS OF HYDROGEN SULFIDE

Rates of reaction of hydrogen sulfide with steel and iron were studied at temperatures from 247° to 347° C. and for contact times up to 90 minutes. At hydrogen sulfide pressures of 0.5 or 1 atmosphere it was found possible to represent the total amount of reaction per unit area as a function time t by an equation of the type:

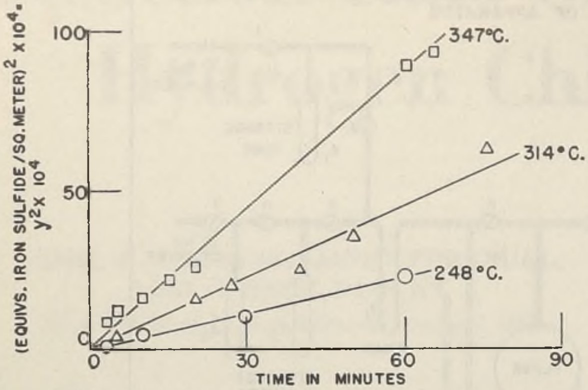
$$y^2 = Kt + A \tag{1}$$

where K and A are constants dependent upon temperature and pressure of hydrogen sulfide. In the figures and subsequent discussion, y is expressed in gram equivalents of sulfide (or chloride) per square meter, and time in minutes.

Figure 2 shows y^2 plotted against time for the S.A.E. 1112 steel at three temperatures; Figure 3 presents similar plots for electrolytic iron wire. These curves are linear as required by Equation 1, and deviations of the plotted points from the lines correspond to deviations not exceeding ±10% for the y values in most instances. Table I summarizes the constants of Equation 1 for the various types of steel and iron used.

For the most part, K values for the samples investigated are in close agreement, particularly when it is recalled that an error in y will square the error in K. Only at 314° C. between the S.A.E. 1112 and the other two types is the disagreement in K values somewhat larger than the experimental uncertainty. Values of intercept A are positive and in fair agreement for electrolytic iron

FIG. 2. TEST OF RELATION y^2 Kt FOR REACTION OF H_2S WITH STEEL AT VARIOUS TEMPERATURES



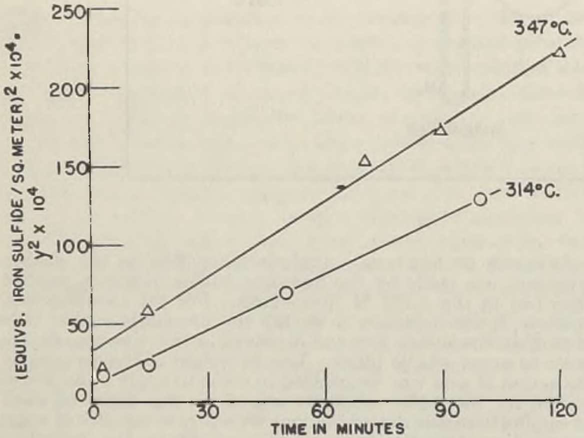


FIG. 3. TEST FOR LINEAR RELATIONS BETWEEN y^2 AND t FOR REACTION OF H_2S WITH C.P. ELECTROLYTIC IRON AT TWO TEMPERATURES

and the S.A.E. 1113 steel, but are zero, within experimental error, for the S.A.E. 1112 steel.

Agreement of the experimental data with Equation 1 indicates that the rate of formation of iron sulfide in a hydrogen sulfide atmosphere is probably controlled principally by the rate of diffusion of one of the reactants through the iron sulfide lattice. Pilling and Bedworth (*12*) found that, in the oxidation of a number of pure metals (copper, iron, nickel, lead, and zinc) at high temperatures, the relation between y and t was given by:

$$y^2 = Kt \tag{2}$$

They showed that such a relation could be derived on the basis of the assumptions that the rate of oxidation was determined by the diffusion rate of oxygen through the oxide lattice, that the rate of chemical reaction was sufficiently rapid to make the concentration of diffusing reactant negligibly small at the reaction interface in comparison with its concentration at the interface at which it goes into solution, and that the oxide film was less dense than the metal displaced.

Since Pilling and Bedworth's investigation, much evidence (*6*) has accumulated which indicates that, in the growth of tarnish films on metals, ions rather than molecules diffuse through the film. Furthermore, in most reactions investigated, it appears to be the cations rather than the anions which diffuse. Pfeil (*11*) presented convincing evidence that, in the oxidation of iron at 800° C., iron ions as well as oxide ions diffused through the film lattice during oxidation. Wagner (*14*) proved that in the reaction between solid sulfur and silver only silver ions diffused through the lattice during the reaction. He further demonstrated that an equation of type 2 was satisfied, irrespective of which reactant diffused when lattice diffusion was the rate determining step and was able to calculate values of K in satisfactory agreement with experiment in a number of instances.

Generally, whenever the cation lattice of a tarnish film exhibits an appreciable concentration of Schottky defects while the anion lattice remains virutally filled, the film is an oxidation semiconductor and during the oxidation only the cations diffuse. It is known (*9*) that as much as 15% sulfur may be dissolved in the ferrous sulfide lattice; the x-ray diffraction investigations of Hägg and Sucksdorf (*5*) upon such solid solutions indicate that vacancies (or Schottky defects) are created in the ferrous iron lattice with addition of sulfur. It might, then, be predicted that, in the reaction of hydrogen sulfide or sulfur with iron, diffusion of iron ions outward through the sulfide lattice would control the reaction rate when chemical reaction is relatively rapid.

On the basis of such a mechanism, fairly close agreement between K values for various iron samples is to be anticipated, since K will be determined primarily by the pressure of hydrogen sulfide or sulfur, the properties of the iron sulfide lattice, and the activity of iron at the iron–iron sulfide interface.

Evans (*3*) discussed various interpretations of intercept A in Equation 1. A positive value for A may indicate that, in the earliest stages of reaction where the film is forming rapidly, some cracking might occur in order to relieve the internal stresses set up in the film. This would expose more surface and thus lead to a higher rate in the early stages of reaction. In the case under consideration, why this should occur for the S.A.E. 1113 and not for the S.A.E. 1112 steel is not entirely clear. It is more understandable that films formed on wires of small diameter should exhibit a greater tendency to crack under internal stress than those on samples of larger diameter. At any rate, the important feature of the present results is that, once a film of iron sulfide is established, further growth proceeds at nearly the same rate regardless of the samples investigated.

For the S.A.E. 1112 steel it was possible to represent K as a function of absolute temperature by the expression:

$$\log_{10}K = -2350/T + 0.12 \tag{3}$$

where T = absolute temperature, ° K.

Figure 4 shows that a plot of $\log_{10} K$ against $1/T$ is linear as required by Equation 3. Lennard-Jones (*8*) discussed the justification of an equation of the same type as 3, as applied to reactions of this character.

At 347° C. and a reaction time of 20 minutes some measurements were taken on the effect of hydrogen sulfide pressure on the extent of reaction. For the S.A.E. 1112 steel under these condi-

TABLE I. CONSTANTS K AND A OF EQUATION 1 FOR THE REACTION OF DIFFERENT TYPES OF IRON WITH HYDROGEN SULFIDE AT ONE ATMOSPHERE

Temp., ° C.	Designation of Iron or Steel	$K\left(\frac{\text{equiv.}^2}{\text{sq. meter}^2 \times \text{min.}}\right)$	$A\left(\frac{\text{equiv.}}{\text{sq. meter}}\right)^2$
314	S.A.E. 1112	0.83×10^{-4}	0×10^{-4}
	S.A.E. 1113	1.16×10^{-4}	6.2×10^{-4}
	Electrolytic iron	1.17×10^{-4}	10.8×10^{-4}
347	S.A.E. 1112	1.32×10^{-4}	0.0
	S.A.E. 1113	1.67×10^{-4}	22×10^{-4}
	Electrolytic iron	1.60×10^{-4}	32×10^{-4}

TABLE II. EXTENT OF REACTION OF DRY HYDROGEN SULFIDE WITH AN IRON OXIDE FILM AND WITH PURE STEEL

Time, Min.	Temp., ° C.	Pressure, Atm.	(Equiv. FeS/Sq. Meter) $\times 10^3$	
			H_2S + oxidized steel	H_2S + steel
15	347	0.50	5.00	7.14
30	347	0.50	5.90	9.00
30	248	1.00	2.66	3.28

tions y could be represented as a function of hydrogen sulfide-pressure ($P_{\text{atm.}}$) by the equation,

$$y = 0.050\, P_{\text{atm.}}^{0.27} \tag{4}$$

with deviations of 10% or less.

At 314° C. some experiments were conducted in which the amount of reaction of S.A.E. 1113 steel with hydrogen sulfide containing 4% oxygen was measured after reaction times of 15 and 30 minutes. These results were somewhat erratic because of heavy scaling of the films when oxygen was present, but the amount of reaction was three to five times larger than when oxygen was absent. During these tests deposits of sulfur formed on the cooler portions of the system. This was undoubtedly due to the reaction:

$$2H_2S + O_2 \longrightarrow 2H_2O + S_2 \tag{5}$$

which, according to equilibrium calculations, should go nearly to completion at this temperature. Presence of a relatively high partial pressure of sulfur in this case probably accounts for the increased reaction.

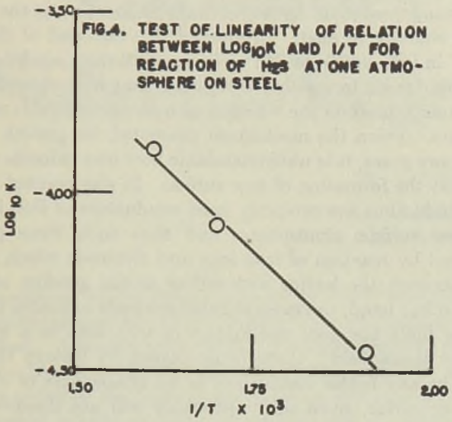


FIG. 4. TEST OF LINEARITY OF RELATION BETWEEN $\text{LOG}_{10}K$ AND 1/T FOR REACTION OF H_2S AT ONE ATMOSPHERE ON STEEL

This result suggested that perhaps the mechanism of reaction between hydrogen sulfide and steel might involve dissociation of hydrogen sulfide into hydrogen and sulfur vapor prior to reaction. Equilibrium calculations, using the data of Preuner and Schupp (*13*) indicated that sufficient sulfur could be formed at the temperatures of the investigation to account for the amount of reaction. Dependence of the rate of formation of iron sulfide upon either the partial pressure or activity of the reactant carrying sulfur is not inconsistent with the mechanism whereby the reaction rate is determined by the diffusion of ferrous ions outward through the film, since the sulfur excess in the lattice will be determined by both the activity and the pressure of the sulfur reactant. Assuming that sulfur is intermediate in the reaction between hydrogen sulfide and iron, K should vary as $P_{S_2}^{1/6}$ on the basis of Wagner's theory (*15*), whereas from the sparse data taken it varies as $P_{S_2}^{3/4}$. This discrepancy could be due to one of the following possibilities: (*a*) a different reaction mechanism at low sulfur pressures or (*b*) incomplete ionization of iron sulfide in the lattice and the operation of interionic effects.

An oxide coating formed on samples of steel by baking for 20 minutes at the reaction temperature under an oxygen pressure of 50 mm. materially lessened the rate of attack of steel by hydrogen sulfide. Table II compares the amounts of iron sulfide formed on the coated and uncoated surface.

These results might be attributed to the resistance offered by iron oxide to the outward passage of ferrous ions not only by virtue of its thickness but also of its lower conductivity toward ferrous ions as compared with iron sulfide containing dissolved sulfur. Addition of about 1% water vapor to the hydrogen sulfide increased the amount of iron sulfide formed by about 10% over that formed by dry hydrogen sulfide.

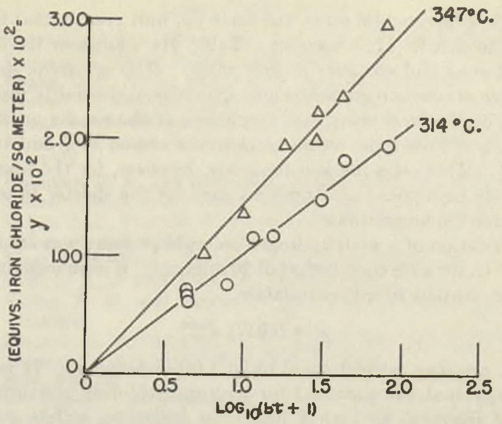


FIG. 5. EXTENT OF REACTION OF STEEL WITH HCl GAS PLOTTED AGAINST $\text{LOG}_{10}(bt+1)$ WHERE t = TIME, MINUTES, AND b IS CONSTANT FOR A GIVEN TEMPERATURE

REACTIONS OF HYDROGEN CHLORIDE

Reaction of hydrogen chloride with S.A.E. 1112 steel and electrolytic iron was studied at 314° and 347° C. For steel the following relations were found to hold between y and t at one atmosphere hydrogen chloride pressure:

$$314°\text{ C.}:\ y = 0.0104 \log_{10}(0.7t + 1) \tag{6}$$

$$347°\text{ C}:\ y = 0.0144 \log_{10}(0.9t + 1) \tag{7}$$

Figure 5 shows the expected straight lines at both temperatures when y is plotted against $\log_{10}(bt + 1)$.

There is considerable disagreement (*3, 10*) on the interpretation of a logarithmic relation between y and t as given by Equations 6 and 7. For relatively thick films, however (thicker than 300–500 Å.), an interpretation suggested by Evans (*3*) seems plausible. He derived the logarithmic law by assuming that the rate of reaction was determined by the diffusion rate of reactant along gross structural defects in the film such as pores, fissures, and grain boundaries. Transport of reactant by this mechanism undoubtedly occurred in the reaction of hydrogen sulfide with steel and iron but was overshadowed by lattice diffusion. Since the amount of iron chloride formed on iron by hydrogen chloride in a given time is only about one fifth the amount of iron sulfide, on an equivalents basis, formed by hydrogen sulfide on iron, it appears that the resistance of the iron chloride lattice in an atmosphere of hydrogen chloride must be much greater toward the reactant ions than the iron sulfide lattice in an atmosphere of hydrogen sulfide.

For short periods the amount of iron chloride formed on flat samples of Armco iron surfaced by a magnetic grinder was,

TABLE III. COMPARISON OF AMOUNT OF REACTION OF HYDROGEN CHLORIDE AT ONE ATMOSPHERE PRESSURE WITH STEEL AND WITH ELECTROLYTIC IRON

Time, Min.	Temp., ° C.	(Equiv. Iron Chloride/Sq. Meter) × 10^2 On steel	On electrolytic iron
5	314	0.66	0.78
30	314	1.42	1.10
45	314	1.62	1.30
60	314	1.74	1.71
5	347	1.04	1.21
15	347	1.60	1.63
30	347	2.12	1.74
60	347	2.66	1.81

within experimental error, the same per unit area as that formed on the S.A.E. 1112 samples. Table III compares the S.A.E. 1112 steel and electrolytic iron wires. It is apparent that the degree of reaction on electrolytic iron wire agrees fairly well with that on the steel samples. Deviations of the results on electrolytic iron from those on the steel do not exceed 25% and average 15%. There is a marked tendency, however, for the results on iron to be higher than those on steel for the shorter times, but less for the longer times.

Variation of y with hydrogen chloride pressure was studied at 314° C. for a reaction period of 20 minutes. Within experimental error, the data fitted the equation,

$$y = 0.0121\ P_{\text{atm.}}^{0.26} \tag{8}$$

in a pressure range from 0.10 to 1.00 atmosphere. It is noteworthy that the exponent for hydrogen chloride pressure is almost identical with that found for hydrogen sulfide pressure (Equation 4).

When hydrogen chloride was permitted to react at 347° C. with steel on which an oxide coating was baked in a manner similar to that described for hydrogen sulfide, the amount of iron chloride formed was only about 8–15% greater than that formed on an uncoated surface.

REACTION OF MIXTURES OF HYDROGEN CHLORIDE AND SULFIDE

A 1 to 1 mixture by volume of hydrogen chloride and sulfide at 1 atmosphere total pressure was reacted with steel at 314° and 347° C. for various times. Since the pressure of each of the reactant gases in the mixture was 0.5 atmosphere, it was necessary for comparison to have the amounts of reaction due to each of the pure gases at 0.5 atmosphere under these conditions. Hydrogen chloride was measured directly by reacting pure hydrogen chloride with steel at 0.5 atmosphere pressure for various times at both temperatures. For hydrogen sulfide the amounts of reaction of the pure gas with steel at 0.5 atmosphere was calculated from the results at 1 atmosphere upon the assumption that y varies with $P_{\text{H}_2\text{S}}^{0.27}$ as given by Equation 4 for both temperatures (314° and 347°) at all times.

Table IV compares the amounts of iron compounds formed by the mixture of the two gases with those formed by the pure gases acting separately at the same pressure as for the mixtures. Amounts of iron chloride formed by the mixture of gases are of the same order of magnitude as, but somewhat less than, those formed by hydrogen chloride acting alone. More striking is the result that the amounts of iron sulfide formed by the mixtures of gases are only small fractions (one third to one tenth) of those formed by hydrogen sulfide acting by itself. Results for iron sulfide are somewhat erratic because of the difficulty in analyzing for the very small amount of sulfur in these films. It is also noteworthy that, on an equivalents basis, iron chloride predominates over iron sulfide after the longer periods of reaction; for the shorter periods iron sulfide seems to predominate.

Table IV. Comparison of Amounts of Iron Sulfide and Chloride Formed by a 50-50 Mixture of Hydrogen Sulfide and Chloride at 1 Atmosphere Total Pressure with That Formed by the Pure Gases Acting Separately at 0.5 Atmosphere

Time, Min.	Temp., ° C.	(Equiv. $FeCl_2$/ Sq. M.) × 10^2		(Equiv. FeS/ Sq. M.) × 10^2		Total Reacted with Mixt., (Equiv. Iron/ Sq. M.) × 10^2
		HCl	HCl + H_2S	H_2S	H_2S + HCl	
5	314	0.40	0.47	1.58	0.56	1.03
15	314	0.92	0.53	2.99	0.88	1.41
30	314	1.28	0.87	4.21	0.47	1.34
45	314	1.42	1.10	5.10	0.22	1.32
60	314	1.48	1.23	5.91	0.47	1.70
5	347	0.70	0.61	2.48	0.53	1.14
10	347	1.00	0.65	3.26	0.78	1.43
15	347	1.24	0.73	3.90	0.61	1.34
30	347	1.68	1.09	5.49	0.57	1.66
45	347	1.92	1.29	6.65	0.96	2.25
60	347	2.12	1.71	7.70	1.07	2.78

In considering possible reactions of mixtures of hydrogen chloride and sulfide on iron, information on equilbria in the system ferrous sulfide–ferrous chloride–hydrogen chloride–hydrogen sulfide is desirable and has been reported (*9*). Calculations made from the equilibrium data indicated that at 314° C. in a 1 to 1 mixture of hydrogen chloride and sulfide under an atmosphere total pressure the stable solid phase is $FeCl_2$, while at 347° C. the stable solid phase is $FeS_{1.14}$. This would indicate that at 314° iron sulfide could form only by reaction of hydrogen sulfide with iron and not by reaction with iron chloride. This probably explains why at this temperature the amount of iron sulfide does not accumulate with time but actually appears to be less after the longer periods. Although hydrogen sulfide may react with iron chloride at 347° C., both iron chloride and iron sulfide accumulate with time. This probably indicates that reaction between hydrogen sulfide and iron chloride is slow in comparison with the reaction between iron and hydrogen chloride, even with a film interposed.

It is significant that the "deficiency" of iron sulfide at 314° C. is not compensated for by any detectable increase in the amount of iron chloride formed. In view of this fact and of the "deficiency" in iron sulfide at 347° where equilibrium conditions were favorable for its formation, it appears that iron chloride in the film actually inhibits the reaction of hydrogen sulfide (or sulfur) with iron. From the mechanism presented for growth of films in the pure gases, it is understandable how iron chloride may act to inhibit the formation of iron sulfide. It was pointed out that iron sulfide films are probably good conductors of iron ions in a hydrogen sulfide atmosphere, and that such films probably thickened by reaction of iron ions and electrons which had diffused through the lattice with sulfur at the gas-film interface. On the other hand, the experimental evidence indicates that iron chloride films are poor conductors of iron ions in a hydrogen chloride atmosphere; there is no reason to believe that they should be any better conductors in an atmosphere of hydrogen sulfide or sulfur, since sulfur probably will not dissolve in the iron chloride lattice. When iron chloride and iron sulfide are forming simultaneously on the surface, no continuous film of iron sulfide exists, and diffusion of iron ions from the metal surface to the gas-film interface through an iron sulfide layer can no longer take place because of the interposition of the poorly conducting iron chloride. Consequently, the number of iron ions and electrons reaching the gas-film interface will be much less, and the amount of iron sulfide formed will be correspondingly less.

These results offer further evidence that the assumed reaction mechanisms are the correct ones; if reaction of hydrogen sulfide with iron involved substantial diffusion of reactant along gross structural faults in the film rather than through the crystal lattice, there would be no reason for a diminution in the rate of iron sulfide formation since a film of iron sulfide and iron chloride should exhibit as many, if not more, structural defects than a film of iron sulfide. On the other hand, since hydrogen chloride apparently reacts with iron after diffusion through such structural defects, its reaction rate should be little affected by the difference between an iron chloride film and a film of iron chloride–iron sulfide.

DISCUSSION

Addition of hydrogen sulfide to hydrogen chloride had been expected to increase the formation of iron chloride, when equilibrium conditions were favorable, but no evidence of "cooperation" was found in the kinetic data. This does not prove, of course, that "cooperation" does not take place in the earliest stages of reaction.

In view of the inhibition of iron sulfide accumulation by iron chloride, it is apparent that films formed of organic sulfur and chlorine extreme-pressure additives must contain a large proportion of iron chloride if they are more than a few molecular layers thick. Another important consequence of this inhibition is that, apart from their function in improving extreme-pressure lubrication, chlorine additives in sulfur-chlorine stocks should prevent excessive attack of the hot parts of the gear surface by the sulfur additive which usually contains "active" sulfur.

These conclusions have been further supported by investigation of the reaction of chlorine and sulfur additives in oil solution on iron powder in the temperature range 200° to 300° C. These and other results will be presented in a forthcoming publication.

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Viscosities and Densities of Solvent–Vegetable Oil Mixtures

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A pycnometer and a viscometer suitable for use with volatile mixtures and for low-temperature determinations are described. Density and viscosity measurements are made from incipient crystallization to a temperature near the boiling point of the solvent for the complete binary systems cottonseed oil–Skellysolve B (commercial hexane), cottonseed oil–acetone, cotton seed oil–2-butanone, peanut oil–Skellysolve B, and soybean oil–Skellysolve B. From these data it is possible to construct for any of these systems the density-composition and viscosity-composition curves for any temperature as well as the density-temperature and viscosity-temperature curves for any composition. The various systems are compared and their idealities discussed. The density-composition curves for the binary systems of Skellysolve B with the three oils practically coincide. The viscosity-composition curves for these systems almost coincide up to about 60% by weight of oil and then diverge to the values for 100% oil. The same is true of the binary systems of cottonseed oil with the three solvents, except that the curves start to converge again at about 90% to meet at the 100% oil value. The applicability of these data to other random samples of these vegetable oils is discussed.

WITH the introduction and increasing use of solvent extraction and low-temperature solvent crystallization in processing vegetable oils, the need for data on the viscosities and densities of oil-solvent mixtures over the pertinent temperature range has become apparent, particularly in connection with the designing of processing equipment. Data for mixtures of soybean oil with hexane, ethylene dichloride, and trichloroethylene at 25°, 37.8°, and 50° C. were reported by Johnstone, Spoor, and Goss (*3*). Keulegan (*4*) determined the kinematic viscosities of mixtures of poppyseed, neat's-foot, castor, or linseed oils with various solvents between −18° and 30° C. Some isolated values on mixtures of peanut, castor, or linseed oil with toluene were reported by Tausz and Rabl (*6*). The present investigation was undertaken to determine the variation of density and viscosity as a function of oil concentration and temperature for various binary systems of cottonseed, peanut, or soybean oils with Skellysolve B, acetone, or 2-butanone, from the point of incipient crystallization to a temperature near the boiling point of the solvent.

The cottonseed oil was refined, bleached, and winterized, and had a Wijs iodine number of 110.6 and 0.11% free fatty acid. It was winterized in admixture with Skellysolve B at −17° C. using a solvent-oil ratio of 1 to 1 by weight. The peanut oil was a refined oil, winterized in admixture with Skellysolve B at −20° C. using a solvent-oil ratio of 3 to 1 by weight. It had a Wijs iodine value of 92.6 and a free fatty acid content of 0.41%. The soybean oil was a commercial sample of an edible oil having a Wijs iodine value of 132.6 and containing 0.10% free fatty acid.

Skellysolve B, a commercial hexane (*2*), was used as received without further treatment. Acetone (C.P. grade) and 2-butanone (Eastman Kodak practical grade) were purified by treating with potassium permanganate, drying over anhydrous potassium carbonate, and finally rectifying by a thirty-plate, helix-packed distilling column, operating at 40% take-off. The refractive indices (n_D^{25}) of the purified acetone and 2-butanone were 1.3568 and 1.3764, respectively.

Measurements below room temperature were made in a thermostat-controlled ethanol bath. The bath liquid was cooled by circulation through copper coils, immersed in a second bath containing a sludge of solid carbon dioxide and ethanol. A sensitive mercury thermoregulator was employed to actuate the circulating pump. This type of regulation provided a temperature control, as recorded by a mercury thermometer, of ±0.05° C. at temperatures as low as −20° C., which was the lowest temperature required. A conventional aquarium water bath with thermostatic control within at least ±0.05° C. was employed in the measurements above room temperature.

Densities were determined in a 25-ml. Pyrex pycnometer (Figure 1) consisting of expansion chamber *A* for densities below room temperature, capillary plug *B*, and a main or equilibrium bulb, *C*. In determining densities below room temperature, the main bulb and plug were filled and a small amount of

Table I. Density and Viscosity Data for Cottonseed Oil–Skellysolve B Mixtures

Wt. % of Oil	−20° C.	−10° C.	0° C.	+10° C.	+25° C.	+40° C.
			Density, Gram per Ml.			
0.00	0.7131	0.7066	0.6980	0.6908	0.6773	0.6637
11.15	0.7373	0.7294	0.7208	0.7121	0.6993	0.6859
19.22	0.7524	0.7445	0.7350	0.7276	0.7149	0.7020
29.06	0.7735	0.7659	0.7569	0.7494	0.7369	0.7245
38.98	0.7935	0.7855	0.7772	0.7693	0.7574	0.7452
49.00	0.8160	0.8087	0.8010	0.7931	0.7818	0.7697
58.28	0.8378	0.8302	0.8224	0.8149	0.8036	0.7924
71.73	....	0.8633	0.8555	0.8485	0.8374	0.8266
78.76	....	0.8813	0.8740	0.8669	0.8561	0.8455
88.00	....	0.9073	0.9004	0.8933	0.8830	0.8725
100.00	....	....	0.9322	0.9253	0.9151	0.9056
			Viscosity, Centipoises			
0.00	0.54	0.48	0.43	0.39	0.33	0.29
11.15	0.83	0.71	0.62	0.55	0.46	0.40
19.22	1.12	0.97	0.84	0.74	0.62	0.54
29.06	1.74	1.48	1.25	1.07	0.88	0.74
38.98	2.89	2.32	1.90	1.59	1.26	1.04
49.00	5.46	4.06	3.22	2.64	1.95	1.54
58.28	....	7.14	5.43	4.29	3.01	2.30
71.73	....	18.60	13.00	9.61	6.25	4.50
78.76	....	34.02	22.54	15.84	9.80	6.75
88.00	....	90.4	54.79	34.87	19.91	12.79
100.00	....	....	198.5	112.3	54.76	31.48

the mixture was introduced into bulb *A*. The pycnometer was then immersed in the bath until temperature equilibrium was attained. Excess mixture was pipetted out of bulb *A*, which was then removed, cleaned, dried, and replaced on the pycnometer. The whole was then removed from the bath, allowed to reach room temperature, dried, and weighed. Weighings were made as soon as practical, to minimize solvent evaporation through the ground glass joints, and were corrected for buoyancy of air. An additional correction was applied to densities determined below 0° C. to compensate for the volume change of the pycnometer. Determinations were made in sequence, beginning at the lowest temperature. Pycnometers were calibrated with water at 25° C.

Viscosities were determined in the modified Ostwald viscometer shown in Figure 1. Standard taper joints were used in both arms of the viscometer to facilitate connection, through three-way stopcock *H*, to a gas buret. The latter contained dry air which could be forced into arm *D* of the viscometer under a slight pressure by means of a mercury leveling bulb. Bulb *E* was filled by increasing the pressure in the gas buret and adjusting three-way stopcock *H* to apply pressure to arm *D* of the viscometer. After the liquid level had dropped to point 3 in arm *D*, the stopcock was turned to equalize the pressure in both arms of the viscometer, and the flow time between points 1 and 2 was recorded. A closed system was thus employed throughout the viscosity measurements to minimize evaporation of solvent and also to prevent moisture condensation at the lower temperatures.

Determinations on a system of mixtures at any one temperature were completed within a period of several hours with in-

Table II. Density and Viscosity Data for Cottonseed Oil–Acetone Mixtures

Wt. % of Oil	−10° C.	0° C.	+10° C.	+25° C.	+40° C.
		Density, Grams per Ml.			
0.00	0.8218	0.8111	0.8017	0.7850	0.7678
9.53	[a]	0.8227	0.8122	0.7960	0.7797
19.44	[a]	0.8327	0.8233	0.8075	0.7919
29.99	[a]	0.8440	0.8351	0.8203	0.8052
39.64	[a]	0.8558	0.8462	0.8322	0.8177
48.51	0.8749	0.8664	0.8573	0.8438	0.8296
59.26	0.8875	0.8790	0.8707	0.8577	0.8446
68.53	0.8978	0.8905	0.8824	0.8702	0.8589
78.96	0.9116	0.9038	0.8960	0.8844	0.8729
88.86	0.9245	0.9173	0.9100	0.8991	0.8884
100.00	....	0.9322	0.9253	0.9151	0.9056
		Viscosity, Centipoises			
0.00	0.45	0.41	0.37	0.32	0.29
9.53	[a]	0.55	0.50	0.43	0.37
19.44	[a]	0.82	0.72	0.60	0.51
29.99	[a]	1.29	1.09	0.88	0.74
39.64	[a]	2.03	1.66	1.29	1.06
48.51	4.11	3.12	2.50	1.94	1.47
59.26	7.35	5.50	4.28	3.16	2.33
68.53	13.11	9.47	7.18	5.00	3.58
78.96	29.82	19.99	14.20	9.22	6.35
88.86	82.8	50.82	32.78	19.16	12.30
100.00	....	198.5	112.3	54.76	31.48

[a] Separated into two liquid phases.

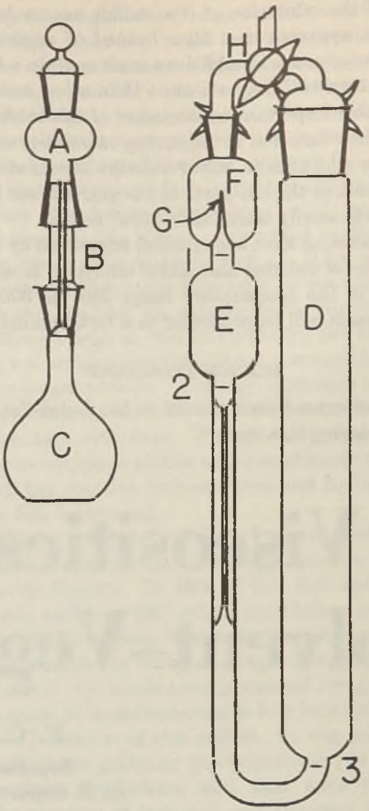


Figure 1. Pycnometer and Viscometer

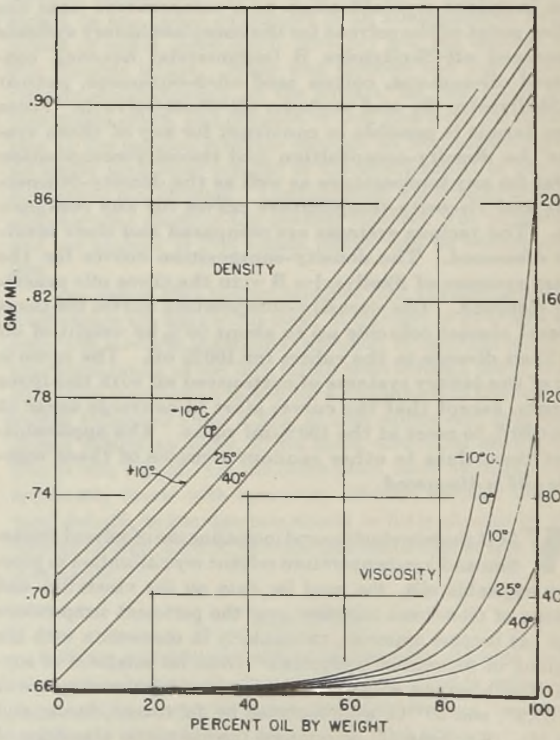


Figure 2. Density-Composition and Viscosity-Composition Isotherms for the System Cottonseed Oil–Skellysolve B

Table III. Density and Viscosity Data for Cottonseed Oil–2-Butanone Mixtures

Wt. % of Oil	−20° C.	−15° C.	−10° C.	0° C.	+10° C.	+25° C.	+45° C.	+60° C.
			Density, Grams per Liter					
0.00	....	0.8384	0.8345	0.8249	0.8147	0.7996	0.7785	0.7627
13.46	0.8577	0.8477	0.8479	0.8381	0.8278	0.8137	0.7947	0.7788
18.75	0.8624	0.8578	0.8530	0.8433	0.8338	0.8194	0.7994	0.7851
27.58	....	....	0.8619	0.8524	0.8426	0.8293	0.8101	0.7955
37.04	....	....	0.8716	0.8621	0.8533	0.8397	0.8222	0.8083
47.28	....	....	0.8812	0.8726	0.8638	0.8512	0.8332	0.8202
55.92	....	....	0.8898	0.8821	0.8732	0.8607	0.8440	0.8313
66.47	....	....	0.9014	0.8932	0.8851	0.8731	0.8577	0.8455
74.81	....	....	0.9103	0.9025	0.8948	0.8831	0.8681	0.8569
89.51	....	....	0.9260	0.9186	0.9116	0.9006	0.8870	0.8762
100.00	....	....	....	0.9322	0.9253	0.9151	0.9015	0.8926
			Viscosity, Centipoises					
0.00	....	0.61	0.58	0.51	0.47	0.39	0.33	0.29
13.46	....	1.61	0.96	0.83	0.73	0.61	0.53	0.41
18.75	....	1.23	1.13	0.97	0.85	0.71	0.57	0.49
27.58	....	....	1.64	1.37	1.19	0.97	0.76	0.66
37.04	....	....	2.55	2.09	1.75	1.39	1.05	0.89
47.28	....	....	4.27	3.30	2.71	2.11	1.53	1.28
55.92	....	....	6.75	5.13	4.08	3.01	2.13	1.75
66.47	....	....	12.86	9.40	7.11	4.96	3.39	2.69
74.81	....	....	23.70	16.41	11.92	7.84	5.06	3.89
89.51	....	....	94.3	56.69	36.38	20.85	11.69	8.26
100.00	....	....	....	198.5	112.3	54.76	26.34	16.84

dividual viscometers chosen to give approximately the same flow time.

Runs were made in sequence beginning at the lowest temperature and thus obviating any refilling in determinations below room temperature; above room temperature, fresh samples were used for each determination. To keep the total volume constant as temperature was raised, the viscometer was designed with an overflow tip *G* of sufficient height to permit discharge of excess volume, resulting from thermal expansion, into bulb *F*. The viscometers were calibrated at 25° C. with standard viscosity oils supplied by the National Bureau of Standards. For the accuracy and range considered, no temperature correction for the viscometer is necessary (*1*). The viscosities reported are believed to be accurate within ±0.5%.

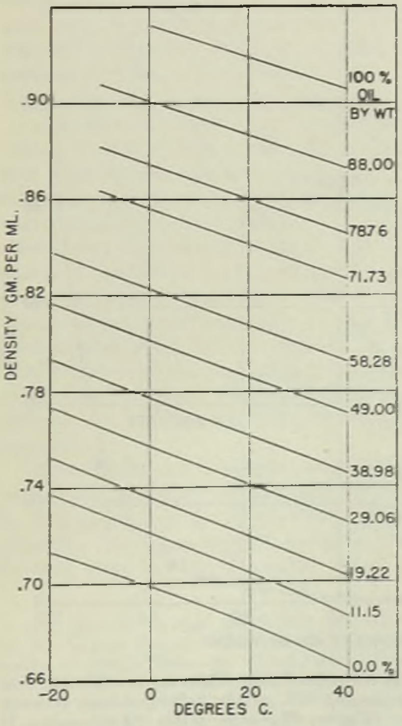
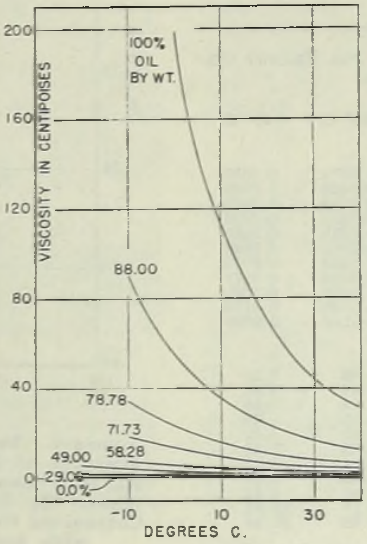


Figure 3. Density-Temperature Curves at Constant Composition for the System Cottonseed Oil–Skellysolve B

Figure 4. Viscosity-Temperature Curves at Constant Composition for the System Cottonseed Oil–Skellysolve B



The results of density and viscosity measurements for the binary mixtures of oil and solvent are shown in Tables I to V. The density-composition and viscosity-composition isotherms were plotted for each oil-solvent system; Figure 2, representing the data for cottonseed oil–Skellysolve B mixtures given in Table I, is typical of the results for each case. A family of curves is also obtained when these data are plotted to show the change in density (Figure 3) and viscosity (Figure 4) with temperature for the compositions investigated.

The density-composition isotherms of the solvent-oil mixtures investigated are not straight lines but are slightly concave upward. An empirical equation was fitted to each of the isotherms of the form,

$$D = a + bP + cP^2 + dP^3$$

where D = density at composition P
a, b, c, d = arbitrary constants

The constants so determined are listed in Table VI. The average deviation of the experimental data from the curves represented by these equations is ±0.0004.

The curves of Figure 3 can be constructed directly by solving the equations of Table VI at the various compositions. For example, the curve for 11.15% cottonseed oil with Skellysolve B could be obtained by substituting 11.15 for P in each of the equations for this system, solving for D, and thus finding the value of density at that temperature. These equations can be used to construct the density-temperature curve for any desired mixture of oil and solvent, from which it is possible to read accurately the density of this mixture at any desired temperature.

Conversely, it is possible to find the composition of a mixture of the cottonseed oil and Skellysolve B from its density at a given temperature. To accomplish this, the density-composition curve for that temperature is plotted from the points where this temperature coordinate intersects the curves of Figure 3.

Similar families of curves can be drawn for the density of the other solvent-oil systems studied. In each case the data of Table VI are sufficient to determine the density of any composition at a given temperature or the composition corresponding to any density at a given temperature.

The data of Table VI were used to test the ideality of behavior of these oil-solvent systems. If two substances form an ideal solution, there is by definition no change in total volume on mixing; therefore, when the density is plotted against volume per cent, or when specific volume is plotted against weight per cent, a straight line is obtained. Table VII shows the deviation from a straight-line relation of the specific volumes of various oil mixtures at 10° C. By this test acetone and 2-butanone at this temperature seem to approach ideality in mixtures with cottonseed oil. Skellysolve B, on the other hand, deviates slightly from ideality with cottonseed, peanut, or soybean oils, the maximum deviations being

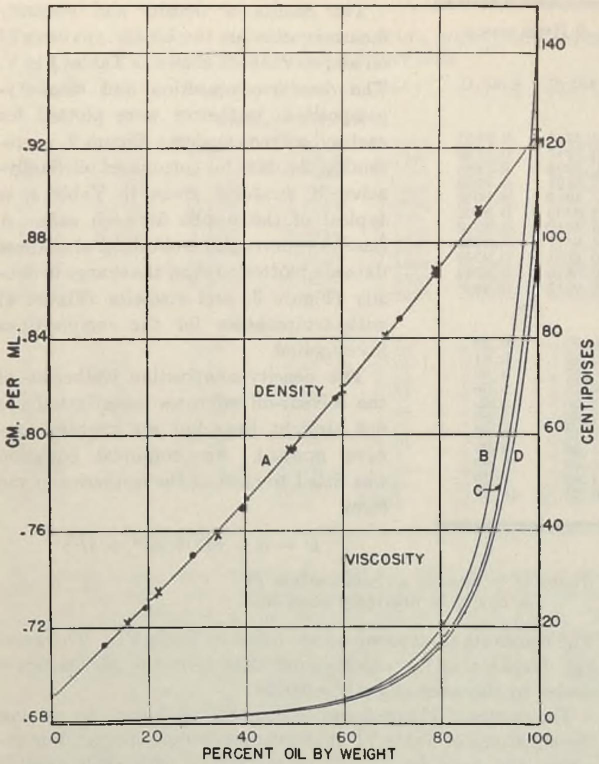


Figure 5. Density-Composition Curve at 10° C. for Mixtures of Skellysolve B with Cottonseed Oil (Curve *A*), with Peanut Oil (•), and with Soybean Oil (×); Viscosity-Composition Curve at 10° C. for Mixtures of Skellysolve B with Peanut Oil (Curve *B*) with Cottonseed Oil (Curve *C*), and with Soybean Oil (Curve *D*)

0.0073, 0.0059, and 0.0064 ml. per gram, respectively. Similar calculations at 40° C. show that the corresponding deviations at that temperature are greater (0.0105, 0.0097, and 0.0097 ml. per gram, respectively).

The viscosity-composition isotherms for cottonseed oil–Skellysolve B mixtures in Figure 2, which are typical of all the oil-solvent systems studied, show that the viscosity of an oil is decidedly changed by adding 10% of its weight of solvent especially at lower temperatures; on the other hand, the viscosity of the solvent is changed very little by adding 100% of its weight of oil. This is also apparent from the curves of Figure 4 which were constructed from the original data to show the change of viscosity with temperature for the compositions studied. The corresponding curves for other compositions could be constructed by reading the points for that composition from the viscosity curves in Figure 2. By graphical interpolation the viscosity at

Table IV. Density and Viscosity Data for Peanut Oil–Skellysolve B Mixtures

Wt. % of Oil	−10° C.	0° C.	+10° C.	+25° C.	+40° C.
		Density, Grams per Ml.			
0.00	0.7066	0.6980	0.6908	0.6773	0.6637
11.35	0.7286	0.7210	0.7124	0.6994	0.6862
19.42	0.7442	0.7366	0.7285	0.7156	0.7029
28.72	0.7628	0.7557	0.7475	0.7351	0.7225
39.63	0.7865	0.7799	0.7707	0.7588	0.7469
49.04	0.8072	0.7996	0.7919	0.7802	0.7681
63.07	....	0.8323	0.8249	0.8139	0.8025
68.96	....	0.8471	0.8398	0.8288	0.8177
76.45	....	0.8659	0.8587	0.8480	0.8372
89.90	....	0.9011	0.8940	0.8838	0.8736
100.00	....	....	0.9231	0.9122	0.9023
		Viscosity, Centipoises			
0.00	0.48	0.43	0.39	0.33	0.29
11.35	0.72	0.64	0.57	0.48	0.42
19.42	0.99	0.86	0.78	0.64	0.55
28.72	1.51	1.27	1.10	0.89	0.75
39.63	2.59	2.11	1.76	1.37	1.12
49.04	4.37	3.42	2.78	2.08	1.63
63.07	....	7.97	6.10	4.29	3.12
68.96	....	12.07	8.99	6.05	4.24
76.45	....	21.21	15.10	9.55	6.61
89.90	....	....	47.52	26.14	15.81
100.00	....	....	142.2	66.68	36.88

Table V. Density and Viscosity Data for Soybean Oil–Skellysolve B Mixtures

Wt. % of Oil	−20° C.	−10° C.	0° C.	+10° C.	+25° C.	+40° C.
			Density, Grams per Ml.			
0.00	0.7131	0.7066	0.6980	0.6908	0.6773	0.6637
15.44	0.7439	0.7379	0.7294	0.7209	0.7081	0.6948
21.61	0.7566	0.7492	0.7417	0.7334	0.7209	0.7083
34.13	0.7809	0.7738	0.7666	0.7582	0.7463	0.7341
40.30	0.7967	0.7902	0.7820	0.7741	0.7620	0.7501
49.21	0.8173	0.8092	0.8018	0.7941	0.7824	0.7707
60.04	0.8421	0.8346	0.8272	0.8196	0.8083	0.7970
69.20	....	0.8561	0.8486	0.8413	0.8306	0.8193
79.31	....	0.8835	0.8766	0.8692	0.8586	0.8484
88.55	....	0.9084	0.9011	0.8943	0.8838	0.8736
100.00	....	0.9410	0.9347	0.9276	0.9175	0.9075
			Viscosity, Centipoises			
0.00	0.54	0.48	0.43	0.39	0.33	0.29
15.44	0.96	0.83	0.72	0.64	0.54	0.46
21.61	1.24	1.06	0.91	0.80	0.67	0.56
34.13	2.26	1.84	1.53	1.30	1.06	0.85
40.30	3.10	2.49	2.04	1.70	1.34	1.12
49.21	5.10	3.40	3.15	2.57	1.97	1.52
60.04	....	7.51	5.69	4.48	3.26	2.44
69.20	....	14.30	10.34	7.83	5.43	3.81
79.31	....	32.23	21.88	15.40	9.88	6.68
88.55	....	80.0	49.03	31.78	18.61	11.95
100.00	....	....	172.9	99.7	50.09	28.86

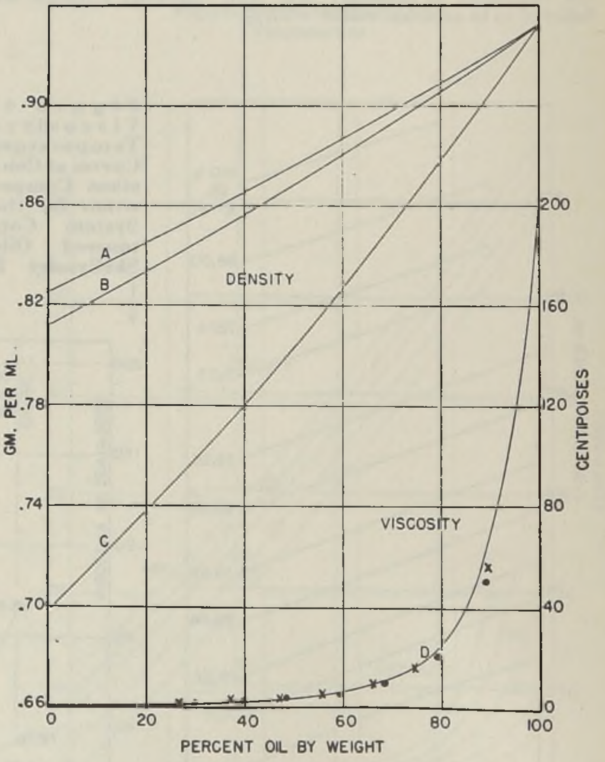


Figure 6. Density-Composition Curves at 0° C. for Mixtures of Cottonseed Oil with 2-Butanone (Curve *A*), with Acetone (Curve *B*), and with Skellysolve B (Curve *C*); Viscosity-Composition Curve at 0° C. for Cottonseed Oil Mixtures with Skellysolve B (Curve *D*), with Acetone (•), and with 2-Butanone (×)

TABLE VI. CONSTANTS FOR DENSITY-COMPOSITION EQUATION OF OIL-SOLVENT MIXTURES AT DIFFERENT TEMPERATURES

Constants	−20° C.	−10° C.	0° C.	+10° C.	+25° C.	+40° C.	+60° C.
			Cottonseed Oil–Skellysolve B Mixtures				
a	0.7131	0.7066	0.6980	0.6908	0.6773	0.6637	......
b	2.0875×10^{-3}	2.0511×10^{-3}	1.9560×10^{-3}	1.9085×10^{-3}	1.9146×10^{-3}	1.9469×10^{-3}	......
c	-3.000×10^{-6}	-1.221×10^{-6}	2.582×10^{-6}	3.356×10^{-6}	4.456×10^{-6}	4.320×10^{-6}	......
d	6.87×10^{-9}	4.32×10^{-9}	1.25×10^{-9}	1.02×10^{-9}	1.83×10^{-9}	4.14×10^{-9}	......
			Cottonseed Oil–Acetone Mixtures				
a	......	......	0.8111	0.8017	0.7850	0.7678	......
b	......	......	1.1101×10^{-3}	1.0717×10^{-3}	1.1252×10^{-3}	1.2050×10^{-3}	......
c	......	......	4.59×10^{-10}	1.424×10^{-6}	1.838×10^{-6}	1.380×10^{-6}	......
d	......	......	1.02×10^{-8}	2.31×10^{-9}	-9.53×10^{-10}	3.68×10^{-9}	......
			Cottonseed Oil–2-Butanone Mixtures				
a	......	0.8345	0.8249	0.8147	0.7996	0.7785[*]	0.7627
b	......	9.975×10^{-4}	9.969×10^{-4}	1.0085×10^{-3}	1.0469×10^{-3}	1.1292×10^{-3}	1.1595×10^{-3}
c	......	-2.500×10^{-7}	4.990×10^{-8}	3.719×10^{-7}	5.087×10^{-7}	3.728×10^{-7}	8.760×10^{-7}
d	......	6.25×10^{-9}	6.92×10^{-9}	5.99×10^{-9}	5.53×10^{-9}	6.45×10^{-9}	5.06×10^{-9}
			Peanut Oil–Skellysolve B Mixtures				
a	......	0.7067	0.6980	0.6908	0.6773	0.6637	......
b	......	1.9344×10^{-3}	1.9333×10^{-3}	1.8212×10^{-3}	1.8742×10^{-3}	1.9338×10^{-3}	......
c	......	-2.435×10^{-6}	1.835×10^{-6}	4.503×10^{-6}	4.594×10^{-6}	3.629×10^{-6}	......
d	......	9.86×10^{-9}	2.03×10^{-8}	5.49×10^{-9}	1.37×10^{-9}	9.25×10^{-9}	......
			Soybean Oil–Skellysolve B Mixtures				
a	0.7131	0.7066	0.6980	0.6908	0.6773	0.6637	......
b	1.9158×10^{-3}	1.9797×10^{-3}	1.9686×10^{-3}	1.8505×10^{-3}	1.9277×10^{-3}	2.0030×10^{-3}	......
c	3.627×10^{-6}	8.787×10^{-7}	1.938×10^{-6}	4.777×10^{-6}	3.817×10^{-6}	2.529×10^{-6}	......
d	4.12×10^{-9}	2.82×10^{-6}	2.03×10^{-9}	3.68×10^{-9}	9.18×10^{-9}	1.80×10^{-9}	......

[*] These values are for 45° C.

TABLE VII. DEVIATION[a] FROM IDEALITY OF SPECIFIC VOLUME OF OIL-SOLVENT MIXTURES AT 10° C.

Solvent	Oil	0% Oil	10% Oil	20% Oil	30% Oil	40% Oil	50% Oil	60% Oil	70% Oil	80% Oil	90% Oil	100% Oil
Skellysolve B	Cottonseed	0.0000	0.0036	0.0055	0.0067	0.0072	0.0073	0.0071	0.0065	0.0060	0.0054	0.0000
Skellysolve B	Peanut	0.0000	0.0023	0.0037	0.0042	0.0049	0.0059	0.0050	0.0048	0.0034	0.0017	0.0000
Skellysolve B	Soybean	0.0000	0.0022	0.0035	0.0048	0.0056	0.0062	0.0064	0.0053	0.0039	0.0032	0.0000
Acetone	Cottonseed	0.0000	0.0001	0.0001	0.0002	0.0002	0.0000	0.0002	0.0000	0.0001	0.0004	0.0000
2-Butanone	Cottonseed	0.0000	0.0005	0.0006	0.0007	0.0005	0.0004	0.0002	0.0000	−0.0001	−0.0004	0.0000

[a] Deviation equals the specific volume (ml./gram), assuming ideality, minus the experimental value.

any temperature for that composition could then be determined. The curves in Figure 4 can be used, in turn, to construct the viscosity-composition curve for any desired temperature. Examination of Figure 4 shows that the thermal coefficient of viscosity is relatively small for oil-solvent mixtures up to approximately 60% of oil and that it then becomes increasingly larger, especially at the lower temperatures.

Application of the data here presented, particularly viscosity values, to any random cottonseed, peanut, or soybean oil mixture with the solvents mentioned must be modified by a consideration of variations in composition such as is evidenced by the iodine value of the oil in question. Previous investigations (*5*, *7*) showed that the viscosity of an oil varies according to its iodine value. It is therefore only reasonable to expect a corresponding effect with solvent mixtures of oils. This variation will probably be particularly noticeable at high oil concentrations and temperatures below 25° C. The data of Johnstone, Spoor, and Goss (*3*) for soybean oil (iodine value 130.1) and Skellysolve B show close agreement with the data here reported, the largest deviation at 25° C. being 0.3% for density and about 3% for viscosity[1].

The densities and viscosities of Skellysolve B mixtures with cottonseed, peanut, or soybean oil at 10° C. are plotted in Figure 5. The density curves for these three binary systems practically coincide. The corresponding viscosity-composition curves also lie very close together, especially for oil concentrations up to about 70%; above 70% they start to spread slightly to approach the values for the pure oils (112.3, 142.2, and 99.7 centipoises, respectively). It seems probable that for oils of the same iodine value the viscosity-composition curves with a given solvent would show even closer agreement.

Figure 6 shows the density-composition and viscosity-composition curves at 0° C. for mixtures of cottonseed oil with Skellysolve B, acetone, or 2-butanone, respectively. As would be expected, the density curves are different for each solvent. The viscosity curves, however, are very close together, especially for oil percentages below 75%. The viscosity curve for mixtures with Skellysolve B is slightly lower than those with 2-butanone and acetone at low oil concentrations, and crosses these curves at about 55 and 80% oil concentration, respectively, so that it lies as much as 15% above the other two curves for high oil concentrations. At higher temperatures the agreement between the three viscosity curves is much closer.

ACKNOWLEDGMENT

The authors are indebted to W. S. Singleton and H. R. R. Wakeham for their interest and cooperation in this work, and to the Analytical Section for certain analyses.

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[1] The data for viscosity and fluidity reported by these authors are incorrect because the kinematic viscosities actually determined were converted to absolute values by inadvertently dividing instead of multiplying by the density. For this reason, all the viscosities which they reported must be corrected by multiplying by the square of the density, and the fluidities must be similarly corrected by dividing by the same quantity (personal communication). The viscosity values were thus corrected before the comparison with our values was made.

OXIDATION OF LUBRICATING OILS

Mechanism of Sulfur Inhibition

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The reactions by which organic sulfur compounds stabilize normally refined lubricating oils against oxidation have been studied. Monothioethers, which contain at least one aliphatic or cycloaliphatic group attached to the sulfur atom, appear to be the most effective sulfur-type antioxidants tested. Their effectiveness seems to vary with the rapidity with which they reduce peroxides. The thioethers studied were relatively resistant to autoxidation but susceptible to oxidation by peroxides. Thioethers function as inhibitors as the result of reducing peroxides, thus breaking the oxidation chain. In this reaction thioethers are converted to sulfoxides and probably to sulfones. The latter two types of compounds are readily autoxidized and in part are so converted to sulfonic acids.

THE first paper of this series (*3*) demonstrated that the oxidation stability of normally refined petroleum lubricating oils is the result of small quantities of natural sulfur compounds and not of any inherent stability of the hydrocarbon fraction itself. In the absence of the natural sulfur compounds the hydrocarbon fraction oxidizes rapidly and, in the initial stages of the reaction, autocatalytically. The rate of oxidation of an inhibitor-free white oil was shown to be a function of the concentration of the peroxide formed in the oil, obeying the empirical relation:

$$\frac{d(O_2)}{dt} = -k\,(\text{peroxide}) \qquad (1)$$

Likewise, when a peroxide-containing white oil was heated with a sulfur-containing lubricating oil in the absence of air, the peroxides were reduced. It was concluded, therefore, that the overall oxidation rate of a normally refined lubricating oil was determined by a combination of reactions similar to those established for white oil. These reactions are the peroxide-catalyzed autoxidation of the hydrocarbons and the reduction of these peroxides by reaction with the natural sulfur compounds present in the oil. It is believed that the oxidation of the hydrocarbon fraction is a chain reaction in which peroxides play an essential part and that inhibitors such as the natural sulfur compounds serve to break the reaction chains by reducing the peroxides. The oxidation of the hydrocarbon fraction thus induces oxidation of the sulfur compounds in a manner analogous to the induced oxidation of alcohols and anthracene studied by Bäckstrom and co-workers (*1*). The previous article (*3*) mentioned that in the course of reducing peroxides the natural sulfur compounds present in the oil were themselves oxidized to deleterious products. The nature of these products was not determined, but it was shown that they were probably responsible in part for the development of undesirable service characteristics in many oxidized oils. It therefore seemed of fundamental importance to study in detail the reactions at work during the oxidation of a sulfur-inhibited oil. Such a study might shed light on inhibition in general, and specific information might be gained on the development of undesirable characteristics during the oxidation of sulfur-inhibited lubricating oils. The present paper reports the results of such an investigation.

EFFECT OF SULFUR COMPOUNDS ON HYDROCARBON OXIDATION

Initially, attempts were made to extract the natural sulfur compounds from various finished lubricating oils. The methods McKittrick (*11*) found so useful for isolating sulfur compounds from kerosene failed in this instance. The mercuric chloride addition compounds of the sulfur compounds present in lubricating oil either do not form or are completely soluble in the oils. Some concentration of the sulfur compounds could be achieved by selective adsorption on fuller's earth, but the results were far from quantitative. The sulfur-rich extracts obtained proved to be intractable, and could not be separated or purified by ordinary chemical means. There was every indication that, as might be expected, the sulfur-containing fractions of the oils were quite as complicated mixtures of individual compounds as the hydrocarbons. These extract fractions did inhibit the oxidation of sulfur-free oils.

In view of the complexities of the natural sulfur compounds, the "synthetic method" was adopted for the present study, and a series of sulfur compounds similar to those which might be expected in lubricating oils was prepared and tested. The significant properties of these materials are given in Table I. Several are new compounds which were synthesized and carefully purified before testing.

Figures 1, 2, and 3 show the effect of a number of these sulfur compounds on the oxidation rates at 171° C. (340° F.) of two desulfured lubricating oils. The absorption of oxygen as recorded was measured in an apparatus of the type described by Dornte (*4*). Desulfured oils were chosen as base stocks so that the final blends would duplicate as closely as possible normally refined lubricating oils except for the substitution of synthetic sulfur compounds for the naturally occurring sulfur inhibitors. The properties of the original base oils and the desulfured oils are given in Tables II and III. Oil A is a moderately refined California naphthenic SAE 30 oil, E is a Pennsylvania SAE 30 oil, and F is a medicinal white oil. Unfortunately the data presented in Figures 1, 2, and 3 were compiled from runs that were often made with other objects in mind and so contain curves for two different base stocks and in some cases for varying concentrations of the inhibitors. As a broad generalization it may be said that all the monosulfides except the diaryl compounds were good inhibitors. The diaryl sulfides were inactive. This generalization was confirmed for a number of other symmetrical and unsymmetrical monosulfides not shown in the figures and for desulfured oils prepared from Pennsylvania, Gulf Coastal, California naphthenic, and California paraffinic stocks.

Members of several groups of sulfur compounds other than the sulfides were also tested (Figure 3). The compounds in which the sulfur was part of the thiophene ring were comparatively inactive. Mercaptans and disulfides were not so active on an equivalent sulfur basis as the corresponding monosulfides. Because of difficulty in preparation, no synthetic thiophanes were evaluated. It is believed, however, that thiophanes will behave similarly to the other aliphatic or cycloaliphatic monosulfides.

For more detailed study representative members of what appeared to be the three most interesting classes of sulfur compounds were chosen. Figure 4 shows their effect on the oxidation of a typical desulfured oil at 171° C. The sulfides were tested in desulfured base oil E. Oxidator curves for this oil and for the

Table I. Properties of Sulfur Compounds

Sulfur Compound	Boiling Point ° C.	Boiling Point Mm. Hg	Melting Point, ° C. Obsvd.	Melting Point, ° C. Recorded	% Sulfur Exptl.	% Sulfur Theory	n_D^{20}
Acetone diamyl mercaptole	109–111	2	......	......	24.6	25.8	1.4870
Bis(phenyl ethyl)sulfide	150–152	1.5	Liquid[a]	92 (*2*)	13.0	13.2	1.5842
Bis(phenyl propyl)sulfide	172–174	2	Liquid[a]	73 (*2*)	11.7	11.9	1.5687
Cetyl cyclohexyl sulfide	192–198	1.5	Liquid[a]	......	9.2	9.4	1.4793
Cetyl mercaptan	151–158	2	18	18 (*6*)	11.7	12.3	1.4632
Cetyl β-naphthyl sulfide	......	...	56	......	8.1	8.4	....
Cetyl phenyl sulfide	201–212	2	46	......	9.1	9.6	1.4937[b]
α-Cetyl thiophene	199–204	3	......	......	9.0	10.4	....
Dibenzothiophene	......	...	96–97	99 (*13*)	16.7	17.4	....
Dicetyl disulfide	......	...	47–48	50 (*6*)	11.3	12.5	....
Dicetyl sulfide	......	...	57.5	57.5 (*7*)	6.4	6.6	....
Dicetyl sulfone	......	...	94–95	100 (*9*)	6.2	6.2	....
Dicetyl sulfoxide	......	...	92	97–98 (*9*)	6.7	6.4	....
Phenyl α-naphthyl sulfide	175–176	2.5	41.5	41.5 (*10*)	..	13.5	....
Thianthrene			E. K. Co., White Label				

[a] Apparently slow to crystallize; melting points of $HgCl_2$ derivatives check Bermejo and Jiménez Herrera values.

[b] n_D^{50}.

Table II. Properties of Oils Studied

Oil Designation	Gravity, ° A.P.I.	Flash Point, ° F.	Viscosity, Saybolt Univ. Sec. 100° F.	Viscosity, Saybolt Univ. Sec. 210° F.	Viscosity Index	Pour Point, ° F.	A.S.T.M. Color	Neutralization No.	Conradson Carbon, %	Sulfur, %
A	21.3	385	627	56.5	8	−20	3	0.04	0.08	0.53
E	28.2	445	530	66.4	102	20	6	0.04	0.48	0.10
F	27.0	395	343	51.0	61	−25	Water-white	0.01	0.00	0.03

Table III. Effect of Sodium Treatment on Composition

Oil Designation	% Sulfur Orig.	% Sulfur Final	% Aromatic Rings Orig.	% Aromatic Rings Final	% Naphthene Rings Orig.	% Naphthene Rings Final	% Paraffin Side Chains Orig.	% Paraffin Side Chains Final	Specific Dispersion Orig.	Specific Dispersion Final
A	0.53	0.07	15	14	33	33	52	53	120	121
E	0.10	0.01	7	4	16	20	77	76	111	110

same oil before desulfurization are included in Figure 4 for comparison. Equimolar quantities of the sulfides were added in each case, and the sulfur content of the sulfide-inhibited oils was 0.13% plus a small amount of sulfur (less than 0.01%) left after sodium treatment. The sulfur content of the base oil before desulfurization was 0.10%.

Several conclusions can be drawn from Figure 4. The diaryl sulfide was completely inactive, the dialkyl sulfide was the most effective in the initial portion of the run, and the alkyl aryl sulfide was intermediate. The alkyl aryl sulfide, while less effective in the initial stages of the reaction than the dialkyl compound, gave rise to an autoinhibited type of oxidation. It is noteworthy that both the dicetyl sulfide and cetyl phenyl sulfide had the same order of activity as the natural sulfur compounds in original oil E.

Although the data showed that oils were inhibited by the addition of certain sulfides, they did not prove that the sulfides themselves, and not some of their oxidation products, were actually responsible for the inhibitory action. The effect of dicetyl sulfoxide and dicetyl sulfone on the oxidation of an oil was therefore studied. These compounds were synthesized and tested in the oxidator at 171° C., as solutions in desulfured oil A. Par-

FIG. 1

ANTIOXIDANT ACTION OF VARIOUS SULFIDES ON DESULFURED OIL A AT 171°C.

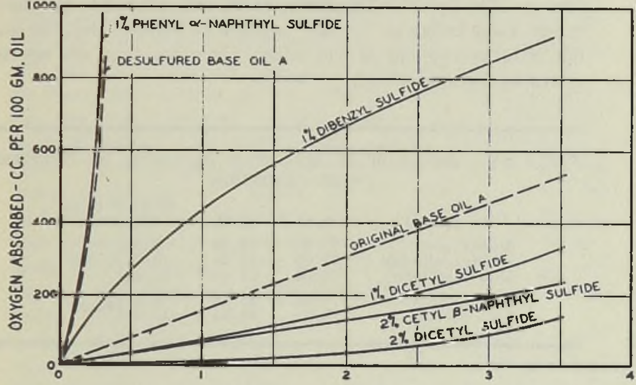


FIG. 2

ANTIOXIDANT ACTION OF VARIOUS SULFIDES ON DESULFURED OIL E AT 171°C.

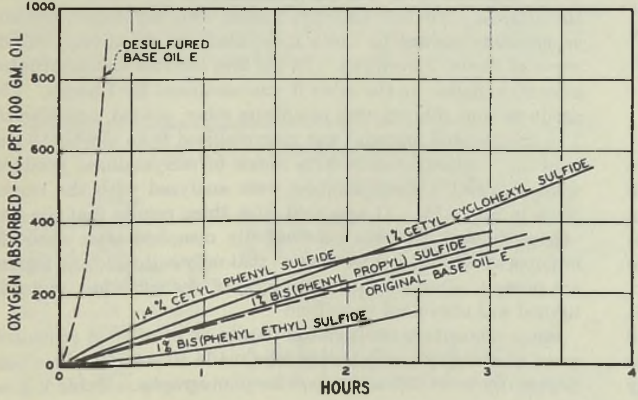


FIG. 3

ANTIOXIDANT ACTION OF VARIOUS SULFUR COMPOUNDS ON DESULFURED OIL A AT 171°C.

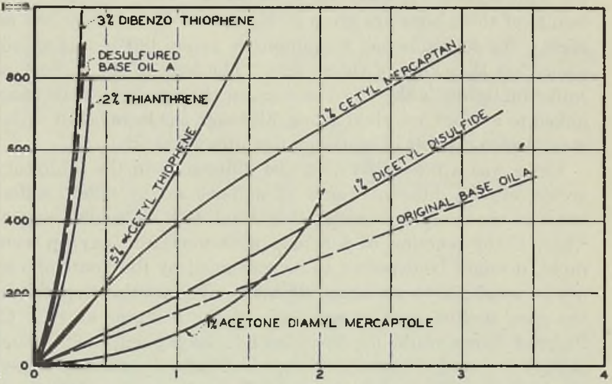


FIG. 4

EFFECT OF SULFIDE TYPE ON ANTIOXIDANT ACTION IN DESULFURED BASE OIL E AT 171°C.

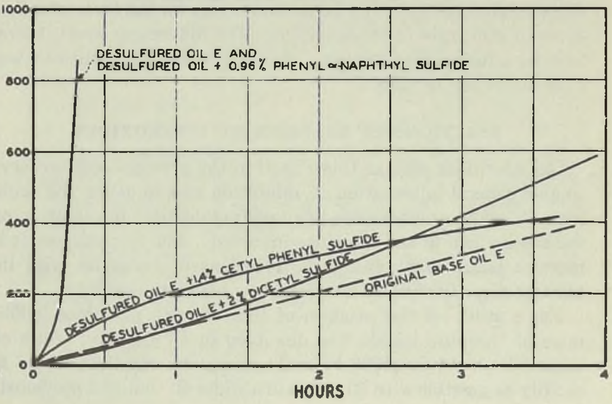


FIG. 5

ANTIOXIDANT ACTION OF DICETYL SULFIDE, SULFOXIDE, AND SULFONE ON DESULFURED OIL A AT 171° C.

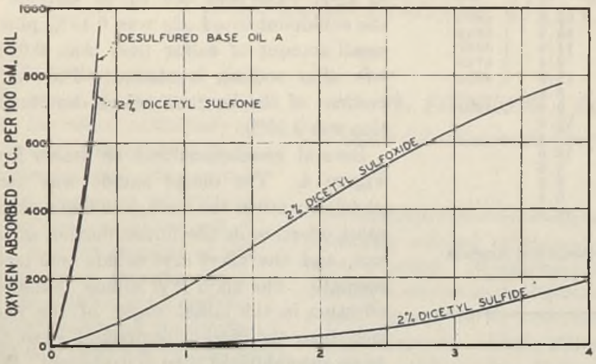
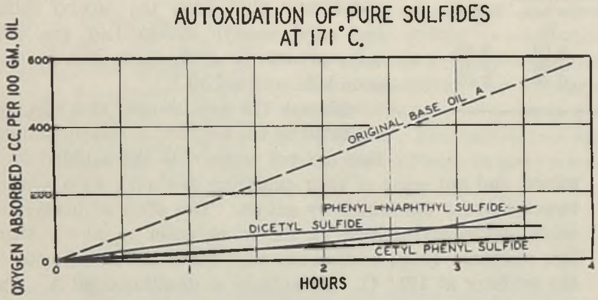


FIG. 6

AUTOXIDATION OF PURE SULFIDES AT 171° C.



ticular care was taken to remove all traces of dicetyl sulfide from the sulfoxide by repeated recrystallization from benzene. The results of these tests are given in Figure 5. The sulfone had no effect; the sulfoxide had an inhibitory action but it was appreciably less than that of the sulfide. The bulk of the activity of sulfur inhibitors is therefore resident in the divalent sulfur atom linked to at least one alkyl group, although the tetravalent sulfur atom is also capable of exerting an inhibitory action.

There was a possibility that the differences in the inhibitory action of the different types of sulfides might reflect differences in the rates with which they react with molecular oxygen. Thus, if the reaction of a sulfide with molecular oxygen were rapid, it might be expected to be consumed by this route and so not be available to act as an inhibitor. To test this hypothesis, the pure molten sulfides were run in the oxidator at 171° C. Figure 6 shows results for dicetyl sulfide, cetyl phenyl sulfide, and phenyl α-naphthyl sulfide. Because of lack of material, phenyl α-naphthyl sulfide was run in a different type of oxidator cell, and the results are not so accurate as in the other two examples. The curves show that the differences in inhibitory activity of the three sulfides could hardly be accounted for on the basis of differences in their rate of autoxidation. The differences must, therefore, be a function of the rates of reaction with oil peroxides, not with molecular oxygen.

REACTIONS OF SULFIDES WITH PEROXIDES

Oxidator data such as those cited in the previous section serve to give general information on inhibition and to define the problem. They are not capable of providing detailed information on the mechanism of the reactions involved. For this purpose it is more satisfactory to study the reactions of peroxides with inhibitors directly and in a simpler system than the oxidator.

For a study of the reaction of sulfides with peroxides 0.0031 mole of the pure sulfide was dissolved in 10 grams of white oil heated to 65.6° C. (150° F.). The solution was then mixed as rapidly as possible with 50 grams of a white oil that had previously been autoxidized to a peroxide number of 360. This peroxidized oil was also at 65.6° C. at the time of mixing. The mixture, contained in a stoppered flask, was immersed in a bath thermostatically controlled at 65.6° C. Samples were pipetted out periodically, weighed, and titrated by the method of Wheeler (*14*). The results were calculated as peroxide numbers—i.e., cc. of oxygen (standard temperature and pressure) per hundred grams of oil. A peroxide number of 100 is equal to 0.0089 equivalent of peroxide per 100 grams of oil. By controlling all of the conditions with the utmost care, a reproducibility of ±5% could be obtained. These figures do not represent the total peroxide oxygen in the lubricating oil but only a relatively constant fraction of it; for example, certain dialkyl peroxides are not titrated at all. If the reaction of the peroxides with hydriodic acid is allowed to proceed for more than the specified 3 minutes, as shown by Yamada (*16*), or at higher than room temperatures, significantly higher numbers result.

Figure 7 gives peroxide reduction curves for dicetyl sulfide and dicetyl sulfoxide. A blank run in which the sulfur compound was omitted showed no measurable drop in peroxide number over the time interval of these tests. If the initial reactions of the sulfur compounds were

$$R_2S + R'OOH \longrightarrow R_2S{=}O + R'OH \tag{2}$$

$$R_2S{=}O + R'OOH \longrightarrow R_2SO_2 + R'OH \tag{3}$$

it may be calculated from the quantities taken that, for the conversion of the sulfide to sulfoxide, the peroxide numbers would fall to the line on Figure 7 marked "Theoretical Limit". The sharp discontinuity in the dicetyl sulfide curve at 0.3 hour and the fact that the remainder of the curve roughly parallels the sulfoxide curve strongly suggest that the oxidation of the sulfide by peroxides follows the stepwise reactions shown by Equations 2 and 3, and that the first is a much more rapid step than the second. The fact that the sulfide curve does not fall to the theoretical value before it "breaks" is taken to indicate that the sulfide reduces fractions of the mixed peroxides that are not titrated by hydriodic acid.

Table IV. Analysis of Reaction Products of Sulfides with Peroxides

Compound	% C	% H	% (O + S) by Difference	
Dicetyl sulfide	79.67	13.69	6.64	Calcd.
Dicetyl sulfoxide	77.03	13.34	9.63	
Dicetyl sulfone	74.64	12.92	12.44	
30-min. product	77.08	13.50	9.42	Found
7-hr. product	75.75	13.34	10.91	

From the curve of Figure 7 it appears likely that the reaction of the sulfide with oil peroxides consists of a rapid initial oxidation to the sulfoxide followed by a slow oxidation of the sulfoxide to the sulfone. To test this hypothesis, two peroxide reduction experiments similar to those illustrated by the dicetyl sulfide curve of Figure 7 were run. In the first the run was interrupted after 30 minutes; in the other it was continued for 7 hours. The products were diluted with petroleum ether, chilled, and filtered. The precipitated material was recrystallized from alcohol to free it of oil. Approximately 85% yields of recrystallized products were obtained. These samples were analyzed with the results given in Table IV. It appeared from these results that the conversion to sulfoxide was substantially complete after about 30 minutes at 65.6° C.; if we assume that only sulfoxide and sulfone are present, after 7 hours some 45% of the sulfoxide originally formed was converted to sulfone.

Since elementary analysis can hardly be considered conclusive proof of structure, an attempt was made to confirm these conclusions by x-ray diffraction powder photographs. Table V gives these x-ray data for pure synthetic dicetyl sulfide, sulfoxide, and sulfone and for 50-50 mixtures of the first and second and of the second and third compounds. The mixtures were prepared by dissolving weighed quantities of the components in white oil; they were precipitated by, as nearly as possible, the same procedure used for the isolation of the reaction products of sulfides and peroxides.

The interplanar distances of the three pure compounds are quite distinctive, and the mixture of sulfide and sulfoxide gives values intermediate between its pure constituents. The diffraction patterns of the mixtures indicate that these compounds form solid solutions. This, however, does not invalidate the conclusions based on the x-ray diffraction patterns. It should be possible to identify any major quantity of the sulfide in admixture with the sulfoxide. In the case of the sulfone and sulfoxide, the interplanar distances of the mixtures are close to those of the pure sulfoxide and are, therefore, of little use in detecting the presence of sulfone in a sample containing large quantities of sulfoxide.

The interplanar distances of the 30-minute sample are those of the sulfoxide (Table V). However, because of the existence of solid solutions, the possibility that the sample may contain some sulfone is not precluded. To establish the fact that the sulfoxide is further oxidized to sulfone, a sample was prepared and isolated exactly as before, except that the reaction in the white oil peroxides was allowed to proceed for 25 hours. The interplanar distances of this sample (Table V) suggest that it is a mixture of sulfoxide and sulfone although the identification of the latter is not conclusive. Because the solubilities, melting points, and mixed melting points of dicetyl sulfoxide and dicetyl sulfone are very close together, a chemical method was used to separate the sulfone from this mixture. Since sulfoxides may be reduced to sulfides readily while sulfones resist reduction (*15*), the following method was applied: 0.5 gram of the 25-hour product was dissolved in 50 cc. of glacial acetic acid and agitated with 5 grams of zinc dust for 14 hours at 80° C. The reduction product was freed of acetic acid and recrystallized from petroleum ether to yield about 0.25 gram of material; the data in Table V on the reduced 25-hour product indicated clearly that this material was dicetyl sulfone. A similar treatment of the 30-minute product yielded only dicetyl sulfide, as identified by melting point. Because of the losses involved in isolating and handling these reaction products, neither the data given above nor the carbon and hydrogen analyses in Table IV permit exact quantitative determinations of the amount of sulfone formed under a given set of conditions. They leave no doubt, however, that the reaction of sulfides with oil peroxides follows the stepwise course indicated in Equations 2 and 3.

With this information as a basis, peroxide reduction experiments were carried out with phenyl α-naphthyl sulfide and cetyl phenyl sulfide, and repeated with dicetyl sulfide. The results are shown in Figure 8. In this case samples of oxidized white oils with higher peroxide numbers were used. One hundred grams of reaction mixture was made up, and the sulfides were tested at a concentration of 0.0083 mole per 100 grams. The initial points of the three curves were calculated from the titration of the original peroxidized oils and differed slightly in the three cases. The results are in qualitative accord with the inhibitory activity of the three compounds as demonstrated by the initial portions of the oxidator curves given in Figure 4. Thus phenyl α-naphthyl sulfide does not reduce peroxides and is not an inhibitor. Cetyl phenyl sulfide reduces peroxides at a moderate rate and is a fair inhibitor. Dicetyl sulfide reduces peroxides rapidly and is the best inhibitor early in the runs.

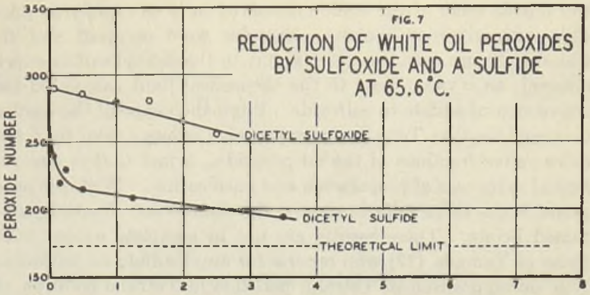


Fig. 7

REDUCTION OF WHITE OIL PEROXIDES BY SULFOXIDE AND A SULFIDE AT 65.6 °C.

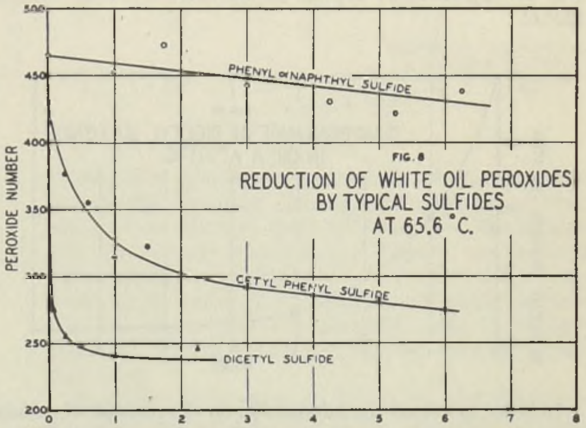


Fig. 8

REDUCTION OF WHITE OIL PEROXIDES BY TYPICAL SULFIDES AT 65.6 °C.

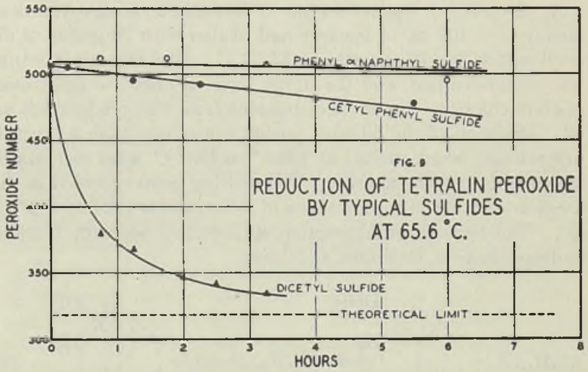


Fig. 9

REDUCTION OF TETRALIN PEROXIDE BY TYPICAL SULFIDES AT 65.6 °C.

Table V. X-Ray Diffraction Data

Sample	Interplanar Distance, Å. (Relative Intensities in Parentheses)
Dicetyl sulfide	4.54 (3), 4.09 (10), 3.70 (5), 2.97 (1), 2.45 (1)
Dicetyl sulfoxide	4.66 (3), 4.20 (10), 3.67 (3), 2.55 (1)
Dicetyl sulfone	13.00 (3), 7.75 (2), 4.43 (4), 4.27 (5), 4.02 (10)
50% dicetyl sulfide–50% dicetyl sulfoxide (by wt.)	4.61 (3), 4.12 (10), 3.71 (3)
50% dicetyl sulfoxide–50% dicetyl sulfone (by wt.)	4.59 (3), 4.23 (10), 3.81 (3)
30-min. product	4.63 (3), 4.20 (10), 3.65 (3), 2.56 (1)
25-hr. product	4.71 (3), 4.22 (10), 3.70 (3)
Reduced 25-hr. product	13.00 (3), 7.75 (2), 4.45 (4), 4.27 (5), 4.02 (10)

Since results with oil peroxides are always subject to some uncertainty because of the mixed nature of the peroxides and the inherent inaccuracies of the titration, it seemed worth while to repeat these experiments with a pure hydrocarbon peroxide of known constitution. For this purpose Tetralin hydroperoxide was synthesized by the method of Hock and Susemihl (*8*) and carefully recrystallized from benzene–petroleum ether until it gave the theoretical peroxide number and recorded physical properties. This peroxide titrates completely by the method of Wheeler (*14*), and peroxide numbers were obtained on its solutions with an accuracy of ±2%. For the peroxide reduction runs, 5.5 grams of the peroxide were dissolved in 145 grams of benzene and titrated. Enough of this solution to make 100 grams of final reaction mixture was heated to 65.6° C. in a stoppered flask and 0.0083 mole of the sulfide dissolved in it as rapidly as possible with vigorous shaking. Samples were removed and titrated as before. In this case (Figure 9) the dicetyl sulfide curve descends to a value close to the theoretical limit calculated for conversion of sulfide to sulfoxide. From the shape of the curves it is obvious that Tetralin hydroperoxide is less active than the more active fractions of the oil peroxides, a fact that is also reflected in its ease of preparation and purification. With the pure peroxide the three sulfides showed the same order of activity obtained before. These results are not in complete accord with those of Yamada (*17*) who reports for amyl sulfide an autocatalytic decomposition of Tetralin peroxide in Tetralin solution at 120° C.

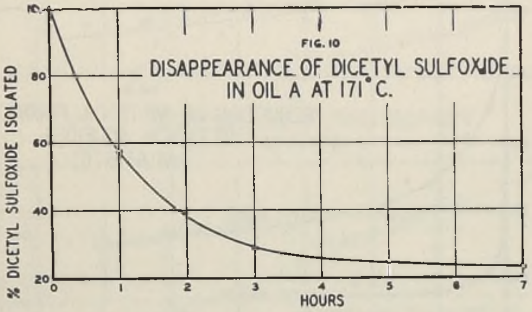
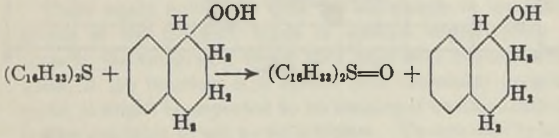


FIG. 10 DISAPPEARANCE OF DICETYL SULFOXIDE IN OIL A AT 171° C.

In order to extend the information on the reaction of sulfides with peroxides, a 4-gram sample of Tetralin hydroperoxide was dissolved in 100 cc. of benzene and heated with 20 grams of dicetyl sulfide for 70 minutes at 65.6° C. The reaction mixture was steam-distilled, and the upper layer of distillate dried over calcium chloride. Removal of benzene from this product left an oil. Reaction of the oil with phenyl isocyanate gave a crystalline product which melted at 122.5° to 123° C. after recrystallization from petroleum ether. The melting point recorded in the literature for the phenylurethane of α-Tetralol is 122° to 123° C. (*8*). The over-all initial reaction of dicetyl sulfide with Tetralin hydroperoxide is, therefore, as follows:



(4)

For oil peroxides no such equation has been established, but it is reasonably certain that the reaction follows the course given in Equations 2 and 3.

PRODUCTS OF SULFIDE INHIBITOR

The best confirmation for the reaction scheme outlined above would be the isolation of a sulfoxide or sulfone from an autoxidized sulfur-inhibited oil. In the hope of obtaining such proof, 100 grams of a 2% solution of dicetyl sulfide in white oil was run in the oxidator at 171° C. until it had taken up 226 cc. of oxygen per 100 grams of oil, or 2.5 moles of oxygen per mole of sulfide. This required 6 minutes. The data show that the sulfide is a much less active inhibitor in white oil than in the desulfured stocks. The oil from this run was diluted with 9 volumes of petroleum ether and chilled to −30° C. After standing at this temperature for several hours, it was filtered cold and washed with petroleum ether. A product amounting to about 85% of theory was recovered. After one recrystallization from alcohol the sample melted at 89–92° C. and gave an x-ray diffraction pattern identical with that of the pure synthetic dicetyl sulfoxide.

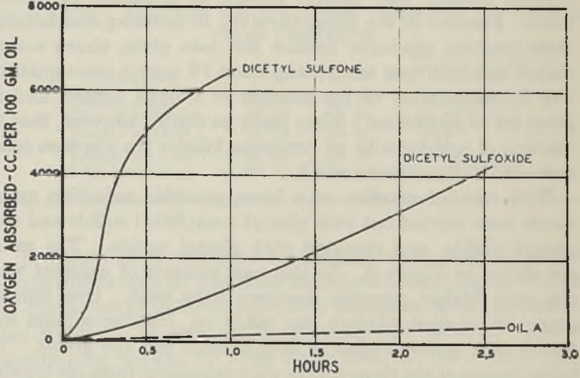
To extend this work to a base oil more closely resembling an actual lubricating oil, 100 grams of a 5% solution of dicetyl sulfide in desulfured oil A was run in the oxidator at 190.6° C. (375° F.) until 638 cc. of oxygen had been consumed per 100 grams of oil. This required 3.6 hours. The oil was then subjected to the isolation procedure used before. No precipitate separated.

In a second experiment under less drastic conditions, 25 grams of desulfured oil A inhibited with 3% of dicetyl sulfide was run for $7^1/_4$ hours in the oxidator at 171° C. Only 73 cc. of oxygen per 100 grams of oil were absorbed, and the oil had not reached the end of its inhibition period. It may be calculated that the 73 cc. of oxygen are equivalent to 0.52 mole of oxygen per mole of sulfide. Fifteen grams of the oil recovered from this oxidator run were treated as before, and 0.275 gram of a solid precipitate was isolated. After one recrystallization from alcohol 0.15 gram of a product melting from 57° to 77° C. was obtained. The melting point indicated that the material was largely dicetyl sulfide contaminated with small quantities of a higher melting material. The contaminant was present in too small amounts to permit separation, but it seemed probable on the basis of the results with white oil that the contaminant was the sulfoxide.

Calculations, based on the quantity of crude material isolated in the last experiment described above, showed that some 40% of the original dicetyl sulfide had disappeared completely. Control experiments indicated that this was several times the quantity of sulfide that would be lost simply through the method of isolation. The peroxide reduction experiments had already shown that both dicetyl sulfoxide and dicetyl sulfone could be isolated in excellent yield by this method. There was, therefore, the serious problem of accounting for the disappearance of the products formed from dicetyl sulfide during its inhibition of the oxidation of the desulfured oil.

It seemed possible that dicetyl sulfoxide or sulfone might be consumed by either or both of two reactions: (*a*) condensation or reaction with the oxidized oil and (*b*) direct oxidation by molecular oxygen. Each mode of disappearance was checked for both the sulfoxide and the sulfone.

FIG. 11 AUTOXIDATION OF DICETYL SULFONE AND DICETYL SULFOXIDE AT 171° C.



The possibility that dicetyl sulfone had disappeared by the first course was tested by dissolving 0.5 gram of the pure compound in 25 cc. of the oil recovered from the 190.6° C. oxidator run described above. The blend was then heated at 171° C. for 7 hours and subjected to the isolation procedure used before; 0.48 gram of material was recovered, which had the proper melting point for the sulfone when recrystallized once from alcohol. The recovery of crude material was 96%.

The case of dicetyl sulfoxide is more complicated, and when the above experiment was repeated with this compound, none could be recovered. Since some reaction or condensation obviously took place with the oxidized oil, it seemed of interest to determine whether a similar reaction took place on heating the com-

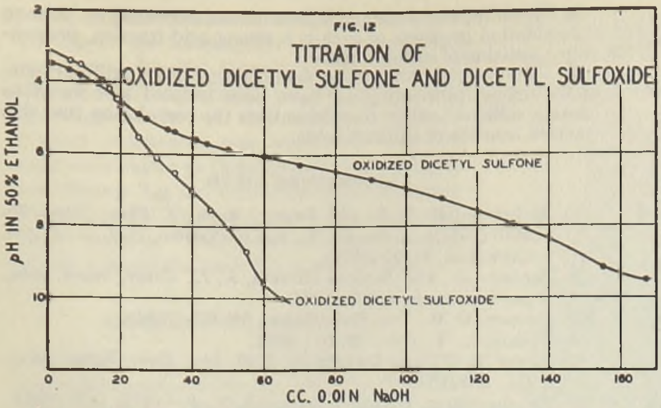


FIG. 12
TITRATION OF OXIDIZED DICETYL SULFONE AND DICETYL SULFOXIDE

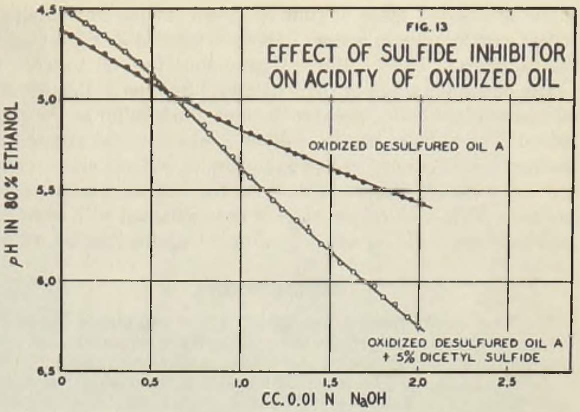


FIG. 13
EFFECT OF SULFIDE INHIBITOR ON ACIDITY OF OXIDIZED OIL

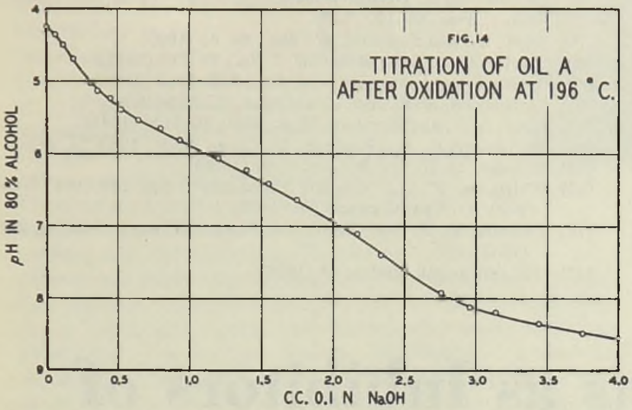


FIG. 14
TITRATION OF OIL A AFTER OXIDATION AT 196 °C.

pound with unoxidized base stock. Four grams of pure dicetyl sulfoxide were therefore dissolved in 196 grams of oil A and heated at 171° C. under an atmosphere of nitrogen. Samples of 50 cc. each were pipetted from the mixture at intervals and subjected to the isolation procedure. Figure 10 shows the percentage recovery of the sulfoxide plotted against time. The melting points of all the samples isolated lay between 84° and 89° C. without recrystallization. As a control, 5 grams of pure dicetyl sulfoxide were heated under the same conditions but with no oil present for 7 hours. At the end of this period it had darkened slightly and showed a melting point of 83° to 87° C. The data in Figure 10 show clearly that the sulfoxide does disappear when heated with oil while the control experiment indicates that purely thermal decomposition could not account for all of this loss. The only conclusion possible is, therefore, that the sulfoxide condenses or reacts with oil while the sulfone does not. The products of this reaction have not been identified. While these data provide one explanation for the disappearance of the products of inhibition in the oxidation experiments when it was necessary to run the oil for an extended period, they should not be interpreted to mean that part of this product could not also have been consumed by direct reaction with oxygen.

To determine whether dicetyl sulfoxide or sulfone could be rapidly consumed by direct autoxidation, samples of the pure compounds were run in the oxidator. Figure 11 shows that both compounds consume oxygen much more rapidly than an ordinary oil. The rapidity of this reaction with oxygen makes it seem probable that, while the sulfoxide may be lost by condensation with the oil, at least some of it must undergo further oxidation with molecular oxygen.

Samples (12.5 grams) of the sulfoxide and sulfone were run in the oxidator at 171° C. until each had adsorbed 4800 cc. of oxygen per 100 grams. The materials were washed from the cells with 50 cc. of alcohol, and 50 cc. of water were added to each sample. Potentiometric titrations with 0.01 *N* sodium hydroxide gave the curves of Figure 12. Both curves show two distinct regions of inflection, one at a pH of about 4.5 and the other, at about 8.7. Therefore two different acid fractions are present in the samples, one of which has a dissociation constant of about 10^{-7} and another which must consist of strong acids. It seemed probable that the weaker acids were carboxylic acids. The most reasonable possibility for the strong acid fraction was sulfonic acids.

To check the presence of this strong acid fraction in an actual oxidized oil, a sample of desulfured oil A that had taken up 1770 cc. of oxygen per 100 grams and a sample of the same oil that was inhibited with 5% dicetyl sulfide and had adsorbed 640 cc. per 100 grams were titrated in 80% alcohol solution.

The oxidized desulfured oil (Figure 13) showed no point of inflection indicative of a strong acid fraction. The point of inflection at pH 5.5 in the curve for the oxidized sulfide-inhibited oil shows the presence of a strong acid fraction. The difference in the point of inflection in this case from those shown in Figure 12 is probably due to the difference in the solvent. The curve for the sulfide-inhibited oil indicates the presence of a strong acid fraction whereas the uninhibited oil shows no such fraction in spite of its greater total acidity. The data still do not furnish adequate proof that this strong acid fraction actually consists of the postulated sulfonic acids. The formation of a strong acid fraction by the oxidation of an insulating oil, and the possibility of its being a sulfonic acid has been discussed by Evans and Davenport (*5*) and Piper and Kerstein (*12*).

As a means of obtaining information on the chemical nature of the strong acid fraction, a 1500-gram sample of base oil A was blown with oxygen for 3 hours at 196° C. A 15-gram sample was titrated in 80% alcohol with 0.1 *N* potassium hydroxide. The titration curve is shown in Figure 14. The curve shows the same strong acid fraction previously noted for the oxidized samples of pure sulfoxide and sulfone and for the oil inhibited with the synthetic sulfide. The remainder of the oxidized oil A was extracted with 1200 cc. of 40% alcohol to remove oxygen-containing fractions. The first extract separated well, but attempts at further extraction failed because of emulsion difficulties. The alcoholic extract was concentrated on the steam plate, taken up in 80% alcohol, and neutralized to a pH of 5.4 with 0.1 *N* potassium hydroxide in order to form soaps of the strong acids present. It was then diluted with water and extracted three times with chloroform to remove from the aqueous solution of the strong acid soaps, the carboxylic acids and other oxidized material not saponified. The combined chloroform extracts were washed with aqueous alcohol to recover entrained strong acid soaps, and these washings were combined with the previous aqueous solution of soaps and evaporated to dryness on the steam plate. The last traces of water were removed in vacuo over calcium chloride.

A few tenths of a gram of gummy brown residue was obtained. It was very soluble in water. Analysis showed 3.54% sulfur in this residue and 0.53% sulfur in the sample of base oil A used.

The potassium soaps of the strong acid fraction of the oxidized oil therefore contained over six times as much sulfur as the original oil. These data can leave little doubt that the strong acid fraction contains considerable quantities of sulfonic acids. They are also a strong indication that the reaction mechanism which has been postulated on the basis of data obtained with synthetic sulfides is also valid for natural-sulfur-containing lubricating oils.

CONCLUSIONS

1. The most effective synthetic sulfur inhibitors found for lubricating oil hydrocarbons are monosulfides containing at least one aliphatic or cycloaliphatic group attached to the sulfur atom.
2. The monosulfides react with hydrocarbon peroxides to give sulfoxides. This reaction is relatively rapid, removes peroxides as they are formed, and thus breaks the hydrocarbon oxidation chain.
3. The effectiveness of various types of sulfide inhibitors appears to depend upon the rapidity with which they reduce peroxides. The sulfides themselves autoxidize much less rapidly than ordinary lubricating oils.
4. The sulfoxide formed by the reactions of the sulfide with oil peroxides can react further with peroxides at a less rapid rate to give a sulfone. In so doing the sulfoxide also functions as an inhibitor although a less active one than the original sulfide. The sulfone is not an inhibitor.
5. In addition to reacting with peroxides, the sulfoxide also reacts or condenses with oil hydrocarbons to give oil-soluble products. These have not yet been identified.
6. Both the sulfoxide and sulfone autoxidize rapidly. Among the oxidation products of each is a strong acid fraction, presumably consisting of sulfonic acids.
7. The soaps of the strong acid fraction of an oxidized, normally refined lubricating oil have been isolated and found to contain sufficient sulfur to substantiate the postulation that this fraction consists of sulfonic acids.

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Redwood Products as Inhibitors of Oxidation in Petroleum Hydrocarbons

INHIBITION OF OXIDATION IN CYCLOHEXENE AND GASOLINE[1]

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SOME ninety years ago Chevreul (*3*) called attention to the ability of oakwood to retard the drying of linseed oil. Poplar and pine were found to have these characteristics to a much smaller degree. This property of oakwood was ascribed by Moureu and Dufraisse (*8*) to the presence of tannin in the wood. The latter investigators studied a long list of organic compounds from the standpoint of their activities as "antioxygenic catalysts" and "autoxidizable substances". Under the former they listed catechol, pyrogallol, the naphthols, and tannins. No mention was made of the tannin type in the article cited (*8*). Among the "autoxidizable" substances were aliphatic aldehydes, substituted aliphatic aldehydes, and cyclic aldehydes; unsaturated hydrocarbons, such as styrol, phenylbromoethylene, diphenylethylene, and turpentine; complex organic substances such as caoutchouc, fats, and oils; and finally sodium sulfite and inorganic salts. A patent (*9*) described the use of "tannic acid" in 1930.

Earlier experiments showed that the tannin obtained from the redwood tree (*Sequoia sempervirens*) possesses antioxidant characteristics to a surprising degree (*5*). In this earlier work the tannins and the products of destructive distillation of the tannins and of redwood were tested as inhibitors of acid formation in mineral oils. In view of their activity in this field, it was decided to investigate the products as inhibitors of gum formation. The characteristics of redwood tannin have already been described (*2*).

The autoxidation of gasoline has been the subject of many researches since, as a result of this autoxidation, a nonvolatile gum is formed which is objectionable in any motor fuel. Diolefins present in the gasoline will oxidize readily to form this gum. The autoxidation of petroleum distillates was reviewed some years ago (*4*). The reaction has been studied in detail by Morrell, Dryer, Lowry, and Egloff (*6*), who oxidized gasoline under carefully regulated conditions in steel bombs and measured the period before serious absorption of oxygen occurred with resultant formation of gum. The addition of antioxidants to the gasoline serves to increase this "induction period", which is dependent on the nature and concentration of the antioxidant.

The evaluation of these various inhibitors was studied extensively by the same investigators (*7*). They suggested the term "cyclohexene number" or the number of minutes the induction

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[1] The first article in this series appeared in October issue (*5*).

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period of pure cyclohexene will be retarded by 0.002% of the antioxidant. Instead of using cyclohexene directly, Morrell *et al.* recommended the use of reference fuels. In our study of the inhibiting action of the redwood products purified cyclohexene was employed. The test units were similar to those described by Winning and Thomas (*11*) and were made by the Tagliabue Manufacturing Company (*10*). The explosion-proof cabinets were manufactured locally. Figure 1 shows the assembly of three units.

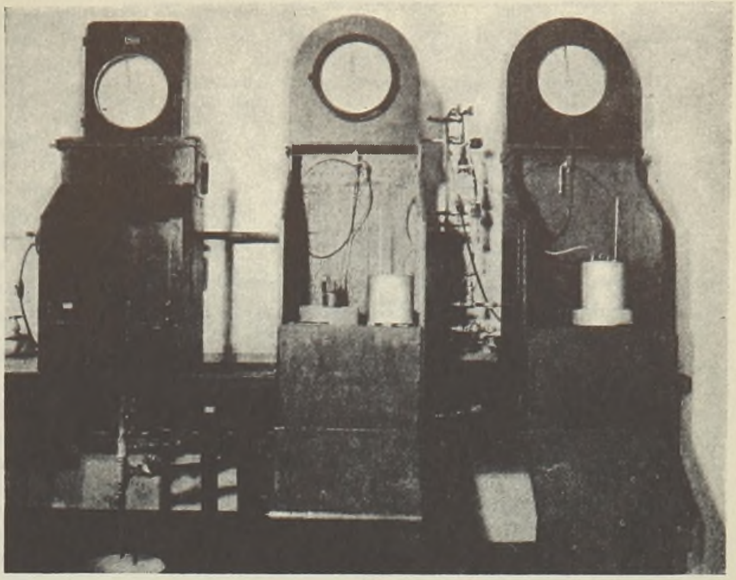

Figure 1. Bombs Used in Tests

Solvent-purified redwood tannins are effective in preventing the oxidation of cyclohexene but are of little value in protecting gasoline because of their solubility characteristics. Products prepared by reacting the tannin with benzoyl chloride, caproyl chloride, chloroacetic acid, formaldehyde, and amines appear to have little interest as antioxidants. Condensation of tannin with acetone or other ketones results in a good yield of ether-soluble products which are good inhibitors for cyclohexene. However, the addition of water to the treated cyclohexene results in the loss of approximately half of the inhibiting action. The acetone-tannin condensation products have poor solubility in gasoline and are of questionable value as gasoline antioxidants. Products obtained by condensing catechol with acetone have excellent inhibiting properties for cyclohexene and appear somewhat promising as antioxidants for gasoline. In using cyclohexene in the Winning-Thomas breakdown test, it is necessary to remove the peroxides in order to obtain duplicate results.

EXPERIMENTAL PROCEDURE

A long period was required for establishing a standard and readily reproducible test with cyclohexene. In the preliminary experiments, the cyclohexene purchased from Eastman Kodak Company was freshly distilled before each use. In spite of this precaution, the induction period of a given antioxidant appeared to diminish gradually with time. Investigation indicated that the cyclohexene sample was contaminated with peroxides which partially distilled with it. The peroxides were removed by shaking the cyclohexene with solid potassium hydroxide and then washing with aqueous ferrous thiocyanate. The product was stored over potassium hydroxide in a refrigerator, and sufficient was withdrawn each day for the required test. Before use it was washed with ferrous thiocyanate and with water, dried over calcium chloride, and distilled. A test for peroxides by the method of Young, Vogt, and Nieuwland (*12*) showed that only small amounts of peroxide remained in the cyclohexene.

It should be pointed out that the bomb test is empirical; except for Table V, the results reported are averages of two or more tests. The data show a maximum variation in most cases of less than 10%.

The redwood tannin was prepared in a pilot plant large enough to extract 100 pounds of wood, which was chipped and run through a hammer mill. Tannin was extracted either with hot water or with 95% ethyl alcohol. When the latter was used as solvent, the extract was first distilled in a twenty-plate column vacuum still until most of the ethyl alcohol had been removed. The residual water in the still was sufficient to keep the tannin in solution. Phlobaphenes and other water-insoluble, alcohol-soluble extractives precipitated on removal of the alcohol and were separated from the tannin by filtration. Residual water was evaporated in stainless steel pans in a vacuum pan evaporator at temperatures which never exceeded 60° C.

Three types of redwood waste were available—conveyor waste, (which is a reject from the sawmill operation and is entirely heartwood) stumpwood, and rootwood. The particular tannin samples were tested either directly or after further purification. During each day's operations, blanks were run on the cyclohexene without any inhibitor; at intervals, checks were made using benzyl-*p*-aminophenol as a control.

A study was made of tannins purified in a number of ways with the hope of concentrating the active principle of the tannin. Dry crude tannin extracted from the rootwood (run 37) was first treated with 12 volumes of acetone at room temperature, which dissolved about 85% of the crude tannin. The insoluble and soluble fractions were tested. In another experiment a part of the rootwood tannin (run 41) was extracted with 10 volumes of acetone, and the acetone-soluble product was tested. In a third experiment a sample of the same tannin was dissolved in 3% sodium bicarbonate solution, and the solution extracted with ethyl acetate. Removal of the solvent from the extract gave an ethyl acetate-soluble fraction which amounted to 49% of the original tannin. Other samples were prepared by extracting similar sodium bicarbonate-tannin solutions with methyl amyl ketone and with amyl isobutyl ketone; these solvents gave yields of 43 and 53% tannin, respectively. Table I shows the induction times of the tannin samples. It is apparent that the inhibitor is concentrated in the acetone-soluble tannin, since the acetone-insoluble material has no antioxidant activity.

Shortly after these tests were run, a sample of the crystalline material found in the green cones of the redwood was received. This material contains about 85% of material soluble in methanol-acetone; the other 15% is largely fibrous material, cone scales, dirt, etc. About 15% of the fraction soluble in methanol-acetone was insoluble in acetone; the acetone-soluble fraction is chiefly tannin. The tannin fraction was a satisfactory tanning agent, but neither the crude cone tannin nor its acetone-soluble and -insoluble fractions showed any antioxidant activity.

Experiments were conducted to determine the effect of storage conditions on the stability of redwood tannin itself in terms of its

Table I. Effect of Solvent Purification of Redwood Tannin on Induction Period

(0.005% antioxidant, treated to remove peroxides and distilled)

Run No.	Description	Induction Period, Min.
Control	No antioxidant	35
37	Crude tannin	225
	Acetone-sol. tannin	245
	Acetone-insol. tannin	35
41	Acetone-sol. tannin	255
	Ethyl acetate-sol. tannin	260
	Methyl amyl ketone-sol. tannin	235
	Hexone-sol. tannin	285

Table II. Inhibiting Activity of Condensation Products of Tannin with Organic Acid

(0.005% antioxidant in cyclohexene treated to remove peroxides and distilled)

Description of Tannin	Yield, %	Induction Period, Min.
Benzoylated (crude product)	40	45
Benzoylated (ether-extracted)	...	30
Treated with 2.7 moles caproyl chloride	136	105
Treated with 0.2 mole caproyl chloride	26	215
Treated with crude chloroacetyl chloride	92	65
Treated with chloroacetyl chloride, ether-sol. fraction	93	130

antioxidant activity. Conditions investigated included the effect of high and low temperature, sunlight and ultraviolet light, and moisture. In general, there was little indication of deterioration of the tannin stored under widely varying conditions.

Previous work has shown that tannin can be prepared from redwood having about the same degree of inhibiting action with cyclohexene as does benzyl-*p*-aminophenol. These products were prepared in a number of ways and were stable over a 4-month test period. The next problem was to improve the solubility of the tannin in cyclohexene or gasoline and lower its solubility in water without, at the same time, altering its inhibiting activity.

CONDENSATION PRODUCTS WITH ACIDS AND AMINES

Benzoic Acid. Ethyl-acetate-soluble stumpwood tannin was treated with 1.1 moles (assuming a molecular weight of 510 for the tannin) of benzoyl chloride in the presence of pyridine. The crude product was insoluble in ether and was purified by extraction with ether to remove the benzoic acid.

Chloroacetic Acid. Acetone-soluble rootwood tannin was heated on the steam bath with 2 parts of chloroacetyl chloride for 8 hours; the product was largely ether soluble.

Caproic Acid. Ethyl-acetate-soluble stumpwood tannin was treated with 2.7 moles of caproyl chloride in the presence of pyridine. The product was ether soluble and was purified by dissolving in ether. A second product was prepared using only 0.2 mole of caproyl chloride in the presence of pyridine. The product was purified by dissolving in ether. The data in Table II show that tannin treated with 0.2 mole of caproyl chloride had good antioxidant activity, but the yield was low. None of the other esterification products had sufficient activity to be of further interest. All these products had low solubility in water.

Table III. Yield and Induction Period of Catechol-Acetone Condensation Products

(0.005% antioxidant in cyclohexene treated to remove peroxides and distilled)

Condensation Product	Reagents Used/10 Grams Catechol			Hours Heated	Yield, %	Induction Period, Min.
	Acetone, cc.	Acetic acid, cc.	Concd. HCl, cc.			
Recrystallized	16	27	22	25	...	390
Tar from mother liquor	16	27	22	25	...	300
Recrystallized	16	27.5	22	25	28	260
Crude	16	27.5	22	24	113	290
Ether soluble	20	6	5	8	30	200
Ether soluble	15	12	10	8	57	310
Ether soluble	16	27.5	22	8	90	290
Ether soluble	20[a]	..	..	8	50	315
Ether soluble	20	6	5	25	105	255
Catechol	..	..	..	..	...	410

[a] One gram $AlCl_3$ used.

Amines. Experiments made to neutralize the acid material had shown that the addition of tributylamine to an aqueous tannin solution caused the separation of an insoluble product. Accordingly, redwood tannin was reacted with a variety of amines (such as tributylamine, aniline, *p*-aminophenol, ethylenediamine, and 2-amino-1-butanol) to form products which in some cases have fair antioxidant activity. In most cases the yields were small and further work was dropped.

CONDENSATION WITH FORMALDEHYDE AND CATECHOL

Redwood tannin was reacted with formaldehyde in an effort to obtain water-insoluble and gasoline-soluble products having antioxidant activity. . The solubility of these products was very poor, and they had little or no antioxidant activity.

Since catechol may be recovered in good yield from the destructive distillation of redwood phlobaphene, tests were run both with catechol and with a number of its condensation products. Catechol was found to have good antioxidant activity but is not used for protecting gasoline because of its high solubility in water. Baker (*1*) described the preparation of a water-insoluble product by the condensation of catechol with acetone in the presence of acids. This product was prepared and found to have considerable promise as an antioxidant. Several experiments were made to study the conditions necessary to produce a satisfactory antioxidant in good yield. The general procedure was to heat the catechol, acetone, and acid mixture on the steam bath under reflux. The reaction product separated as a tar when poured into water. After washing with water, this tar was either recrystallized from alcohol–acetic acid or was purified by dissolving in ether and washing the ether free of acid. In most cases the product was completely soluble in ether.

The data in Table III indicate that large amounts of acids or long periods of heating are necessary for high yields of the product. Substitution of anhydrous aluminum chloride for the acid resulted in poor yield. These products have good antioxidant activity and appear to have reasonably good solubility in cyclohexene and gasoline, with low solubility in water.

CONDENSATION WITH KETONES

Since catechol condenses with acetone to form a product having good antioxidant activity with improved solubility characteristics, an investigation was made of the effect of acetone on redwood tannin under similar conditions. Tannin was found to react with acetone and other ketones in the presence of concentrated hydrochloric acid and glacial acetic acid or in the presence of anhydrous aluminum chloride to form water-insoluble products. The product from the tannin always consisted of both ether-soluble and ether-insoluble fractions. The ether-soluble fraction had good antioxidant activity and was nearly insoluble in water. The ether-insoluble fraction had poor antioxidant properties and was somewhat soluble in water.

Apparently the acetone or other ketone is essential to the reaction, because tannin heated under similar conditions without acetone resulted in a low yield of inactive material. Other ketones can be substituted for acetone in this reaction, but no advantage was found in their use, particularly since the high-boiling ketones were difficult to remove from the product. The various conditions used in preparing the condensation products, the yield data, and the induction periods of the products are summarized in Table IV.

The most satisfactory of the condensation products were then tested for solubility behavior. The general procedure was to shake 100 cc. of cyclohexene, to which had been added the antioxidant, with two 25-cc. portions of water and determine the in-

Table IV. Yield and Induction Period of Condensation Products of Redwood Tannin with Ketones

(0.005% antioxidant in cyclohexene treated to remove peroxides and distilled)

Tannin (10 G.)	Ketone, Cc.	Acetic Acid, Cc.	Concd. HCl, Cc.	Hours Heated	Ether-Sol. Reaction, Products, %	Induction Period, Min.
Rootwood	Acetone, 20	6	5	22.5[a]	60	215
	Acetone, 20	6	5	8[a]	41	160
	Acetone, 20	6	5	10	44	210
	Acetone, 20	6	5	6	66	255
Cone	Acetone, 20	6	5	8	41	170
Rootwood	Acetone, 20[b]	...	...	6	60	275
	Acetone, 20[b]	...	...	6	43	240
	Acetone, 10	3	2.5	10	54	250
	Acetone, 20	6	5	10[c]	57	215
	Acetone, 10	3	2.5	8	26	255
	Acetone, 10	3	2.5	8	29	310
Stumpwood	Acetone, 10	3	2.5	8	28	245
Rootwood	Hexone, 20	6	5	8	78	250
	Cyclohexanone, 20	6	5	8	120	225
	Methyl ethyl ketone, 20	6	5	8	80	270
	Mesityl oxide, 5	6	5	8	65	250
	Isophorone, 5	6	5	8	25	250
	Acetophenone, 20	6	5	8	54	150

[a] 60 cc. acetic acid and 50 cc. hydrochloric acid added and heating continued for 2 hours.
[b] One gram anhydrous aluminum chloride used.
[c] Heated to 50° C. only.

Table V. Solubility Behavior of Condensation Products

(Cyclohexene treated to remove peroxides but not distilled; 0.005% used in each case; water washed after addition of antioxidant)

Condensation Product	Induction Period, Min.
Benzyl-*p*-aminophenol	310
Acetone-condensed tannin	105
Hexone-condensed tannin	75
Cyclohexanone-condensed tannin	80
Methyl ethyl ketone–condensed tannin	60
Acetophenone-condensed tannin	45
Benzophenone-condensed tannin	35
Chloroacetyl chloride–condensed tannin	50
Acetone-condensed phlobaphene	50
Acetone-condensed catechol	300
Acetone-condensed catechol	250

duction period on 25 cc. of the washed cyclohexene. In some cases 25 cc. of the washed cyclohexene were evaporated, and the residue was weighed in an attempt to determine the amount of antioxidant left in solution. This washing procedure was probably more drastic than would be encountered in commercial practice but, since the condensation products are ether soluble and water insoluble, it was originally believed that they would easily withstand such a test.

This treatment of cyclohexene protected with tannin condensation products caused the separation of a sludge between the two layers, and a decrease of more than 50% in the induction period. The water treatment had much less effect on the induction period of cyclohexene protected with the catechol condensation product, and had no apparent effect on cyclohexene protected with benzyl-*p*-aminophenol or with isobutyl-*p*-aminophenol. The tests made to determine the amount of antioxidant left in solution indicate that the water treatment removed a considerable amount in each case. The quantity of the tannin condensation products left in solution was approximately equal to that left in solution with substituted aminophenols and the catechol condensation product.

In one test the addition of about 0.5% water was sufficient to decrease the induction period more than 50%. On the other hand, the use of cyclohexene which had been shaken with water before addition of the antioxidant did not result in any loss in protection. The experimental data are given in Table V.

The extraction of the treated cyclohexene with water appears to cause the antioxidant to separate at the interface. It was believed that the presence of small amounts of some surface-active material might prevent this separation. Accordingly, the treated cyclohexene was washed with water containing varying amounts of NOPCO 2090-M (sulfonated teaseed oil), Surpasol 630 (double sulfonated castor oil), and Vel (glyceryl lauryl sulfate). The results were essentially the same as those obtained in the absence of surface-active materials.

TESTS ON GASOLINE

From the beginning of this investigation it was known to be impossible to obtain and keep a standard gasoline for test. Different samples of gasoline have widely different oxidation stabilities and, in addition, the stability of an unprotected gasoline undergoes considerable change under normal storage conditions. However, a few tests were made on different gasolines.

In general, the results indicated that the tannins and their condensation products are much less effective than benzyl-*p*-aminophenol in preventing the oxidation of gasoline. This may be due to the poor solubility of the tannins in gasoline, but there are some indications that the redwood products protect a considerably narrower field of chemical structures than is the case with the substituted aminophenols.

SUMMARY

1. The Winning and Thomas breakdown test involving the use of cyclohexene has been standardized. Satisfactory checks are obtained when the cyclohexene is treated to remove peroxides, followed by distillation.
2. Satisfactory antioxidants for use with cyclohexene are made by extracting redwood with 95% alcohol, precipitating the phlobaphene with water after the alcohol is mainly removed, and evaporating. The active fraction is removed from the residue by extraction with acetone or ethyl acetate.
3. Such tannins are too soluble in water to be satisfactory for use in water-sealed gasoline tanks. A variety of condensation products have therefore been made. Of greatest interest is that formed by condensation with acetone. Caproyl chloride and *p*-aminophenol can also be used as condensing agents.
4. Although the solubilities of these derivatives have been greatly improved, there is a concentration of the antioxidant at the interface when solutions in cyclohexene are washed with much water; antioxidant effectiveness is thus lost. Surface-active oils have been added in the hope of reducing the concentration of the antioxidant at the interface. The results have not been successful.
5. The solubility of the redwood products in several gasolines is less than in cyclohexene. Poorer protection is afforded than with benzyl-*p*-aminophenol. Tests with gasolines have only directional value.
6. Some interest in catechol condensation products is indicated; this is in line with the possible production of catechol from the destructive distillation of redwood phlobaphene.

ACKNOWLEDGMENT

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Correlating Viscosity and Vapor Pressure of Liquids

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Viscosity data may be plotted directly to give straight lines on log paper against a temperature scale readily calibrated from the vapor pressures of a reference substance. The method follows from that previously suggested for vapor pressures (*14*), vapor compositions, and other properties (*17*). A thermodynamic derivation indicates the soundness of the plot and of the governing equation:

$$\log \mu = -(E/L) \log P' + C$$

The use of reduced temperatures correlates even better, since it tends to make the lines for all liquids converge in a narrow range at the extrapolated points corresponding to the critical. Fluidities, the reciprocal of viscosities, may be correlated by similar plots, either against the temperature scale or against the reduced temperature scale obtained by this method.

MANY physical properties of liquids, of solids, and of liquid solutions of other liquids, solids, or gases have been correlated by a simple method of logarithmic plotting and the correspondingly simple algebraic equations (*14*). For vapor pressures and latent heats,

$$\log P = (L/L') \log P' + C$$

where at the same temperatures, P and P' are vapor pressures and L and L' molal latent heats, respectively, of two compounds (the latter in each case being that of a standard or reference substance), and C is a constant. Log P' really serves as the temperature variable and is obtained directly from vapor pressure data of the standard substance. L/L' is nearly independent of temperature. A log plot gives a substantially straight line whose slope (L/L') provides latent heat data at any temperature for the compound in question from that of the reference substance. This vapor pressure plot was extended (*15*) for use with reduced pressures at reduced temperatures in order to increase the precision. Further applications were made to gas solubilities and partial pressures (*19*) and to the pressures of adsorbed materials from adsorbents (*18*). Other properties, such as vapor composition, equilibrium constant, activity coefficient, relative volatility, and electromotive force, were also shown to correlate as straight lines by this method (*16, 17*); and the slopes of the lines were identified with the heats of vaporization and of solution.

In most cases the equation is not needed, and vapor pressure (or other function) is plotted on log paper (or logarithms are plotted on ordinary graph paper) by three steps: (*a*) Corresponding temperatures and vapor pressures of the reference substance are read from a table; temperatures are indicated on the X-axis at appropriate values of pressures, with ordinates erected accordingly. (*b*) Pressure (or other function) is plotted from the logarithmic scale of the Y-axis on the respective temperature ordinates. The same units do not have to be used on both the X and Y axis, since there is a constant ratio between any two units; this ratio would merely move the line up or down on the plot without changing its form of slope. (*c*) Points so obtained are connected by a line, usually straight.

APPLICATION TO VISCOSITY DATA

Plotted by the same method previously standardized for many functions, Figure 1 in the upper graph gives viscosity of different substances *vs.* temperature, indicated in the regular way from the corresponding vapor pressure of water as the reference substance.

The correlation is good, and viscosities may be so plotted as straight lines for any of these materials; many others have also been checked. In some cases the data for a substance are best expressed as a series of two or three connected straight lines. While each section is straight, to indicate the validity of the relation over the particular temperature range, the breaks (and corresponding changes in slopes) are due to the change of the physical and often chemical nature of the material at that particular temperature. With water, for example, there is an abrupt break in the line for viscosity between 30° and 40° C.; this corresponds to the postulated change in the molecular structure of water at 40° C. (*5, 12*).

The equation of the straight lines in the upper graph of Figure 1 is:

$$\log \mu = -A \log P + C \tag{1}$$

where μ is viscosity and P is vapor pressure of any liquid, both expressed in any desired units; A and C are constants. In the usual case this equation will be less useful than the simple graph which, for a new compound (in most cases), gives a single straight line right up to the boiling point. Only two points are thus needed to establish the entire range of values, but a third intermediate point, also on the line, will check the continuity of the straight line. If breaks are shown, two points will be required for each straight line section.

The plotted viscosity data are at atmospheric pressure; in general, lines of such a plot must be isobaric. If there is a pressure change, there is a change in viscosity. For example, data at the boiling point may tend to fall slightly away from the indicated straight lines, since the experimental method may have included some application of superatmospheric pressure to prevent vaporization from interfering with the experimental determinations.

Another useful function is fluidity, ϕ, the reciprocal of viscosity; when a comparable plot of fluidity of the same liquids is made in the lower graph of Figure 1, a similar series of straight lines is obtained; because of the properties of logarithmic plotting, this plot is the mirror image of the upper graph of Figure 1, with the lines having identical algebraic slope but negative sign:

$$\phi = 1/\mu; \quad -\log \phi = \log \mu$$

From Equation 1:

$$\begin{aligned} -\log \phi &= -A \log P + C \\ \log \phi &= A \log P - C \end{aligned} \tag{2}$$

THERMODYNAMIC BACKGROUND

The Clausius-Clapyron equation relates P (pressure), T (temperature), and L (latent heat of vaporization per mole) with R (the gas constant):

$$\frac{d \ln P}{dT} = \frac{L}{RT^2}$$

Guzman (*10*) indicated a similar derivation:

$$\frac{d \ln \phi}{dT} = \frac{E}{RT^2}$$

where E is related to the heat of fusion of the liquid or the activation energy of viscosity.

If these equations are combined, there results at the same temperature:

$$\frac{d \log \phi}{d \log P} = \frac{E}{L} \text{ or}$$

$$\frac{d \log \mu}{d \log P} = \frac{-E}{L} \qquad (3)$$

This relation indicates that a log plot of viscosity or of fluidity against pressure at the same temperatures for a given substance would be a straight line with slope equal to the ratio of the energy of activation and the heat of vaporization. Others (*1–4*) have also contributed to this idea of the relation of viscosities and vapor pressures of the same substance.

It was previously shown (*14*), however, that

$$\frac{d \log P}{d \log P'} = \frac{L}{L'}$$

where P' is the pressure and L' the molar heat of vaporization of a second fluid. When this is combined with Equation 3:

$$\frac{d \log \mu}{d \log P'} = -\frac{E}{L'} \text{ or}$$

$$\frac{d \log \phi}{d \log P'} = \frac{E}{L'} \qquad (4)$$

These may be integrated to give approximately:

$$\log \mu = -\frac{E}{L} \log P' + C$$

$$\log \phi = \frac{E}{L'} \log P' + C \qquad (5)$$

Hence it follows that Equation 1 is correct, assuming the constancy of E/L; the proposed relation and method of plotting are thermodynamically sound within the assumptions of the derived equations. The relation E/L or its reciprocal L/E was discussed by Glasstone (*9*) and indicated to be a constant for a given substance by Eyring and Ewell (*6, 7, 8*). For large groups of substances it may be regarded as substantially constant, depending on molecular structure and related properties. As indicated here, this ratio may conveniently be found or checked as the relation between the slopes of the lines on a log plot of vapor pressures and of a log plot of viscosities when both are made against temperatures as determined by the vapor pressures of the same reference substance.

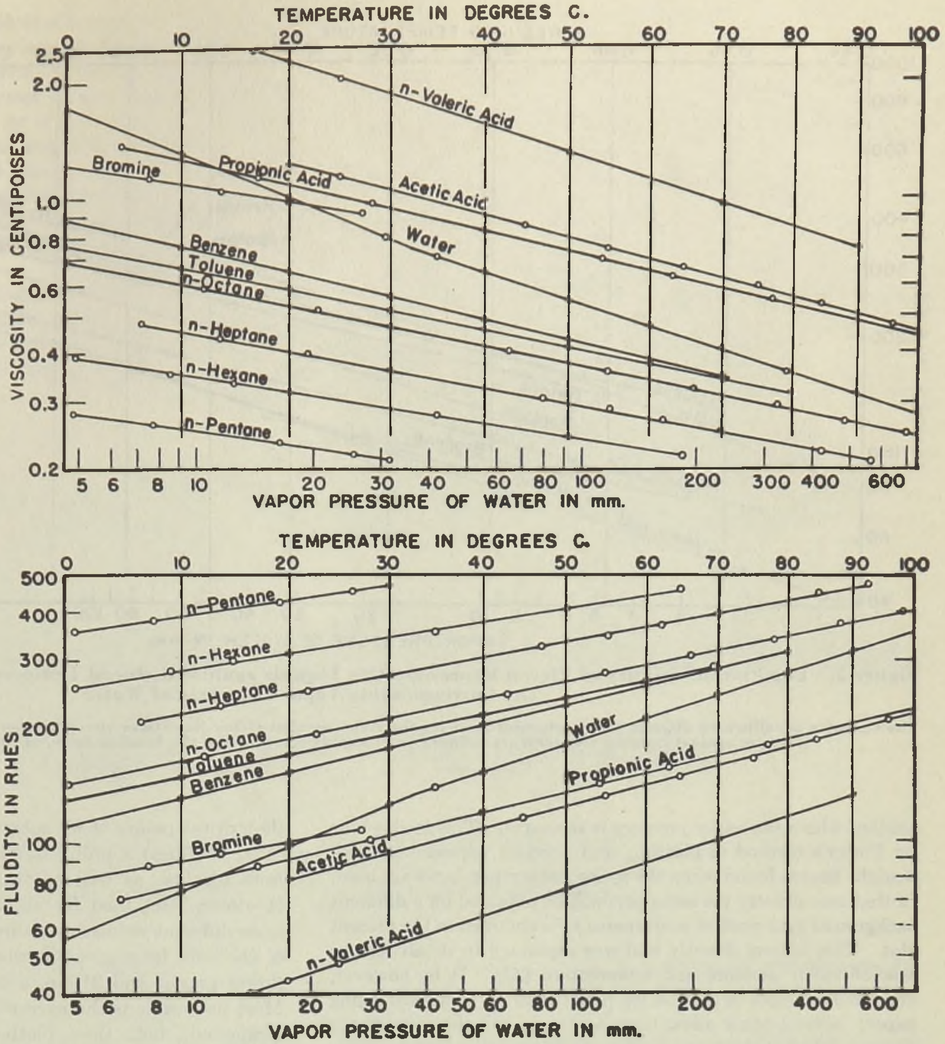

Figure 1. Log Plot of Viscosity (*above*) and of Fluidity (*below*) of Eleven Representative Liquids against Temperature Which is Obtained from the Corresponding Vapor Pressures of Water

RELATION TO OTHER CORRELATIONS

A method which follows from the equation of Andrade (*1, 2, 3*) is to plot logarithms of viscosity or logarithms of fluidity against $1/T$, which is comparable to the familiar plot of log P against $1/T$. The latter does not give lines which are nearly so straight as does the plot of log P against log P', as has been shown (*14*). The plot of log μ or log ϕ against $1/T$ also does not give lines which are nearly so straight as does a plot of log μ or log ϕ against log P'. The reason is that the $1/T$ plot assumes the constancy of E, which is not so correct as the assumption of the constancy of E/L in the present plot. In other words, E varies as does L; while neither is constant, the ratio is practically constant.

Numerous other more or less empirical relations of viscosity, temperature, and vapor pressure have been presented. One closely related to the present method is the so-called Porter rule (*21*), a plot of temperature of one liquid *vs.* temperature of another liquid where it has the same viscosity. This is directly analogous to the Dühring plot for the temperatures at which two liquids have the same vapor pressure. It has been shown (*14, 20*) that reciprocal temperatures should be used for the Dühring plot; i.e., the reciprocal of the temperature of one substance should be plotted against the reciprocal of the temperature of

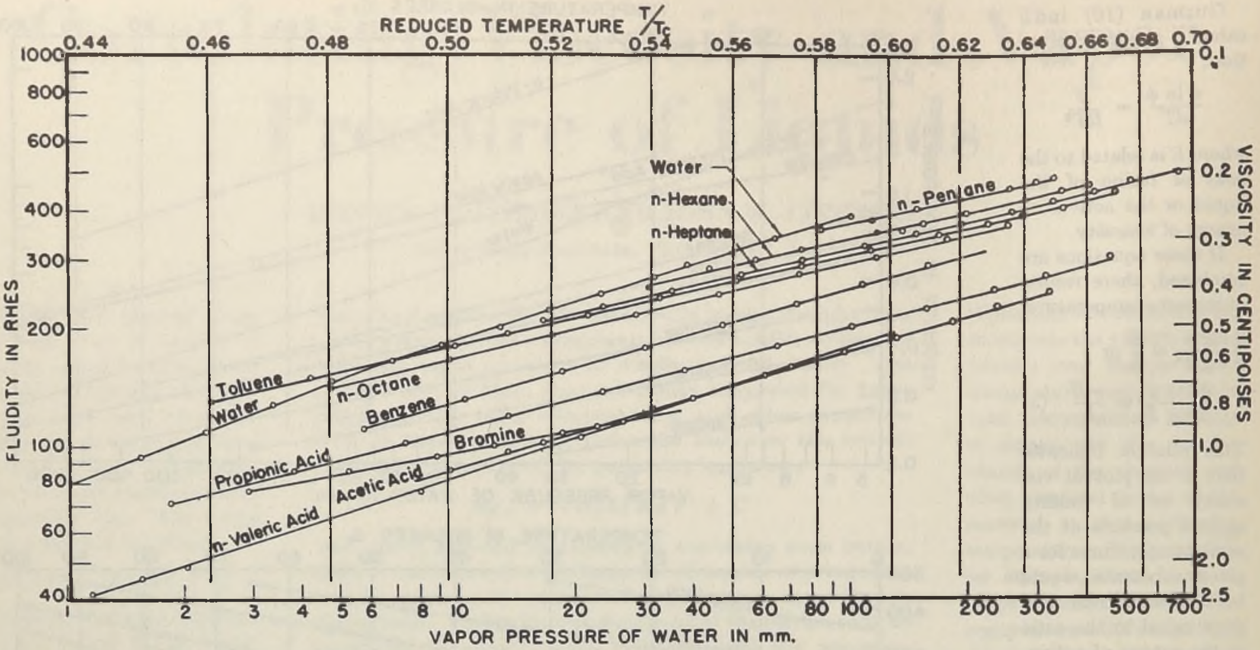

Figure 2. Log Plot of Fluidity of Eleven Representative Liquids against Reduced Temperature Which is Obtained from the Corresponding Vapor Pressures of Water

The viscosity is calibrated directly on a reciprocal scale on the right, so that either fluidity or viscosity may be read from the same chart. This plotting against reduced temperature reduces considerably the width of the band of lines, as compared with Figure 1.

another where the vapor pressure is the same. This is also true for Porter's method of plotting, and a better approximation to straight lines is found when the reciprocal temperatures are used. In that case exactly the same plot will be obtained on a different background grid work of coordinates as is obtained in the present plot. This follows directly and was explained in detail for the case of vapor pressure and temperature (*14*). It is, however, much more simple to plot on log paper than on reciprocal ruling paper; several other advantages are explained there for vapor pressure which hold here also for viscosity. Furthermore, it is much more convenient to plot and to use a graph of viscosity as indicated above than a graph of temperatures at which viscosities are equal.

Others have also considered similar more or less empirical functions (*11*, *13*) which may be related to the thermodynamic derivations given above. Many other empirical formulas have been particularly related to the viscosities of petroleum fractions.

USE OF CRITICAL CONSTANTS

The use of reduced temperature (*15*) tends to straighten log plots of reduced pressure as compared to those of pressure itself. Figure 2 is a plot of fluidity against the vapor pressure of water at the same reduced temperature (T/T_c). A series of ordinates was erected against the vapor pressure log scale on the horizontal axis at values of the corresponding temperatures divided by the critical temperature of water; the fluidity of the several materials was plotted on this grid work against the reduced temperature for that material. Since the lines against temperature, as determined by vapor pressure of reference substance (Figure 1), are straight within experimental error of the determination of data, the use of critical temperature cannot improve the presentation substantially. An interesting point, however, is that if these lines are extended to their respective critical temperatures (i.e., where $T_R = T/T_c = 1$), they tend to converge to a narrow band, except for water and the halogens. The fact that they do not converge to a point (i.e., the extended lines at the critical points of all substances do not give the same indicated fluidities) is probably due to the divergence of the liquids from ideality, as well as the fact that the isobaric pressure (1 atmosphere) used for all determinations of viscosity represents different reduced pressure for each substance. The slopes of the lines for a given substance on the two plots [Figures 1 (lower graph) and 2] are in each case substantially the same. Most noticeable is the narrowing of the band of the lines of all compounds, both those plotted here and others which fall directly on top of this representative group. Presumably, a general relation might be worked out. If it could include corrections for the fundamental properties of the individual fluid, it might bring even closer together all of the viscosity data for fluids. Even on the present basis these data do not vary more than 50% as a maximum from the values of a representative material such as benzene.

Also investigated was a plot of fluidity at the same value for the difference between critical and experimental temperature. This log plot of ϕ against $T_c - T$ (from calculated values for water which are calibrated on the X-axis against the log of vapor pressure) also gives straight lines, but there is no other reason to warrant its complicated preparation and use.

VISCOSITY FUNCTION AGAINST VISCOSITY FUNCTION

Still other methods of expression which follow directly from Figures 1 and 2 would be plots of viscosity of the compound against viscosity of a reference substance (not water, since it forms a broken line) at the same temperature; or of fluidity against fluidity at the same temperature; or of viscosity against viscosity or of fluidity against fluidity at the same reduced temperature. These plots would also give straight lines and could be employed. However, in the usual case it may be somewhat easier to calibrate the log paper used for plotting on the basis of the vapor pressure scale rather than of the viscosity scale in order to obtain the temperature ordinates used for the actual plotting.

Proof of the previous paragraph is self-evident. In the upper graph of Figure 1, for example, the viscosity of both benzene and of acetic acid is a straight-line function as plotted logarithmically against the vapor pressure of water at the same temperature. Hence, the viscosity of benzene (or of any other material which gives a straight line on this graph) would be a straight-line function of the viscosity of acetic acid taken at the same temperature. The same would hold for a plot of fluidity at the same temperature against that of a reference substance, or for either viscosity or fluidity against that of a reference substance at the same reduced temperature.

The last mentioned plot is analogous to the plot of vapor pressure for one substance against vapor pressure of another at the same temperature (*14*) or critical temperature (*15*). The slopes of the lines on such a plot are the ratio of activation energies of viscosity of the two liquids (or of reduced activation energy).

ACKNOWLEDGMENT

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Hydrolysis and Catalytic Oxidation of Cellulosic Materials

DETERMINATION OF STRUCTURAL COMPONENTS OF COTTON LINTERS[1]

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A BOILING aqueous solution containing 2.5 moles of hydrochloric acid and 0.6 mole of ferric chloride per liter evolves carbon dioxide rapidly from glucose at a nearly constant rate which is proportional to the glucose present in the system (*6*). This reagent under the same conditions also liberates carbon dioxide from cellulosic materials but at slow, initial rates which increase as hydrolysis is continued (*4, 6*). These observations have led to the conclusions that some of the cellulose is hydrolyzed to simple sugars which, by oxidation, yield carbon dioxide, and that the course of the hydrolysis can be determined from instantaneous rates of carbon dioxide evolution (*5*). The technique and apparatus originally employed in this laboratory were modified and improved by Conrad and Scroggie (*2*), who verified and extended some of the earlier work.

Hydrolysis-time curves obtained by this method for a number of different cellulosic materials have in common a shape that indicates rapid, early disintegration of part of the cellulose and a subsequent slower and more constant breakdown of the remainder. As Badgley and collaborators (*1*) stated in a recent review, such curves are generally regarded as evidence of a structural heterogeneity. The rapid initial hydrolysis represents the easily accessible or disordered fraction; the slower and more constant, subsequent hydrolysis, the denser less accessible or highly ordered fraction of the material. However, these two parts of a typical hydrolysis-time curve are not sharply differentiable and, consequently, only a rough approximation of the distribution between ordered and disordered states can be obtained from the test.

The study described in this paper was undertaken to yield deeper insight into the meaning of hydrolysis-time phenomena and, if possible, to develop a practical method of resolving the typical curve. Samples of cotton linters were subjected to acid hydrolysis for varying times under controlled conditions, and the resulting insoluble residues were washed and dried. This series of hydrocelluloses was then investigated by the hydrolysis-oxidation method.

MATERIALS AND METHODS

A well-blended batch of processed, high-viscosity, acetate-grade cotton linters was used without additional purification as starting material. Hydrocelluloses, representing 0, 0.07, 0.2, 0.8, 2, 4, and 7 hours of treatment with boiling hydrochloric acid-ferric chloride reagent or its equivalent, were isolated for investigation by the methods described below.

The intact sample (0 hours) was boiled 4 minutes in water; the 0.07- and 0.2-hour samples were digested singly in boiling 2.5 *N* hydrochloric acid for 4 and 12 minutes, respectively. The rest of the series was prepared by refluxing a suitable batch of linters in hydrochloric acid-ferric chloride reagent. siphoning off portions of the boiling suspension 5–10 minutes short of the times indicated, and, as quickly as possible, filtering the hot suspension on coarse alundum crucibles. Crucible and residue were then given preliminary washes with cool, dilute hydrochloric acid and water; finally, the crucible containing moist residue was transferred to boiling 2.5 *N* hydrochloric acid for 5–10 minutes to complete the digestion. A volume of 40 ml. of hydrolyzing solu-

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[1] For previous papers in this series, see literature citations *3–6*.
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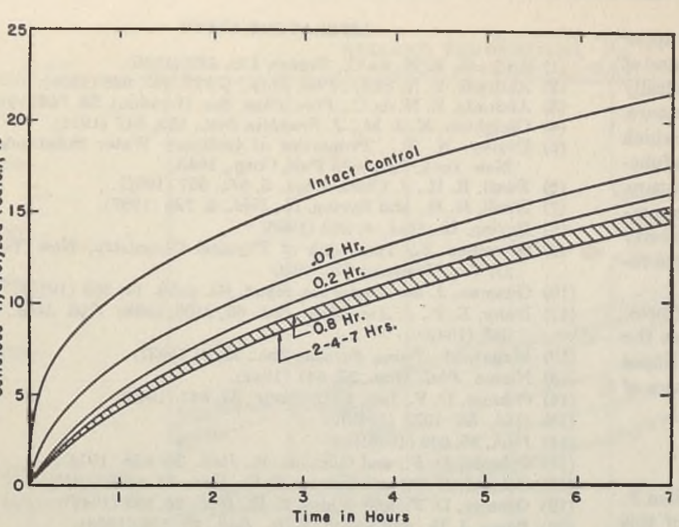

Figure 1. Hydrolysis-Time Curves Calculated for Linters and Derived Hydrocelluloses

The times indicate amounts of hydrolytic pretreatment employed in preparation of samples.

tion per gram of starting material was found to be satisfactory. The use of ferric chloride reagent for the longer periods of hydrolysis hinders the accretion of undesirable tarlike products, while the double digestion is designed to extract occluded iron salt.

Directly after receiving the treatment just outlined each sample, including the intact control, was purified in the following way: The solid was filtered on a coarse alundum crucible, and washed in the crucible with hot water, with several floodings of warm 5% ammonia, and then successively with boiling water, acetone, and benzene. It was removed from the crucible and air-dried.

Approximately 2 grams of the hydrocelluloses were placed in tared weighing bottles, dried at 105° C., and weighed accurately before use. Time–carbon dioxide evolution data covering a 7-hour period were then determined for each preparation by a method similar to that used previously (*5*, *6*). The apparatus, however, was modified so that weighing bottle and sample could be dropped into the boiling hydrochloric acid–ferric chloride reagent through a port in the digestion flask. Time for the hydrolysis-oxidation reactions was reckoned from the entrance of the sample into the boiling liquid. In previously reported experiments it was necessary to introduce the sample and assemble the apparatus before the digestion mixture was heated and to count time from the onset of boiling. The change in technique was designed to eliminate any spurious effects the warming-up period might have caused.

A further modification of the apparatus was made in the substitution of an ascarite-gravimetric absorption system for the aqueous barium hydroxide–titrimetric system used earlier for carbon dioxide determination. The gravimetric method proved to be simpler and less time consuming than the titrimetric and fully as accurate. Since suitable absorption trains have been adequately described by Whistler, Martin, and Harris (*8*) and by Conrad and Scroggie (*2*), only the novel feature of that used in the present investigation needs mention here.

Ten similar ascarite-filled, U-shaped absorption tubes with short side arms, and two pairs of detachable, right-angled, glass extensions for the arms were employed in each run. Fitted with a pair of the extensions by means of rubber connections, an absorption tube could be seated over two vertical orifices provided with mercury cups and, so placed, would bridge a gap in the train. At the end of a prescribed time interval the absorption tube was quickly removed and replaced by another absorption tube extension assembly.

In practice the ten tubes were conditioned together overnight in a large desiccator and weighed. Nine of the tubes were then used to cover a 7-hour hydrolysis-oxidation period. After further overnight conditioning in the desiccator, all ten tubes were reweighed, and the weight increments were corrected for changes in the blank. The series of tubes was then ready for a new run.

CARBON DIOXIDE EVOLUTION

The assumption that soluble hydrolytic products derived from cellulose yield carbon dioxide in the same manner as glucose receives support from the data in Table I. Presented on a comparable basis as cumulative moles of carbon dioxide per mole of glucose, these data indicate that glucose and cellobiose behave the same within experimental error. This basis of presentation was suggested by Scroggie (*7*).

Table II shows the variation of cumulative carbon dioxide output, as moles per mole of anhydroglucose, with time for intact linters and for hydrocelluloses derived from them. These data on conversion by the method of slopes (*5*) yield the percentage hydrolyzed–time curves of Figure 1. In both forms these observations indicate that prior hydrolysis reduces the yield of carbon dioxide, at first rapidly and then at a decreasing rate to practical constancy in about one hour. In fact, this result might almost have been anticipated from the relative densities of intact linters and of the various hydrocelluloses prepared for use in the runs. Figure 2 also suggests that constancy of a sort is attained in about an hour of hydrolysis.

At the end of each 7-hour hydrolysis-oxidation run, the insoluble cellulosic residue in the digestion flask was filtered off, washed, dried, and weighed. From the known starting weights of each sample, the percentages of unhydrolyzed matter were readily calculated. In Figure 3 these percentages are plotted against the hours of hydrolysis the samples received prior to the actual runs. The amounts of recoverable residue, represented by the solid line, rise sharply and then level off after the first hour. Similarly, the estimated quantities of cellulose hydrolyzed during the 7-hour runs taken from Figure 1 and shown by a dotted line decrease rapidly with hydrolytic pretreatment, and become more or less constant after an hour. Incidentally, the sums of the corresponding values on the solid and dotted curves are approximately 100 in most cases and tend to confirm the validity of the calculations.

In sum these observations indicate that the linters starting material is structurally heterogeneous and that virtually complete homogeneity is produced by about an hour of hydrolysis

Glucose, cellobiose, cotton linters, and a series of derived hydrocelluloses were examined by the hydrolysis-oxidation method for the purpose of obtaining more information on linters structure and on the method itself. Carbon dioxide evolution data for these materials and for a dextrose-hydrocellulose mixture that simulates intact linters are reported. Other variables investigated include moisture adsorption and insoluble matter recoverable after hydrolysis-oxidation runs. The linters starting material appears to contain, as distinguishable parts, highly disordered, highly ordered, and transitional components in amounts by weight of approximately 3, 94, and 3%, respectively. The highly disordered component is readily differentiated by its hygroscopic nature and hydrolytic susceptibility, the crystalline or ordered component, by its uniformly low hydrolytic reactivity. A single hydrolysis-oxidation run is probably insufficient to characterize a sample, but the differential approach may be used advantageously.

under the conditions of the experiments. The evidence suggests that the major change occurring in the first hour of hydrolysis and resulting in homogeneity is the removal of part of the structure. Further information on this change can be obtained from the data in Table II by utilization of differences. For example, subtraction of values in column B from those for corresponding times in column A gives a series of differences which indicate how the ability of linters to yield carbon dioxide is reduced by 0.07 hour of hydrolytic pretreatment. If, as might be expected, these differences represent the loss of some easily hydrolyzed anhydroglucose from intact linters, it should be possible to express them in terms of glucose by use of the data in Table I. However, while column A values are yielded by one equivalent of intact linters, column B data are based upon one equivalent of hydrocellulose, which must necessarily represent more than one equivalent of starting material. In other words, it is assumed that the carbon dioxide values for intact linters are sums of carbon dioxide derived from a fraction that behaves like column B and a fraction that behaves like glucose. This assumption may be expressed by the equation,

$$A_t = (1 - x)B_t + xG_t \tag{1}$$

where x is the mole fraction of glucoselike material; A, B, and G are carbon dioxide values at time t for corresponding items in columns A and B of Table II, and for glucose in Table I, respectively. Solution of this equation for x gives

$$x = \frac{A_t - B_t}{G_t - B_t} \tag{2}$$

a more convenient form for calculation.

The results obtained by applying Equation 2 to several pairs of columns in Table II are shown in Table III. Despite considerable experimental error, the data, especially those derived from the 0 – 0.07-hour pair, indicate clearly that intact linters responds as if it contained 0.033 mole of glucose or, as is more likely, 0.033 mole of easily hydrolyzed anhydroglucose. Other pairs, such as 0 – 0.2-hour and 0 – 0.8-hour columns, yield not constants but series of increasing values which, plotted against the elapsed times of Table III, give essentially straight lines. In each case where intact linters (column A) is the minuend, extrapolation of the straight line so obtained to zero time[4] produces an intercept at about 0.03 mole, as can be confirmed qualitatively by Table III. Thus, preparations representing longer pretreatment than 0.07 hour respond to hydrolysis-oxidation as if they differ from intact linters by 0.033 mole of immediately hydrolyzed anhydroglucose and, in addition, some gradually available cellulosic material. Column $B - D$, corresponding to the 0.07 – 0.8 hour pair, shows how the gradually hydrolyzed cellulosic material accumulates and indicates that the maximum of it present in intact linters is about 3.0 mole %. This estimate agrees fairly well with the vertical spacing of the 0.07- and 0.8-hour curves in Figure 1, after they have been adjusted for the concentration effect mentioned above.

Table I. Carbon Dioxide Evolved by Glucose and Cellobiose in Hydrochloric Acid–Ferric Chloride Reagent

Elapsed Time, Hr.	Moles CO_2/Mole Glucose: Glucose	Moles CO_2/Mole Glucose: Cellobiose	Cellobiose/ Glucose
0.8	0.047	0.045	0.96
1.3	0.124	0.118	0.95
1.9	0.211	0.219	1.04
2.5	0.310	0.322	1.04
3.1	0.414	0.428	1.03
4.0	0.562	0.568	1.01
5.0	0.711	0.710	1.00
6.0	0.855	0.845	0.99
7.0	0.979	0.967	0.99

Table II. Carbon Dioxide Evolution of Linters and Derived Hydrocelluloses in Hydrochloric Acid–Ferric Chloride Reagent

Elapsed Time, Hours	A	B	C	D	E	F	G
	Moles CO_2/Mole Anhydroglucose after Prior Hydrolysis for:						
	0	0.07 hr.	0.2 hr.	0.8 hr.	2 hr.	4 hr.	7 hr.
0.8	0.0031	0.0015	0.0015	0.0013	0.0015	0.0013	0.0011
1.3	0.0086	0.0052	0.0044	0.0041	0.0037	0.0042	0.0039
1.9	0.0185	0.0117	0.0099	0.0089	0.0079	0.0101	0.0091
2.5	0.0277	0.0198	0.0163	0.0151	0.0131	0.0147	0.0139
3.1	0.0412	0.0284	0.0245	0.0225	0.0206	0.0222	0.0204
4.0	0.0635	0.0458	0.0387	0.0361	0.0338	0.0370	0.0344
5.0	0.0900	0.0675	0.0572	0.0531	0.0505	0.0531	0.0494
6.0	0.1190	0.0930	0.0777	0.0716	0.0697	0.0704	0.0689
7.0	0.1499	0.1180	0.0995	0.0915	0.0888	0.0891	0.0875

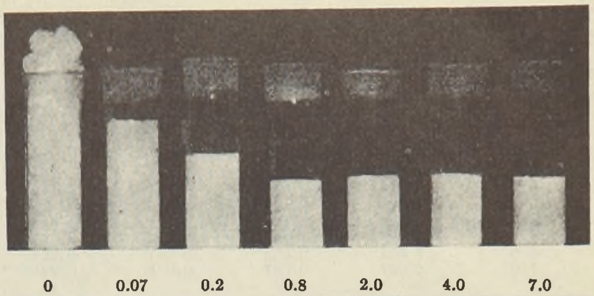

Figure 2. Appearance of Dry, 1-Gram Samples of Linters and Derived Hydrocelluloses

Numbers indicate hours of hydrolytic digestion received by each sample.

The foregoing calculations yield the result that the linters starting material contains approximately 3.3% of readily hydrolyzed anhydroglucose, 3% of a gradually hydrolyzed fraction, and, consequently, between 93 and 94% of slowly hydrolyzed, resistant cellulose. Support, especially for the latter estimate, is provided by the data of Figure 3; they suggest not only that resistant material of uniform behavior is produced by an hour or more of hydrolysis under the conditions, but also that about 84% of this material is recoverable at the end of a 7-hour hydrolysis-oxidation run. The 84% recovery value holds over an appreciable range of pretreatment times and may be assumed to hold for intact linters. Thus, the 77.2% recovery for intact linters may represent about 84% of the total resistant cellulose of this starting material. The ratio of these two quantities yields an estimate for total resistant cellulose in intact linters of 92% which agrees very well with the independent value derived by the other method.

The above differential analysis suggests that intact linters behaves like the sum of glucose and 0.07-hour hydrocellulose fractions during hydrolysis-oxidation. This surmise was confirmed experimentally. A mixture of crystalline glucose (reagent dextrose) and this hydrocellulose preparation, in the calculated proportions of 0.033 to 0.967 mole, was subjected to hydrolysis-oxidation. Carbon dioxide–time data yielded by this mixture follow:

Time, hr.	0.8	1.3	1.9	2.5
CO_2, moles/mole anhydroglucose in mixt.	0.0031	0.0086	0.0188	0.0285

Time	3.1	4.0	5.0	6.0	7.0
CO_2	0.0441	0.0640	0.0901	0.1180	0.148

These data compare favorably with those for intact linters in Table II and indicate that the behavior of the starting material can be simulated almost perfectly by this means.

The variation of moisture-adsorbing capacity of certain unsubstituted cellulosic materials with amount of hydrolysis has already been demonstrated (*5*). These observations show that a

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[4] Owing to a low initial rate of carbon dioxide evolution from glucose (*2*), an apparent lag seems to occur between additions of glucose and appearance of carbon dioxide. For this reason zero time for the extrapolation is at approximately 0.4 hour.

Table III. Calculated Glucose Equivalents of Carbon Dioxide Differences Produced by Prior Hydrolysis

Elapsed Time, Hr.	Moles of Glucose Equivalent to Column Differences (from Table II)			
	A − *B*	*A* − *C*	*A* − *D*	*B* − *D*
0.8	0.035	0.036	0.039	0.004
1.3	0.029	0.035	0.038	0.009
1.9	0.034	0.043	0.048	0.014
2.5	0.027	0.039	0.043	0.016
3.1	0.033	0.043	0.048	0.015
4.0	0.034	0.047	0.052	0.018
5.0	0.035	0.050	0.056	0.021
6.0	0.034	0.053	0.061	0.027
7.0	0.037	0.057	0.065	0.028

rapid initial fall in regain capacity is followed by a continual, slow rise. Moisture vapor sorption determinations were also made on the present series of preparations. The dry samples were simultaneously exposed at 70° F. and 65% relative humidity until weights became constant. The data obtained follow:

Time hydrolyzed, hr.	0	0.07	0.2	0.8	2	4	7
Regain of residue							
Per cent	7.66	6.26	6.43	6.77	7.14	7.71	8.17
Moles water/mole anhydroglucose	0.689	0.563	0.579	0.609	0.643	0.694	0.735

In addition to confirming the previously reported variation of hygroscopic behavior with progress of hydrolysis, these data may be used in the calculation of an interesting result: Since intact linters appears to be composed of 0.033 mole of a glucose-analogous cellulose and 0.967 mole of 0.07-hour hydrocellulose, the preceding table shows that 0.145 mole of water are associated with the 0.033 mole of quickly hydrolyzed cellulose [from 0.689 − (0.967) (0.563), since intact linters is considered to contain only 96.7% of 0.07-hour hydrocellulose]. This represents about 4.4 molecules of water per anhydroglucose unit or about 1.5 molecules of water per hydroxyl group for this part of the structure. Unreported observations indicate that the 0.07-hour hydrocellulose shows about one third less adsorption-desorption hysteresis than intact linters; presumably, therefore, a part of this moisture may be condensed in capillaries which the hydrolysis destroys. Even so it is evident that there must be a high percentage of free hydroxyls, each having one molecule of water, in the easily hydrolyzed regions of intact linters.

STRUCTURAL COMPONENTS

The evidence presented can leave little doubt that the intact linters starting material is structurally heterogeneous. In fact, examination of the data suggests that the structure is composed of three different parts or, more specifically, of three distinguishable degrees of association of the anhydroglucose chains. For want of more descriptive terms, these three parts are designated as crystalline, amorphous, and mesomorphous components.

The crystalline component comprising the bulk of the linters is characterized by its low hydrolytic susceptibility. The data in Table II and the curves in Figures 1 and 3 show that hydrolysis for about an hour under the conditions produces a residue which is remarkably uniform in its behavior towards further hydrolysis. It is reasonable to assume that this residue represents the highly organized or crystalline regions of the linters whose low reactivity per unit weight is caused by their relative impermeability and inaccessibility. It is estimated that this component constitutes about 94% of the starting material.

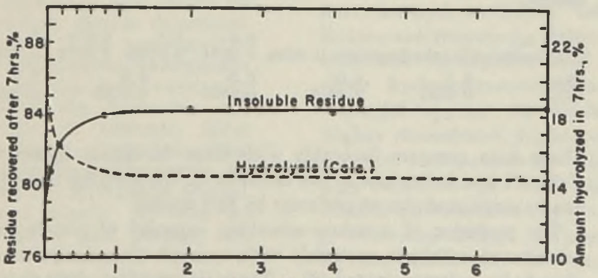

Figure 3. Effect of Hydrolytic Pretreatment of Linters on Yield of Insoluble Residue and on Amount of Cellulose Hydrolyzed during Hydrolysis-Oxidation Runs

The amorphous component, on the other hand, is characterized by its complete accessibility. It quickly hydrolyzes to glucose or soluble glucoselike products which can be separated from the rest of the structure. In addition to exhibiting the greatest hydrolytic susceptibility, this component is the most hygroscopic; it apparently has at least one molecule of water per hydroxyl group at standard textile testing conditions. These results suggest that the amorphous component consists of extremely random or disordered portions of anhydroglucose chains. The data indicate that intact linters contains about 3.3% by weight of this component. The role of this disorganized part of the linters structure is very important for, as Figure 2 shows, its removal reduces the linters to a coarse powder.

The mesomorphous component is intermediate in hydrolytic susceptibility. It appears to be less accessible than the amorphous and more accessible than the crystalline component. Furthermore, its behavior suggests that it is less homogeneous in itself than either of the other components since it exhibits all degrees of hydrolytic susceptibility between those of the amorphous and crystalline components. In short, it acts precisely as if it were the transitional state of matter between two extremes of structural organization. It seems to be rather sharply differentiable from the amorphous component but not from the crystalline. The mesomorphous material is estimated to constitute about 3% by weight of the intact linters. The photographic evidence suggests that further powdering of the linters occurs when this component is removed.

From these results it is apparent that a single hydrolysis-oxidation run may not be sufficient to characterize a sample completely. The amorphous component, set free at the start, falls in the range where measurements are least accurate. Furthermore, extrapolation as a means of estimating the total noncrystalline cellulose presents an uncertainty in that the point of transition from mesomorphous to crystalline is, at best, obscure. However, it seems reasonable to expect that a differential method of the type employed in this investigation will overcome both of these difficulties.

Present results should facilitate the application of the differential method to other materials. For example, it is conceivable that the amorphous component of other cellulosic materials would hydrolyze completely under roughly the same time and concentration conditions as were observed for linters. In support of this suggestion is the fact that similar hydrolyzing conditions produce moisture regain minima in about the same time for a variety of natural and modified cellulosic materials (*5*). However, it should be noted that more precise methods than that employed may be adapted for glucose determinations, and that somewhat milder hydrolyzing conditions requiring a longer time than 0.07 hour may also be desirable for greater accuracy. Some work along these lines has already been completed.

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Changes in Stored Dried Eggs

SOURCE OF FLUORESCENCE

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The fluorescence of 10% salt extracts of dried eggs is currently used as a simple criterion of palatability. This fluorescence, the source of which has not been recognized, appears to be due to the brown reaction products of glucose and the free amino groups of proteins. Similar fluorescing brown products also result from the interaction of simple amines and aldehydes. These can be used as model systems for the study of the glucose-protein reaction.

DURING the past few years it has become increasingly apparent that the brown color which develops in food products during storage is in part the result of a condensation of reducing sugars with proteins and protein hydrolytic products. Ramsey, Tracy, and Ruehe (*18*) attributed the darkening of condensed milk sweetened with dextrose to sugar-protein condensation products. Balls and Swenson (*2*) suggested that the accelerated darkening of trypsin-treated unfermented egg white might be due to a similar reaction. Fermented egg white which contains no glucose does not darken on storage. Stewart and Kline (*21*) and Stewart, Best, and Lowe (*20*) studied the effect of glucose concentration, temperature, pH, and moisture content on the changes in properties of egg white and spray-dried eggs. Darkening was favored by increased concentrations of glucose, high temperature, alkaline reaction, and moisture contents higher than 5%. Weast and Mackinney (*23*) demonstrated that the darkening of apricots and other fruit products is due in part to the reaction of reducing sugars and amino acids.

Since Maillard (*13*) described the reactions of amino acids with reducing sugars with formation of artificial "humin" substances, a number of investigators have contributed further information (*1*). The development of brown products takes place in concentrated aqueous solutions of glycine and glucose in a few hours at slightly elevated temperatures. As with dried eggs, the reaction is favored by high temperature and an alkaline reaction. Enders (*5*) showed that the glucose-glycine phenomenon is a specific example of a very general aldehyde-amine reaction.

Pearce and Thistle (*17*) first proposed that the fluorescence in salt extracts of dried eggs could be used as a measure of their deterioration during storage. Later Pearce (*16*) described the development of fluorescing materials during the storage of a number of different types of foodstuffs. Stewart, Best, and Lowe (*20*) concluded that the fluorescence changes in dried eggs were due to the reaction of glucose with some other component in the egg.

Although the fluorescence test has been widely used as an index of palatability of dried eggs, the origin and nature of the fluorescing substance have been obscure. Pearce (*15*) suggested that it was due to protein hydrolytic products. During the course of work related to dehydrated eggs at this laboratory, it was observed that the brown solutions developing during the interaction of simple aldehydes and amines were highly fluorescent. The experiments to be reported in this paper indicate that products of the reaction between glucose and the amino groups of proteins are responsible, at least in part, for both discoloration in dried eggs and fluorescence in salt extracts.

Dutton and Edwards (*4*) suggest that the brown fluorescent substance which can be extracted from stored dehydrated eggs with ether arises from an aldehyde-amine reaction. The fluorescence of the ether-soluble lipide fraction should be differentiated from that observed by Pearce *et al.* (*15*, *16*, *17*), who measured this property in aqueous salt extracts.

FLUORESCENCE MEASUREMENTS

METHODS. The development of color during the course of reaction of glucose and glycine was followed by measuring the optical density (log I_o/I_x at wave length 440 mμ in a cell of 1-cm. path length) with a Cenco spectrophotometer. The fluorescence of the substances measured was bluish white and consisted of a continuous emission band that extended throughout the visible region of the spectrum. Fluorescence was measured with a Coleman electronic fluorophotometer (filters B_1 and PC-1). The wave length of the exciting light was 365 mμ (mercury). The instrument was adjusted to give a scale reading of 100 with a quinine sulfate solution containing 0.0004 mg. per ml. in 0.1 *N* sulfuric acid. Amino nitrogen was determined by the manometric method of Van Slyke (*22*); proteins were permitted to react for 15 minutes, hydrolyzates for 3 minutes.

Crystalline egg albumin was prepared by the method of Kekwick and Cannon (*11*). Egg-white globulin was obtained from fresh egg white by precipitation with half-saturated ammonium sulfate at pH 6.0. The procedure of solution in distilled water followed by precipitation was repeated twelve times. The protein was then dialyzed against distilled water and dried by lyophilization. Lipovitellin was prepared as directed by Chargaff from fresh egg yolks (*3*). Livetin was recovered from the water-soluble fraction of egg yolks by lyophilization after dialysis. The acid casein was a preparation supplied by the Eastern Regional Research Laboratory.

BROWN COLOR AND FLUORESCENCE WITH PROTEINS AND GLUCOSE. One half gram of recrystallized egg albumin was dissolved in 10 ml. of distilled water. The solution was at pH 4.6. To one half, 0.0125 gram of glucose (5% of the weight of the protein) was added. The two portions were separately dried before a fan at room temperature, ground, and equilibrated in a closed vessel adjusted to contain 70% relative humidity at room temperature (23–25° C.) for 2 days. The samples then contained approximately 11% moisture. They were transferred to small vials, stoppered with rubber, and held at 50° C. for 6 days. The sample containing glucose had become yellow brown; the control remained colorless. The two samples were dissolved in water, and aliquots were analyzed for amino nitrogen. The control sample contained 0.66% amino nitrogen (dry basis); the sample with glucose contained 0.31% amino nitrogen (corrected for glucose and moisture). The fluorescence value for the brown, glucose-treated egg albumin (0.1% solution in distilled water) was 26.9; that for the colorless control, 1.5.

In a parallel experiment, 1.0-gram samples of egg albumin, egg-white globulin, livetin, lipovitellin, and casein were dissolved or suspended in 20 ml. of distilled water, and sufficient 0.1 *N* sodium hydroxide was added to adjust the pH to 8.0. (Homogenized eggs are usually at pH 8.0 or somewhat higher.) To half of each of the solutions 25 mg. of glucose were added. The samples were then dried before a fan at room temperature equilibrated at 70% relative humidity, stoppered, and stored at

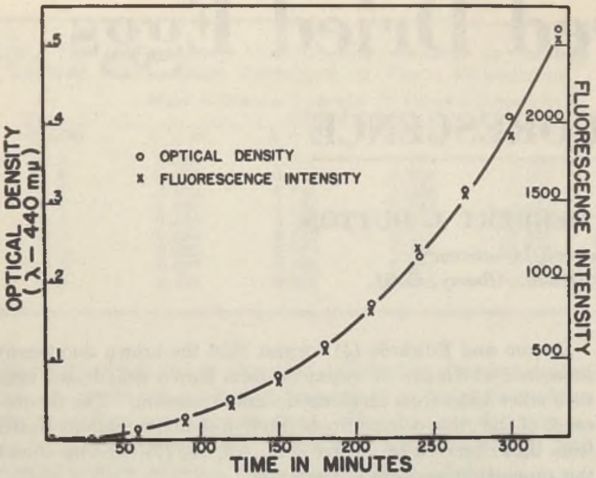

Figure 1. Development of Color and Fluorescence in Glucose-Glycine-Phosphate Solution with Time

At 0 time, 17.5 grams glucose, 7.5 grams glycine, and 5 grams disodium phosphate dodecahydrate were dissolved in 25 ml. of water at 50° C. (pH 7.3). The solution was kept in a bath at 50° C. during the course of the experiment.

50° C. for 7 days. The samples were analyzed for nitrogen and amino nitrogen. The results for amino nitrogen are summarized in Table I. For each protein the samples stored with added glucose were considerably browner than their controls. The insolubility in water of some of these products prevented fluorescence measurements. Egg albumin gave fluorescence values of 62.5 and 2.0 for the samples with and without glucose, respectively. The results indicate that the reaction of proteins with glucose is not confined to any one protein constituent of the egg.

Table I. Effect of Glucose on Amino Nitrogen Content of Protein Stored at 50° C. for 7 Days

Protein	Amino N as % of Total N		
	Without glucose	With glucose	Loss
Egg albumin	4.5	2.6	44
Egg-white globulin	3.9	2.2	45
Livetin	6.2	3.7	40
Lipovitellin	5.6	3.6	35
Casein	5.4	3.7	34

Absence of Fluorescence in Enzyme-Digested Egg Albumin. Crystalline egg albumin solutions were adjusted to pH 2.0 and 8.0 and digested with crystalline pepsin and commercial pancreatin at 37° C. The fluorescence and amino nitrogen content of the solutions were measured at intervals during the digestion. There was no increase in fluorescence in 48 hours, although by this time approximately 10% of the peptide bonds had been released. A similar experiment with fresh egg white gave comparable results. The fluorescence of the pepsin-digested egg white was compared with that of a 10% potassium chloride extract obtained from a sample of defatted spray-dried egg (containing 5% moisture) which had been stored for 9 months at 37° C. The two solutions were adjusted to equal nitrogen contents. The salt extract was considerably browner than the pepsin digest and the fluorescence was twenty-six times stronger. Reeder and Nelson (*19*) state that hydrolysis of proteins by hydrolytic enzymes or alkalies produces only a slight increase in fluorescence, as compared with that which develops during acid hydrolysis.

Glucose-Glycine Reaction. This reaction was typical of a number of aldehyde-amine systems studied. When these two compounds were ground together in a mortar and stored at 50° C., there was no apparent change. However, mixtures containing 2, 5, and 10% added water turned brown in 24 hours at 50° C. The color was deepest in the mixture with the highest moisture content. These results are analogous to those obtained in experiments with egg white by Stewart *et al.* (*20, 21*) and in this laboratory, in which browning was inhibited by low moisture contents.

Figure 1 shows the rate of development of a brown color in a concentrated, heavily buffered solution (pH 7.0) of glycine and glucose. The rate is accelerated by increasing temperature, pH, and concentration. Air or oxygen is not necessary, since the reaction proceeds at equal rate in a high vacuum. In the absence of buffers, the pH of such a mixture falls from 7 to below 5.

To show that the colored products were also responsible for the fluorescence, the two properties were measured simultaneously during the course of the reaction. By appropriate adjustment of the scales for optical density and fluorescence, the curves could be shown to be directly superimposable (Figure 1); this agreement is regarded as evidence of the identity of the colored and fluorescing compounds.

Glucose-Amine Condensation Products. Glucosides of amyl, butyl, and ethanol amines were synthesized by the method of Mitts and Hixon (*14*). During storage at room temperature the white crystalline compounds gradually turn yellow and then brown, and after several weeks melt to a deep brown sirup. At 50° C. this reaction is considerably accelerated, and the first stages are detectable in a few hours. Solutions of the brown products are highly fluorescent. These decompositions do not appear to require the presence of added water, in contrast to the behavior of glucose-glycine mixtures.

DISCUSSION

The suggestion of Pearce (*15*) that protein hydrolytic products are responsible for the fluorescence of salt extracts of dried egg was based in part on his observation that solutions of peptones are highly fluorescent. They are also highly colored. It appears more probable that the substances responsible for these properties are due to an interaction of amino acids with carbohydrates during some subsequent process (possibly drying) in the preparation of such materials, since peptic or tryptic digestion alone did not cause an increase in fluorescence or color.

The instability of the dry glucosidyl-*N*-amines suggests that aldehyde-amine addition products once formed do not require moisture in order to decompose. However, the browning reaction in stored foods is markedly inhibited at low moisture contents (*20, 21*). These observations lead to the hypothesis that the role of moisture may be to furnish a reaction medium for the aldehydes and amines.

The chemical reactions responsible for the browning are apparently complicated (*1, 5, 6*). The amino groups of proteins seem to be primarily involved in the glucose-protein color reaction, since, of a number of proteins, only zein failed to develop a deep brown color when evaporated to dryness at 100° C. with a solution of glucose. Zein is known to contain very few free amino groups. The degree of browning obtained with all proteins was markedly increased after partial hydrolysis. However, it is possible that other protein polar groups may also react with glucose. Formaldehyde has been shown to combine with protein amide, thiol, guanidyl, and possibly other groups, as well as with the amino groups (*8*).

Loiseleur (*12*) described a progressive increase in the intensity of fluorescence of proteins during treatment with formaldehyde. The amount of fluorescence was proportional to the concentration of formaldehyde and developed more quickly at elevated temperatures. Proteoses gave a more intense fluorescence than did proteins. These reactions are, in all likelihood, parallel to those described above with glucose.

The work of Enders (*5*) and Fischer and Marschall (*7*) suggests that amino compounds "catalyze" caramelization of the glucose or other aldehyde under milder conditions than when these materials decompose alone. The brown colors obtained from glucose, either by heat or in stronger alkaline solutions, have much the same characteristics as do those obtained in the presence of amino compounds. However, the amines are not true catalysts for such decomposition, since they participate in the reaction. "Humins" prepared in their presence contain varying amounts of nitrogen, depending upon the amount of amine originally present (*5*).

Several investigators have studied the development of brown pigments in heated milk products (*10*, *18*). The reactions are apparently closely related to those which occur during prolonged storage.

The color changes that take place in stored foods undoubtedly reflect a number of independent reactions. Joslyn (*9*) summarized those that are important for fruit products. The parallel development, during storage, of color (reflectance) and fluorescence, when measured after the removal of lipides, is in accord with the results described above for model systems. Dutton and Edwards (*4*) have shown that carotenoid destruction and the development of brown substances in the lipide fraction of dried egg contribute to the color changes.

ACKNOWLEDGMENT

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ROLE OF PHOSPHOLIPIDES AND ALDEHYDES IN DISCOLORATION

B. G. EDWARDS AND H. J. DUTTON

A brown material from dehydrated whole egg powder, found in both the total ether extract and the cephalin fraction, has been concentrated. Evidence indicates that this material arises from the reaction of a cephalin amino group with aldehydes.

DEHYDRATED egg powders tend to acquire a brown color during storage. In a study of the sources of this discoloration, an ether-soluble brown substance has been traced to the cephalin fraction of the phospholipides. Evidence obtained supports the hypothesis that this substance is the product of a reaction of an aldehyde with an amino constituent of the cephalin fraction.

Dehydrated whole egg powder that had darkened markedly during nine months of storage in air at 37° C. was used in this investigation. From the ether-soluble fraction of the powder a brown product was prepared in concentrated form. It was not removable from the ether extract by water, but after the saponifiable fraction had been strongly acidified with sulfuric acid, the brown material was found in the acid aqueous layer and was no longer soluble in ether. Inorganic salts were largely precipitated and removed from the aqueous solution by addition of absolute ethanol to give a concentration of 80% alcohol. The alcohol, water, and most of the glycerol were then removed by vacuum distillation. The pressure was reduced to less than 1 mm. of mercury toward the end of the process; the temperature did not exceed 135° C. By this step the water solubility of the brown material was markedly diminished although its ether insolubility was not affected. The material was washed by two consecutive suspensions in distilled water, followed by centrifugations. From 60 grams of dehydrated whole egg, 86 mg. of brown amorphous material containing 1.1% nitrogen (micro-Kjeldahl) and 1.6% phosphorus (colorimetric method) was obtained. Its absorption spectrum (obtained with a Beckman spectrophotometer) is given in Figure 1.

Since the phosphorus and nitrogen contents of the product suggested derivation from phospholipides, lecithin and cephalin were separated from the stored dehydrated egg, from freshly lyophilized yolk, and from yolk of fresh shell egg by a modification of the method of Sueyoshi (*10*). This method is based on the tendency of phospholipides to precipitate from extracted egg oil, the comparative insolubility in acetone of phospholipides as compared to fats, and the differences in solubility in alcohol between lecithin and cephalin. In the preparation of the cephalin fraction, the alcohol-insoluble material obtained after separation of the lecithin was further purified by elimination of ether-insoluble matter and subsequent acetone precipitation of the concentrated ether extract.

It is well to mention at this point the uncertainty regarding the purity of phospholipide preparations in general. Complete separation as indicated by total nitrogen, phosphorus, and amino nitrogen values of phospholipide preparations is seldom claimed (*5*). Such caution has been justified by recent work showing that the brain cephalin fraction is a mixture of phosphatidyl compounds (*4*) of different solubilities in alcohol. The presence in many preparations of products of partial hydrolysis, as well as the incompleteness of separation of lecithin and cephalin, permits only qualitative conclusions from experimental results involving the isolated compounds.

In a concurrent study under the direction of E. B. Kester on isolation and purification of egg phospholipides, it was observed that the cephalin-containing fraction from stored dehydrated egg powder appeared as an opaque brown substance in contrast to the transparent yellow of the lecithin. Although both lecithin and cephalin preparations were impure, their marked differences in color were considered significant in view of the practical absence of color from phospholipides similarly prepared from freshly lyophilized yolk and from fresh shell egg. (The cephalin samples average 1.5% nitrogen and 3.5% phosphorus; the lecithins averaged 1.8% nitrogen and 3.9% phosphorus.)

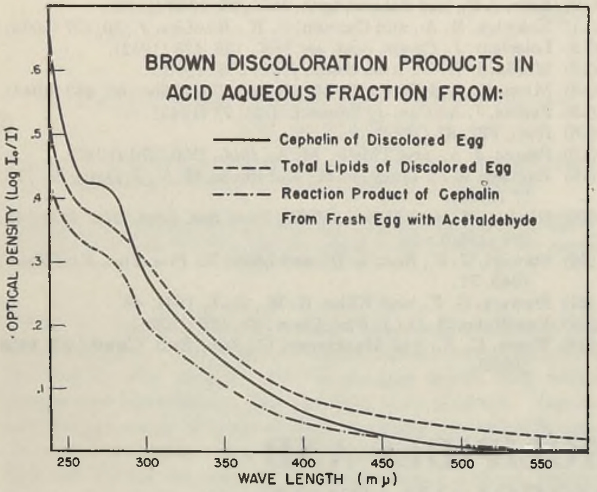

Figure 1

When the dissolved cephalin fraction was saponified, acidified, and treated with ether, the brown material remained in the acid aqueous phase, as was true with the total lipide extract of the stored egg powder. (This material differs from the well-known brown substance of aging lecithin and cephalin preparations, which enters the ether phase under the same conditions of treatment.) Spectrophotometric measurements ($\lambda = 270$ mμ) of the acid aqueous layer of the cephalin fraction showed that the brown reaction product in this fraction was concentrated ten to fourteen times its value in the original lipid extract. Moreover, different preparations showed three to seven times as much absorption at this wave length in the cephalin as in the lecithin fraction.

NATURE OF DISCOLORATION

The nature of the reactions involving discoloration is suggested in the reports of various workers. Balls and Swenson (*1*) and Stewart, Best, and Lowe (*9*) obtained brown products from glucose-protein interaction. Maillard (*6*), Weast and Mackinney (*11*), and Enders (*3*) demonstrated brown humin substances from interaction of reducing sugars and amino acids. Olcott and Dutton (*7*) showed that the reaction product of glucose with the amino groups of proteins was responsible in part for the brown color of stored dried eggs. These reports prompted a study of the reactions of the two phospholipides, cephalin and lecithin, and of ethanolamine and choline with aldehydes.

Weighed amounts of cephalin and lecithin preparations from lyophilized fresh egg yolk were reacted with approximately tenfold molar excess of acetaldehyde at room temperature in sealed glass tubes. The cephalin turned intensely brown within 30 minutes, while the lecithin darkened only slightly. Spectrophotometric measurements ($\lambda = 270$ mμ) of the acid aqueous fractions of these samples after removal of acetaldehyde under vacuum showed six times as much brown material in the cephalin as in the lecithin product. More decisive results were obtained when the more nearly pure ethanolamine and choline, which are nitrogenous constituents of cephalin and lecithin, respectively, were reacted with acetaldehyde. Ethanolamine hydrochloride and acetaldehyde gave a deep brown within 24 hours. The choline hydrochloride–acetaldehyde mixture, however, showed only a light translucent brown after 7 months.

Figure 1 gives the absorption curves of the brown materials obtained directly from the lipide extract and from the cephalin fraction of discolored dehydrated egg powder, and also from the cephalin fraction of fresh egg upon reaction with acetaldehyde. Lecithin and cephalin from fresh egg and freshly dehydrated egg in the absence of acetaldehyde gave negligible absorption. The curves for brown products from the cephalin of discolored egg and from cephalin reacted with acetaldehyde are practically identical in shape. The absorption curve for the brown material isolated directly from the lipide extract gives less indication of a maximum near 270 mμ than do the other two. The presence of other absorbing ether-soluble materials in the brown complex isolated from the whole dehydrated egg powder may account for the more general absorption characteristics observed.

The brown reaction products not only yield characteristic absorption curves but have been shown to be fluorescent. These two optical properties have made possible some analytical methods useful as quality criteria. The methods are now being applied to the study of dehydrated eggs during storage.

Since the brown materials have been found concentrated in the cephalin fraction, and since both cephalin and ethanolamine hydrochloride react rapidly with acetaldehyde in contrast to the slight reactivity of lecithin and the nonreactivity of choline hydrochloride, it seems apparent that at least one brown discoloration product in stored dehydrated egg arises from the reaction of a cephalin amino group with aldehydes. While the aldehydes involved may arise in the course of fat oxidation, their exact origin or character is not known. It is probable, moreover, that lipide amines other than cephalin may contribute to the browning of egg fat.

The evidence that cephalin reacts with aldehydes may be significant in connection with its antioxidant activity (*8*). It is possible that the common failure to detect aldehydes in egg fat is due to the prompt reaction of these compounds with lipide amines. The cephalin-aldehyde reaction may also be of interest when regard to the masking of amino groups in purified phospholipides as previously reported (*2*).

ACKNOWLEDGMENT

The writers are indebted to E. B. Kester and Julia S. Furlow for the phospholipide preparations used in these studies, and to L. M. White and G. E. Secor for the nitrogen and phosphorus determinations.

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SPECTROPHOTOMETRIC AND FLUOROMETRIC MEASUREMENT OF CHANGES IN LIPIDES

H. J. DUTTON AND B. G. EDWARDS

Changes that occur in the lipide fraction of dehydrated eggs during storage have been studied by spectrophotometric and fluorometric techniques. The reaction of lipide amines with aldehydes, the destruction of carotenoids, and a process that has been interpreted as polymerization of the unsaturated fatty acids were found to proceed faster at 98° than at 70° F.; little change was detected at 15° F. The fluorescing substance that develops in the fat of dehydrated eggs during storage has been tentatively identified as the reaction product of lipide amines with aldehydes.

CHANGES in color of the lipide fraction of dehydrated egg during storage arise presumably from three chemical changes: destruction of naturally occurring carotenoid pigments, production of yellow-to-brown materials from unsaturated fatty acid groups, and development of brown products resulting, probably, from the interaction of amine and aldehyde groups of lipides (*6*). While carotenoid destruction results in loss of color, the other two changes tend to darken the color of the dried egg product.

The decomposition of carotenoids in egg powders may be expected to be primarily oxidative, involving atmospheric oxygen either directly (*7*, *12*), or indirectly through enzymic or chemical intermediates (*1*, *21*). The alteration of unsaturated fatty acid groups in this product may also involve oxidative reactions. Although complex and partly obscure, the latter reactions are believed to result in the formation of peroxides and aldehydes and to yield brown polymers (*4*, *14*). However, polymerization and browning of unsaturated fatty acids may not involve oxidation but may occur as a result of a Diels-Alder type of reaction (*15*).

Attempts to follow the course of oxidation of the fats of dehydrated egg during storage by means of peroxide determinations have demonstrated little change; in fact, initial peroxide values have been found to decrease during storage (*3*). These data have led to the impression that the fat of dehydrated egg is quite stable. The present report, however, describes several changes found to occur in egg lipides during storage.

The "amine-aldehyde" interaction in egg lipides (*6*) is apparently a condensation process analogous to the glucose-protein reaction of the protein fraction (*2*, *16*, *19*, *20*). The brown substances produced, which will be referred to subsequently as lipide amine-aldehyde reaction products, absorb light throughout the

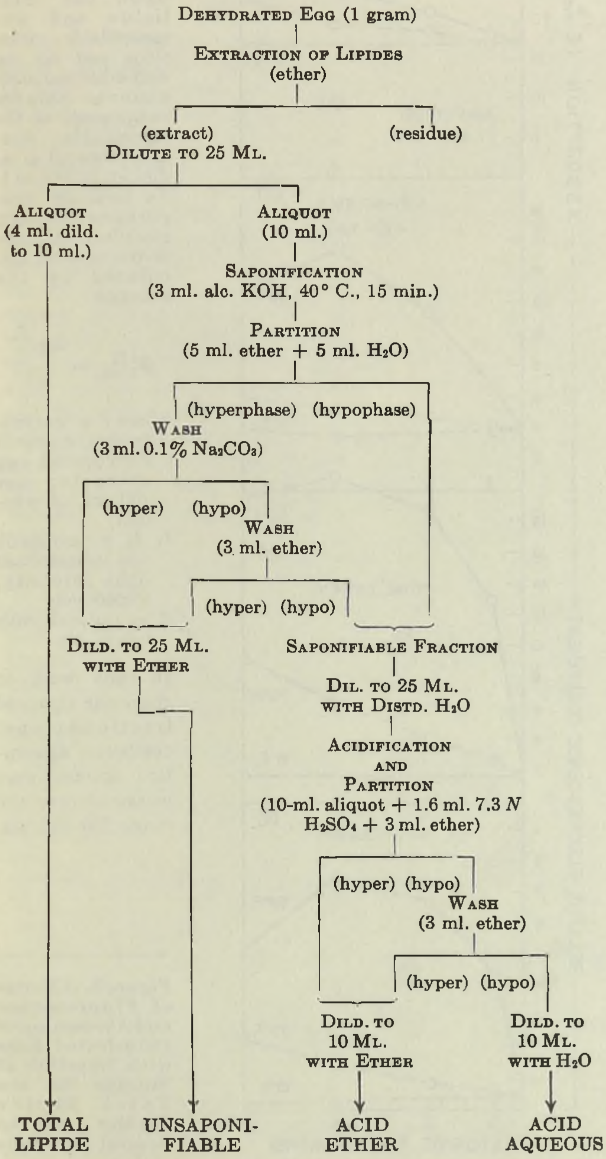


Figure 1. Flow Sheet of Analytical Procedure

USE OF DIETHYL ETHER. Despite the fact that other solvents have been reported to extract the fat more completely (*13*), diethyl ether was chosen because of its low boiling point and the resultant minimizing of deleterious effects upon the color of the residue.

LENGTH OF EXTRACTION. Extraction time was 4 hours, since longer periods produced no significant increases in the amounts of either fat or carotenoid pigment extracted.

PURITY OF SOLVENTS. This is a critical factor in spectrophotometric and fluorometric procedures. However, satisfactory results were obtained by using, without redistillation, the highest purity grades of anhydrous ether and ethanol.

SAPONIFICATION MIXTURE. The use of a completely reproducible saponification mixture was found desirable for the preparation of fractions whose absorbing components are cleanly separated. Such a mixture, modified from Olcott and Mattill (*17*), was made as follows: 28 grams of KOH were dissolved in 40 ml. of distilled water with thorough mixing in a stoppered flask. The mixture while hot was added to 90 ml. of 95% alcohol. (This was prepared from absolute alcohol of the best grade, since commercial 95% alcohol after treatment with alkali was not satisfactory for spectrophotometric purposes.) The alcoholic alkali was well mixed in a stoppered flask. To compensate for unavoidable inaccuracies in weighing the KOH, three 3-ml. aliquots of the solution were titrated with standard acid. On the basis of the titrations, the alcoholic alkali was diluted to a concentration of 2.92 normal; 3 ml. of the 2.92 *N* alkali were used for saponification.

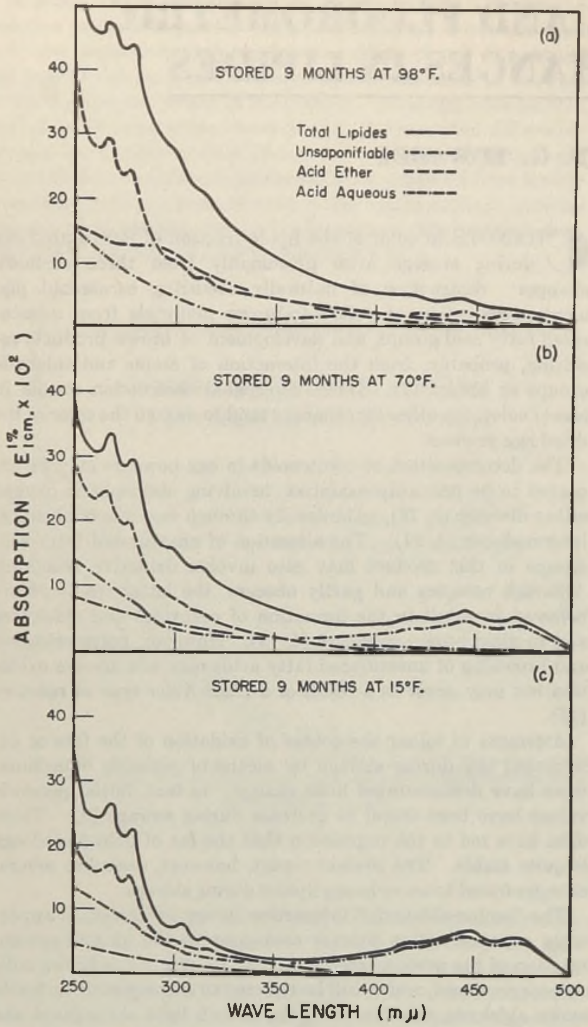


Figure 2. Absorption Spectra of Total Lipide Extracts and of Absorbing Components of Dehydrated Eggs Stored for 9 Months at Three Temperatures

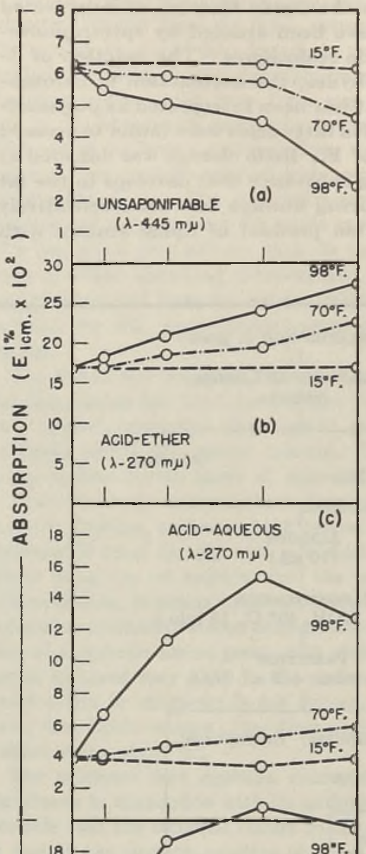
visible and ultraviolet regions. This absorption diminishes with increasing wave length and shows a slight maximum at 270 mμ. In addition to these absorption properties, solutions of the brown product show marked fluorescence. The reported correlation of fluorescence, both in the salt-soluble potassium chloride protein fraction and in the whole egg powder, with loss of palatability (*9, 18*) led to this investigation of fluorescence as well as of spectral absorption properties of the stored egg.

Spectrophotometric and fluorometric studies were carried out upon commercially spray-dried egg powders. Samples prepared at Lynden, Wash., by the Washington Cooperative Egg and Poultry Association for a previous investigation (*11*) were available for the present study. The egg powders had been stored in paper-lined barrels at 98°, 70°, and 15° F. Samples were collected at intervals of 1, 3, 6, and 9 months from the approximate centers of the barrels. In the absence of other controls, the powder stored at 15° F. for 1 month was used. During the intervals between sampling and analysis the materials were kept at −30° F.

ANALYTICAL METHODS

Completeness of chemical separation and washing was checked spectrophotometrically, and spectrophotometric data were interpreted in conjunction with chemical reactions. Experience has shown that either spectrophotometric measurements or chemical methods alone may lead to erroneous conclusions.

One gram of dehydrated egg powder was continuously extracted for 4 hours in a micro-Soxhlet apparatus with anhydrous diethyl ether from a freshly opened bottle. From the extract, diluted to 25 ml. with the solvent, two aliquots were removed: (*a*) 4 ml. were diluted to 10 ml. with the anhydrous ether, to give the sample designated as total lipide, which thus had a dilution equal to that of the samples to be subsequently described; (*b*) 10 ml. were transferred to a 65-ml. separatory funnel, freed from ether by evaporation, saponified, and fractionated according to flow sheet of Figure 1.



Absorption measurements were made with a Beckman Model DU spectrophotometer upon the total lipide and unsaponifiable fractions and on the acid-ether and acid-aqueous soluble components of the saponifiable fraction prepared as indicated in Figure 1. To facilitate comparisons between samples, the absorptions were calculated by the equation:

$$E^{1\%}_{1\ \text{cm.}} = \frac{\log \frac{I_0}{I_x}}{cd}$$

where c = concentration, grams of dehydrated egg extracted per 100 ml. of solution
I_0, I_x = incident and transmitted light intensity, respectively
d = optical path length, cm.

In early work to check the chemical fractionations, complete absorption spectra were measured over the range 250–550 mμ.

Figure 3. Change of Fluorescence and Absorption of Dehydrated Eggs with Duration of Storage in the Total Lipide Extract and in Several Fractions

After the chemical method was established, it sufficed for analytical purposes to measure optical density at a few specified wave lengths. Complete absorption data are given, however, for the final (9-month storage) samples (Figure 2).

Fluorometric measurements were made on the total lipide extract and the three fractions (diluted from 3 to 10 ml.) by means of a Coleman electronic photofluorometer with filters B_1 and PCI (excitation, 365 mμ, mercury). The fluorescence standard was a solution of quinine sulfate dissolved in 0.1 N sulfuric acid at a concentration of 0.4 microgram per ml. Blank readings for the solvents, either ether or water, were subtracted from the observed readings. A function designated as the relative fluorescence coefficient, Φ, was calculated by the equation:

$$\Phi = \frac{100\ (I_s/I_{qu})}{c}$$

where I_s/I_{qu} = ratio of fluorescence intensities of sample (corrected for solvent fluorescence) to that of standard quinine sulfate solution

c = concentration, grams of egg powder extracted per liter of solution

ABSORPTION SPECTRA

The absorption spectra of the total lipide extracts of dehydrated egg stored for 9 months at 98°, 70°, and 15° F. are plotted in Figure 2. Absorption spectra of significant fractions derived from the total extract are also shown. With increasing temperature of storage, the absorption of the total extract decreases in the visible region of the spectrum and increases in the ultraviolet. Apparently the lowering of absorption in the visible region is caused by destruction of the carotenoid pigments (unsaponifiable fraction, maxima 425, 445, and 475 mμ), and the rise in the ultraviolet is accounted for by a rise in the absorption of the acid-ether and acid-aqueous fractions. The increased absorption of the acid-aqueous fraction is apparently caused by the reaction of lipide amines with aldehydes (*6*). Two hypotheses are suggested to explain the intensified absorption of the acid ether fraction—an increase in amount of conjugation of fatty acid double bonds and the development of polymerization products from the unsaturated fatty acids. Some conjugation has been found in freshly dehydrated eggs as indicated by maxima at 268 and 280 mμ (triene conjugation) and at 305 and 315 mμ (tetraene conjugation). Conjugation is also evident in the sample stored at 15° F. (Figure 2*c*). The absorption coefficients at these maxima are larger on the material stored at the higher temperatures, and the increase might be explained as formation of conjugated products. However, the increases could result from the development of generally absorbing polymerization products. In fact, analysis of the data by the method of Brice and Swain (*5*) does not reveal any increase in conjugation. It appears probable, therefore, that polymerization accounts for the observed rise.

Figure 3 shows the rates at which changes take place in the absorption and fluorescence coefficients of the total lipide extract and component fractions during storage. The points plotted represent averages of two to four separate determinations. Results were producible to ±5%. The breaks in many of the curves after 6 months of storage were unexpected. However, anomalies of this sort had been observed previously (*8, 19*).

The rate of destruction of carotenoids (Figure 3*a*) as revealed by absorption measurements upon the unsaponifiable fraction (λ = 445 mμ) rises both with temperature and duration of storage. The loss of 27% of carotenoids during 6 months of storage at 98° F. is comparable to the 29% loss during 6 months of storage at room temperature reported by the Purdue University Agricultural Experiment Station (*10*).

Figure 3*b* shows the increase during storage in the absorption at wave length 270 mμ of the acid-ether fraction, which is tentatively interpreted as being due to polymerization. This increase appeared to proceed at a nearly constant rate, which was greater at higher temperature; little or no change was found at 15° F.

The course of the lipide amine-aldehyde reaction with time and temperature is illustrated in Figure 3*c*. The zero time intercept of 3.8×10^{-3} probably represents absorption due to substances other than the lipide amine-aldehyde reaction products, which were present in the acid-aqueous fraction. Evidence on this point has been presented (*6*), and further evidence is suggested in the legend for Figure 4. At the highest temperature (98° F.) the initial rate of reaction was high but decreased with time. At the intermediate temperature (70° F.) the reaction proceeded more slowly and at a nearly constant rate. No reaction was observed at 15° F.

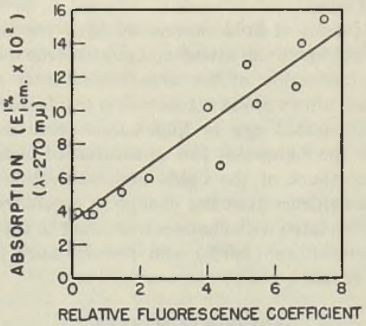


Figure 4. Relation of Absorptions to Relative Fluorescence Coefficients of Acid-Aqueous Fraction

The zero fluorescence intercept of the absorption for the acid-aqueous fraction has a value of 3.5×10^{-3}. This value is equivalent to that for the zero-time-storage sample (Figure 3c) and, therefore, probably represents the absorption due to substances other than the lipide amine-aldehyde reaction product present in the acid-aqueous fraction.

FLUORESCENCE

Comparison of the fluorescence values of the total lipide extract from samples stored 9 months at 98° and 15° F. showed that the extract of the high-temperature sample fluoresced ten times as strongly as that of the low-temperature sample. The effect of storage upon the fluorescence coefficients of the total lipide extract was then determined (Figure 3*d*). The rate of development of fluorescence for the egg powder stored at 98° F. was initially high but decreased, at 70° it was approximately constant, and at 15° it was zero.

An attempt was made to learn something of the chemical nature of the compound that gives rise to fluorescence in the total lipide extract by measuring the changes in fluorescence of the chemically separated, unsaponifiable, acid-ether and acid-aqueous fractions. From a consideration of the chemical separations indicated in Figure 1 and the fluorescence results in Figure 3, *d* and *e*, it is evident that the fluorescing material passed from the total lipide to the acid aqueous phase upon ether partition of the acidified saponifiable fraction. No fluorescing material could be demonstrated in the unsaponifiable and acid-ether fractions. Their relative fluorescence coefficients did not increase significantly but varied at random between 0.47 and 1.8 (data not shown). It is therefore apparent that the fluorescing materials of the total lipide extracts are released from their lipide combinations in the stored egg powder by the saponification process and are isolated in the acid-aqueous fraction (compare reference *6*).

Since the curves describing development of fluorescence in the total lipide extract (Figure 3*d*) and acid aqueous fraction (Figure 3*e*) appear to parallel the curves for absorption at 270 mμ (Figure 3c) in the acid-aqueous fraction, the identity of the fluorescing and absorbing substances is indicated. This conclusion is supported by the approximately linear relation that exists in the acid-aqueous fraction between absorptions and relative fluorescence coefficients (Figure 4). Thus the fluorescing material appears to be the same as the substance responsible for the absorption in the acid aqueous fraction. This substance is believed to be the fluorescent lipide amine-aldehyde reaction product (*6*).

Evidence is now at hand to indicate that oxidative changes take place in the fat and fat-soluble components of egg powders stored in the presence of air, as follows: Loss of carotenoid pigments as reported here, as well as of vitamin A (*11*), during storage indicate oxidative reactions; the formation of lipide amine-aldehyde reaction products likewise implies oxidative change, since aldehydes have been shown to develop during the oxidative breakdown of fats.

The development of lipide amine-aldehyde reaction products in egg fat tends to give the extracted lipides a brown color as does also the polymerization of the unsaturated fatty acids. Formation of these brown lipide substances is one factor in the color change of dehydrated egg in high-temperature storage. Another factor is the coincident loss of carotenoid pigment. Aside from the importance of the lipide amine-aldehyde reaction to color, there is evidence that the change in concentration of this substance is correlated with changes that occur in the palatability of both high-moisture (>5%) and low-moisture (<1%) eggs (unpublished results).

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Hygroscopicity of Softened Glue Composition

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ALTHOUGH it is widely recognized that the functioning of industrial glue compositions is closely related to their water contents, no data are found in the literature concerning the hygroscopicity of glue compositions containing the usual softeners. As part of a study of the evaluation of sorbitol as a plasticizer for glue, hygroscopicities of a typical hide glue softener with sorbitol, glycerol, and a mixture of sorbitol and glycerol were investigated along with the hygroscopicities of the individual components.

In use, a glue composition is seldom at a given set of conditions long enough for equilibrium to be reached. Equilibrium values, however, represent the point toward which the composition will always be changing, and a knowledge of how the equilibrium moisture content varies with humidity is of value in calculating the maximum changes expected within established humidity limits. A second attribute of hygroscopicity which was not investigated in the present study is the rate at which moisture is exchanged between the composition and the air under nonequilibrium conditions. This rate of moisture exchange is a complex function depending upon such variables as film thickness, velocity of water diffusion within the composition, rate of air circulation, distance of the composition from equilibrium moisture content, etc., and it was not considered feasible to undertake such an investigation at the present time.

Briefly, the method used for the glue compositions was to cast thin films on glass and to expose them to circulated air of a chosen constant humidity and temperature until they attained constant weight. From known initial compositions and final weights, the equilibrium moisture contents were calculated.

MATERIALS AND APPARATUS

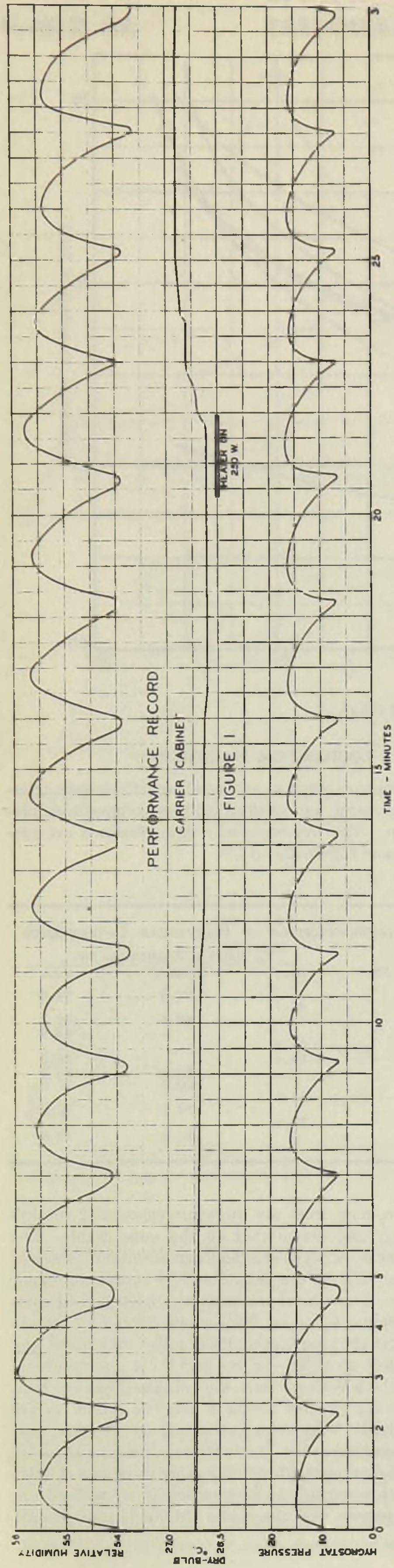
The ingredients employed in compounding the experimental softened glue samples follow. Their moisture contents were determined by titration with Karl Fischer reagent (*1*):

Glue. A balanced grade of hide glue containing approximately 16% water (analyzed 15.3%), 410 to 415 grams gel strength (Bloom), 135 millipoise viscosity, ground to 24–26 mesh, pH 5.9 in 20% solution.

Glycerol. Dynamite grade, 0.5% water.

Sorbitol. Commercial solution (Arlex), 16.0% water. The differences introduced by using this product in place of pure sorbitol have been found to be within the experimental error of the method employed.

The test samples were conditioned in a laboratory model Carrier processing cabinet in constantly recirculated air of con-



Equilibrium water content data for a hide glue, with and without softeners, are presented for a wide range of humidities. Both glycerol and sorbitol were studied as softeners. Glycerol alone is more hygroscopic than sorbitol. In glue compositions at high softener contents, this relationship is still true. At low softener contents, particularly at low humidities, the softened glue compositions hold less water than the unsoftened, and the glycerol-softened glue appears to hold less water than the sorbitol-softened glue.

trolled temperature and humidity. The air was continuously dehumidified by passing a portion of it over ice, the desired humidity being maintained by an intermittent water spray. The water spray was controlled by a silk-wick pneumatically operated hygrostat. The controls were adjusted so that the variation of temperature was ±0.3° F. and that of relative humidity was ±1%. A complete control cycle for humidification occurred every few minutes; hence the effective variation in humidity was less than the ±1% extremes.

Figure 1 illustrates the fluctuations in humidity and temperature of the conditioning atmosphere. The variation of relative humidity (top curve) was indicated by changes in the readings of wet- and dry-bulb thermometers. The middle curve shows the dry-bulb temperature. The bottom curve shows the air pressure of the hygrostat control system. The water spray for humidification of the air in the cabinet is on when the air pressure is less than 8 to 10 pounds per square inch gage. There is a lag of 15 to 20 seconds in the wet- and dry-bulb relative humidity compared with the pressure that is controlled by the silk-wick system.

The methods of determining the equilibrium moisture contents were based on the principle of bringing a thin film of the sample to equilibrium with the desired conditions, varying the manipulative details to suit the physical nature of the several substances. For all compositions containing glue, whether softened or unsoftened, mixtures of known solids content were weighed into tared weighing bottles, 40 mm. inside diameter and 100 mm. high. The bottle and the liquid sample were placed in a device which rotated the bottle in a tilted position over a heater while a stream of clean dry air was directed into the bottle. This dried the glue

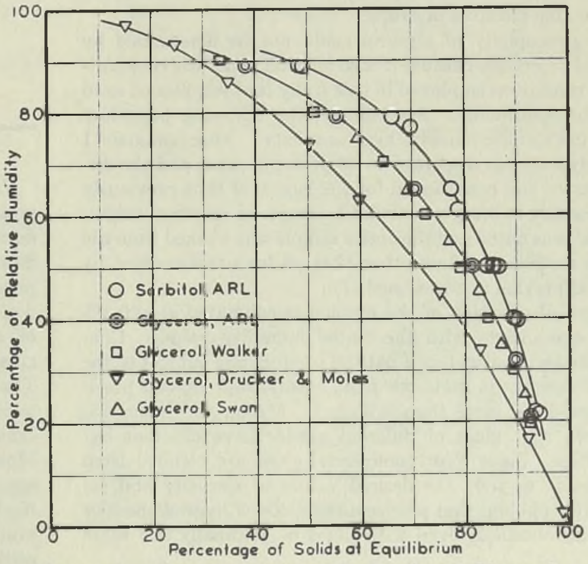


Figure 2. Hygroscopicity of Sorbitol and Glycerol

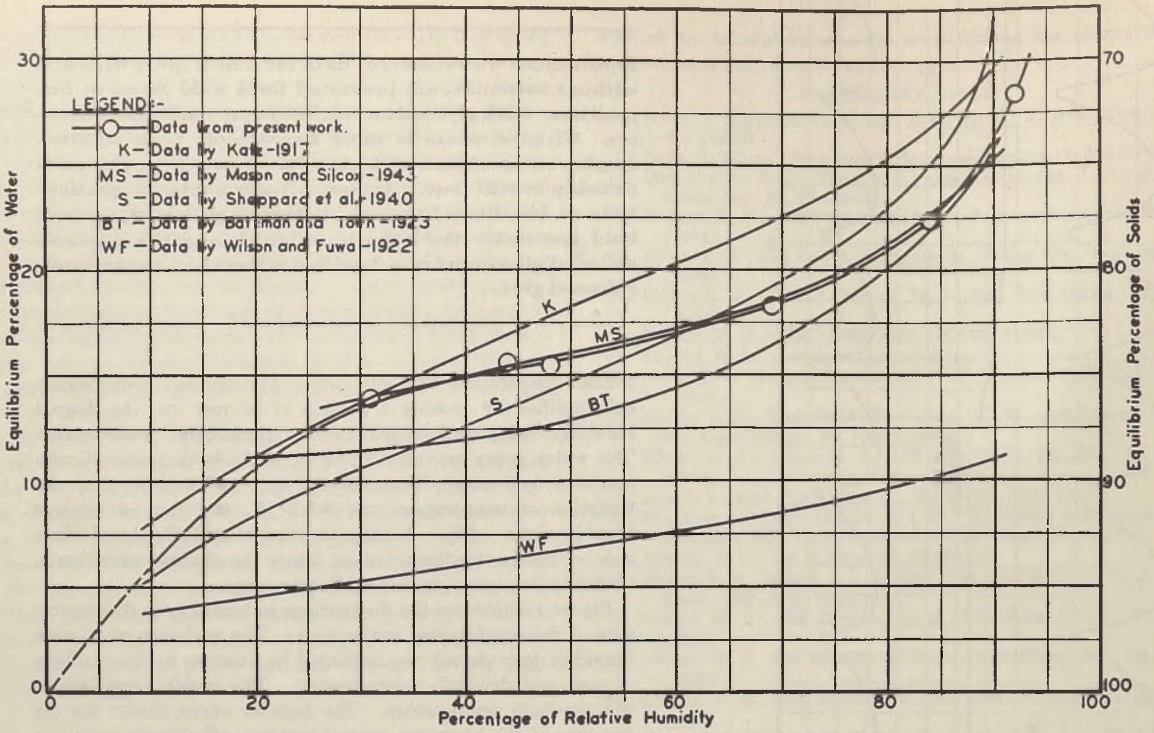


Figure 3. Hygroscopicity of Unsoftened Glue

in a thin film inside the weighing bottle. The drying was not carried beyond the point at which the glue film was gelled at room temperature.

The weighing bottles were then placed in the constant temperature–constant humidity cabinet, and the glue films were allowed to reach equilibrium successively at various humidities. All of the data were obtained at a dry-bulb temperature of 80° F. Relative humidities were determined by frequent wet- and dry-bulb readings. Weight changes of the samples were considered to be moisture gain and loss and were calculated as such.

For determining the hygroscopicities of the nonfilm-forming polyols employed as softeners for the glue, the above procedure could not be used. The nonvolatile polyol, sorbitol, was investigated using a modification of the official A.O.A.C. method (*6*) for determining moisture in sirups.

The hygroscopicity of glycerol could not be determined by this official procedure because it is so volatile under the constant-humidity conditions employed in this study that samples on sand lose weight continually. Accordingly, the following procedure was adopted to determine its hygroscopicity. Approximately 1 gram of glycerol was dispersed on 40 grams of sand, and the dispersed sample was conditioned for the length of time previously found necessary to bring a nonvolatile sample to constant weight. The weight was noted and the entire sample was washed from the sand with methanol and was then titrated for water content by the method previously mentioned (*1*).

The over-all precision of the method is estimated at ±0.3% solids at equilibrium with the stated humidity values. Considering the fact that glue is a natural product and subject to the variations inherent in materials from natural sources, this precision is considered more than sufficient. Mason and Silcox (*8*) have shown that glues of different grades have different hygroscopicities. Since most commercial glues are blended from several stocks to yield the desired values of viscosity and gel strength, it is obvious that precise duplication of hygroscopicities may not be obtained, even with glues of nominally the same grade.

EQUILIBRIUM MOISTURE

Equilibrium moisture contents at several humidities were determined for glue, glycerol, and sorbitol, and for compositions prepared from them. The hygroscopicity data obtained are presented in Table I and Figures 2 and 3.

Table I. Hygroscopicities of Individual Ingredients

% Relative Humidity	% Solids at Equilibrium for: Glue	Glycerol	Arlex
23	..	92.6	94.0
31	86.1	...	..
32	..	89.4	91.6
40	..	...	88.9
44	84.3	...	..
48	84.5	...	86.2
50	..	80.9	83.9
65	..	70.2	77.3
69	81.7	...	..
79	..	55.2	66.3
84	77.6	...	..
89	..	37.9	48.3

For comparison, data from the literature concerning the hygroscopicity of glycerol are plotted on the same graph. The data of the present work are in excellent agreement with those of Swan (*10*), whose values were determined by measuring vapor pressures in a closed system of solutions of predetermined compositions. The values found by Walker and quoted by Carson (*3*) are consistent in showing slightly lower solids contents at any given humidity than do those of Swan and those reported here. The method by which Walker's data were obtained has not been published so that the relative merits of the two sets of values cannot be adjudged. The values obtained by Drucker and Moles (*4*) and presented in the International Critical Tables (*5*) are in pronounced disagreement with the other three sets of data. No literature data covering the hygroscopicity of sorbitol are available for comparison with the values obtained in the present work.

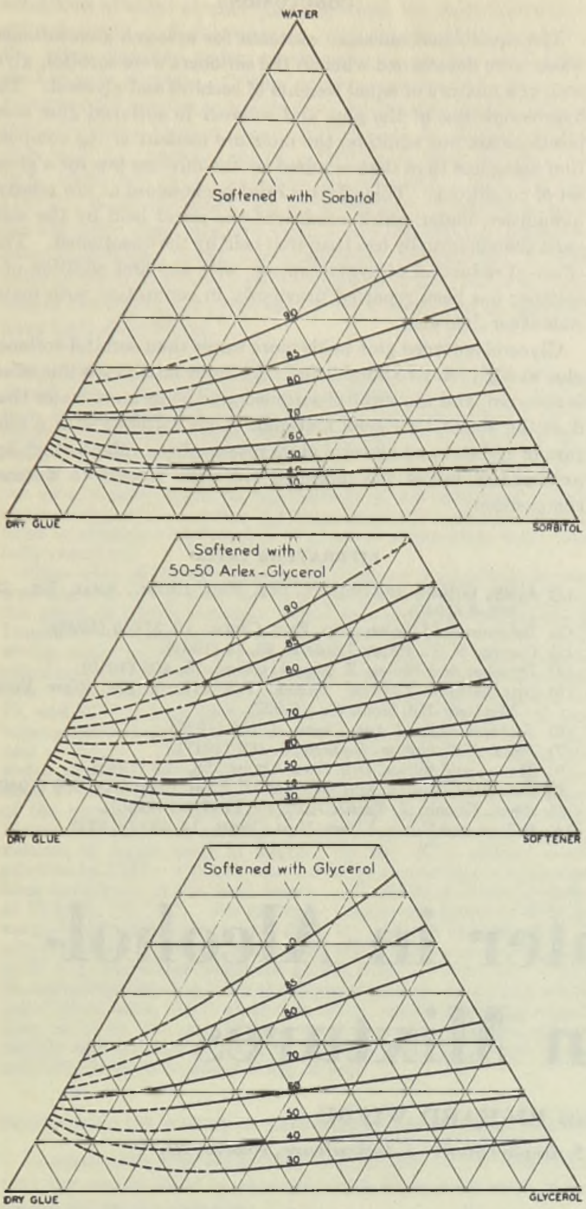


Figure 4. Hygroscopicity of Softened Glues

Lines of constant relative humidity (per cent R. H. at 80° F.)

The data for unsoftened glue are plotted in Figure 3; curves from several literature sources are included for comparison. At humidities above 30% the data of the present work are in excellent agreement with those of Mason and Silcox (*8*). The curve presented by Bateman and Town (*2*) is parallel to those of Mason and Silcox and the present work but the moisture content is 2 to 3% lower. This strongly suggests a difference in determination of the dry solids of the glue, although the effect might simply be due to inherent variations in the glues from different sources. The data presented by Katz (*7*) and by Sheppard and co-workers (*9*) were obtained with purified gelatin rather than hide glue. These curves are parallel, and although they differ in shape from the curves presented for glue, the moisture contents are of the same order of magnitude. The data of Wilson and Fuwa (*11*) are considerably lower than any of the others reported. They worked with a ground glue but did not prepare solutions or cast films from them; it is likely that they did not attain equilibrium.

HYGROSCOPICITY OF GLUE COMPOSITIONS

The softened glue compositions are listed in Table II. The solids content of each composition was calculated from the analyses of the ingredients.

The data obtained on these compositions, used in preparing the graphs for the three-component systems glue (415 grams)-softener-water, are summarized in Table III. The chronological order of the conditions was as follows: 84, 69, 44, 31, 48, and 91%. An approximately full cycle was covered to determine if there was any hysteresis effect. At the return to 91% relative humidity the values obtained correlate well with former data; hence no hysteresis was observed.

These data are presented in ternary plots (Figure 4). The curves are derived from binary plots of weight per cent solids *vs.* relative humidity at each of the several glue-softener ratios. From these intermediate curves the solids content of the compositions at equilibrium with atmospheres of 30, 40, 50%, etc., relative humidity were read. Knowing the solids content and the glue-softener ratios, the percentage composition corresponding to each point thus observed could be calculated and plotted on a ternary graph. Through points so obtained, curves of constant humidity were drawn.

The curves of Figure 4 emphasize that the plasticizing effect of certain polyols on glue is not due solely to the retention of increased amounts of water in the film. Actually, in the low-humidity range less moisture is held by the glue-softener mixture at a given humidity than by either the softener or the glue alone. Even at high humidities the curves drop below the straight lines called for by the mixtures law, an indication that this effect persists to high water contents. Swan (*10*) pointed out a similar effect for a starch-glycerol-water system. In this instance it is evident that the polyols and the glue are mutually satisfying, to a certain extent, their respective water-binding capacities. It is reasonable to infer that hydrogen bonding between the polyols and the protein brings about a reduction in the water-binding capacities of both.

Table II. Percentage Composition Used in Tests

Compn. No.	Composition (as Is)			Water Added	Calcd. Solids Content
	Glue	Arlex	Glycerol		
1	15	..	...	85	12.7
2	11.25	3.75	...	85	12.7
3	7.5	7.5	...	85	12.7
4	3.75	11.25	...	85	12.7
5	11.25	..	3.75	85	13.2
6	7.5	..	7.5	85	13.8
7	3.75	..	11.25	85	14.9
8	11.24	1.88	1.88	85	13.0
9	7.5	3.75	3.75	85	13.3
10	3.74	5.63	5.63	85	13.8
11	7.5	1.87	5.63	85	13.5
12	7.5	5.63	1.87	86	13.0

Table III. Hygroscopicity of Softened Glue Compositions

Solids Compn., %			% Solids at Relative Humidity of:					
Glue	Arlex	Glycerol	91%	84%	69%	48%	44%	31%
75	25	...	64.2	73.9	82.5	89.9	91.6	93.6
50	50	...	57.0	70.5	80.0	89.2	90.9	93.6
25	75	...	49.4	63.0	76.1	86.9	88.7	92.8
75	..	25	59.2	69.5	79.1	90.2	90.3	95.4
50	..	50	48.4	59.0	74.2	89.0	88.7	94.2
25	..	75	39.4	54.0	68.6	84.6	85.6	92.5
75	12.5	12.5	62.3	69.7	8.10	90.0	90.8	93.0
50	25	25	55.3	64.1	76.9	89.1	89.8	94.9
25	37.5	37.5	44.4	59.0	72.1	86.8	87.3	93.2
50	12.5	37.5	52.6	60.1	75.3	88.5	88.9	94.0
50	37.5	12.5	57.5	67.0	78.3	89.2	90.2	94.2

The data presented in the ternary plots may be used to formulate compositions, embodying these softeners and a similar glue, to be at equilibrium with a given humidity.

Industrial flexible glue compositions are commonly formulated on the basis of arbitrary softener-glue ratio, and at various percentages of Arlex in the softener. These ratios are based on the products as supplied, with their customary water content. Since the ternary plots are calculated to anhydrous glue and softeners, it is desirable to calculate the formula amounts for the ingredients as supplied commercially. This can be done readily with the following formulas:

$$G = \frac{100 - A}{(0.87 - 0.15BC + 0.99B)} \qquad (1)$$

$$S = CBG$$

$$X = (1 - C)\,BG; \quad W = 100 - (G + S + X)$$

where G = % glue of 13% water content
S = % Arlex of 16% water content
X = % glycerol of 1% water content
W = % make-up water, %
A = % total water in composition = analyzed water
B = % softener-glue ratio = $(S + X)/G$
C = fraction of Arlex in softener

Equation 1 is based on typical water contents for the components. For the contents given under "Materials and Apparatus", the constants would have slightly different values:

$$G = \frac{100 - A}{(0.84 - 0.175\,BC + 0.995\,B} \qquad (2)$$

G, S, X, and W calculated from Equations 1 and 2 for $B = 5$, $C = 0.5$, and $A = 19.23$, follow:

Equation	G	S	X	W
1	15	37.5	37.5	10
2	14.83	37.07	37.07	11.02

Equation 1 will be sufficiently accurate for most purposes.

CONCLUSIONS

The equilibrium moisture contents for systems glue-softener-water were determined wherein the softeners were sorbitol, glycerol, or a mixture of equal weights of sorbitol and glycerol. The hygroscopicities of the glue and softener in softened glue compositions are not additive, the moisture content of the composition being less than that required by the mixture law for a given set of conditions. This effect is most pronounced at low relative humidities, under which conditions the water held by the softened glues is actually less than that held by the unsoftened. This effect of reduction of hygroscopicity with the first addition of a softener has been reported previously in connection with materials other than glue.

Glycerol-softened glue holds more water than sorbitol-softened glue at high relative humidities. At lower humidities this effect is reversed, and the sorbitol-softened glue holds more water than does the glycerol-softened material. Glue softened with a mixture of sorbitol and glycerol gives intermediate values which approximately follow the mixtures law with respect to softener composition.

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Solubility of Water in Alcohol-Hydrocarbon Mixtures

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THE most objectionable feature of alcohol-gasoline blends, according to Howes (*8*), is their tendency to separate into two layers if water is present in excess of the amount in equilibrium at the particular operating temperature. If justifiable, such a statement seems to imply that, when separation occurs, the engine will stop running immediately and nothing short of emptying the fuel tank will remedy the situation. Further investigation, however, will reveal that, aside from some possible irregular operation, no real trouble will necessarily be experienced; the simple explanation is that (*a*) both layers contain a combustible mixture, (*b*) one layer may be only a small fraction of the total volume, and (*c*) because of the motion of the car, a more or less homogeneous mixture may result. In freezing weather the accidental presence of water in the fuel system may be more harmful in the case of straight gasoline than when alcohol-gasoline blends are used, since water is only slightly soluble in gasoline and ice formation in the fuel lines may starve the engine. On the other hand, an alcohol-gasoline blend may dissolve all the water, but if the amount is in excess of the equilibrium concentration, an emulsion or two phases will form which, at worst, may stop the engine temporarily. Nobody, however, will deny that phase separation is undesirable and must be avoided. For the purpose of avoiding this apparent difficulty, experimental data on the phase relations of ethyl alcohol–gasoline–water are being obtained. When reasonable precautions are observed in preparation and storage, blends containing from 10% or more of alcohol have been used over long periods under practical conditions without trouble (*5*, *9*). Experiments conducted at this laboratory as well as elsewhere (*5*, *7*) show that, in ternary mixtures of alcohol-gasoline-water, the temperature at which separation occurs is unchanged or lower after exposure to the atmosphere than before. This happened frequently under conditions more severe than likely to be encountered in practice and is a phenomenon similar to the one utilized in the dehydration of alcohol. In gasoline or hydrocarbon blends with ethyl alcohol, the solubility of water becomes less with decreasing temperature. The temperature of phase separation is called the "critical solution temperature".

In this paper the term "ethyl alcohol" is used in the chemical sense, meaning anhydrous ethyl alcohol. The ternary system consisting of ethyl alcohol–gasoline–water has been investigated extensively (*2, 4, 5, 8*); however, with the exception of benzene, the other possible major constituents of gasoline have been studied only slightly. Critical solution temperatures have been measured for a number of blends of ethyl alcohol with 2,2,4-trimethylpentane (boiling point 99.25° C.), 2,2-dimethylbutane (b.p. 49.7° C.), cyclohexane (b.p. 78–81° C.), methylcyclohexane (b.p. 99.85–100° C.), iso-octene (commercial grade, b.p. 80–171° C.), and cyclohexene (b.p. 82.55–82.65° C.); these representing the three remaining principal classes constituting gasoline—namely, paraffins, olefins, and naphthenes. In addition, the solubility of water in several blends containing ethyl alcohol in a mixture of two hydrocarbons as well as the effectiveness of stabilizers have been determined.

The apparatus and procedure were similar in principle to those described by King and Manning (*10*), Hubendick (*9*), and Bridgeman and Querfeld (*4*). A glass tube with stirrer containing the hydrocarbon–ethyl alcohol–water mixture was immersed in a bath, the temperature of which could be varied at any desired rate of heating or cooling. Mixtures were prepared directly in the tube, special pipets for the transfer of the individual components being used. During the experiment all necessary precautions to exclude moisture and to prevent evaporation were carefully observed.

Since some of the solutions had a tendency to supercool by several degrees, the critical solution temperature was taken to be the point at which turbidity would just disappear on warming. Duplicate determinations on separate samples would check within about 0.3° C. The experimental error in making up the solutions is estimated to be less than 0.2% of either volume fraction. Measurements were made on mixtures containing 25, 50, 75, and 90% of hydrocarbons and solutions of ethyl alcohol containing various amounts of water at temperatures between −45° and +45° C. The experimental results are expressed as the water tolerance of the blend. For practical purposes this is defined as the volume per cent of water which, at the temperature of the experiment, can be added before separation will occur. Water tolerance was calculated by multiplying the per cent by volume of water used in making up the ethyl alcohol–water solution by $(100 - P)/100$, where P is the percentage of hydrocarbons contained in the final blend. All mixtures were prepared at 15.5° C. (60° F.). For example, assuming a blend of 50% by volume of hydrocarbons and 50% by volume of a solution of ethyl alcohol, the latter containing 6% by volume of water (at 15.5° C.), the water tolerance equals $6(100 - 50)/100 = 3\%$. No correction was made for the slight expansion in volume which takes place when ethyl alcohol is mixed with various hydrocarbons since in the case of iso-octane, for example, the volume change will amount at most to no more than 0.4%, and in the majority of cases to about 0.2% or less.

SOLUBILITY OF WATER IN ALCOHOL-HYDROCARBON BLENDS

In agreement with Bridgeman and Aldrich (*3*), it was found that the results could be expressed with a probable error of less than 0.5% by the equation:

$$\log S = a - (b/T) \qquad (1)$$

where S = water tolerance, % of water by volume
a, b = constants depending on type and concentration of hydrocarbon
T = absolute temperature, ° K.

Table I gives the numerical values of the constants determined from plots of $\log S$ against $1/T$; Table II lists the data calculated at +25°, 0°, and −45° C. by means of Equation 1.

TABLE I. CONSTANTS OF EQUATION 1[a] FOR ETHYL ALCOHOL-HYDROCARBON-WATER MIXTURES

Hydrocarbon	Hydrocarbon, Vol. %	*a*	*b*
2,2,4-Trimethylpentane (iso-octane)	90	1.383	553.5
	75	1.894	554.5
	50	2.151	504.4
	25	2.001	352.5
2,2-Dimethylbutane (neohexane)	90	1.235	473.1
	75	1.679	444.9
	50	1.911	388.5
Iso-octene	90	0.637	229.4
	75	1.520	357.9
	50	2.120	475.2
	25	1.870	290.6
Di-isobutylene[b]	75	1.400	340.3
	50	1.842	355.4
Cyclohexane	90	1.856	628.7[c]
	75	2.421	693.4[c]
	50	2.850	693.4[c]
	25	6.328	1526.0[d]
Methylcyclohexane	75	2.058	587.6
	50	2.210	504.9
	25	2.047	347.3
Cyclohexene	90	1.312	477.5
	75	2.051	530.4
	50	2.332	487.6

[a] The equations are valid for the range from +45° to −45° C. except where otherwise stated.
[b] Only a few measurements were made on a very small sample as received.
[c] Valid only for temperature range +4° to +25° C.
[d] Valid only from −45° to 0° C. (solution in equilibrium with solid cyclohexane).

TABLE II. WATER TOLERANCE OF ALCOHOL-HYDROCARBON MIXTURES

Hydrocarbon	Temp., ° C.	Water Tolerance at Following Hydrocarbon Content:			
		90 vol. %	75 vol. %	50 vol. %	25 vol. %
2,2,4-Trimethylpentane	+25	0.337	1.08	2.89	6.59
	0	0.228	0.733	2.02	5.14
	−45	0.0908	0.291	0.873	2.86
2,2-Dimethylbutane	+25	0.446	1.54	4.05	...
	0	0.319	1.13	3.08	...
	−45	0.145	0.536	1.62	...
Iso-octene	+25	0.738	2.09	3.37	7.87
	0	0.626	1.63	2.41	6.40
	−45	0.429	0.895	1.09	3.95
Di-isobutylene	+25	...	1.82	4.47	...
	0	...	1.43	3.48	...
	−45	...	0.81	1.93	...
Cyclohexane	+25	0.560	1.25	3.35	...
	0	...	...	...	5.53[a]
	−45	...	...	...	0.438[a]
Methylcyclohexane	+25	...	1.25	3.29	7.64
	0	...	0.807	2.30	5.97
	−45	...	0.304	0.995	3.35
Cyclohexene	+25	0.514	1.88	4.98	...
	0	0.367	1.29	3.52	...
	−45	0.166	0.533	1.57	...

[a] Solution in equilibrium with solid cyclohexane.

The results show that 2,2-dimethylbutane has approximately a 50% greater water tolerance than 2,2,4-trimethylpentane. This is equivalent to the statements by Bridgeman and Querfeld (*4*) and Heinze *et al.* (*6*) that increase in volatility produces a marked lowering in the critical solution temperature. This tendency is also shown in values for pentane and hexane obtained by Ormandy and Craven (*11*). Their values for hexane are lower than those for 2,2-dimethylbutane; the reason is the presence of higher boiling impurities as well as the fact that their sample contained considerable amounts of *n*-hexane, and that isomers have a greater water tolerance than the normal compounds. These authors state that, while there is relatively little difference between benzene and toluene, the water tolerance of ethyl alcohol–xylene is definitely lower. It is also of interest to note in Table II that the percentage difference among the various compounds is greatly diminished at the higher alcohol concentrations, and that, under these circumstances, structural difference appears to be less important.

BLENDS OF ALCOHOL WITH GASOLINE AND WITH HYDROCARBON MIXTURES. Bridgeman and Aldrich (*3*) found that the water tolerances of blends of alcohol with twenty-three different gasolines could be expressed by a single equation, containing one characteristic constant. Thus a single measurement on each gasoline should be sufficient to determine S at any value of P and T. It was not possible to express the data for individual hydrocarbons in a similar manner since any two gasolines appear to resemble each other more closely than, for instance, iso-octane and cyclohexene.

Using their equation, Bridgeman and Aldrich (*3*) calculated the water tolerances of an "average gasoline" in blends with 5 and 10% alcohol. For the 10% blend at 0° C. the value found was 0.25%. Table II shows that the water tolerance at 0° C. of a 10% blend lies between 0.23 and 0.63% for the hydrocarbons studied in this investigation. Similarly, for a 50% blend, the same "average gasoline" has a water tolerance of 2.06%, whereas the values for the compounds investigated vary from 2.02 to 3.52%.

TABLE III. CONSTANTS OF EQUATION 1 FOR BLENDS OF 50% AQUEOUS ALCOHOL–50% HYDROCARBON MIXTURE

% Hydrocarbon in Mixture	*a*	*b*	*S* at 0° C.
Iso-octane 45–benzene 5	2.073	459.5	2.47
Iso-octane 40–benzene 10	2.038	428.0	2.97
Iso-octane 35–benzene 15	1.919	373.4	3.57[a]
Iso-octene 45–benzene 5	2.046	433.6	2.88
Iso-octene 40–benzene 10	1.930	382.7	3.39
Iso-octene 35–benzene 15	1.781	326.7	3.85[a]
Iso-octane 37.5–neohexane 12.5	2.068	469.2	2.24 (2.28)[b]
Iso-octane 25–neohexane 25	2.103	468.6	2.45 (2.55)[b]
Iso-octane 12.5–neohexane 37.5	2.026	439.1	2.63 (2.81)[b]
Iso-octene 25–methylcyclohexane 25	2.233	508.0	2.37

[a] Equation valid only to approximately −30° C. at which temperature benzene begins to crystallize.

[b] Calculated on the basis of linear variation from data in Table II.

While ethyl alcohol is miscible in all proportions with ordinary gasoline even at temperatures as low as −50° C., this is not true in case of distillate fuels. Barger (*1*) found that low-octane distillate fuels are not completely miscible with ethyl alcohol even at moderate temperatures. A 25% blend of alcohol in a distillate fuel of 4.3 octane number had a critical temperature of 24° C. Special precautions must therefore be taken when ethyl alcohol–distillate fuel blends are used. Piazza (*12*) used butyl alcohol to stabilize kerosene-alcohol blends. Since his ethyl alcohol contained 3.5% of water by volume, the amounts required were quite large.

Table III shows the water tolerance of blends containing 50% of ethyl alcohol and 50% of a mixture of two hydrocarbons in various proportions. The water tolerance of blends with iso-octane and neohexane is an approximately linear function of the composition at 0° C.; no such simple relation was found in the remaining cases.

EFFECT OF VARIOUS COMPOUNDS. Relatively small additions of various compounds will lower the critical solution temperatures or, in other words, increase the water tolerance of ethyl alcohol–hydrocarbon blends. The experimental data in Table IV show that the higher alcohols are the most suitable agents to lower the critical solution temperatures. This result corroborates earlier findings (*2*, *9*). In addition to their primary purpose, denaturants containing a large proportion of these higher alcohols would also be useful in increasing the water tolerance; however, some of the hydrocarbons in the blend also act as denaturants.

Unless the ethyl alcohol used for blending already contains a mixture of various higher alcohols resulting from the method of production, it is not considered economically practical to add any compounds for the purpose of increasing the solubility of water. In the first place, the amounts needed will be relatively too large, and secondly, ethyl alcohol–gasoline blends will remain stable when reasonable precautions are observed.

CONCLUSION

The solubility of water in ethyl alcohol–paraffin hydrocarbon blends decreases with increase in molecular weight of the hydrocarbon; a similar conclusion was reached by Ormandy and Craven (*11*) in the case of aromatics. This rule probably holds for naphthenes and olefins as well. The statement is equivalent to saying that the more volatile gasolines have a higher water tolerance (*4*, *6*).

With the exception of distillate fuels, the solubility of water in ethyl alcohol–hydrocarbon blends or, in general, in ethyl alcohol–gasoline blends is large enough so that if reasonable precautions are observed, no trouble from this source should be experienced. Past experience has shown that this is true for blends containing 10% or more of alcohol. The introduction of an excessive amount of water into any fuel will cause trouble, and alcohol-gasoline blends are no exception to the rule. Storage above water is required by law in some sections of the country; this is impossible for alcohol fuels, if only for the fact that alcohol will progressively diffuse into the water and cause serious loss of fuel.

Unless higher alcohols are present in ethyl alcohol as a denaturant or in consequence of the method of production, it would not seem practical to add them in order to increase the solubility of water in blends; if deemed necessary, this might be better accomplished by the further addition of ethyl alcohol.

TABLE IV. EFFECT OF ADDING 2 VOLUMES OF STABILIZER TO 100 VOLUMES OF 90% ISO-OCTANE–9.69% ALCOHOL–0.31% WATER BLEND, WITH A CRITICAL SOLUTION TEMPERATURE OF 20° C.

Stabilizer	Change in Critical Soln. Temp., ° C.
3-Methyl-1-butanol (isoamyl alcohol)	−33.1
n-Hexyl alcohol	−32.3
n-Amyl alcohol	−31.2
Octyl alcohol (2-ethylhexanol)	−31.1
2-Methyl-1-butanol	−31.0
sec-Butanol	−30.2
Lauryl alcohol	−27.6
Lauric acid	−25.8
Terpineol	−23.3
Naphthenic acids	−20.0
Benzylamine	−18.6
Dicyclohexylamine	−17.4
Oleic acid	−16.8
n-Butyric acid	−16.7
Cyclohexanone	−13.2
Methyl *n*-amyl ketone	−12.7
Isopropyl propionate	−10.4
Ether	−10.0
Fenchone	− 9.0
2-Ethylhexaldehyde	− 8.9
1,4-Dioxane	− 8.1
Acetone	− 7.8
Di-isobutyl ketone	− 7.5
Aniline	− 7.1
Amyl ether	− 3.6
Morpholine	+ 2.2
Methyl Cellosolve	+ 2.2
Pyridine	+ 2.9
Diacetone alcohol	+ 3.5

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Unfermentable Reducing Substances in Molasses

ANHYDRIDES AND AMINO ACID CONDENSATION PRODUCTS OF REDUCING SUGARS

The formation of unfermentable reducing substances from reducing sugars in the absence and presence of amino acids, under the conditions of sugar manufacture, has been investigated. Glucose alone gives only traces of unfermentable material. Fructose furnishes considerable amounts; the product, formerly considered to be glutose, consists of a mixture of 1,2-fructopyranose anhydride, its nonreducing dimer whose constitution has been established by methylation and oxidation, and dark-colored fructose caramel. Glutosazone is shown to be impure glucosazone. Large amounts of unfermentable reducing substances are formed from glucose and fructose in the presence of amino acids, more from glucose than from fructose. They constitute a mixture of simple condensation products and melanoidins, and also yield impure glucosazone. The hydrolysis curves of the unfermentable reducing substances in cane molasses are similar to the curves of those prepared from glucose and fructose, with or without amino acids. The presence of nitrogenous unfermentable reducing substances is confirmed by correlations of the reducing power of the unfermentable portion and of its nitrogen content with the total nitrogen in molasses. Minor unfermentable reducing substances that may occur in molasses are discussed.

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THE occurrence of the unfermentable ketohexose *d*-allulose in distillery slop from cane molasses was reported in a previous paper in this series (*51*). This sugar was found to represent only a small fraction of the total unfermentable reducing substances in molasses, and the investigation was continued to identify those whose chemical nature is still unknown.

Lobry de Bruyn and Alberda van Ekenstein (*27*) expressed the opinion that the unfermentable reducing substance in molasses is identical with that obtained in the interconversion of hexoses of the glucose series in a weakly alkaline solution. According to this view, which has been accepted generally by sugar technologists, the glucose and fructose in cane juice are partially converted during the alkaline clarification process into mannose, allulose, and glutose. Lobry de Bruyn and Alberda van Ekenstein erroneously considered allulose to be a fermentable sugar, and chose the name "glutose" for the unfermentable portion of the reaction mixture. During the present investigation it was found that unfermentable reducing substances are formed not only from reducing sugar alone, but also by the interaction of reducing sugars with asparagine, the principal amino acid derivative in cane juice. It will therefore be necessary to consider the two types of unfermentable reducing substances separately.

I. UNFERMENTABLE REDUCING SUBSTANCES FROM REDUCING SUGARS ALONE

Lobry de Bruyn and Alberda van Ekenstein prepared glutose in the form of a sirup which would not crystallize, either directly or after solution in any solvent. This product gave the general reactions characteristic of ketoses—namely, Seliwanoff's test, complete destruction by prolonged boiling with dilute hydrochloric acid, ready formation of acids upon treatment with strong alkali. But the substance differed from fructose by yielding an osazone melting at 165° C. To account for these facts, a 3-ketohexose structure was suggested but not supported by any experimental evidence.

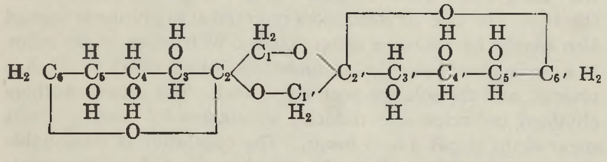
The voluminous literature on the nature of the unfermentable reducing substances in molasses was reviewed by Prinsen-Geerligs (*34*), and since none of the workers was able to draw definite conclusions, only certain points relevant to the present discussion will be referred to.

Lobry de Bruyn and Alberda van Ekenstein were unable to obtain glucose, fructose, and mannose by treating glutose with alkali in the same manner in which they prepared the supposed equilibrium mixture of hexoses from glucose or fructose. This indicates that it is not a true equilibrium mixture of isomers, and that the glutose must be formed by some other reaction. Furthermore, the same investigators reported that glutose is formed also simply by boiling a water solution of fructose under reflux in a platinum vessel—that is, under conditions where no alkali is present, and the solution soon turns acid. The present authors obtained unfermentable reducing substances by heating invert sugar sirup at pH 4.5 or lower. The conclusion is inescapable that alkalinity is not essential for the formation of unfermentable reducing substances from reducing sugars.

Waterman and van der Ent (*47*) found that, when cane juice is clarified at pH 8.0–9.5, unfermentable reducing substances are formed. The same result was obtained with an artificial juice containing both glucose and fructose; but when the fructose was omitted, no unfermentable reducing substances could be detected. Kilp (*24*) also reported that glutose is formed from fructose when cane juice is clarified. If the Lobry de Bruyn–Alberda van Ekenstein transformation took place under the conditions of cane juice clarification, then fructose should have been formed from glucose alone in the experiments just mentioned, and this fructose should have given rise to unfermentable reducing substances. It is possible that the glucose alone, or any fructose formed from it, may have yielded too little unfermentable reducing substance to be detected by the method used; nevertheless, the experiments show that fructose is the principal source. It may be concluded that the Lobry de Bruyn–Alberda van Ekenstein transformation can play only a minor part in the formation of unfermentable reducing substances during juice clarification.

During the factory operations subsequent to clarification the products are maintained for hours at an elevated temperature, averaging around 70° to 75° C. The pH gradually drops to about 7 in the evaporator sirup, and to 6 or below in the final molasses. Since high pH is not a necessary condition for the formation of unfermentable reducing substances, it may be expected that they increase during the manufacturing process. No data have been published on this particular point, but it has been observed in Java (*36*) that, when final molasses is stored for six months under tropical conditions, the unfermentable reducing substances increase as much as 1.5% on the weight of the molasses. Even though this increase may be due partly to the formation of unfermentable nitrogenous condensation products (to be discussed later), it is nevertheless significant.

A definite advance in this field was made by Mathews and Jackson (*29*) who studied the decrease in rotation and reducing power when fructose solutions are heated under varying conditions of pH, temperature, and time. They concluded from their experiments that the changes observed could be explained by the formation of glucose and mannose through the Lobry de Bruyn–Alberda van Ekenstein transformation and by the simultaneous formation of fructose anhydrides. The former reaction predominates at high pH, the latter at low pH; but there is no strict dividing line between the two. Fructose shows maximum stability at pH 3.3. Computation of the rotation values of the fructose anhydrides in the reaction mixture indicated that they were probably identical with the heterolevulosan and diheterolevulosan which Pictet and Chavan (*33*) obtained by treating fructose with concentrated hydrochloric acid at 0° C. On the basis of the analysis and the molecular weight, Pictet and Chavan considered heterolevulosan to be a fructose anhydride, and diheterolevulosan a difructose anhydride, but they made only certain suggestions as to the chemical structures, based on analogies and unsupported by experimental evidence. Mathews and Jackson repeated Pictet and Chavan's work and confirmed their observations, but did not study the nature of the products. About the same time, Schlubach and Behre (*40*), by treating fructose with liquid hydrogen chloride at room temperature, obtained a difructose anhydride which they showed to be a pyranose derivative, with a dioxane ring:



This compound may exist in at least three different modifications: α,α, α,β, and β,β. Still further modifications are possible, depending on whether carbon atom 1 in one fructose unit is linked with carbon atom 1′ or with carbon atom 2′ in the other fructose unit.

Mathews and Jackson did not carry out fermentation experimentation experiments nor did they discuss the possible relation between the fructose anhydrides and the glutose of Lobry de Bruyn and Alberda van Ekenstein. They merely concluded that the well-known reversion products in cane molasses probably consist of the same anhydrides. The term "reversion product" was first introduced by Wohl (*49*) for the sugar anhydrides formed when highly concentrated fructose or invert sugar solutions are heated in the presence of acid. He anticipated Mathews and Jackson's observation that a minimum of reversion products is formed at a definite acidity; he also found that at low sugar concentration the reversion products are hydrolyzed by acid. This indicates an equilibrium between reversion and hydrolysis, depending on sugar concentration, acid concentration, time, and temperature, provided no further decomposition of the primary reversion products has taken place.

Wohl also discovered that glucose is much more stable than fructose. Englis and Hanahan (*10*) showed recently that in pure aqueous solution glucose can be autoclaved for 30 minutes at 15 pounds pressure per square inch without detectable change. However, in the presence of certain impurities, such as potassium dihydrogen phosphate or ammonium chloride, at pH 6.4–6.6, it is partially transformed to fructose, and at the same time "some ketose other than fructose, with dextro or less levorotation than fructose" is produced. Phosphates and other salts are always present in sugar cane products, and it is possible that under manufacturing conditions the glucose is partially converted into fructose, but probably to a lesser extent than observed by Englis and Hanahan who employed a much higher temperature, although the pH is in about the same range. The "ketose other than fructose" mentioned by them is evidently glutose.

All the previous work here related indicated that the unfermentable reducing substances in cane molasses should contain fructose anhydrides. The next problem was to ascertain the chemical nature of the unfermentable products formed when a fructose sirup is heated under mildly acid conditions, as prevail in sugar manufacture.

UNFERMENTABLE REDUCING SUBSTANCE FROM FRUCTOSE

In the first experiments an 80% fructose solution was gently boiled under reflux for 16 hours. Then it was diluted to 7% and fermented with 3 grams of Fleischmann baker's yeast per gram of sugar. After standing 3 days at room temperature, the yeast was removed by filtration, and the filtrate clarified with a slight excess of neutral lead acetate solution. The precipitate was removed and the filtrate deleaded with hydrogen sulfide. The resulting filtrate was concentrated in vacuo at 50–60° C. In a typical experiment 300 grams of fructose gave 130 grams of unfermentable solids in the residual solution. The sirup obtained was freed of water by repeated distillation with ethanol-benzene mixtures.

The water-free sirup was found to be soluble in methanol but insoluble in acetone. It was therefore dissolved at room temperature in a minimum of anhydrous methanol, and the solution was poured in a thin trickle into a large volume of dry acetone which was vigorously stirred. The precipitated substance was rapidly filtered on a Büchner funnel, washed with acetone and then vacuum-dried at 60° C. The solid was creamy white and very hygroscopic, and reduced Fehling solution. It was stored in a ground-stoppered bottle over phosphorus pentoxide in a vacuum desiccator.

An attempt was made to purify the solid by redissolving it in methanol and reprecipitating it in acetone; a considerable portion of the substance did not go into solution in the methanol whereas previously it had been abundantly soluble. Repetitions of this purification process with new, acetone-precipitated material yielded increasing amounts of the alcohol-insoluble substance. This behavior recalls the observation of Pictet and Chavan that heterolevulosan, which is soluble in alcohol, readily dimerizes to diheterolevulosan, which is alcohol insoluble. Mathews and Jackson also concluded from their experiments that both monomer and dimer may be formed simultaneously. With the conversion of the monomer into the dimer, the reducing power decreases; Spoehr and Strain (*43*) found that when glutose is treated repeatedly with yeast, and the solution after each fermentation is heated to 80° C. for 15 minutes, the copper reduction gradually diminishes.

To preclude the possibility of incomplete fermentation, P.P. Regna was requested to carry out the yeast treatment of a new batch of fructose sirup. A solution of 730 grams of pure fructose in 230 grams of distilled water was gently refluxed for 16 hours. After cooling, it was carefully neutralized with calcium hydroxide and filtered. Addition of 6 liters of methanol produced a small quantity of gummy precipitate which was filtered off but not further investigated. It was probably Wohl's (*49*) levulosin, $(C_6H_{10}O_5)_n$. The filtrate was evaporated in vacuo to remove the methanol, diluted to 7 liters with distilled water, sterilized, and fermented for 6 days with yeast. The product was filtered, and the alcohol removed by distillation in vacuo. The solution was again made up to 7 liters, sterilized, and treated with fresh yeast for 4 days at the end of which time there was no further evolution of carbon dioxide. After filtration the solution was concentrated in vacuo to a weight of 400 grams and returned to the writers.

The sirup was dried by repeated distillation with ethanol and benzene, in the final stage with absolute alcohol and benzene. The dried material was dissolved in hot anhydrous methanol, filtered rapidly through a Büchner funnel, and poured with rapid stirring into 10 volumes of dry acetone which precipitated a pale yellow solid. The acetone was quickly decanted and the moist solid transferred to a vacuum-drying oven heated to 60° C. for a preliminary drying. It was then placed in an Abderhalden dryer where it was further heated over phosphorus pentoxide at the temperature of boiling chloroform and 1 mm. pressure.

The specific rotation of the product obtained in the earlier work was −28.3° (c = 1.5335 in water); that of the new batch −23.2° (c = 0.2981). The copper reducing power by the Munson and Walker method was 7.4 and 13.9%, respectively, of that of fructose. The molecular weight of the second preparation, determined by the freezing point method in water, was found to be 206, an indication that it contained about three parts of the monomer to one of the dimer.

ACID HYDROLYSIS OF UNFERMENTABLE MATERIAL

If the unfermentable material consists of fructose anhydrides, as suggested by the work of Mathews and Jackson, its levorotation and reducing power should, upon treatment with dilute acid, increase by conversion into fructose. When its solution was heated with hydrochloric acid to 60° C. under the conditions used in inverting sucrose according to Jackson and Gillis (*23*), the specific rotation increased from −28.3° to −31.1°, or about 10%. When the acid solution was heated to 100° C. for 1 hour the specific rotation rose to −65.6°. When the heating period at 100° C. was extended to 4 hours, the specific rotation dropped again to −24.9° because of decomposition. Similarly, hydrolysis according to Jackson and Gillis increased the reducing power from 7.4 to 14.3% of that of fructose, and heating to 100° C. for 4 hours to 28%. The original levorotation of the unfermentable material and its slow hydrolysis by acid are characteristic of the fructose anhydrides described by Pictet and Chavan and Schlubach and Behre. Pictet and Chavan reported that heterolevulosan is nonreducing, but they may not have boiled with Fehling solution long enough to obtain a precipitate of cuprous oxide. The presence of a reducing substance was confirmed by osazone formation from the unfermentable material.

OSAZONE FROM UNFERMENTABLE MATERIAL

Treatment of the unfermentable product with phenylhydrazine hydrochloride and sodium acetate in a boiling water bath under the usual conditions slowly produced an osazone which, when recrystallized from 50% alcohol, had a melting point of 194° C. Repeated crystallization from 50% alcohol did not alter the melting point of this substance whose crystalline form does not resemble that of phenylglucosazone. Recrystallization from isopropyl alcohol was tried next. The osazone was suspended in water, the suspension boiled under reflux, and isopropyl alcohol added until the crystals dissolved completely. The solution was filtered hot through a hardened filter, with the addition of decolorizing carbon. Upon cooling overnight in a refrigerator, crystals formed which had a melting point of 194.5° C. After four additional recrystallizations by the same method, but without the use of carbon, the melting point was 195° C. But after two more recrystallizations it fell to 165° C. The writers (*50*) had previously obtained an osazone of melting point 194.5–195° C. from the unfermentable residue of an invert sugar sirup which had been kept at 55° C. for 10 weeks. Reindel and Frey (*37*) also reported an osazone of the same melting point, prepared from the unfermentable residue of a cane molasses. The melting point of glutosazone, according to Lobry de Bruyn and Alberda van Ekenstein, is 165° C. Nagel (*32*) found the same melting point for glutosazone, but upon recrystallization it fell to 140° C. Spoehr and Wilbur (*44*) reported 163–166° C.; but in further work Spoehr and Strain (*43*) found that, after each recrystallization, glutosazone becomes more soluble and its melting point decreases. A preparation difficultly soluble in alcohol gave a melting point as high as 207° C. Coltof (*9*) observed melting points ranging from 97° to 157° C. for the osazones of various glutose preparations; the unfermentable residue from a cane molasses produced an osazone melting at 163° C. The extreme range of melting points reported for different glutosazone preparations demonstrates that they must have contained impurities. The solution of this problem was finally found by utilizing the observation of Benedict, Dakin, and West (*4*) that, when glutose is treated with phenylhydrazine in weakly alkaline solution, the osazone of methylglyoxal is produced. Since this osazone is readily soluble in dry acetone, it was decided to extract the glutosazones with this solvent. When osazones melting at 165° and 195° C., respectively, were simply washed with dry acetone, the melting point of both went up at once to 209–212° C., that of glucosazone. A mixture with authentic glucosazone gave the same melting point. To confirm this result, the crude unfermentable residue from the heated fructose sirup was treated directly with phenylhydrazine. When the resulting osazone, contaminated with tarry matter, was washed with dry acetone and recrystallized once, glucosazone of the correct melting point was obtained. For final identification, the osazone was converted by the method of Hann and Hudson (*16*) to the osotriazole which melted correctly at 195–196° C.; upon mixing with osotriazole prepared from glucose, the melting point remained unchanged.

Work on the substance or substances which contaminate the glucosazone is under way. They may be formed during the reaction with phenylhydrazine, but they may also be by-products of the yeast fermentation or derived from the fructose by purely chemical reactions. Possible impurities other than methylglyoxal are: acetylmethylcarbinol, identified by Browne (*7*) as a by-product of fermentation of cane juice, or glucic acid (reductone), formed by the effect of alkali on glucose or fructose during juice clarification; hydroxymethylfurfural; diacetyl or acetol.

In connection with a somewhat different problem, dealing with the effect of hydrogen fluoride on sugars, a low-melting phenylosazone has been prepared from the purified unfermentable product of glucose thus treated. This osazone (melting at 112° C.) yielded, on recrystallization from 30% ethanol, lemon-yellow needles which melted, but not sharply, at 125° C. Instead of attempting to purify the osazone further by recrystallization, the product was converted directly to the osotriazole. This melted sharply at 195–196° C. and gave exactly the same mixed melting point, which showed that it was glucose osotriazole.

According to Lobry de Bruyn and Alberda van Ekenstein, galtose is obtained from galactose in the same manner as glutose from glucose. Since glutosazone has been shown to be an impure glucosazone, it is probable that galtosazone is an impure galactosazone, and that galtose, like glutose, is not another hexose. Significantly, the melting point of galtosazone was found to be 182° C.; that of galactosazone has been variously reported in the range from 182° to 201° C.

The glucosazone just identified must have been formed from a fructose derivative which, judging from previous work, is evidently some anhydride. A large number of intra- and intermolecular anhydrides are theoretically possible, and several of them have been reported in the literature. The following experiments were carried out to establish the structure of those present in our unfermentable product.

METHYLATION OF UNFERMENTABLE MATERIAL

Seventy-five grams (dry weight) of the unfermentable sirup was fully methylated, as in previous work (*51*), by treating it in three 25-gram portions with methyl sulfate and then with methyl iodide and silver oxide. The resulting product was distilled at 1.1 mm. pressure, the bulk of the distillate going over at 216° C. There was a low-boiling fraction consisting mainly of methylated glycerol, from the glycerol formed as a by-product of the fermentation. The yield of high-boiling material was 28.6 grams. It reduced Fehling solution only slightly on boiling. However, when first hydrolyzed with dilute hydrochloric acid, the resulting solution vigorously reduced Fehling solution.

An analysis of the sirupy methylated product gave C = 52.74, H = 8.04 (calculated for trimethylfructose anhydride or hexamethyl difructose anhydride: C = 52.94, H = 7.84). The molecular weight in camphor was found to be 350 and 368, intermediate between that of the monomer (204) and the dimer (408); this indicated that it was a mixture of the two, the dimer predominating. This was not unexpected because of the tendency, previously mentioned, of sugar anhydrides to form dimers, which property had also been observed for their benzoylated and acetylated derivatives.

The $[\alpha]^{20^\circ}_{D}$ of the sirupy methylated product in chloroform was + 15.9 (c = 3.0464). Upon standing for five months at room temperature, crystals began to form in the sirup. The viscous material was diluted slightly with absolute ether, stirred, and allowed to stand in the refrigerator for 2 weeks. The crystals were then removed on a small fritted glass funnel, washed with absolute ether, and then dissolved in anhydrous methanol.

The solution was filtered and evaporated to incipient crystallization. The crystals which formed were collected and dried, and recrystallized twice from petroleum ether (boiling point, 70–90° C.). The melting point was 96° C., unchanged after recrystallization. From 14 grams of sirup, 0.41 gram of crystals was obtained; the $[\alpha]_D^{20}$ in chloroform was −41.9° C. (c = 0.9500). Schlubach and Behre reported for their hexamethyldifructose anhydride a melting point of 143–145° C. and a specific rotation of −46.5°. The differences in these physical constants indicate the presence of different modifications mentioned previously.

The structure of the hexamethyldifructose anhydride was proved by hydrolysis to trimethylfructose, from which osazones were prepared without loss of methoxyl groups; this showed that carbon atoms 1 and 2 are not methylated. The levorotation of the methylated product classes it as a pyranose derivative. It is therefore methylated on carbon atoms 3, 4, and 5.

HYDROLYSIS OF HEXAMETHYLDIFRUCTOSE ANHYDRIDE

Five grams of the methylated sirup were heated at 80° C. for 18 hours with 30 ml. of 1.5 N sulfuric acid in a glass-stoppered Erlenmeyer flask. At the end of the heating, the solution had turned dark brown. Powdered calcium carbonate was added in excess and the mixture stirred until all the acid was neutralized. The mixture was evaporated to dryness in a glass dish on the water bath and placed in a desiccator over sulfuric acid. The powdered material was then extracted in a Soxhlet apparatus with chloroform. This yielded 2.5 grams of a pale yellow, viscous oil with a boiling point of 154° C. at 1.5 mm. pressure. It reduced Fehling solution strongly and readily gave the Seliwanoff test for ketoses. The elementary analysis showed C = 48.62, H = 8.17 (calculated for $C_6H_9O_3(OCH_3)_3$: C = 48.44, H = 8.46). The $[\alpha]_D^{20}$ in chloroform (c = 1.7036) was −17.7°; in water (c = 1.4388) it was −20.5° initial, −24.2° after 2 days. These values compare with Schlubach and Behre's −55.2° in chloroform and −75.3° in water.

The rotation of the trimethylfructose varies somewhat with the conditions under which the hexamethyldifructose anhydride is hydrolyzed. Two further experiments were made with hydrochloric instead of sulfuric acid. In one, 2.5 ml. of 6.4 N hydrochloric acid was added to 0.5254 gram of the methylated sirup in a 25-ml. volumetric flask, and the volume was completed with water. The flask was placed in a boiling water bath for 2 hours and cooled to room temperature, and 4 grams of silver carbonate were added. After filtration the excess silver was removed with hydrogen sulfide, and the refiltered solution made up to 100 ml; $[\alpha]_D^{20}$ = −13.2° (c = 0.5254). In the other experiment, 0.4436 gram of the methylated sirup was hydrolyzed with hydrochloric acid as in the first but was heated for only 1 hour. After standing for 20 hours at room temperature, the hydrochloric acid was neutralized with sodium hydroxide. The $[\alpha]_D^{20}$, in the presence of the sodium chloride, was found to be −15.6°. All three specific rotations, although differing somewhat, are in the same range.

OSAZONES OF 3,4,5-TRIMETHYLFRUCTOSE

Treatment with phenylhydrazine produced a red, oily osazone which could not be crystallized by any method tried. After solution in isopropyl alcohol and drying in an Abderhalden dryer at 60° C. it analyzed only 13.2% nitrogen, against 14.0% theoretical. All attempts to convert it into a crystalline osotriazole were likewise unsuccessful. For this reason substituted osazones were next prepared.

The p-nitrophenylosazone was made by treating 0.25 gram of the trimethylfructose with 1 gram of p-nitrophenylhydrazine in 6 ml. of 50% acetic acid plus 0.5 ml. of 99% isopropyl alcohol. The mixture was heated for 30 minutes in boiling water and allowed to stand overnight. The red solid was collected and recrystallized from 50% isopropyl alcohol. Whereas nitrophenylosazones are generally little soluble in organic solvents, the three methoxyl groups greatly increase the solubility of the compound which was moderately soluble even in ether. The brick-red osazone analyzed C = 51.36, H = 5.21, N = 16.92, 16.98 (calculated for $C_{21}H_{26}O_8N_6$: C = 51.41, H = 5.34, N = 17.14). The osazone began to shrink at 206° C. and melted at 210° C. It gives the characteristic indigo blue color reaction observed by Hyde (*19*) with sodium hydroxide in dilute alcohol.

Identification of the p-nitrophenylosazone by converting it into the corresponding triazole according to the directions of Hann and Hudson (*16*) was attempted; refluxing was continued for 6 hours. The solution was filtered to remove decomposition products and evaporated to a small volume. No crystals appeared, but after standing in the refrigerator for a few days, large brownish needles formed in good yield. They melted at 209° C. Recrystallization from 30% isopropyl alcohol produced yellow needles, 1 inch long and melting at 210–211° C. A small crystal dissolved in alcohol and treated with 5 N sodium hydroxide solution gave a reddish-orange solution. The analysis gave C = 49.08, H = 4.42, N = 21.47 (calculated: C = 51.13, H = 5.72, N = 15.90). The $[\alpha]_D^{20}$ in pyridine was +5.64° (c = 1.3200). The presence of a nitro group in the para position seems to have a profound influence on the course of the reaction; instead of the expected osotriazole, a cleavage product is obtained which energetically reduced Fehling solution as well as Tollens silver solution.

The p-bromophenylosazone was prepared according to the directions of van der Haar (*15*). It comes down as an oil, but on standing over water, it gradually solidifies. Recrystallized from petroleum ether it yields orange-yellow crystals melting, but not sharply, at 100° C. The analysis gave Br = 28.70 (calculated for $C_{21}H_{26}O_4N_4Br_2$: Br = 28.65).

OXIDATION OF METHYLATED FRUCTOSE ANHYDRIDE

The conclusion drawn previously that carbon atoms 1 and 2 in the unfermentable anhydride obtained from fructose are involved in the anhydride formation has been confirmed by oxidation of the methylated product according to the method of Haworth, Hirst, and Learner (*17*):

Five grams of the constant-boiling methylated anhydride were placed in a Pyrex evaporating dish and 72 ml. of 27% nitric acid were added. The resulting mixture was heated on the water bath until the volume was reduced to about 10 ml. The reaction product was transferred to a 125-ml. Claisen flask, and distilled water was added continuously during distillation at 14 mm. pressure. When two liters of distillate had been collected, it was assumed that most of the residual nitric acid had been removed. The contents of the distilling flask were washed into a glass evaporating dish and concentrated to a small volume on the water bath. The material did not form crystals while standing in a refrigerator over the week end. It was therefore diluted to 30 ml. with distilled water and neutralized with sodium hydroxide. The solution was treated with activated carbon, evaporated until the salt began to precipitate, and then allowed to stand in the refrigerator. A voluminous amorphous solid separated out and was collected on a Hirsch funnel. After drying, the salt was purified three times by dissolving it in methanol, treating the solution with activated carbon, and evaporating as before. The white sodium salt weighed 3.5 grams and vigorously reduced Fehling solution. The analysis gave Na = 9.05, 8.96; OCH_3 = 35.0 [calculated for $C_6H_6O_4(OCH_3)_3Na$: Na = 8.91, OCH_3 = 36.0]. The $[\alpha]_D^{20}$ was found to be −15.4° (c = 3.8280). There was no mutarotation.

The analysis showed conclusively that a trimethyl ketogluconic acid was formed. If the original trimethylfructose anhydride had a methoxyl group on carbon atom 1 it would, according to Haworth, Hirst, and Learner, have been oxidized to carboxyl, and a dimethyl ketogluconic acid would have been obtained as the oxidation product. This would have happened if carbon atom 2 were linked by oxygen with carbon atoms 3, 4, or 5. The oxidation thus furnishes further evidence that the anhydride oxygen ring links carbon atoms 1 and 2.

When a few crystals of the sodium salt are ground together with an equal amount of resorcinol and mixed with two drops of concentrated sulfuric acid, and the mixture is carefully heated, the solution turns a dark cherry red. Upon washing the reaction product into about 400 ml. of dilute potassium hydroxide solution, an intense purplish-red color is obtained. When the mixture of sodium salt and resorcinol is heated with 0.5 ml. of 5 N hydrochloric acid in a boiling water bath for 2 minutes and the solution then made alkaline with 5 N sodium hydroxide, it turns a bright yellow resembling the color of a potassium dichromate solution. The coloring matter acts as an indicator, being colorless in acid and yellow in alkaline solution; it is not extracted by amyl alcohol.

HEXABENZOYLDIFRUCTOSE ANHYDRIDE

Two grams of the dry, crude anhydro sugar were treated in a 50-ml. glass-stoppered Erlenmeyer flask with 25 ml. of freshly prepared anhydrous pyridine and 5 grams of benzoyl chloride. The mixture was shaken on a machine for 4 hours and allowed to stand 2 days at room temperature. It was then poured with vigorous stirring into a large volume of ice water. The gummy solid which formed was repeatedly washed with fresh ice water. On further standing under water the material solidified. It was filtered on a Hirsch funnel, air-dried, and recrystallized from methanol. The melting point was 116° C. The elementary analysis gave C = 68.02; H = 4.60 [calculated for $C_{12}H_{14}O_{10}(C_6H_5CO)_6$: C = 68.34, H = 4.68]. The $[\alpha]_D^{20}$ in benzene was −125° (c = 1.5200). Although the compound was not distinctly crystalline, it is interesting to note that the melting point and specific rotation agreed closely with the values reported by Pictet and Chavan for hexabenzoyldiheterolevulosan (melting point 118° C., [α] in benzene −122.5°).

HEXA-ACETYLDIFRUCTOSE ANHYDRIDE

The directions of Hurd and Cantor (*18*) were followed. The anhydride was purified by dissolving in 50% methanol and refluxing for a few minutes with activated carbon. The water-white filtrate was brought to a boil, and distilled water was added in small quantities until the mixture became turbid at the boiling point. It was found that the acetylated compound tends to separate out in the form of thin, plastic sheets, and for this reason the flask was shaken vigorously. This purification process was repeated twice. In spite of the fact that the product does not form well-defined crystals, its analysis gave values in good agreement with the theoretical: C = 49.72, H = 5.56 [calculated for $C_{12}H_{14}O_{10}(CH_3CO)_6$: C = 50.00, H = 5.56]. Its molecular weight in camphor was found to be 579, compared to 576 theoretical, which showed that it contained little or none of the monomer. The melting point and specific rotation are compared in Table I with previous data in the literature. While the specific rotations agree fairly well, there are large differences in the melting points, which indicates the possible existence of several modifications.

Table I. Physical Constants of Hexa-acetyldifructose Anhydride

Method of Preparing Anhydride	M.P. of Acetate, ° C.	$[\alpha]_D^{20}$ (Benzene)	c	Citation
Fructose and concd. HCl at 0° C.	94	−43.5°	...	(*33*)
Fructose and liquid HCl	171–73	−41.7°	1.01	(*40*)
Fructose heated in water soln.	71	−44.4°	0.896	Authors

DISCUSSION OF RESULTS

The experiments prove that glutose, prepared by heating a fructose sirup and removing fermentable sugars by means of yeast, is not a 3-ketohexose, as suggested by Lobry de Bruyn and Alberda van Ekenstein, because glutosazone, when freed from accompanying impurities, is identical with glucosazone. Since glutose gives the reactions characteristic of ketoses, the glucosazone obtained from it must be derived from fructose. The methylation and oxidation experiments have shown that the reducing substance which yields the osazone is the 1,2-anhydride of fructopyranose. In common with other hexose anhydrides—for example, the fructofuranose anhydride of Schlubach and Elsner (*41*)—this anhydride readily dimerizes to a difructopyranose anhydride, by the opening up of the anhydride oxygen rings and linking between the two fructose units with formation of a dioxane ring. This compound is nonreducing, does not give an osazone, and is difficult to hydrolyze. Glutose, formed from a heated fructose sirup, consists principally of a mixture of these two fructose anhydrides. The dark color of the glutose indicates that it contains also more complex anhydrides of higher molecular weight (fructose caramel), in addition to minor quantities of other reducing substances, such as hydroxymethylfurfural, methylglyoxal, etc.

The difructose anhydride appears to have the same structure as that prepared by Schlubach and Behre and the diheterolevulosan of Pictet and Chavan. Like the former, it consists of two fructose units linked together by oxygen bridges between carbon atoms 1 and 2 of one unit with carbon atoms 1 and 2 of the other; various modifications of this structure are possible. The hexabenzoate of the difructose anhydride prepared by the writers has the same properties as that of heterolevulosan. The identity of the monomeric fructose anhydride and of heterolevulosan is problematical.

The results obtained by the writers explain the findings of Spoehr and Strain (*43*) that glutose can, by the cyanohydrin reaction, be converted into a heptonic acid which upon reduction yields methyl-*n*-butylacetic acid and is therefore derived from a 2-ketohexose—namely, fructose. They also explain the behavior of glutose in the animal body, observed by Benedict, Dakin, and West (*4*); it is physiologically inert since it is excreted unchanged, and it does not form a hexose phosphate when treated with yeast and sodium phosphate because the anhydride ring is evidently resistant to biochemical hydrolysis.

Glutose, formed not from fructose alone but from cane juice, is a much more complex mixture, as will be shown in Part II. Further experiments are in progress to ascertain whether the unfermentable fructose anhydrides prepared by heating a fructose solution are actually present in cane molasses, as may be inferred from the heat treatment of cane juice in the factory.

II. Unfermentable Reducing Substances from Interaction of Reducing Sugars with Amino Acids and Their Amides

Reducing sugars react with amino acids and their amides, such as aspartic acid, glutamic acid, asparagine, and glutamine; the last two have been isolated from cane juice, and all are present in molasses. Ambler (*2*) reviewed the literature on this subject, covering the period up to 1928. Maillard (*28*), who was the first to study this reaction, found that it takes place at room temperature but much more vigorously if heat is applied, especially when solutions of high concentration are used. Under these conditions carbon dioxide is given off, and dark brown to black, amorphous substances of varying composition are produced which Maillard termed "melanoidins". He suggested that the first step in the reaction is condensation of the sugar with the amino acid or amide, followed by evolution of carbon dioxide and further condensation with additional moles of the sugar. There is no distinct line of separation between the two types of products, but for practical reasons they will be discussed separately.

PRIMARY CONDENSATION PRODUCTS OF REDUCING SUGARS AND AMINO COMPOUNDS

Although the condensation of sugars with arylamines, and the molecular rearrangements of the resulting products have been extensively studied (*21*), there is only scant information about the chemical nature of the substances which are formed initially by the interaction of sugars and amino acids. It is known that in the early stages of the reaction no carbon dioxide is given off, and little color is formed. Chemical combination between the constituents has been deduced by various investigators from the observed changes in the chemical and physical properties of the reaction mixture. Kostytchev and Brilliant (*25*), Borsook and Wasteneys (*5*), Frankel and Katchalsky (*13*), and Ågren (*1*) found a reduction in amino nitrogen during the course of the reaction, as determined by the methods of Van Slyke and of Sörensen. Temperatures as high as 55° C. and varying pH were used in these experiments. Up to pH 10, simple condensation between one mole each of the constituents, with the formation of *N*-glycosides, was indicated, but above that point decomposition took place and the reaction became more complex. Von Euler and co-workers (*11*) observed changes in the rotation and freezing point of the mixture. A considerable increase in the electrical conductance of solutions containing invert sugar and sodium aspartate or asparaginate was reported by Sattler and Zerban (*39*). Later, Frankel and Katchalsky (*14*) studied the pH changes taking place during the reaction. Ripp (*38*) and also Shiga (*42*) found that fructose reacts less readily than glucose.

Only four crystalline *N*-glycosides have been prepared directly from the components: alanine glucoside by Irvine and Hynd (*20*), glycine ester glucoside by von Euler and Zeile (*12*), the calcium salt of glycine glucoside by Kuzin and Polyakova (*26*), and cysteine glucoside by Ågren (*1*). These glucosides were found to be rather unstable and to be readily hydrolyzed, with the exception of cysteine glucoside to which a thiazole structure has been ascribed because of its great stability.

All the remaining known condensation products of sugars and amino acids have been obtained by Maurer (*30*), by von Euler and Zeile (*12*), and by Maurer and Schiedt (*31*) from the acetobromo derivatives of glucose or cellobiose and the ethyl esters of sarcosine, glycylglycine, or sarcosylglycine, as acetylated ester glycosides. Some of the corresponding acid amides have also been prepared by treating the esters with ammonia in methanol.

It is important to note that the *N*-glycosides of amino acids and amino acid amides reduce Fehling solution and yield the osazone of the parent sugar. Glycine ester glucoside, derived from the lowest member of the amino acid series, was found to be fermentable, but not the amide of sarcosine glucoside.

EXPERIMENTS WITH GLUCOSE OR FRUCTOSE AND ASPARAGINE

To obtain information on the possible formation of unfermentable nitrogenous condensation products in the factory treatment of cane juice, the following experiments were made:

Six grams of glucose or 6 grams of fructose were dissolved in a phosphate–citric acid buffer solution of pH 7 to a total volume of 100 ml. In two further experiments the same quantity of sugar plus 5.5 grams of asparagine (1.1 mole per mole of sugar) was used instead of the sugar alone. The solutions were heated side by side at 60° C. for 10 days, during which time the color of those containing asparagine had darkened much more than those without asparagine—that is, to about the color of a factory evaporator sirup. Each solution was diluted and completely fermented with a large excess of Fleischmann baker's yeast in a 500-ml. flask; the solution was then clarified with neutral lead acetate solution, made up to the mark, filtered, deleaded with dry potassium oxalate, and refiltered. The copper reducing power was determined in 50 ml. of the final filtrate by the Munson and Walker method, and the total nitrogen in 20 ml. by the Kjeldahl method; Table II gives the results.

Only a trace of unfermentable reducing substance, expressed as hexose, was formed from the glucose alone, but there was a fairly large quantity from fructose alone, as expected. Much greater amounts than from fructose alone were obtained in the presence of asparagine, and in this case glucose produced more than fructose. This makes it probable that a considerable part of the unfermentable reducing substances in molasses is formed by the interaction of reducing sugars with asparagine. The small quantity of nitrogen found in the fermented solution of the fructose alone is probably only apparent, since there were slight fluctuations in the blank used for correction. Where asparagine had been added, a substantial portion of the nitrogen originally present (46.7 mg. in 20 ml.) is present in the solution after fermentation. It is interesting to note that the fermentation residue from fructose and asparagine contains more nitrogen than that from glucose and asparagine, whereas the reducing power is smaller.

Table II. Reducing Power and Nitrogen Content of Unfermentable Condensation Products

	Glucose Alone	Glucose + Asparagine	Fructose Alone	Fructose + Asparagine
Mg. Cu from 50 Ml.	0.7	154.8	25.9	101.3
Mg. reducing substance calcd. as glucose or fructose, respectively	0.3	77.2	13.6	54.6
Reducing substance as % of sugar originally present	0.05	12.9	2.3	9.2
Mg. N in 20 ml.	0.0	21.3	1.4	39.6

An additional experiment was made, under the same conditions, with fructose in the presence of aspartic acid instead of asparagine. In this case the unfermented reducing substance, calculated as fructose, amounted to only 0.5% of the sugar originally used, against 9.2% in the presence of asparagine. This is in line with the observation of Ripp (*38*) that under comparable experimental conditions 50% of the nitrogen in asparagine reacts with fructose, but only 2.6% of that in aspartic acid.

No attempt has been made to isolate and identify the products formed in these experiments. That condensation products of sugars and amino acids are present in the reaction mixtures may be safely concluded from the work of previous investigators. For further information on this point, various analytical methods have been used to ascertain whether unfermentable products, having the same characteristics as those prepared from the pure components, occur in molasses. In one series of experiments the course of the hydrolysis of the unfermentable products listed in Table II was compared with that of the unfermentable substances in molasses. In the second series the correlation between total nitrogen and total unfermentable reducing substances in molasses was studied. In the third, the proportion of the total nitrogen in molasses that is still present in the unfermentable material was determined.

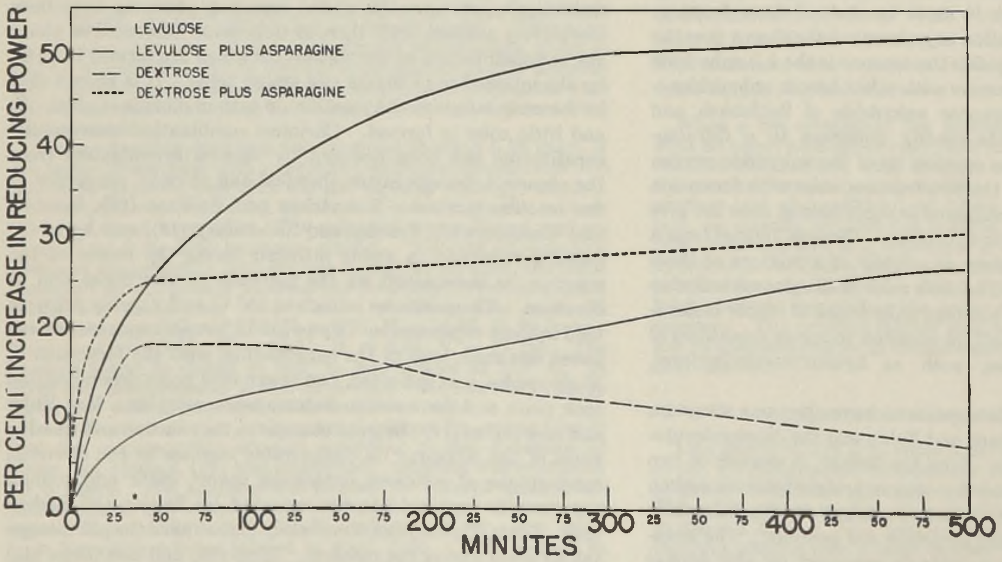


Figure 1. Rate of Hydrolysis of Condensation Products

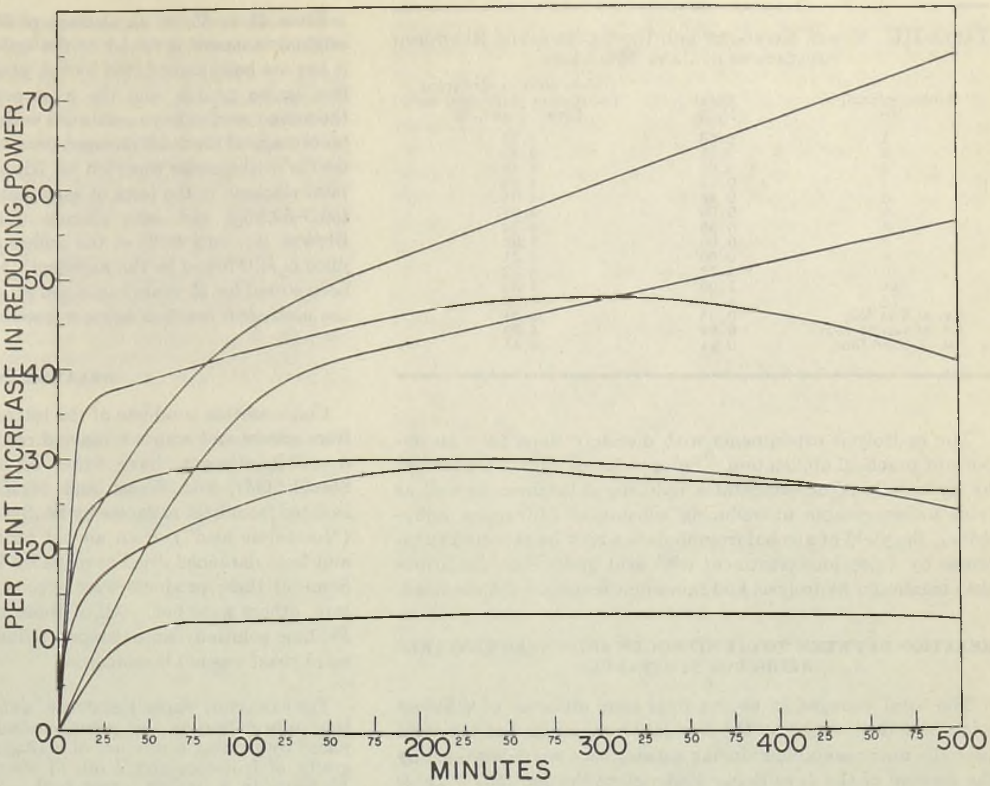


Figure 2. Rate of Hydrolysis of Unfermentable Reducing Substances in Cane Molasses

HYDROLYSIS OF CONDENSATION PRODUCTS

New batches of unfermentable material, similar to the products in Table II, were prepared. To duplicate factory conditions more closely, solutions of about 70° Brix were made by dissolving 140 grams of glucose or fructose, respectively, in 60 grams of Sörensen's phosphate buffer solution of pH 5.9, the buffer taking the place of the ash in cane juice. In two further solutions the same quantity of glucose or fructose and buffer solution, plus 3 grams of asparagine, was used. This gave about the same ratio of amino acid amide to sugar as in cane juice. The four solutions were kept side by side in an oven heated to 60° C. They were then diluted to about 15° Brix and fermented with a large excess of Fleischmann baker's yeast. After complete fermentation the solutions were clarified with a little more than the calculated amount of neutral lead acetate solution and filtered. The excess lead was removed with solid disodium phosphate, and the precipitate removed by filtration. Of each final filtrate, 500 ml. were concentrated in vacuo to a small volume and transferred to a 200-ml. volumetric flask. Ten milliliters of concentrated hydrochloric acid were added, and the volume was completed with water. For the analyses 10-ml. aliquots of this solution were placed in test tubes closed with rubber caps and were heated side by side to 65° C. in a thermostat. At the end of measured time intervals one tube at a time was removed from the bath, and the contents were washed into a 100-ml. volumetric flask containing 2 ml. of sodium carbonate solution (160 grams of the anhydrous salt in 1 liter). The quantity of this solution necessary to neutralize the 10 ml. of acid solution had been previously determined by titration of the unheated solution. After completing the volume of the neutralized solution, 10-ml. portions were analyzed by the method of Isbell, Pigman, and Frush (*22*). A Precision electric heater in series with a Variac, to control the heating, was used to bring the solution to the boiling point in exactly 4 minutes, and boiling was then continued for another 6 minutes. The flask was removed exactly 10 minutes after being placed on the heater; the solution was then rapidly cooled and analyzed.

Figure 1 shows the results of these analyses in terms of the percentage increase in copper reducing power upon extended heating with acid. The curves show that all of the four products are, under the conditions chosen, rapidly hydrolyzed during the first 45 minutes, after which the hydrolysis slows up more and more. In the case of the unfermentable product from glucose alone, reversion becomes predominant after the initial 45-minute period. In the same interval the products from fructose alone and from glucose plus asparagine have about the same hydrolysis rate, but later the former gains rapidly over the latter. The product from fructose plus asparagine has the lowest initial hydrolysis rate, but after 75 minutes total time its rate curve crosses that of the product from glucose alone. For a complete understanding of the reactions an extensive investigation on the effect of each variable on the kinetics involved will have to be undertaken. But until methods for separating and differentiating between the unfermentable products formed from sugars alone and by their interaction with amino compounds become available, only a qualitative comparison can be made between the curves in Figure 1 and those showing the hydrolysis rate of the unfermentable substances in cane molasses (Figure 2).

HYDROLYSIS OF UNFERMENTABLE REDUCING SUBSTANCES

Samples of distillery slops were furnished by six alcohol producers who use cane molasses as raw material. These slops were found to be much more highly buffered than the solutions prepared from the pure sugars without and with asparagine; consequently the amount of acid used for the hydrolysis had to be increased to produce approximately the same hydrogen ion concentration as before. The samples of the slops, which had previously been concentrated in the distillery, were diluted with water and the solutions were clarified with a slight excess of neutral lead acetate solution. The excess lead was removed from the filtrates with disodium phosphate, and the solutions were refiltered. Some preliminary experiments had to be made with the final filtrates to secure a concentration of reducing substances falling in the proper range of the method of Isbell, Pigman, and Frush. The hydrolysis was then carried out as described previously; the only difference was that potassium hydroxide was used for neutralizing the acid instead of sodium carbonate, to avoid the heavy foaming caused by the evolution of carbon dioxide. Figure 2 shows the curves obtained in these experiments. The qualitative similarity with those in Figure 1 is evident. All of the curves show a fairly high initial rate of hydrolysis. After this first period the hydrolysis slows up, and in three cases there is noticeable reversion.

The experiments indicate that the unfermentable reducing substances in molasses behave, upon hydrolysis, much like those prepared from glucose or fructose alone or in the presence of asparagine. Exact coincidence cannot be expected because of the many possible combinations between at least two sugars and at least four amino compounds.

TABLE III. TOTAL NITROGEN AND UNFERMENTABLE REDUCING SUBSTANCES IN CANE MOLASSES

Molasses Sample No.	Total N, %	Unfermentable Reducing Substances Expressed as Invert Sugar, %
1	0.28	2.75
2	0.34	3.55
3	0.36	3.48
4	0.41	4.24
5	0.49	4.05
6	0.50	4.01
7	0.55	4.34
8	0.60	3.97
9	0.69	4.21
10	0.72	4.32
11	1.06	4.39
12	1.27	4.72
Av. of first four	0.35	3.51
Av. of second four	0.54	4.09
Av. of third four	0.94	4.41

The hydrolysis experiments with distillery slops have an important practical application. Since reducing sugars are formed by hydrolysis of unfermentable reducing substances as well as from unfermentable nonreducing substances (difructose anhydride), the yield of alcohol from molasses may be expected to increase by a previous treatment with acid under such conditions that maximum hydrolysis and minimum reversion are obtained.

RELATION BETWEEN TOTAL NITROGEN AND UNFERMENTABLE REDUCING SUBSTANCES

The total nitrogen in twelve final cane molasses of different origin was determined by the Kjeldahl method, and at the same time the unfermentable reducing substances were determined by the method of the Java Sugar Experiment Station (*35*). Table III shows the results; the molasses are arranged in the order of increasing nitrogen content.

The percentage of unfermentable reducing substances increases, in a general way, with the total nitrogen. This is shown even better by the averages of Table III. It is evident that there is good correlation between the two constituents of molasses, although these were produced in widely separated parts of the world. According to analyses by Browne (*8*), 90% of the Kjeldahl nitrogen in cane juice, exclusive of that coagulated during clarification, is present in the form of amino acids and their amides (55% as amides, 35% as amino acids), 8% as soluble peptides, and 2% as ammonia. Hence practically all the Kjeldahl nitrogen in the clarified juice occurs in the form of groups which are capable of reacting with reducing sugars, and it may be expected that much of the nitrogen in molasses is present in the form of nitrogenous condensation products with sugars. Baars and Bogtstra (*3*) observed that the nitrogen in cane molasses is not utilized by the yeast *Torula utilis*, whereas nitrogen in the form of amino groups is readily assimilated.

COMPARISON OF NITROGEN IN UNFERMENTABLE PORTION TO TOTAL NITROGEN

The nitrogen in molasses was determined before, and again in the residue after fermentation. Table IV shows the results.

TABLE IV. NITROGEN IN UNFERMENTABLE PORTION COMPARED WITH TOTAL NITROGEN IN CANE MOLASSES

Origin of Molasses	N as % of Molasses: Total, *A*	N as % of Molasses: Unfermentable portion, *B*	*B* as % of *A*
Santo Domingo	0.37	0.22	60
Cuba	0.39	0.33	85
Cuba	0.44	0.21	48
Hawaii	0.45	0.20	45
Puerto Rico	0.50	0.42	84
Cuba	0.58	0.49	85
Florida	1.07	0.78	73

From 45 to 85, or an average of 68%, of the nitrogen in the original molasses is found in the unfermentable residue. Since it has not been assimilated by the yeast, it is not in the form of free amino groups, and the most probable explanation is that the amino groups have combined with the reducing sugars. The percentage of the total nitrogen present in the unfermentable portion is in the range reported by Ripp (*38*) for the percentage of total nitrogen in the form of asparagine that reacts with fructose (50.0–52.3%) and with glucose (80.8–85.1%). According to Browne (*6*), only 60% of the amino nitrogen in Louisiana cane juice is still found in the molasses; a Cuban molasses that had been stored for 15 years contained no α-amino nitrogen whatever, the ninhydrin reaction being negative.

MELANOIDINS

Condensation products of the intensely colored type, prepared from sugars and amino acids and containing from less than 3 to over 7% nitrogen, have either been described by Ripp (*38*), Staněk (*45*), and Weast and McKinney (*48*), or have been isolated from beet molasses by Stoltzenberg (*46*) and Staněk (*45*) ("fuscazinic acid"), from an old cane molasses by Browne (*6*) and from darkened dried apricots by Weast and McKinney (*48*). Some of these products were precipitated by neutral lead acetate, others were not. All of those that have been tested with Fehling solution cause copper reduction. Their behavior toward yeast was not investigated.

PREPARATION FROM FRUCTOSE AND ASPARTIC ACID. To obtain information on this point, a condensation product was prepared by heating a mixture of 8.42 grams of aspartic acid, 34.19 grams of fructose, and 7 ml. of water in a pressure bottle for 12 hours in a boiling water bath. The reaction product was brownish black and very viscous. It was diluted with water and fermented with a large excess of Fleischmann baker's yeast at pH 4.6; disodium phosphate was added as yeast food. After completion of the fermentation, the yeast was removed by filtration, the solution was treated with a slight excess of neutral lead acetate solution, and the excess lead was removed from the filtrate with hydrogen sulfide. The unfermented residue reduced Fehling solution.

OSAZONES FROM UNFERMENTABLE CONDENSATION PRODUCT. Depending on the particular method of purification, phenylosazones of different degrees of purity, as shown by analysis and physical properties, were obtained which were exactly like those obtained by the writers from the unfermentable residue of heated fructose sirup and by others from various "glutose" preparations. All these osazones were prepared long before the method of purification with dry acetone had been discovered, and before the paper by Hann and Hudson (*16*) on osotriazoles had appeared. The common characteristic of all these osazones is that the materials from which they were prepared were first fermented with yeast and were therefore liable to be contaminated with phenylhydrazine derivatives of fermentation by-products. The $[\alpha]^{20}_{D}$ of an osazone melting at 184–185° C. in pyridine-alcohol was −56.5° initial, −42.1° final; the corresponding figures for a preparation melting at 196.5° C. were −70.7° and −48.8°, respectively. They are in the general range of the values for glucosazone (−62° and −35° C., respectively) but are sufficiently different to disclose the presence of impurities. An osazone melting at 191.5° C. contained 61.20% carbon and 14.57% nitrogen, while glucosazone has 60.31% carbon and 15.64% nitrogen. Another osazone, with a very low melting point (134° C.) contained 68.40% carbon and 19.55% nitrogen, approaching the composition of the osazone of methylglyoxal (C = 71.40, N = 22.21). There is little doubt that all these osazones were impure glucosazones.

THIOBARBITURIC ACID DERIVATIVE OF MELANOIDIN. The dark-colored condensation product of fructose and aspartic acid was found to react with thiobarbituric acid in 12% hydrochloric acid, which is generally used in the determination of furfural. A yellow precipitate formed which was insoluble in alcohol and cold water, sparingly soluble in hot water, and readily soluble in pyridine and dilute alkali solutions from which it could be precipitated by acid. The reaction product was allowed to stand overnight, removed by filtration, washed with water, and then dissolved in dilute ammonium hydroxide. The solution was filtered, and the compound was reprecipitated with dilute sulfuric acid, collected on a filter, washed with water, and dried at 60° C. in vacuo. All attempts to obtain it in crystalline form were fruitless; this was not unexpected since the condensation product with furfural is also an amorphous substance.

An elementary analysis of the compound gave C = 49.40, H = 4.20, N = 6.87, which corresponds to the empirical formula $C_{25}H_{26}O_{13}N_3S$ (C = 49.34, H = 4.28, N = 6.91, S = 5.26, O = 34.21). If the thiobarbituric acid remainder is deducted from this formula, the fructose–aspartic acid condensation product itself has the formula $C_{21}H_{24}O_{12}N$, containing C = 52.28, H = 4.98, N = 2.90, O = 39.84. This composition agrees closely with that of the two melanoidins isolated by Browne (*6*) from cane molasses: C = 52.68 and 50.61, H = 5.18 and 4.59, N = 2.71 and 2.90, O = 39.43 and 41.90. Such a product may be formed by the condensation of three moles of hexose and one mole of aspartic acid, with the loss of eight moles of water and one of carbon dioxide. Actually, it is a complex mixture of substances of unknown constitution. If the lead purification is omitted in the preparation of the condensation product, the thiobarbituric acid derivative has a higher carbon content than that obtained after lead clarification.

Although the composition of these hexose–amino acid condensation products may vary widely, depending on the individual constituents and the conditions of their formation, there is no doubt that they form part of the highly colored unfermentable reducing substances in molasses.

OTHER UNFERMENTABLE REDUCING SUBSTANCES

SUBSTANCES CONTAINING PHOSPHORUS. The presence of a strongly reducing, crystalline substance of the empirical formula $C_{30}H_{54}O_{18}N_5P$ in the unfermentable residue of heated invert sugar sirup was announced in the previous paper (*51*). It must be partly or wholly derived from the yeast, since the material subjected to fermentation contained neither nitrogen nor phosphorus; on the other hand, unheated invert sugar sirup treated with yeast gives only traces of reducing substances. The previous heat treatment also seems to play a part in the formation of the reducing compound.

VOLATILE SUBSTANCES. Earlier work (*50*) disclosed that about 10% of the unfermentable reducing substances in molasses is volatile. This suggests the presence of methylglyoxal, acetylmethylcarbinol, or hydroxymethylfurfural, mentioned previously. The nature of these substances is being investigated.

CONCLUSIONS

In this study on the nature of the unfermentable reducing substances derived from sugar cane products it has been found that the "glutose" of Lobry de Bruyn and Alberda van Ekenstein is not a 3-ketohexose, as suggested by them. It is a complex mixture of substances whose composition varies with the raw material from which it has been prepared and with the method of preparation. The unfermentable residue from cane molasses contains a small quantity of *d*-allulose, as previously reported, but this sugar has not been found in glutose prepared from invert sugar by the method of Lobry de Bruyn and Alberda van Ekenstein. Alkaline reaction is not essential for the formation of unfermentable reducing substances, because they are obtained also below pH 7. The important factor for their formation is high temperature. Considerable quantities are formed at the temperatures used in cane sugar manufacture. The unfermentable portion of a fructose solution that has been boiled under reflux contains, principally, 1,2-fructopyranose anhydride which reduces Fehling solution and the corresponding difructose anhydride which does not reduce. The glutosazones, of varying melting point as well as other physical and chemical properties, which have been reported by a number of investigators, are merely glucosazone contaminated with impurities; the principal one appears to be the osazone of methylglyoxal.

The unfermentable reducing substances obtained by heating solutions of glucose, fructose, or mannose in the presence of alkali have not been investigated because alkalinity is only a minor factor in the formation of unfermentable reducing substances in cane sugar manufacture, but it has been found that glucose, unlike fructose, when heated in aqueous solution, gives only traces of unfermentable reducing substances. However, when glucose or fructose sirups are heated in the presence of asparagine, the principal amino acid derivative occurring in cane juice, large quantities of unfermentable reducing substances are formed, evidently condensation products of amino acids and their amides with reducing sugars. These substances are well known, but their exact nature has not been established except for some of the simpler members of the series which are considered to be *N*-glycosides. Still less is known about the dark-colored condensation products (melanoidins) formed by prolonged heating at high temperatures. A melanoidin prepared from fructose and aspartic acid yielded impure glucosazone when treated with phenylhydrazine. With thiobarbituric acid it gave an amorphous precipitate whose composition showed that it is quite similar to a melanoidin prepared previously from cane molasses by Browne.

Neither the fructose anhydrides nor any of the nitrogenous condensation products have been isolated from the unfermentable residue of cane molasses, but hydrolysis experiments have shown that they are essentially the same as those obtained synthetically from the constituents. Upon hydrolysis the sugars are regenerated, and utilization of this fact may increase the alcohol yield in distilleries. The conclusion that condensation products of reducing sugars with amino acids occur in cane molasses is supported by the high correlation between unfermentable reducing substances and total nitrogen in molasses, and further by the fact that a large percentage of the nitrogen in the original molasses is found in the unfermentable portion. In addition to an organic reducing compound containing not only nitrogen but also phosphorus, which had been announced previously, volatile reducing substances have also been found in the unfermentable residue; these are being further investigated.

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Evaluation of Malts for Production of Alcohol from Wheat

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Knowledge of the amylase content of a malt is helpful but is not adequate for complete evaluation of the malt. Other factors also operate, and probably only a fermentation test can give an accurate evaluation. A possible method for evaluating malts for production of alcohol from wheat is to employ a 5% level of malt in a 36-hour fermentation. If two fermentations are run, 24- and 72-hour periods give both the rate of conversion and the final degree of conversion of the wheat starch to alcohol. In laboratory fermentations of wheat, malt in the amount of 8% of the total grain bill, as commonly used in industrial plants, was found to be in excess. Many malts at a 5% level gave maximum yields of alcohol in 36 hours. Under the conditions employed, the limiting factor in speed of fermentation appeared to be the action of the malt rather than the fermenting power of the yeast.

THE tremendous increase in the demand for industrial alcohol, together with the use of grains as raw material, placed a great load on malting facilities and barley supply. In the industrial production of alcohol from starchy mashes, the amylase activity of the saccharifying agent is probably of primary concern. The index used classically in the evaluation of malts is the Lintner value; other indices are the alpha- and beta-amylase activity of the malt. The final test must be the yield of alcohol obtained. In this paper the amylolytic criteria are compared with the results obtained by a suitable fermentation procedure to determine which gives the best indication of the malt value.

Dark Northern Spring Wheat No. 2 and Hard Winter Wheat No. 2 were obtained from the Commodity Credit Corporation through the Norris Grain Company. These grains are referred to here as spring wheat and winter wheat. The wheat was ground and sifted to determine the fineness of the meal. All of it passed through a 2-mm. sieve, 63% passed through a 1-mm. sieve, and 38% passed through a 0.5-mm. sieve. The moisture content was determined by drying the ground material at 100–105° C. for 10–12 hours. The starch content of the ground material was determined by the malt-acid method of the A.O.A.C. (*2*). The values obtained on the dry basis were 66.7% for spring wheat and 65.8% for winter wheat.

A barley malt set aside by the Pabst Brewing Company for research on the Wheat Alcohol Project was used as a reference standard. The other barley malts, prepared under varying conditions of malting, represent a number of different barley varieties which are produced commercially and some hybrid selections which are being developed by plant breeders. Tables I and II give information on the varieties of barley, malting conditions, and amylolytic properties of the malts.

FERMENTATION PROCEDURE

Seven liters of a 22.25% suspension [weight equivalent to 22.25 grams of dry grain per 100 ml. of mash or 30.2 gallons per bushel (56 pounds) of dry grain] of meal in water were held at room temperature for 15 minutes. The pH was adjusted to approximately 5.6 with 1 *N* sulfuric acid. With continuous stirring, the mash was heated in a boiling water bath for 1 hour and then cooled, and water was added to make up for loss due to evaporation. Aliquots of 600 ml. of the mash were autoclaved in 1-liter flasks at 15 pounds per square inch pressure for 1.5 hours with 5 drops of Vegifat Y to prevent loss by frothing.

This mashing and cooking procedure was used for both spring and winter wheat, except that with winter wheat 1% malt was added at the beginning of the procedure to accomplish liquefaction. The spring wheat contained enough amylase to produce autoliquefaction, but the amylase was not so abundant in the winter wheat.

For conversion the mash was cooled to 65° C. The desired amount of finely ground malt was made into a 10% slurry with water and added to each of the flasks of mash. The flasks were shaken vigorously for 2 minutes and then cooled quickly under the water tap.

The pH was adjusted to approximately 4.8 with 1 *N* sulfuric acid, and 10 ml. of yeast suspension were added. The yeast (No. 47 of our collection) was a strain of *Saccharomyces cerevisiae* from the Lawrenceburg plant of Joseph E. Seagram and Sons, Inc. It was transferred from an agar slant into a tube containing 10 ml. of medium containing 3% malt sprouts extract and 5% glucose, and was allowed to grow 24 hours at 30° C. The contents of the tube were then transferred to a bottle holding 200 ml. of the malt

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[1] Barley and Malt Laboratory and Departments of Agricultural Bacteriology and Biochemistry in cooperation with the Office of Production Research and Development.

TABLE I. EFFECT OF LOW MALT LEVELS ON ALCOHOL YIELDS FROM SPRING WHEAT IN 72-HOUR FERMENTATIONS WITH MALTS PRODUCED UNDER DIFFERENT CONDITIONS

Malt No.	Variety or Selection	Location Grown	Malting Moisture, %	Malting Time, Days	Diastatic Power		Maltose Equivalent		Alcohol Yield, Proof Gal./100 Lb.		
					° L.	Maltose equiv.	β-amylase	α-amylase	1% malt	2% malt	4% malt
4270–71	Wis. Barbless	Clinton, Wis.	44	5	146	584	547	37	7.76	8.46	9.38
4278–79			44	7	145	578	536	42	7.93	8.87	9.57
4274–75			48	5	159	636	597	39	7.91	8.65	9.57
4282–83			48	7	168	672	627	45	8.21	9.12	9.85
4268–69	Manch., N. D. 2121	Langdon, N. D.	44	5	196	786	746	40	8.21	9.09	9.65
4276–77			44	7	208	830	777	53	8.22	9.10	9.30
4272–73			48	5	219	874	827	47	8.14	9.13	9.56
4280–81			48	7	225	902	850	52	8.37	9.49	9.85
4207–09	Trebi	Edgeley, N. D.	48	5	230	920	874	46	8.80	8.94	9.72
4228–30	Minn. II-31-19	Waseca, Minn.	48	5	89	356	318	38	7.46	8.43	8.90
4234–35	Kindred	Minnesota	48	5	261	1044	956	88	8.91	9.54	9.98
Pabst	Control	......	..	..	183	732	689	43	8.01	8.65	9.66

TABLE II. AMYLASE VALUES ON MALTS FROM DIFFERENT BARLEY VARIETIES AND ALCOHOL YIELDS FROM SPRING WHEAT WITH 5% LEVEL OF MALT

Malt No.	Variety or Selection	Location Grown	Malting Moisture, %	Malting Time, Days	Diastatic Power		Maltose Equivalent		Alcohol Yield, Proof Gal./100 Lb. at Fermentation Time of:	
					° L.	Maltose equiv.	β-amylase	α-amylase	36 hr.	72 hr.
Pabst	Control	......			183	732	689	43	8.95	9.84
4228–30	Minn. II-31-19	Waseca, Minn.	48	5	89	356	318	38	9.55	10.19
4231–33	Olli	Madison, Wis.	48	5	139	556	484	72	9.96	10.39
4219–21	Norwegian	Fargo, N. D.	48	5	248	992	903	89	10.07	10.44
4207–09	Trebi	Edgeley, N. D.	48	5	230	920	874	46	8.53	9.87
4222–24	Manch., N. D. 2121	Brookings, S. D.	48	5	230	920	847	73	9.39	9.84
4189–91	Atlas	Davis, Calif.	48	5	80	320	260	60	8.80	9.84
4174–76	Trebi	Fargo, N. D.	48	5	150	600	563	37	8.10	9.39
4195–97	Sparton	Lincoln, Nebr.	48	5	133	532	486	46	8.63	...
2070	Manch., N. D. 2121	Lincoln, Nebr.	45	6	220	880	793	87	9.39	9.62
4573	Mich. 07930	Waseca, Minn.	45	6	135	540	494	46	9.83	10.23
4574	Nebr. 381162	Waseca, Minn.	45	6	123	492	435	57	9.82	10.18
4575	Minn. II-31-19	Waseca, Minn.	45	6	122	488	415	73	10.22	10.42
4576	Minn. II-31-45	Waseca, Minn.	45	6	105	420	343	77	10.12	10.43
4577	Wis. Barbless	Waseca, Minn.	45	6	150	600	546	54	9.03	9.98
4578	Wis. H35-7-2-1-3	Waseca, Minn.	45	6	196	784	696	88	9.92	10.36
4579	Wis. H35-7-6-4-1	Waseca, Minn.	45	6	246	984	891	93	9.96	10.45
4580	Manch., N. D. 2121	Waseca, Minn.	45	6	203	812	726	86	10.14	10.42
4581	Tregal	Waseca, Minn.	45	6	146	584	532	52	9.95	10.24
4582	Iowa 15	Waseca, Minn.	45	6	158	632	589	43	9.80	10.50
4583	Peatland	Waseca, Minn.	45	6	179	716	590	126	10.27	10.44
4589	Oderbrucker	Madison, Wis.	45	6	161	644	598	48	9.17	...
4467	Reno Winter	Hays, Kansas	45	6	258	1032	924	108	9.99	...
4479	Garton	Canada	45	6	159	636	538	98	10.28	...
4484	Rojo	Davis, Calif.	45	6	91	364	325	39	8.54	...
4609	Trebi	Madison, Wis.	45	6	162	648	612	36	8.91	...
4620	Kindred	Madison, Wis.	45	6	226	904	817	87	10.08	...

sprouts extract–glucose medium and grown for another 24 hours at 30° C. The cells were removed from the medium by centrifugation, and were resuspended in water to make a volume of 20 ml. Ten milliliters of such a suspension were used to inoculate each 600-ml. portion of mash. After inoculation the volume was made to 750 ml. (equivalent to 17.8 grams of wheat per 100 ml.). Duplicate 350-ml. aliquots were placed in 500-ml. Erlenmeyer flasks. A scrubber, consisting of a glass tube leading into an 8-inch test tube, about three fourths full of water, was attached to each of the flasks to catch the alcohol carried over during the evolution of carbon dioxide. The flasks were incubated at 30° C. for the desired time with occasional shaking.

TABLE III. EFFECT OF HIGH MALT LEVEL ON ALCOHOL YIELDS FROM SPRING WHEAT IN 72-HOUR FERMENTATIONS

Malt	Yields, Proof Gal./100 Lb. Dry Grain							
	Experiment 1				Experiment 2			
	5%	6%	7%	8%	5%	6%	7%	8%
Pabst	10.32	10.29	10.45	9.95	10.00	9.94	9.92	9.93
4228–30	10.28	10.44	10.33	10.51	10.21	10.29	10.01	10.16
4234–35	10.60	10.42	10.33	10.60	10.52	10.40	10.33	...
4231–33	10.27	10.29	10.29	10.23	10.39	10.31	10.25	10.19
4207–09	9.85	9.87	9.54	10.15	10.03	10.06	10.10	10.17

TABLE IV. ALCOHOL YIELDS FROM WINTER WHEAT WITH 5% MALT[a] IN 36-HOUR FERMENTATIONS

Malt No.	Proof Gal./100 Lb. Dry Grain	
	Expt. 1	Expt. 2
Pabst	9.31	9.26
4467	9.77	10.21
4479	10.38	10.47
4484	8.66	8.63
4577	8.79	8.63
4580	9.92	10.16
4589	8.77	8.98
4609	8.80	8.86
4620	10.21	10.16

[a] Of the 5% total, 1% was Pabst malt used for preconverting.

At the end of the fermentation period the contents of each flask were diluted to 500 ml. with the water from the scrubber tube and more tap water. A 200-ml. aliquot of the diluted mash was placed in a Kjeldahl flask, and about 95 ml. distilled off. This distillate was diluted to 100 ml., and alcohol was determined by means of a Westphal balance. Weight of alcohol was read from a curve made with known solutions. Yields were calculated as proof gallons of ethyl alcohol per 100 pounds of total dry grain.

The results of duplicate fermentations (duplicate flasks in the same run) agreed closely. The data are not given in the tables, but such flasks usually checked within 0.05 proof gallon per 100 pounds of dry grain. The results obtained with a malt in successive runs did not check so well. The variation was of the order of 0.0 to 0.5 proof gallon per 100 pounds of dry grain. Tables III and IV give data for two runs at different times.

EVALUATION OF MALTS

ALCOHOL YIELDS FROM SPRING WHEAT. Various malts differ in rate as well as in ultimate degree of conversion of wheat starch. Therefore, a method for evaluating malts should provide for comparison of these factors. The reduction of the quantity of malt to a limiting level or the use of short fermentation times are two evident procedures. Several fermentation experiments in which

Table V. Effect of Length of Fermentation Time on Alcohol Yields from Spring Wheat

Malt No.	Yield, Proof Gal./100 Lb. Dry Grain after Fermentation for: 24 hr.	36 hr.	48 hr.	72 hr.
	A. 8% Malt Level			
Pabst	8.50	9.50	9.71	9.81
4228–30	9.17	9.85	10.00	10.19
4234–35	9.74	10.06	10.17	10.25
4231–33	9.81	10.15	10.19	10.18
4207–09	7.77	8.91	9.41	9.73
4222–24	9.39	10.00	10.10	10.16
2070	9.00	10.00	10.26	10.26
4189–91	8.95	10.00	10.26	10.26
4195–97	8.54	9.47	10.10	10.20
4174–76	7.75	9.32	9.85	10.00
	B. 5% Malt Level			
Pabst	7.54	8.95	9.72	9.84
4228–30	8.36	9.54	10.09	10.18
4231–33	9.60	9.95	10.28	10.39
4219–21	9.66	10.07	10.32	10.43
4207–09	7.09	8.52	9.38	9.86
4222–24	7.96	9.39	9.84	9.84
2070	7.26	9.39	9.46	9.62
4189–91	7.75	8.80	9.45	9.84
4174–76	5.17	8.10	8.71	9.39
4195–97	6.72	8.63	9.32	...

malt level and fermentation time varied were carried out to determine the most suitable combination for comparing malts. Pabst malt was used as a control throughout.

A yield of 10 proof gallons of alcohol per 100 pounds of total dry grain was taken as a reasonable final standard in evaluating the fermentations. Such a yield was obtained regularly when proper conditions were observed and has been reported for the same batch of spring wheat by several alcohol producers.

Table I shows the alcohol yields obtained with several malts at levels of 1, 2, and 4% and a fermentation time of 72 hours. The yields are averages of two runs. From approximately thirty malts tried in this manner, data were also arranged to show the influence of malting conditions on alcohol yields. The relation will be discussed later. None of the fermentations with these low levels of malt reached the standard yield of 10 proof gallons.

Table III presents results obtained with higher levels of malt (5, 6, 7, and 8%) in 72-hour fermentations. Two of these were new malts. The yield of 10 proof gallons was obtained with all levels. Therefore levels above 5% appeared to be excessive in a 72-hour fermentation.

Table V*A* shows the effect of shorter fermentation times with a malt level of 8%. None of the fermentations reached the standard yield of 10 proof gallons before 36 hours. The data in Tables III and V*A* seem to show that a concentration of malt less than 8% and a time of fermentation shorter than 72 or even 48 hours would give the best conditions for evaluating a malt. To test this assumption, fermentations with 5% malt for various periods were tried. Table V*B* gives averages of two runs. The figures show that the earliest time at which any of the fermentations reached a 10-gallon yield was 36 hours. At 48 hours three of the fermentations reached this figure and two came within 0.3 gallon of it. At 72 hours three more fermentations were close to the standard figure. The three fermentations yielding 8.4 gallons or better at 24 hours all reached a 10-gallon yield in 48 hours.

Table V*B* seems to indicate that, if a single fermentation is to be relied on to evaluate a malt, a 5% concentration and 36-hour period are best. These conditions permitted some fermentations to reach the 10-gallon level but were rigorous enough to sort out slow fermentations. If two periods are to be used in rating the malt, a 24- and a 48-hour fermentation give a better basis for rating. If it is assumed that industrial practice calls for fermentation lasting approximately 48 hours, three of the malts qualified as excellent, two were good, three rated fair, and one was poor.

Comparison of the data in Table V, *A* and *B*, suggests that malt activity was the limiting factor in the speed of the fermentations. With 8% malt the yield at 24 hours was from 0.21 to 2.58 gallons (average 1.27) higher than at the 5% level. From these data it appears that if the rate of starch conversion could be increased, the yeast would be adequate to convert the sugar to alcohol.

Alcohol Yields from Winter Wheat. Two runs were made with winter wheat. A total of 5% malt was used of which 1% (Pabst malt) was required for liquefaction. Alcohol determinations were made at the end of 36 hours. Table IV gives results of these fermentations. The yields correlated in most cases with those obtained with spring wheat when the same malts were used (Tables II and IV). This was expected since the starch contents of the two wheats were approximately equal.

AMYLOLYTIC ACTIVITY OF MALTS AND ALCOHOL YIELDS

Table II records the characteristics of the malts in the conventional terms used in the malting industry. Diastatic activity was determined according to the Official Method of the American Association of Cereal Chemists (*1*). The results are expressed as degrees Lintner and maltose equivalent (degrees Lintner × 4). The α-amylase dextrinizing activity and β-amylase activity were determined by the methods of Sandstedt, Kneen, and Blish (*5*) and Kneen and Sandstedt (*3*), as modified by Olson, Evans, and Dickson (*4*). The analytical data are given in Tables I and II.

Table I shows the influence of malting moisture and germination time on the amylase values of the malts and the alcohol yields. Increased malting moisture and longer time increased the amylase values somewhat and, in most cases, the alcohol yields. As indicated earlier, alcohol yields were obtained with thirty-one malts at a 2% malting level and 72-hour fermentation time. Correlation coefficients were calculated from the data as an aid to interpretation. In this experiment alcohol yield correlated significantly with both β- and α-amylase when low malt concentrations and long fermentation times were used.

Table II presents analytical data on another group of malts representing several different varieties and selections grown at different locations, and the alcohol yields obtained with 5% malt at 36- and 72-hour fermentations. Significant correlations were found between alcohol yields and α-amylase only at the 36-hour fermentation. No relation between alcohol yield and diastatic power or β-amylase was indicated. When higher malt concentrations and short fermentation times were used, the relations between alcohol yield and amylase values on the malts were different from those given for the previous series of malts. Although only suggestive, the data indicate that α-amylase may be of more importance in the rate of fermentation; in longer fermentations at low malt concentrations, both amylase components assume importance. With a malt concentration of 5% and a 72-hour fermentation, the values level off sufficiently so that no relations with the original amylase values of the malts are indicated. While the amylase activity of a malt is informative, it alone is not adequate for evaluating the malt for alcohol production; other undetermined factors also play an important role. Therefore, the best evaluation of a malt is the determination of the amount of alcohol produced in a fermentation with the malt.

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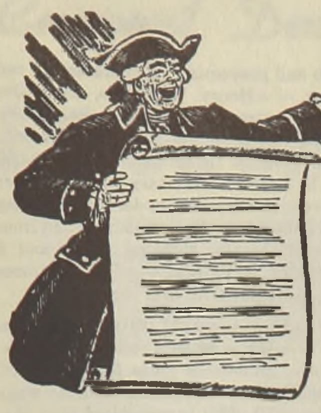


OCTOBER'S HEADLINES

Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

Reviewed by the Editors

¶ October 1. Representatives returned from world tour of U. S. military installations urge President Truman to maintain atomic bomb secrecy pending report of scientists who directed project. ~ ~War Department reveals German scientists are being brought to U. S. on voluntary basis to aid in military research. ~ ~Walter R. G. Baker, vice president GE, says no nation other than U. S. can produce atomic bomb. ~ ~Eight government-owned chemical plants producing synthetic ammonia put up for sale or lease by Reconstruction Finance Corp. ~ ~U. S. Rubber announces fungicide which will control apple scab, a DDT formulation four times as effective as DDT powder, and a herbicide for weeding large acreages of cereal crops. ~ ~A. E. Staley Mfg. completes $2,000,000 soybean oil extraction plant. ~ ~Harold Vagtborg, president Midwest Research Institute, tells Mexican-American Conference on Industrial Research that research in U. S. is destined to be billion-dollar-a-year industry.

¶ October 2. House Committee on Patents opens hearings on Administration's bill to extend temporarily time for filing and acting on patent applications, and for preventing proof of acts abroad with respect to making inventions.

¶ October 3. War Department says new fiber practically equal to nylon has been produced in Germany.

¶ October 4. President Truman, in special message to Congress, says "atomic force in ignorant or evil hands could inflict untold disaster upon the nation and the world" and urges prompt creation of Atomic Energy Commission. ~ ~Senate and House introduce bills to carry out President's proposals. ~ ~R. E. Wilson, Standard Oil of Ind., tells special Senate committee investigating petroleum resources that America's supplies are more than sufficient to meet our needs for generations. ~ ~Corning Glass announces purchase of substantial interest in largest glass plant in Chile. ~ ~President Truman in special message urges Congress to speed authorization of St. Lawrence seaway and power project as necessary to perfection of atomic bomb. ~ ~President Truman orders abolition of WPB, its replacement by a new Civilian Production Administration, effective November 3, and names J. D. Small to head new agency. ~ ~President Truman orders Navy to seize 26 strike-bound oil-producing and refining companies. ~ ~Dow Chemical plans $15,000,000 expansion program at Freeport, Tex., to meet anticipated demand for plastics, according to A. P. Beutel, general manager of Texas division.

¶ October 5. Federal Judge Frank L. Kloeb enters order against Hartford Empire Co., Owens-Illinois Glass, and 11 other glass container companies to settle disputes, setting hearing for October 22. ~ ~WPB revokes important directive controlling war expenditures.

¶ October 7. Justice Department announces termination of civi antitrust suit against Merck & Co. following consent judgment in which Alien Property Custodian agreed. ~ ~Toilet Goods Research Foundation, Inc., New York City, is created to conduct scientific research with special reference to cosmetics and toilet preparations. ~ ~ R. J. Dearborn, chairman Committee on Patents, National Association of Manufacturers, says American supremacy in invention and technological progress will be endangered by compulsory licensing of patents as outlined in bills pending in Congress.

¶ October 8. Irving Langmuir, associate director of G.E.'s research laboratories, at hearing before Senate subcommittee, warns that unless international organization is set up to control atomic energy, U. S. may be destroyed within 20 years. ~ ~Former President Hoover, in address prepared for 50th anniversary convocation of Clarkson College of Technology, warns against certain types of monopolies, labor union rules, and government policies which could cripple scientific expansion. ~ ~Supreme Court denies petition of Associated Press for reconsideration of 5 to 3 decision which held membership by-laws of news agency in violation of Sherman Antitrust Act. ~ ~Department of Commerce foresees potential $3,000,000 glass market in Mexico. ~ ~Department of Commerce reports listing on register of patents available for licensing or sale about 400 patents owned by individuals, corporations, universities, and others.

¶ October 9. Research Corp., New York, N. Y., offers $2,500,000 in grants-in-aid for postwar collegiate research. ~ ~WPB eliminates all end-use restrictions on lead in lead chemicals and establishes an over-all quota for their production. ~ ~Kenneth T. Norris, spokesman for West Coast industrialists and president Norris Stamping and Mfg. Co., says President Truman has given assurance he desires decentralization of industry. ~ ~New Food and Drug Administration labeling regulations effective today make drugs safer for home medication. ~ ~Secretary of War Patterson and Maj. Gen. Leslie R. Groves tell Congressional committee that commission should control atomic bomb. ~ ~ Harlow Shapley, Harvard, Chas. F. Kettering, president American Association for Advancement of Science, Harold E. Moulton, permanent secretary AAAS, and Howard Meyerhoff, executive secretary, appearing before Senate subcommittee back long-range program of fundamental and applied research through government foundation. ~ ~President James B. Conant of Harvard and Vannevar Bush, director Office of Scientific Research & Development, tell Senate subcommittee it would be less dangerous to permit manufacture and sale of narcotics without regulation than to allow unlicensed and uncontrolled experimentation in atomic energy. ~ ~Libbey-Owens-Ford announces expansion program by construction of $250,000 research plant.

¶ October 10. Representative Clare Boothe Luce blocks efforts of House Military Affairs Committee to reach prompt agreement on atomic energy legislation.

¶ October 11. House Naval Committee receives indications from high naval officers that an effective counter measure to atomic bombs has been developed. ~ ~Secretary of Commerce Wallace appearing before Senate subcommittee backs science foundation but says it should be part of world program. ~ ~Niels Bohr in science magazine contends that atomic energy must be subject to international control. ~ ~Francis C. Cary, Hybinette & Cary & Associates, metal research engineers, confirms report that company has offered to buy and run government-owned aluminum plants in competition with Aluminum Co. of America. ~ ~Senate passes S.J. Res. 100 permitting industrial alcohol plants to produce sugars and sirups while continuing production of alcohol.

¶ October 12. R. J. Dearborn, appearing before Senate subcommittee advocates inclusion in national science foundation bill of provision that grants of fellowships and scholarships be contingent upon recipients being on emergency call of Government. ~ ~Lt. Gen. Lucius D. Clay announces confiscation by the Allies of all I. G. Farben properties within Germany. ~ ~Standard Oil of Calif. contracts with RFC to operate major part of government-owned 100-octane plant at Richmond, Calif., for manufacture of premium motor gasoline. ~ ~James B. Conant, speaking at annual meeting of Association of American Universities, expresses fear that colleges will lose their productive men if government and industry set up too many research institutes. ~ ~Department of Commerce, Office of

Publication Board, issues Index No. 1 of available industrial and scientific technical reports of plants investigated or interviews with German scientists declassified for distribution to industry.

¶ October 13. Four hundred experts who helped develop atomic bomb in a statement released by Robert R. Wilson, member of executive council, on behalf of Los Alamos scientists, say efforts to keep atomic secret would be diastrous.

¶ October 14. John W. Thomas, chairman Firestone Tire & Rubber, announces use of first commercial electronic vulcanizer in rubber industry in manufacture of Foamex mattresses.

¶ October 15. Robert C. Hockett, scientific director Sugar Research Foundation, announces foundation has granted awards totaling $38,200 to eight universities and one state experiment station for research on food values of sugar.∼∼Hercules announces $30,000,000 three-year construction program. ∼ ∼Secretary of War Patterson and Vannevar Bush urge federal support of scientific research in backing Magnuson bill before Senate joint committee. ∼ ∼Mathieson Alkali in quarterly report says capacity of sodium chloride plant is being doubled. ∼ ∼Francis C. Frary, director of research Aluminum Co. of America, elected to receive Perkin Medal for 1946, Cyril S. Kimball, secretary American Section, Society of Chemical Industry, announces.

¶ October 16. Sam Husband, head of Defense Plant Corp., tells Senators that Columbia Metals Corp. has offered to buy surplus aluminum plants. ∼ ∼RFC offers two magnesium plants for sale. ∼ ∼Admiral Wm. R. Purnell, testifying before Senate subcommittee, says no nation other than U. S. is equipped to manufacture atomic bombs. ∼ ∼Secretary of Navy Forrestal, testifying before same committee, approves establishment of National Research Foundation.

¶ October 17. Secretary of War Patterson tells Senate Military Affairs Committee country urgently needs unified department of national defense which would not draw funds away from technological research through wasteful duplicating practices. ∼ ∼J. R. Oppenheimer, director of atomic research at Los Alamos, N. Mex., Robert Wilson, of Harvard, and H. J. Curtis, representing scientists at Clinton Laboratories in Oak Ridge, Tenn., appearing before Senate committee urge international commission for world curb of atomic energy. ∼ ∼Aluminum Co. of America offers to lease and operate key unit of government's $700,000,000 aluminum properties and sell product to anyone Government approves. ∼ ∼RFC offers chemical plant formerly operated by Westvaco Products Co., at Newark, Calif., for sale or lease. ∼ ∼I. W. Wilson, Alcoa's vice president, tells Senate Committee on Military Affairs and Postwar Planning that recommendation of SPB for disposal of government-owned aluminum plants would destroy Aluminum Co. of America. ∼ ∼Surplus Property Administrator Symington asks Congress for new directive to clarify government's position in disposal of aluminum plants.

¶ October 18. Eastman Kodak says its German plant in Berlin outskirts has been dismantled and is in hands of Russians. ∼ ∼Standard Oil of Calif. lets contract for construction of new 175-mile 18-inch oil pipe line to supply its refining operations on San Francisco Bay at Richmond. ∼ ∼President Truman says he believes government subsidies necessary to continue peacetime operations of surplus aluminum plants. ∼ ∼State and Commerce Departments assign Edwin C. Jahn to conduct survey of pulp and paper industries in Norway, Sweden, and Finland. ∼ ∼Senate votes to freeze disposal of government-owned aluminum plants for 30 days. ∼ ∼Hercules announces plans for construction of $1,500,000 organic chemicals and resin plant near Burlington, N. J.

¶ October 20. General Eisenhower advises Allies to destroy I. G. Farben empire. ∼ ∼Eleven American oil companies file with Special Senate Committee Investigating Petroleum Resources plea for government support of their plans for foreign expansion. ∼ ∼A Chemicals Division directed by Lawrence Brown, assistant director of WPB's Chemicals Bureau, one of nine industry divisions set up under Bureau of Reconversion Operations in Civilian Production Administration. ∼ ∼Peter C. Reilly, president Reilly Tar and Chemical Corp., makes $1,000,000 endowment to Notre Dame University, income from which to be used for fellowships in chemistry and chemical engineering.

¶ October 21. A. L. Viles, president Rubber Manufacturers Association of America, says synthetic rubber has permanently established itself as basic new world raw material. ∼ ∼Harold C. Urey, as principal speaker at luncheon of American Scandinavian Foundation, says only by abolishing atomic bomb and preventing its manufacture can world escape atomic bomb war. ∼ ∼Henry W. Chase, chancellor New York University, advocates support of college research by defense funds. ∼ ∼Carl Hallaner, vice president Bausch and Lomb, announces $6,000,000 expansion program in addition to $6,200,000 spent during war. ∼ ∼Charles L. Parsons, Secretary ACS, in letter to War Mobilization and Reconversion Director Snyder, urges freeing huge mass of vital scientific and industrial information obtained from enemy sources. ∼ ∼Army seizes 45 plants, 25 sales offices, and 4 miscellaneous installations owned by I. G. Farben. ∼ ∼GE announces 100,000,000 volt x-ray machine, most powerful ever made.

¶ October 22. Corn Products Refining begins $1,000,000 expansion program at Kansas City plant. ∼ ∼Louis Ware, president International Minerals & Chemical Corp., announces plans for $2,500,000 amino products plant at San Jose, Calif. ∼ ∼President Truman signs legislation extending time during which SPB is prohibited from disposing of government-owned aluminum plants.

¶ October 23. Abbott Laboratories break ground for $100,000 building for production of streptomycin. ∼ ∼Rustless Iron and Steel Corp. merges into American Rolling Mill Co. ∼ ∼Deputy Petroleum Administrator Ralph K. Davies says secrets of German oil industry are available to public through Library of Congress. ∼ ∼U. S.-held foreign oil reserves nearly equal those in this country, survey filed with O'Mahoney Senate Petroleum Committee shows. ∼ ∼WPB establishes specific controls of tin and lead scrap and prepared used tin cans in the hands of scrap dealers. ∼ ∼Monsanto Chemical announces plans for construction of $1,500,000 synthetic caffeine plant in St. Louis. ∼ ∼Sixty leading scientists, educators, and civic leaders send telegram to President Truman opposing May-Johnson bill. ∼ ∼Charles A. Thomas, vice president in charge of research for Monsanto Chemicals, says long-range postwar industrial progress is threatened by conscription of young scientists for armed forces.

¶ October 24. Civilian Production Administrator, John D. Small, says WPB policy of industry-government cooperation will be continued, and lists 176 key industry advisory committees to be consulted on reconversion problems including chemicals, forest products, rubber, and textiles. ∼ ∼L. C. Dunn, Columbia University, at Senate subcommittee hearing proposes new government department headed by scientific director or secretary with Cabinet rank.

¶ October 25. Sir Alexander Fleming, discoverer of penicillin, and E. B. Chain and Sir H. W. Florey, his co-workers, to receive 1945 Nobel Prize for physiology and medicine. ∼ ∼K. T. Compton, president MIT, H. De W. Smyth, of Princeton, and H. C. Urey, University of Chicago, at Senate subcommittee hearing condemn secrecy in research activities except in details of bomb manufacture.

¶ October 26. Association of Colleges and Universities of N. Y. asks President Truman for selective service deferment for science and engineering students. ∼ ∼Senator Brien McMahon named chairman of Senate Committee on atomic energy, an 11-member panel.

¶ October 27. President Truman in Navy Day speech says discussion of atomic bomb with Great Britain and Canada and later with other nations cannot wait upon organization of United Nations, but that discussions will not be concerned with process of manufacturing.

¶ October 28. R. T. Haslam, vice president and director Standard Oil N. J., says it will require 3 years to rebuild company's war-damaged plants in Europe. ∼ ∼GE plans to spend $280,000,000 for expansion and research on new products pressing work on atomic energy.

¶ October 30. Colonel Bradley Dewey, ACS President-Elect and former Rubber Director, tells Senate hearing that control of proposed government program for aiding scientific research should be entrusted to board of outstanding scientists and engineers and urges that the phrase "medical, natural, and social sciences" in the pending bill be changed to its original form—"mathematical, physical, and biological sciences". Roger Adams, Chairman of the ACS Board of Directors, appearing before same committee urges establishment of a control board of competent men, a majority to be trained in science. ∼ ∼House Military Affairs Committee approves, 17 to 10, bill establishing 9-man commission with power over atomic research.

¶ October 31. President Truman says entire field of atomic energy and no other subject is on agenda of his forthcoming discussion with Prime Ministers Atlee and Mackenzie-King, and denies rumors that President Roosevelt and Winston Churchill made secret agreement at Quebec for peacetime control of atomic bomb.

Current Developments in EQUIPMENT AND DESIGN

Chemical plants built for war should be maintained for postwar usefulness and as insurance against aggression.

Discussed by Charles Owen Brown

THE readers of this column are familiar with the government's program of new plant construction carried out during the last three years. No one will contest the fact that these plants have served a satisfactory purpose. Most of them have seen an active operating life of less than two years; a few have had over three full years of capacity production. In the main, huge sums of money were spent on them. There are several hundred plants which cost in the neighborhood of three quarters to two million dollars; many, between ten and thirty million dollars; and some, well over one hundred million dollars. These are impressive figures, even in wartime. Never has new productive construction been completed and operated on such a scale as we have recently witnessed in the United States. Most of the new chemical plants are separate projects, but some are mere additions of odd pieces of equipment to privately owned plants—for example, the Defense Plant Corporation's alcohol plants.

Now these plants must be disposed of and in a practical, thrifty manner. This problem was anticipated long before the war ended, but relatively few policies for proper disposition have been adopted. To discuss these plants in the abstract or collectively serves no useful purpose. The nature of the plants and the products they were built to produce vary so widely that each must be discussed on its own merits. This column is mainly concerned with a logical, useful disposition of the chemical plants.

After the last war many of the larger chemical plants were dismantled promptly and completely. After the equipment was demolished, or at best removed to storage, the buildings were torn down. This may have been a logical move at that time. Since those days we have seen that aggressor nations rise again to plan wars, and that each succeeding war is carried on with increased brutality. We believe that all signs point to the fact that some day we will not be able to prepare in time to avoid complete disaster. Therefore the philosophy regarding the major chemical plants which seemed sensible after the first war must not be permitted now. These plants represent the most modern technology. Their usefulness in many lines cannot be overestimated, particularly as a restraining influence on aggressors who will hesitate to start a war if they know we are fully prepared. Except for one unfortunate experiment, the Navy has not demolished its fleets at the end of any war. If the Navy does not sink its battleships just because a war is over, it is no more logical for the country to destroy its large chemical plants. The United States, therefore, should maintain its position as a nation fully prepared for war. As far as practicable all the War Department's productive capacity should be retained. If a lasting peace is possible, this step will justify the maintenance of these plants and solve the problems of proper disposition.

Chemical plants built for the Government but operated by private companies are a minor disposal problem. Generally the companies which built these plants have plans for their peacetime use. In many cases such plants contain more modern equipment than the regular manufacturing facilities of the agent company. It is therefore not much of a problem for such industries to absorb the wartime plants at a reasonable return to the Government. Our general civilian economy and scale of living will profit by such a course.

Plants built for the War Department to produce strictly war materials represent a more difficult problem. Explosive plants are complicated and extremely specialized. Safety requirements in manufacturing operations have led to wide separation of relatively small plant units. In addition, there are large cement barriers between separate plant buildings and between major pieces of equipment. The explosive plants scattered over the country are built in the form of "lines", fairly well connected by a continuous sequence of equipment which converts toluene or cotton into the final explosive. These highly specialized plants will be extremely difficult to modify for the production of other chemicals, and they far exceed peacetime needs for explosives. Nevertheless they should not be demolished as were similar plants after the last war. Let us look at their construction costs. The records indicate that sums spent in acquiring the site for the plant, making access roads, fencing the property, and leveling and grading to make the site suitable for erection and installation of equipment has, in almost every case, amounted to from 50 to 55% of the total cost of the completed plant. In other words, half the cost of these enormous investments went into developing a place to build a plant. Many argue that the cost of maintaining these government plants so they will be usable when war clouds gather is prohibitive. The point we are trying to make here is that, if these plants are locked up and depreciation is controlled as far as possible by simply closing the buildings, making them tight, and preventing access of weather and intruders, 50% of the original investment can always be realized. Of course the plants should first be thoroughly cleaned, and all metal should be protected. Corrosion undoubtedly will be rapid enough so that in fifteen or twenty years the equipment in the plants will have relatively little value. Notwithstanding, this policy of retaining rather than demolishing these plants will still salvage, without any annual expense to the Government, over half of the original investment and construction time. It is the writer's opinion that if these plants were to be revamped and put into operation twenty years from now, although new parts and much new equipment would have to be installed, the salvage value would amount to two-thirds of the original cost of the plant. Another important factor is time. In practically all of the large government plants more than 50% of the total time for completion was consumed in acquiring and preparing the site for building. That time saving may be needed desperately when the next threat arises. There appears to be ample justification for the retention of these plants by the Government.

This course, however, need not be a burden to the taxpayer, and the creation of a few essential jobs is even desirable. Most of the explosive plants are equipped with a modern sulfuric acid plant and a modern, efficient nitric acid plant. The projects are located fairly well to operate the sulfuric acid plants in place. The nitric acid plants can be moved to more desirable locations if necessary. The lease of these acid plants will work out profitably in almost every case, and greatly improve the problem of maintaining the entire project.

Some of the more costly government-built plants, running from seven to fifty million dollars, are modern, fully integrated projects producing heavy chemicals.

(*Continued on page 86*)

They are therefore in a different class, and have more hopeful prospects for a useful peacetime life. Typical of this group are the synthetic ammonia plants. The ammonia-producing capacity of the country was more than doubled to meet war demands. In 1939 privately operated plants were producing, roughly, 1450 tons of anhydrous ammonia per day. The wartime capacity of the plants built for the War Department represented 2440 tons of ammonia per day or an increase of 168% over peacetime production possibilities. Why should all these plants be demolished or put in idle stand-by condition? The ammonia plants can produce at least three, and possibly more, ammonia compounds of value to agriculture. Several plants already have facilities for converting ammonia to nitric acid, and at some plants a further conversion to ammonium nitrate is possible. Nitric acid and limestone, and ammonium nitrate and limestone yield two important products.

Prewar, the average annual increase in the use of fixed nitrogen in agriculture was approximately 14,000–15,000 tons per average year. Since the capacity of the wartime ammonia plants is in the neighborhood of 732,000 tons of nitrogen per year, our fertilizer uses can scarcely absorb the capacity of these plants. The world situation, however, is somewhat different. Some of these plants are in areas where raw materials are relatively expensive. One plant may not be well located to serve any useful market, but it can act as potential capacity for future war needs. If the United States becomes an exporter of fixed nitrogen compounds, if certain of these plants are converted to the manufacture of organic chemicals other than ammonia, if the expected increases in the use of fixed nitrogen fertilizers occur, and if perhaps one plant is withdrawn from production, the gap between consumption and production capacity would be relatively small.

It is therefore logical that certain of these plants should be retained idle by the War Department. In the case of ammonia plants this can be done in a practical way. If an intelligent policy is adopted, it need not be an expensive procedure. If the property is well protected with fences and locks and refenced closely to include just the building areas, and if the vast lands in some of the present sites are returned to usefulness, the plants can be put in stand-by condition for a relatively small sum, with a small expenditure per year for maintaining this condition. Let us assume that twenty years have passed and that the buildings have withstood the elements. The cost of reconditioning a plant and supplying the parts which have corroded or are too weathered for further use would not exceed one fourth of the original investment. This certainly is worth-while insurance.

Many of the War Department facilities include steam supply and power plants which are larger than many of the municipal power plants serving some of our large cities. For example, many of these projects contain boiler plants with five to ten or more units of the latest modern construction, some are capable of raising 200,000 pounds of steam per hour. At several plants turbines and electrical generators are installed to consume approximately the full capacity of the boiler plant. These power plants are a valuable asset. It may not be wise, however, to strip a project of the steam and power facilities just because they can be sold more easily than the rest of the equipment. If no use for the project as a whole can be found, those plants should be leased with the provision that they be maintained and returned to the Government when needed. A relatively large percentage of the value of steam and power facilities should be realized in any sale or leasing arrangement made. In some cases, a logical renter may desire only part of a large plant. Wherever it is possible to separate a plant, this type of arrangement should be made. We believe this is a favorable plan for the project as a whole.

Current Developments in
INSTRUMENTATION

New instruments for measuring vacuum and a new titrimeter are now available.

Discussed by Ralph H. Munch

Devices for measuring low pressures were discussed in the March issue (advertising section, page 77). Among the instruments mentioned were the McLeod gage and the ionization gage. Since that time, a new form of each of these has appeared on the market. In each case serious limitations of the older forms have been eliminated.

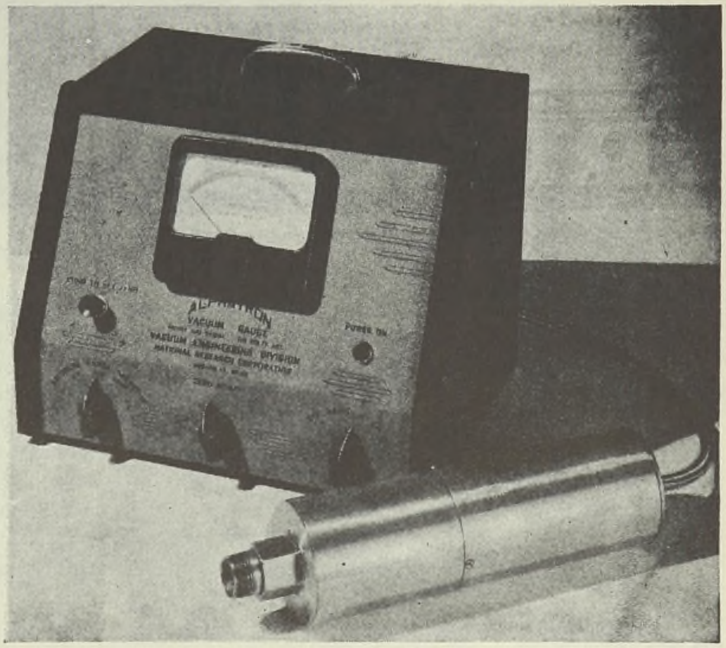
Although the McLeod gage is generally used as a primary standard for laboratory measurement of low pressures, the usual forms suffer from the disadvantage that readings are not continuous but must be obtained by manual operation of the gage. This has kept it from becoming popular as a plant instrument, in spite of its many good points. Among its good points are its simplicity, the fact that it is a primary standard, and the fact that its calibration is the same for all gases so long as they are not condensable. The Stokes Machine Company, Philadelphia 20, Pa., recently announced the Vacorder, an automatic recording form of McLeod gage. This new instrument, shown in Figure 1, provides a continuous visible record of pressures in the range 0 to 5000 microns. It employs a modified Stokes McLeod indicating gage which is mechanically tilted from the horizontal to the vertical position by an electric motor. The height of the mercury in the measuring capillary, and hence the vacuum in the system, is electrically determined and transmitted to the recorder. The recording unit may be located at any distant point, but the gage proper is installed close to the sampling point. The Vacorder thus includes an indicating gage at the sampling point as well as a recorder at either the sampling point or any other desired location. Available in two models, the panel-mounted Vacorder may be furnished as the single-point instrument (Figure 1) or as a multiple-point Vacorder to record vacuum from as many as four different points in sequence on a strip chart.

The conventional ionization gage is a useful instrument for measuring pressures below one micron. It is not usable at higher pressures because the thermionic cathode which serves as a source of electrons to ionize the residual gas becomes inactivated at higher pressures. Even at pressures below one micron, it is necessary to maintain the flow of ionizing electrons constant, since the reading of the gage is in proportion to the electron current. The Vacuum Engineering Division of National Research Corporation, Boston 15, Mass., has just introduced a new form of ionization gage, the Alphatron, shown in Figure 2. In this instrument the ionization is produced by the emanation from a small, permanent radium source instead of by electron bombardment. The ions formed in the residual gas in the gage are collected as in the conventional ionization gage, and the ion current is measured by a sensitive amplifier to indicate continuously the gas pressure in the gage.

(*Continued on page 92*)

Figure 1 (*Left*). Recording McLeod Gage (the Vacorder)

Figure 2 (*Below*). Ionization Gage (the Alphatron)



The Alphatron has three ranges—0 to 10 mm., 0 to 1 mm., and 0 to 100 microns—which are chosen by means of a selector switch. The zero setting of the gage may be adjusted at any time by pressing a button on the panel and turning an adjustment knob. Since the ionization effect is produced by the constant flow of alpha particles from a sealed radium source, there is no filament to burn out and no filament current to set and maintain. Furthermore, the gage cannot be damaged by exposure to atmospheric pressure. It is ruggedly constructed of all-metal parts which are not subject to breakage. No degassing is necessary when the gage is turned on. The scale of the meter is linear and its response is almost instantaneous. As shipped from the factory, it is calibrated for dry air. The Alphatron consists of two units (Figure 2), the gage housing and the control box, connected by a ten-conductor flexible cable 10 feet long. The gage housing contains the radium source, grid and collector plate in the vacuum chamber, and the first stage of the amplifier.

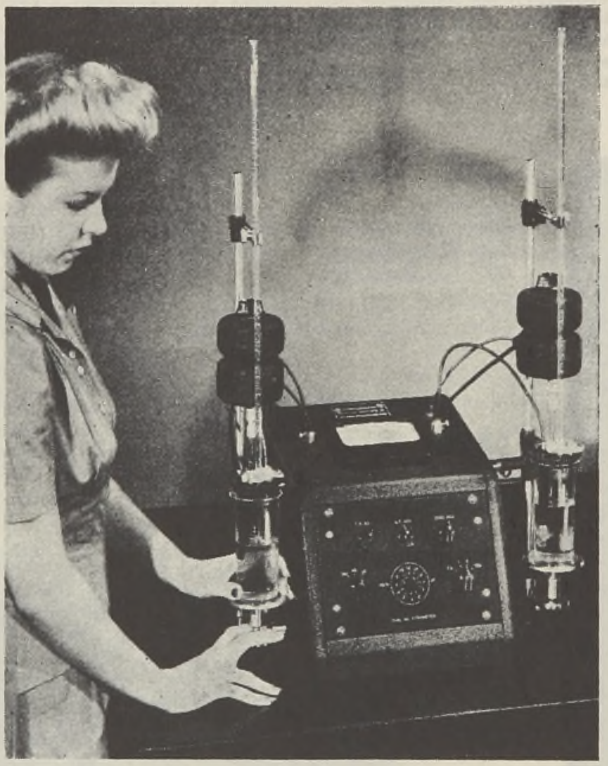


Figure 3. Dual Alternating-Current Titrimeter

The Precision Scientific Company, Chicago 47, Ill., is now offering the Shell dual alternating-current titrimeter. This instrument (Figure 3) is a vacuum tube voltmeter combined with a step potentiometer, which makes possible a wide range along with high sensitivity in a single indicating meter. With this arrangement voltages to 0.5 millivolt over a range of -1.65 to $+1.65$ volts can be read. The instrument is suitable for measuring the electromotive force of cells with a resistance up to 5000 megohms, which makes it available for use with sturdy glass electrodes and high-resistance titration media. This titrimeter has been found suitable for such procedures as the A.S.T.M. Proposed Method of Test for Saponification Number of Petroleum Products by Electrometric Titration and the A.S.T.M. Tentative Method D-664 (Neutralization Number of Petroleum Products by Electrometric Titration).

Current Developments in

WASTE UTILIZATION

Sewage disposal plants provide industrial waters and organic chemicals of considerable significance to industry.

Discussed by Harold R. Murdock

Below Washington, D. C., the Potomac River widens gradually and becomes a tidal stream as it flows into Chesapeake Bay. Its narrow, deep channel is bordered on both sides by spacious tidal flats which are covered with varied aquatic plants. This dense vegetation provides a shelter for small fish and a breeding ground for microscopic plant and animal organisms. At low tide these flats resemble meadows, but when the tide rises, polluted water from upstream flows across them and deposits suspended impurities. Since the water here is not disturbed by winds or river currents, clarification is rapid.

Natural Purification of Rivers

The sunlight penetrates this clear water readily and stimulates the growth of the chlorophyll-bearing plants and microscopic plant organisms. Such green vegetation produces, by this process of photosynthesis, two and one half times as much oxygen as the weight of carbon added to the plant tissue. These flats are, therefore, efficient chemical factories which produce oxygen to counteract the oxygen-consuming sewage burden placed upon the Potomac River.

The tides exert a vital influence upon these flats. They increase many fold the effective length of the river and provide a long retention period for the water and the activity of organisms. They also mix the channel water, the water on the flats, and the sewage, which promotes the biological processes. These tides average about thirty inches. Without them these large shallow basins would become semistagnant bayous, and the virility of plant growth on the flats would be lost. The tides automatically lift huge amounts of contaminated channel water into the flats and 6 hours later they drop the now oxygenated water back into the river channel.

The Huntington flat, just below Alexandria, Va., was particularly interesting to W. C. Purdy in 1916, because the entire sewage of that city passed over this flat on its way downstream. Purdy made extensive chemical and biological tests on the waters and muds of this flat for almost a year. This particular body of water was 1.3 square miles in area and fronted the river for 1.25 miles. A marsh of about 0.18 square mile constituted the extreme upper portion most remote from the river. Three small streams entered the upper end of the marsh, two of which were heavily polluted by raw sewage from Alexandria. The water in these small streams was putrid where they entered the marsh, and when the bottom mud was stirred, the anaerobic decomposition gave rise to foul gases. The water leaving this marsh showed little evidence of pollution. Tests made near the middle of the flat showed dissolved oxygen values of 103% saturation on sunny days; on cloudy days 75% saturation was recorded. Values of 128% saturation were recorded on particularly favorable sunny days.

The water leaving the flat on the morning ebb tide had been on the flat during the night, so it did not receive the sunlight. Nevertheless, it showed an average of 83% oxygen saturation. On the other hand, water which had been on the flat in the daytime showed 93% oxygen saturation. In October and November when the biological activity was lower, the average oxygen value of all water leaving the flat was 88% saturation as compared to the average oxygen value of 75% for all water entering the flat. It should be understood that these waters had also purified the raw sewage from Alexandria. Purdy computed the results per acre of tidal flats. The production of oxygen over that required for the raw sewage pollution was 17.7 pounds per acre per day. He concluded as follows: "This Huntington Flat provides sufficient oxygen for the first 24 hours natural purification of nearly 3,000,000 gallons of raw sewage from Washington. This is in addition to the first 24 hour natural purification of 6,000,000 gallons per day of raw sewage from Alexandria."

Nature has built an efficient waste disposal plant in the Potomac River. All of the factors involved appear to be at their optimum effectiveness in carrying out the cycle of growth and decay, with sunlight and enzymes as the energizing forces. The absence of any one of these factors would seriously impair the balance. The sewage is the fertilizing agent for luxuriant growth of plants and organisms. The flats serve as reaction chambers for the biological process. The tides function as automatic pumps to move the water in and out of the chemical reactor—the flats. The plants and microscopic organisms serve as catalysts in transforming carbon dioxide from decayed organic substances into plant-building chemicals. Coproduct of this reaction is the oxygen which transforms unstable raw sewage into stable, simpler, and nontoxic organic chemicals; these chemicals can break down partially to carbon dioxide. Sunlight is the powerhouse for the cycle of biological and chemical reactions which occur.

Industry Simulates Nature

The trickling filter and activated sludge processes used in industrial sewage disposal plants are based upon the same biological processes which take place in the Potomac River. Such processes have been employed by industry in some instances, but careful attention should be given to the elimination of toxic materials in waste before this biological principle is applied more extensively.

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Waste Utilization

The trickling filter is essentially a bed of crushed stone, 5 to 10 feet deep. The stone is uniform in size and varies from 0.5 to 3 inches in diameter, depending upon the preference of the engineer. After the raw sewage has been screened to remove the coarse suspended solids, it is sprinkled over the stones so that it will pass through the filter in 15 to 30 minutes. A copious deposit of slime is built up on the surface of the stones by the circulation of a suspension of sewage and activating bacteria through the filter. When the slime reaches the desired effectiveness, 75 to 80% of the biological oxygen demand is usually removed.

The activated sludge process is another method which simulates the biological action of self-purifying streams. Slime and bacteria do not coat the stones, as in the trickling filter, but are kept suspended in the sewage by vigorous agitation with air. In this process the removal of B.O.D. can be 90 to 95% of the raw sewage value.

These methods are not utilization processes; they merely dispose of the waste material. More attention should be given to actual utilization of the organic chemicals which result from the biological conversion of sewage. The tremendous volume of sewage available creates a challenge to technical men to find profitable products from the effluent of the trickling filter or activated sludge operations. New absorption chemicals and developments in organic chemistry during the war period should be combed carefully with this purpose in mind. The field is almost unexplored.

Industrial Waters from Disposal Plants

Several versatile industrial companies have gone to the sewage disposal plant in search of water. A certain steel company had overpumped its underground water supply as did other near-by war-expanded industries. Many wells became contaminated with salt or highly acid waters, and the situation was critical. Wartime demands necessitated the expansion of the steel plant. Extensive surveys for water were made. Finally a chemist suggested using the sewage disposal effluent of a large near-by city. After careful study and correction of the sewage by control of industrial wastes which entered the system, it was found feasible to build a plant which could process 50,000,000 gallons per day of trickling filter effluent. The activated sludge effluent was satisfactory to the steel mill without further treatment. A similar use of sewage effluent from an activated sludge plant has been made by a midwestern railroad. An oil refinery is reported to be using trickling filter effluent. Studies have been completed which indicate that trickling filter effluent can be utilized as a substitute for underground waters in the wood pulping industry. In Europe sewage plant effluent is employed for fish culture as the chemicals in the water are considered to be suitable foods for small fish.

Such uses for the effluent of sewage disposal plants will expand, particularly where underground waters are at critically low levels. But the real opportunity is for utilization of the chemicals present in processed sewage effluents. Obviously this suggestion brings up difficult problems, but difficulties encountered are problems to solve, not obstacles to defeat the objective.

Current Developments in
PLANT MANAGEMENT

Company manuals promote good will and coordination in the chemical industry.

Discussed by Walter von Pechmann

THERE is an increasing trend in the chemical industry toward the use of written instructions. This stems from a recognition of the need to coordinate operations and to maintain more personal contact with the working force. The issuance of company manuals is the most effective means to accomplish this. However, manuals are of little or no value if improperly designed or not kept up to date. The purpose of this writing is to assist in the establishment and maintenance of good company manuals by describing the manner in which chemical concerns have successfully converted fundamental information into written form.

A manual is a systematic series of written instructions on duties, policies, and procedures. Because it is often believed that the term "manual" implies arbitrary rulings and inflexible instructions, many concerns prefer to use such titles as general instructions or standard practice information. Frequently attempts are made to establish complete manuals in concerns where only a few written instructions exist. This procedure is not recommended since it results in the issuance of manuals which are usually outdated before they are put into effect. The development of a good company manual takes considerable time, and its maintenance requires continuous change. It is difficult, and sometimes impossible, to keep altering instructions during the period of manual preparation. It is recommended that management outline the work which has to be done and prepare individual instructions whenever the need arises. To accelerate the establishment of the manual, management can make a group of executives responsible for its preparation.

Company manuals are usually subdivided as follows: (1) general or company-wide instructions, (2) departmental instructions, (3) job instructions, and (4) employee handbooks. Since the proper preparation of job instructions has assumed new importance during the reconversion period, special emphasis is placed on a description of this part of the manual. Subdivisions are discussed according to organization, policy, and procedure because most companies develop their manuals along these lines.

General Instructions

ORGANIZATION. This section of the manual should include organization charts and outline the responsibilities of officers and executives. The organization chart should indicate clearly where line, staff, and functional controls are involved. The description of the responsibility of officers and executives should indicate the extent of their authority.

POLICY. This part should cover all general policies of company-wide significance—for instance, in personnel relations, accounting, budgeting, production, sales, and advertising.

PROCEDURE. Those procedures, practices, and clerical routines of a general nature which are necessary to operations throughout the company should be included. This section may also describe procedures established by one division for the guidance of another.

Departmental Instructions

ORGANIZATION. Occasionally the responsibilities and the authority of department heads and supervisors are covered in the general or company-wide instructions. However, manufacturers sometimes prefer to issue individual departmental organization charts and descriptions. The advantage is that minor functions usually not shown on the plant-wide organization chart can be listed, and instructions can be issued to supervisors without revealing the confidential information which is usually contained in the general part of the manual.

POLICY. Departmental instructions should contain only policies which are of interest to employees. Failure to comply with this principle has caused more than one unnecessary and embarrassing discussion between management and labor. Departmental policy instructions are commonly issued by the department head and should not conflict with established plant-wide policies. It is considered good practice to republish in this section the general plant-wide policies which the department head wishes to reveal to his employees.

PROCEDURE. Standard procedures applying to one department only should be included here. Often no distinct separation can be made between departmental policies and certain phases of procedures. The writer considers instructions which apply to all jobs a standard departmental practice and therefore does not cover such matters in his job instructions.

Job Instructions

ORGANIZATION AND POLICY. Job instructions should never contain matters pertaining to organization and policy but should be confined to rulings which apply to the work of employees.

PROCEDURE. Many a good company manual was started with the revision of existing departmental job instructions. The writer favors this approach because it not only encourages department heads to participate actively in the new plan, but also gives them the opportunity to familiarize themselves with the technique employed in working out the manual. Before departmental job instructions can be incorporated in the new plan, it is necessary (1) to standardize instruction forms on a plant-wide basis and (2) to eliminate from existing job instructions those rulings which have no connection with the execution of a job (company and department policies, time-keeping procedures required by employees, etc.).

Some difficulties are to be expected when the first attempt is made to standardize departmental instructions. Chiefs naturally believe that the manner in which they have issued their instructions is best suited for their departments; therefore they may be reluctant to accept changes. They may also feel that the departure from existing forms will cause confusion among employees. Furthermore, opinions often vary as to what extent instructions should be issued; if too detailed, they have to be revised frequently; if not complete, they do not serve the purpose for which they are intended. The writer favors the issuance of instructions in considerable detail, provided arrangements are made for quick and effective revisions when necessary. A job may be divided into three elements—tasks, operations, and key points. Instructions are issued for each operation in which the key points are described. A "task" is considered a job performance which is unrelated to others but contained in one job, an "operation" is a job performance, and a "key point" is a special knack put in form of an instruction which is helpful in bringing about the efficient execution of the job performance.

For example, John Doe is a chemical worker, engaged most of the day in weighing chemicals. In addition to his regular duty, he relieves two operators in the mixing room during lunch periods, and is responsible for distributing working clothes to employees of the entire department. His tasks are: weighing, mixing, and clothes distribution. Every task consists of several operations. Operations embodied in the task of weighing are as follows: obtain chemicals, check chemicals, obtain containers, weigh chemicals, store chemicals weighed. Every operation has several key points. For the operation of obtaining chemicals they might be as follows: Old stock is to be used first. Only chemicals bearing the approved laboratory label shall be removed. Spilled chemicals shall be put into a container marked "Do not use" and shall be returned to the stock room for retesting.

Breaking down jobs into such details may seem unnecessary. However, experience has taught that only this method makes certain no important part of a job is overlooked. Another advantage of such an analysis is that every page of the job instructions is relatively equal in importance since only operations and not key points become instructions.

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Plant Management

It is not uncommon to prepare job instructions together with the job descriptions for a job evaluation system. It should be clearly understood, however, that job descriptions and job instructions are two entirely different matters. Job descriptions should cover only the tasks to be performed and outline employee responsibilities, whereas job instructions should state what is to be done, when the operation is to be performed, how it is to be performed, and, in some instances, why certain regulations have to be observed. For example,

JOB DESCRIPTION	JOB INSTRUCTION
Responsible for submitting samples of shipments to the laboratory.	Upon receipt of shipment, make out test sheet in duplicate; this shall contain the following information: data received, user, material, manufacturer's number and name, indication that material submitted is a shipment. Submit original and duplicate to laboratory with sample of shipment. Retain triplicate in file until original is returned; then destroy.

One of the most important steps in establishing manuals is a provision for keeping the written instructions up to date. Some concerns issue manuals in book form and send out memos requesting changes when needed. Occasionally the manuals are reprinted. This method has sometimes caused the abolishment of manuals because they were too difficult to keep up to date, and the job of making changes could not be properly supervised The writer has used the following procedure with good results:

Instructions are presented in loose-leaf books. Each instruction is headed by a marker which identifies it with the manual to which it belongs, its section, and its correct position within the section—for instance, DC-J-43-9. DC stands for departmental manual, coating department; J means job instruction section, 43 is for job number 43, and 9 means the ninth instruction issued. When revision is necessary, holders of the manual are requested to remove the instruction from the loose-leaf book and return it to the office which is responsible for the upkeep of this record. The following form is used to request the return of canceled instructions:

Please remove instruction No.————, which is herewith canceled,

from your manual and return it to————————————————

☐No other instruction will be issued.
☐Revised page will be sent to you after receipt of canceled instruction.

Date————————

It might be argued that this procedure involves too much office work. The writer has tried several times unsuccessfully to make the holders of manuals responsible for the proper maintenance of the books but has come to the conclusion that the only safeguard against obsolete instructions being used is to ask for their return before the revisions are given out.

Employee Handbooks

Many executives consider employee handbooks to be the most important part of the company manual. Some concerns spend a great deal of money to familiarize new employees with the surroundings of the company for which they will work. This should not be interpreted as extravagance, for these handbooks are of great assistance to the newcomer and can often forestall grievances and promote good will. However, it is not sensible for companies to distribute expensive handbooks to new employees, yet fail to provide old employees, especially the supervisory staff, with information which enables them to conduct business in a more efficient manner. Employee handbooks usually do not contain organization charts although some manufacturers include a broad outline of the functions of their officers and executives.

POLICY. Personnel policies should be covered in this section of the manual as well as general information about the company. This may include an employees' life insurance plan, medical servnice, first aid, salary during absence, transfer of employees, layoff, employment termination code, and personal record.

PROCEDURE. Regulations concerning all employees in a plant are usually found in this section, such as the ringing of the time clock, time allowed for change of clothes, rest periods, etc.

Last-Minute Flashes

FROM THE EDITOR'S DESK

EUROPE will be in a tight spot as far as fertilizer and industrial nitrogen go. Much of the supply must come from Polish plants of rather small capacity, but the Czechoslovakian units may soon be in operation. Some of our surplus material has been shipped to continental Europe to help out.

★ Hemp plants built by the Government during the war (I. & E. C. REPORTS, advertising section, page 14, July issue) are now on the market. Forty-two plants are being offered for sale by Reconstruction Finance Corporation.

★ Domestic production of iodine, which is now running at about half of our needs, will probably continue at this rate even though the war is over.

★ One of the little items that the designers of airplanes had to worry about in their planning of huge bombers was the moisture pickup of insulating materials. On a hot, steamy landing field hundreds of pounds could be added to the load of a bomber by moisture adsorption.

★ Large-scale vacuum equipment used in many war industries must have a leakage rate of only a few microns per hour.

★ The Belgian Congo, now producing quinine at a rate of 24,000 pounds per year, expects to export in a few years about a quarter of the world's total needs of 2,000,000 pounds.

★ The total footage of Fiberglas insulation and boards used on aircraft carriers ran to about 360,000 square feet. In addition, some 326,000 linear feet of tape and cloth were used for insulating pipes.

★ Phosphates will probably continue in short supply for some time until the fat and oil situation is eased. The reason for the phosphate shortage is the greater demand for these compounds as soap substitutes and extenders.

★ The hydrofluoric acid alkylation plants owned by Defense Plant Corporation have ceased operation owing to a lack of demand for high-powered aviation gasoline.

★ The Government has a stock pile of about 15 to 20 million gallons of toluene.

★ Instead of the large aerosol bombs standardized by our armed forces, the British army used a small bomb that contains enough of the insecticide to kill insects in 4000 cubic feet. Tiny and easily held between two fingers, the little bomb was of great use in airplane crash landings in the Pacific jungles.

★ Surpluses now in government hands for disposal have reached the two billion dollar mark.

★ India, always cognizant of its shortage in fertilizer materials, is rapidly pushing the construction of plants which have about 400,000 tons of ammonium sulfate capacity.

★ Oil companies with holdings in the various European countries have finally been granted permission to inspect their properties.

★ Carbon black facilities in the Nation are probably going to run full blast next year to make up the backlog demand.

★ Heat sealing of the pores of egg shells prior to storage is said to be an efficient way of preventing spoilage.